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UNRESTRICTED

THE CHEMICAL WORK OF THOMAS GRAHAM

by

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ABSTRACT

Thomas Graham (1805-1869) was taught Chemistry at the Universities of Glasgow and Edinburgh by the students of Joseph Black: Thomas Thomson and Thomas Charles Hope. Graham devoted himself to Chemistry, despite opposition from his father, and became one of the foremost British chemists of his age.

Essentially inductive in his research work, Graham investigated molecular movements in gases and liquids and the role of water in the constitution of acids and salts. Graham made use of analogy in directing his researches. Thus, he believed that there was a partial analogy between gaseous and liquid diffusion; both processes depended ultimately on inherent molecular motions. The chemical affinity of water for different substances connected his studies of acids and salts with the liquid state.

His first chemical investigations of 1825 were concerned with the absorption of gases by liquids. Inspired by Faraday's liquefaction experiments, Graham emphasised the continuity of the states of matter and suggested an analogy between liquefaction and gaseous absorption. Heat was an important consideration in these changes of state.

Graham was cautious in drawing conclusions from his experiments although he speculated imaginatively. It is possible that Graham's belief in atoms of primary matter, endowed with different, unalterable motions for each element, was conceived at the time of his first studies of gaseous diffusion. However, he did not express this view openly until 1863.

In this thesis, I have traced the development of Graham's chemical work by exploiting: unpublished manuscript material and the views of Graham and his contemporaries. Graham responded to criticisms of his work. When Berzelius dismissed the polybasic nature of the phosphoric acids, Graham countered by rejecting inorganic isomerism and he subsequently investigated polymerism. Bunsen's denial of the diffusion

law and the rejection of Graham's first explanation of osmosis were spurs to further creative experimental investigations.

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TABLE OF CONTENTS

		<u>Page</u>
Chapter 1	Introduction	1
Chapter 2	Graham's Early Studies	9
Chapter 3	Graham's Work on the Motion of Gases	54
Chapter 4	The Role of Water in the Constitution of Acids and Salts	133
Chapter 5	Polymerism and Voltaic Circles	212
Chapter 6	The Liquid State and Molecular Motion in Solution	278
Chapter 7	Speculative Ideas Concerning the Constitution of Matter	347
Appendix 1	An Explanatory Note on the Symbols used by Graham in his Researches on the Phosphates	374
Appendix 2	Graham's Contributions to Physiology	377
Bibliography	A Preliminary Survey	391
	Manuscripts	400
	Printed Sources	408

Chapter 1

INTRODUCTION

1. Graham, Wellcome MS.2584 (Old no.3394) 'On the Molecular Mobility of Gases.' A draft copy with corrections and additions 44 ff. 1863 (?) See 'Theoretical appendix' p.38.

INTRODUCTION

"The physical properties of matter depend so much upon motion as to impress the idea that all differences of property whatever may be ultimately referable to the possession by matter of various kinds and degrees of motion." ¹

Graham stated this fundamental belief in his draft notes of 1863. More than thirty years study of the motion of gases and liquids had convinced him of the inherent activity of matter. Graham was essentially inductive in his mode of thought and this can be seen in his chemical researches. By induction he was able to draw out generalisations and laws gradually from carefully-conceived and often wide-ranging experimental investigations. For example Graham recognised that Dalton's interpretation of the phenomenon of gaseous diffusion was not really adequate. By making a study of the diffusion speeds of different gases Graham was able to infer and then confirm his fundamental diffusion law.

Initially he was reluctant to speculate on this law. Ever cautious, Graham did not want to put forward hypotheses to account for diffusion until he had made a more-detailed experimental investigation of all aspects of the subject. In 1831, he merely concluded that diffusion was an exhibition of the inherent motion of the ultimate particles and that it was subject to a fixed law.

Later in his life Graham did speculate on the inherent motion of matter and despite some opposition he published his views. Indeed, it is even possible that he had worked out these speculative ideas at the time of his first studies of gaseous diffusion. Graham believed in the essential unity of matter and he justified this belief by quoting Newton's demonstration that gravity acted equally on all bodies. Therefore, all elements were constructed from the same primary atoms. These atoms were identical in mass. He now had to explain how all the different elements could be created from the same primary atoms. He suggested that a

primordial influence, presumably God, had invested the primary atoms with different and unalterable motions for each element. Thus a hydrogen atom possessed a quantitatively-different, inherent motion to that of a sulphur atom. This hypothesis, of atoms possessing different, unalterable motions, enabled Graham to explain the observed differences in the diffusion speeds of gases or liquids. The inherent motion of the atom swept out a constant volume in space and this gave the atom its fixed density. Thus, both the density of matter and the speed of its diffusion depended ultimately on its inherent motion.

Graham's chemical researches can be divided into experimental investigations in two major areas: the motion of both gases and liquids; and the constitution of acids and salts. Patiently he performed a vast number of experiments which eventually led him to the laws or principles on which these phenomena were based. To understand how Graham achieved successful examples of induction, two important components of his thought must be considered. Firstly, he often made use of analogy to direct his inductive investigations and secondly, he recognised the importance of continuity as a connecting principle in nature.

From Faraday's 1823 experiments on the liquefaction of gases Graham recognised the essential continuity existing between the gas and liquid states of matter. Both gaseous and liquid molecules possessed characteristic and inherent molecular motions which were essentially repulsive in their action on one another. The liquid state also possessed some analogy to the solid state because liquid molecules attracted one another by the force of chemical affinity although this attractive force was much weaker than that found in solids.

In his very first paper Graham made use of the analogy between the liquefaction of gases and the absorption of gases by liquids. This liquefaction analogy was used again by Graham to account for the passage of gases across various apparently-impermeable partitions, such as: soap films, bladder, rubber and even hot metals. Likewise, Graham drew on

the analogy between gases and liquids when he began to investigate the diffusion of different substances in the liquid state.

The liquid state was important in Graham's researches. The spontaneous spreading out of solutes into different solvents by liquid diffusion was evidence for inherent molecular motions. Also, studies of the liquid state seemed to provide evidence for the polymerisation of elementary molecules. Polymerisation produced both colloid molecules from crystalloid molecules and smaller aggregates of equal weight and identical diffusibility. Polymeric molecules appeared to be present in liquid water and in voltaic circles. Using a less successful analogy, based on the decomposition of polymeric molecules in a voltaic circle, Graham attempted to explain the water movement in osmosis. Graham believed that the different speeds of liquid diffusion could be correlated with the variations in the chemical affinity of different solutes for water. This analogy between the attraction of chemical affinity of salts for water and the different speeds of liquid diffusion connects Graham's work on the constitution of acids and salts with that of liquid diffusion, osmosis, dialysis and the distinction between crystalloids and colloids. The existence of a continuity in all matter was pointed out by Graham when he showed that the latter distinction was not absolute; crystalloids gradually shaded into colloids.

The role of analogy in Graham's thought can be seen clearly in his studies of the phosphoric acids and their salts. He assumed that there was an analogy between water and the strong bases, such as soda and silver oxide, in the phosphoric acids and their salts. The polybasic nature of the three phosphoric acids could then be interpreted by determining the different quantities of 'basic' water found in each acid. By an extension of this analogy, Graham allowed water to assume other roles in salts and so he was able to explain the formation of double salts, acid salts and basic salts. Indeed if water itself could function as a strong base like sodium oxide then hydrogen might possess an analogy to a

metallic vapour and Graham developed this idea in his final researches on 'hydrogenium'. The analogy between water and basic oxides was further extended by Graham when he suggested that nearly all known salts could be incorporated into a single class of salts. These salts were constitutionally neutral and it was even possible to include acids in the same class.

Therefore it can be seen that Graham's researches followed along the lines of gradual induction. But this induction, from copious experiment to generalisation, was greatly promoted by the use of judicious examples of analogy. Further, from the principle of continuity of matter Graham was able to choose bold and often empirically sound examples of analogy to direct his induction. Although Graham was extremely cautious in his use of hypothesis there is evidence that he did use hypothesis and speculation in his work. This can be seen in his work on voltaic circles; in his molecular theories of organic chemistry, and above all in his speculations about the nature of matter itself.

The aim of this thesis is to trace the origins and development of Graham's chemical research work. I shall also attempt to relate Graham's work to that of his contemporaries - previous attempts to do this have been both incomplete and only partially successful. Finally I shall make use of important manuscript materials in order to obtain a better understanding of the development of Graham's research work. Primary source material concerning Graham's researches has not been properly exploited in previous studies of his work.

My thesis will include chapters on: Graham's early studies; his work on the motion of gases; his researches on: the role of water in the constitution of acids and salts, and the problem of isomerism; polarity and chemical affinity, including a consideration of voltaic circles, organic chemistry and polar molecules, and unity of matter; the liquid state; and finally the nature of matter itself.

I have excluded from this thesis: Graham's early life and education; his work as an educationalist, applied scientist and consultant; his work

2. Edith Frame, 'Thomas Graham - A Centenary Account,'
Phil. J. 7 (1970) 116-127.
3. J. S. Rowe, Ph.D. Thesis: Research Work of University College, London
 Chemistry department (1828-1935).
 (University of London, 1955)
 This thesis was developed out of an earlier M.Sc. thesis - see
Bibliography.
4. E. A. Mason, 'Thomas Graham and the Kinetic Theory of Gases',
Phil. J. 7 (1970) 99-115
 See Bibliography for other papers.
5. M. D. Swords, Ph.D. Thesis The Chemical Philosophy of Thomas Graham
 (Case Western Reserve University, 1973).

as Master of the Mint, because these aspects of his life are currently being investigated by Mrs. Edith Frame of Strathclyde University. Mrs. Frame has published a useful introduction to her work in Philosophical Journal.²

Graham's chemical work has not generally received the scholarly attention which it deserves in this century. There are, however, perhaps three exceptions to this opinion and I will now consider them briefly.

In 1955, J.S. Rowe wrote a Ph.D. thesis entitled: The Research Work of University College, London, Chemistry Department (1828-1955). In this thesis Rowe has devoted about 300 out of 800 pages to a study of Graham.³ He has attempted to answer three questions: were there any links between the University College chemists, for example Turner, Graham and Williamson?, how original was their work? and how correct does it turn out to be? The main strength of Rowe's thesis is his attempt to relate Graham's work on gases and liquids to that of his predecessors and contemporaries. However, the last question which Rowe asks regarding the correctness of Graham's work has a distinct ring to it of a Whiggish interpretation of History. He is therefore much less successful in his attempts to evaluate Graham's work on the nature of matter, the atomic theory, etherification, and the role of water in the constitution of acids and salts.

In a useful series of papers, E. A. Mason has stressed the originality and accuracy of Graham's diffusion law. He has also demonstrated the remarkable clarity of thought shown by Graham in his final distinction between the three fundamental modes of gas motion:- diffusion; effusion; and transpiration or viscous flow. Mason's 1970 paper 'Thomas Graham and the Kinetic Theory of Gases' is particularly valuable.⁴

Finally, in 1973, Michael D. Swords wrote a Ph.D. thesis entitled 'The Chemical Philosophy of Thomas Graham'. This short thesis of 92 pages is an important attempt to examine the underlying ideas of Graham's work.⁵ Swords assumes that Graham believed in the unity of matter from the start of his research career in 1826 and he stresses the importance

6. Swords, *ibid.* pp 67-68.

7. Swords devotes two pages to these important topics pp 78-79.

8. On Thomas Reid's philosophy see: L. L. Laudan, 'Thomas Reid and the Newtonian turn of British Methodological Thought,' in: The Methodological Heritage of Newton, edited by R. Butts and J. Davis (Toronto, 1970) pp 103-131.

of atomic motion in Graham's work. Essentially Swords believes that Graham's speculations on matter really date from 1826. But it is important to remember that these speculations were not published until 1863 by which time Graham had expunged caloric from his original vision. Swords believes that these fundamental speculations guided much of Graham's research work. This is an original reconstruction of Graham's thought and I find it largely convincing although I think that Graham's speculations might with more plausibility have been in his mind from 1830. However it must be stressed that there does not seem to be any surviving evidence on which these views, of the possible earlier origin of Graham's speculations, can be firmly based.

The discussion by Swords of the role of water in the constitution of compounds tends to be superficial and is too brief. It is also spoiled by the use of anachronistic formulae such as $\text{Na}^2\text{Ag}^{\cdot\cdot}\text{P}^{\cdot\cdot\cdot}$ for the silver salt precipitated from common sodium phosphate solution.⁶ This salt is not produced by this reaction. As Graham correctly expressed it, the silver salt formed is actually $\text{Ag}^3\text{P}^{\cdot\cdot\cdot}$. Likewise Swords has not discussed Graham's later researches on osmosis, dialysis, crystalloids and colloids, in sufficient detail.⁷

Swords pays special attention to the influence of the common sense school of philosophy on Graham's work and thinking. In particular, Swords emphasises the influence of the writings of Thomas Reid on Graham's work. Also Swords assumes that Graham's hypothetical speculations on matter were a guide for his research work. It does seem problematical however to reconcile these hypothetical speculations of Graham with Reid's known contempt for hypothesis and conjecture.⁸ Also Graham's extensive use of analogy as a guide in obtaining successful examples of induction seems to be more compatible with the version of common sense philosophy advocated by Dugald Stewart. As Christie has recently pointed out, the emphasis of common sense philosophy changed during the early years of the nineteenth century. Common sense philosophers, who succeeded Reid,

adopted more liberal positions towards the use of hypothesis and analogy.⁹ Christie rightly advises caution in deciding on direct links to show the influence of moral philosophy on particular scientific researchers.

Although it is not easy to define the philosophical influences on Graham's thought, his researches certainly demonstrate that he was an inductive thinker. The method of induction was favoured by common sense philosophers and they cited Francis Bacon and Isaac Newton as pioneers in the use of induction. It is quite probable that Graham made a study of Bacon's Novum Organum when he was a student in the moral philosophy class at Glasgow University.¹⁰ Bacon recommended the use of a gradual process of induction in all scientific investigations. In 1821, Graham wrote some student notes on philosophy. These were probably taken down in George Jardine's Logic class and it is interesting to see that Graham wrote down on 'hypothesis':- "It very often happens that the philosopher must suppose a cause; that is take one for granted which he cannot demonstrate. Although these are very often wrong yet philosophy would advance slowly if they were not allowed."¹¹ Therefore he was taught that hypothesis did have a role in philosophy.

In 1838, Graham quoted the views of Sir John Herschel on hypotheses, in his University College lecture notes, on the nature of heat. Herschel had drawn on Bacon's Novum Organum as a source of inspiration when he was writing his influential book: A Preliminary Discourse on the Study of Natural Philosophy. Graham's quotation shows clearly his views on hypothesis were based on Herschel's opinion that: "to lay any great stress on hypotheses..., except in as much as they serve as a scaffold for the erection of general laws, is to 'quite mistake the scaffold for the pile'. Regarded in this light, hypotheses have often an eminent use: and a facility in framing them, if attended with an equal facility in laying them aside when they have served their turn is one of the most valuable qualities a philosopher can possess."¹² And of Chemistry, I think, Graham would probably have echoed Herschel again: "The simple process of

12. cont. Graham wrote that:- "Owing to the rapid advance [in Chemistry, more] than in any other branch of Science - [such a] rapid advancement enlarging our views we think less of the absolute truth of theories than of the assistance they give in leading to new discoveries. The scaffolding of Science is only valuable in erecting the fabric - the means and not the end. I maintain that the material theory has been a most useful one. It has led to many useful results and is likely to lead to more. While other theories which would refer heat to vibrations of particles to some form of motion have proved barren hypotheses in the hands of chemists and have led to nothing."
Wellcom MS. 2579 'Notes and drafts for his lectures on Chemistry at University College, London.' Author's holograph MS. 154 ll. (1838-48) These notes appear to date from 1838.

13. Herschel, *ibid.* pp 299-300.

inductive generalisation grounded on the examination of numerous facts,
....., has sufficed in most instances, to lead, by a clear and direct road
to its highest laws yet known."¹³

Let us now examine Graham's early chemical researches.

Chapter 2

GRAHAM'S EARLY STUDIES

1. R. A. Smith, The Life and Works of Thomas Graham, (Glasgow, 1884) p 12.
Letter from Graham to his mother dated 11th October 1826.

GRAHAM'S EARLY STUDIES

"The present article, although short, is one of considerable importance. There is nothing that I wish more than that somebody should oppose the theory which it contains, as a discussion of that kind is the very thing to make one known." ¹

In this extract from a letter written by Thomas Graham to his mother we see that he was ambitious to establish his reputation as a chemist. He was alluding to his speculative paper 'on the heat of friction' in which he attempted to explain static electricity in terms of material caloric. Graham's determination to succeed in his chosen chemical career was reinforced by his father's disapproval of the choice of chemistry as a suitable pursuit for his eldest son.

In this chapter I will examine Graham's early career in so far as it is relevant to his eventual decision to become a chemist. I will then consider the views of Graham's teachers concerning the nature of chemistry together with Graham's own view of chemistry. Finally, Graham's early researches will be examined. He began his researches at Glasgow in 1825 and continued them in Edinburgh until 1828 when he returned to Glasgow. It is evident that some of his early research work was developed from hints thrown out by his teachers but he added considerably to them through his own acute and frequently original powers of reasoning. Graham first studied chemistry between 1823 and 1824 under Thomas Thomson. He was undoubtedly impressed by the contemporary experiments on the liquefaction of gases carried out by Faraday and Perkins. It will be shown that Graham's interest in the changes occurring when gases were reduced to liquids or solids was most important in his early researches. He was eager to exploit both the material theory of caloric and Black's discovery of latent heat in order to explain these changes of state. At the beginning of his career Graham was particularly concerned with the nature of the liquid and gaseous states. The liquid state appeared to

2. A useful account of the state of Glasgow University in 1825 is given in 'Notice of the University of Glasgow - its professors and students' The Edinburgh Magazine and Library Miscellany, Vol. 95 (Edinburgh, May 1825) 513-523 and for further comments (June 1825) 647-648. I have deduced the probable course followed by Graham from this article. Graham's teachers were:- Josiah Walker (1761-1831), Professor of Humanities from 1815 to 1831; John Young (1747-Nov. 1828), Professor of Greek from 1774-1820 and Daniel Keyte Sandford (1793-1838), Professor of Greek from September 1821 to 1838; George Jardine (1742-1827), Professor of Logic from 1774 to 1824; James Mylne (1776-1839), Professor of Moral Philosophy from 1797 to 1839; James Millar (1762-1832), Professor of Mathematics from 1789 to 1832; William Meikleham (1771-1846) Professor of Natural Philosophy from 1803 to 1846 and Thomas Thomson (1773-1852) lecturer then Professor of Chemistry 1817 to 1852.

3. Wellcome Manuscripts. Thomas Graham 2551. 'Edward's letters to his kinsfolk from Glasgow' 21 pp (1821); 'Fragment of an essay on philosophy' pp 11-24 (1821). It is probable that the latter notes were taken down by Graham at Jardine's lectures. This is deduced from a comparison of these notes with Jardine's description of his course in: George Jardine, Outlines of a Philosophical Education (Glasgow, 1818) 46-48. It is possible that Graham received one of the thirteen prizes for general eminence in the logic class of 1821-2, but his name is mis-spelled 'Thomas Grahame, Glasgow' in W. Innes Addison, Prize Lists of the University of Glasgow, (Glasgow 1902) p 227.

be quite remarkable. Chemical affinity or attraction was an important feature of this state but so also was the force of repulsion exerted by caloric particles which surrounded the liquid molecules. It eventually became evident to Graham that an essential continuity existed between the liquid and gaseous states of matter and that motion was central to any understanding of the different states of matter.

Let us first examine the course of Graham's career which led up to his decision to devote his life to chemistry. Graham was born at Glasgow on December 21st 1805. After attending Glasgow grammar school he entered Glasgow University as an Arts' student in October 1819. He was only 13 years old, but it was then quite usual for students to begin the Arts course at about the age of 14. The first two years were spent studying Latin and Greek. He was taught Latin by Josiah Walker, Professor of Humanities and it is possible that he was taught Greek in his first year by John Young, Professor of Greek. The third year was usually devoted to a further study of Greek; presumably Graham was taught by Young's successor as Professor of Greek, Daniel Sandford.² In this academic year (1821-2) Graham probably also studied logic, or more accurately Belles-lettres and composition, under George Jardine. Two manuscripts survive from this time and they are almost certainly connected with Jardine's course. A draft manuscript of one of Graham's student essays entitled 'Edward's letters to his kinsfolk from Glasgow' is extant. It is signed and dated October ~~the~~ 1821. Also a few lecture notes or 'fragments of philosophy' still exist in Graham's own handwriting. They are dated Friday, October 26th 1821.³

The fourth year was usually devoted to a study of Moral Philosophy and Mathematics. These subjects were probably taught by James Mylne and James Millar respectively. Graham's final year of study from 1823 to 1824 may have included mathematics again. However, in this last session Graham definitely attended lectures on the two subjects which were most germane to his future career: natural philosophy taught by William

4. ibid. Prize Lists. p 247.
Meikleham in his lectures gave an account of the general objects of Natural Philosophy; general mechanics; pure statics and pure dynamics and their applications to practical mechanics and astronomy; affections of heat; electricity and magnetism; hydrodynamics and hydrostatics; hydraulics; pneumatics and finally light and optics.
Evidence, Oral and Documentary Taken and Received by the Commissioners, Great Britain Commission (1826-30) On the Universities of Scotland Vol.2. University of Glasgow, 1837. Evidence given by Meikleham January 8th 1827 p 115.

5. Graham, 'On the absorption of gases by liquids,' read before the University Chemical Society on September 3rd 1825, The Scots Mechanics' Magazine and Journal of Arts, Sciences and Literature, 2, (Glasgow November 1825 - January 1826) January 1826 pp 97-101.

6. Graham, 'On the absorption of gases by liquids,' Ann.Phil. 12 (July 1826) 69-74. The only difference between these two accounts is the omission in this later account of the footnote "Mr. Perkins has subsequently shown the possibility of liquifying many more gases" found in the first account op.cit.(5) p 97.

7. W.Innes Addison, Prize Lists of the University of Glasgow (Glasgow, 1902) p 267.

8. Wellcome Manuscripts. Thomas Graham 2551. 'Whether is the theory of Electricity of Dr. Franklin, or that of Dufay the more probable?' (1825) This is written over the first 12 sides of his student essay 'Edward's letters to his kinsfolk from Glasgow' op.cit. (3).

Meikleham (1771-1846) and chemistry taught by Thomas Thomson (1773-1852). In the natural philosophy class, Graham won one of the ten prizes awarded in the session of 1823-4 "for propriety of conduct, exemplary diligence and specimens of composition on subjects in natural philosophy presented by the Professor, or chosen by the students."⁴ Finally, aged 18, Graham was awarded the degree of Master of Arts on April 28th 1824.

For two further years, Graham continued his studies at Glasgow University, apparently devoting his attention to the study of mathematics and physical sciences under the guidance of William Meikleham, Thomas Thomson and others. Presumably between 1824 and 1826 Graham became convinced that he wanted to take up chemistry as a career. His father, however, did not approve of this plan because he wanted him to study for the ministry. With two of Graham's uncles already being ministers in the Church of Scotland it would have been reasonably easy to secure a position for him in the church. This led to a disagreement and an eventual breach between the strong-willed father and his son over the choice of a career.

Meanwhile, Graham helped to establish a Glasgow University Chemical Society to which he read on September 3rd 1825 what appears to be his first scientific paper: 'On the absorption of gases by liquids.' This paper was published in January 1826 in The Scots Mechanics' Magazine.⁵ This Journal was edited by Robert Wallace, Professor of Mathematics at the Andersonian University, with the assistance of Thomas Thomson amongst others. Thomson appears to have actively encouraged Graham's chemical career. In July 1826 Graham's paper was reprinted in the influential Annals of Philosophy.⁶

Also, in 1825, Graham began his preparations for an essay on the question: 'whether the hypothesis of Franklin, or that of Du Faye, on electricity is the most probable?'⁷ A draft manuscript of Graham's attempt to answer this question still survives.⁸ The essay title was the prize subject for philosophy (or more appropriately, natural philosophy) set by Glasgow University in the 1825-6 session. The prize for

9. John Guthrie Smith, The Parish of Strathblane and its Inhabitants from Early Times (Glasgow, 1886) See 'The Grahams of Ballewan' pp 161-165 particularly p 163.

10. On G. D. Longstaff see his obituary notice in J.Chem.Soc. 63 (1893) 751-3 Longstaff is said to have claimed that "Dr. Graham was his most distinguished pupil." p 753.

11. R. A. Smith, op. cit. (1) pp 9-11. The Hunterian Medical Society was founded in 1824 by eight Edinburgh Medical students and it survived until 1868-9. Richard Owen became a member in 1824.

the best essay was a silver medal. It was awarded on May 1st 1826 to James Finlay Weir Johnston, who was Graham's fellow-student and friend. Subsequently, Johnston became Professor of Chemistry at Durham University in 1833.

From Graham's published letters it can be inferred that he moved to Edinburgh in May 1826. Edinburgh University matriculation records show that he was a student in the medical faculty during the sessions 1825-6 and 1826-7. He does not seem to have started his studies at the beginning of the 1825-6 session. A possible explanation for this, is the death of his brother which took place in November 1825 at the young age of 19. One account of Graham's life suggests that he reached an arrangement with his father. This was that if he must be a minister then he should be educated in Edinburgh where theology was better taught than in Glasgow.⁹

From May 1826, Graham worked in the Edinburgh University chemistry laboratory. He wanted suitable facilities to make a practical study of the liquid state. Nominally this laboratory was under the direction of Professor T.C. Hope, but Hope did not teach any practical chemistry. Instead, practical chemistry was taught by his assistant who, at this time, was George Dixon Longstaff (1799-1892).¹⁰ It is possible that Graham might have known Longstaff before he went to Edinburgh, because G. D. Longstaff had assisted his father, Thomas Longstaff, when he had lectured on Chemistry to the Glasgow Mechanics Institute from 1824 to 1825.

During his stay in Edinburgh, Graham established himself as a practical chemist and scientific writer. He began by founding a University chemical society at Edinburgh in June 1826. In the following month he read an essay on 'liquidity' to the Hunterian Medical Society.¹¹

By the summer of 1826 Graham applied for a teaching post as lecturer on mechanics and chemistry at the Glasgow Mechanics Institute. He had to give a trial lecture at the Institute but failed to secure the

12. See Glasgow Mechanics Magazine 5 (September 9th 1826).

13. A. W. Hofmann, 'Obituary notice of Thomas Graham' Berichte der Deutschen Chemischen Gesellschaft 2 (1869) 753-780 see p 755.

14. Chalmers' Journal of Useful Knowledge and Monthly Miscellany of Arts and Sciences Vol.1 (1827) pp 25-28, 81-87, 121 - 129, 230-232. This Journal existed from March to August 1827 and then presumably ceased publication. Graham's articles were signed with the letter G.

15. R. A. Smith, op. cit. (1) p 18.

position, which went instead to his friend and fellow-chemist, Thomas Clark, on September 4th 1826.¹²

Thus, Graham returned to Edinburgh to continue his research and writing. Hofmann says that Graham attended Hope's Chemistry lectures for two years.¹³ It is evident from his letters that Graham did not like Hope's rather pompous manner. However, Hope was a conscientious teacher who was proficient at lecture-demonstrations. It is probable that Graham derived some benefit from the content of Hope's chemistry lectures. In January 1827, Thomas Thomson sent Graham two letters of introduction; one to John Leslie, Professor of Natural Philosophy and the other to Edward Turner, who was then extra-mural lecturer on Chemistry. These letters helped Graham to gain the friendship and help of both of these teachers.

Early in 1827, the impecunious Graham began to write some popular scientific articles for Charles Chalmers' new journal. Graham admitted that he did not consider them to be important productions.¹⁴ For, as he explained to his brother in February 1827, "eminence purely scientific is more philosophical, more honourable, and more desirable in my eyes. But leave it to time."¹⁵

Edward Turner was appointed to the new Chair of Chemistry at University College, London, in November 1827, and Graham was offered the chance of succeeding Turner as an extra-mural lecturer in Chemistry. The plan was for Graham to take over Turner's practical chemistry classes in February 1828 and to have the free use of all his laboratory apparatus. Then, in May 1828, Graham was to deliver a summer course of chemistry lectures of three months duration. During this period he achieved scientific recognition. For, in April 1828, Graham was elected a Fellow of the Royal Society of Edinburgh. This followed David Brewster's request that he should read some papers to the Royal Society of Edinburgh. This he did in 1827 and 1828.

Graham's stay in Edinburgh was now nearly at an end. He was short

16. John Guthrie Smith, *op. cit.* (9) p 163.

17. MS. letter of application for the Chair of Chemistry at King's College, London from Thomas Graham, Portland Street Lecture Room, Glasgow.
July 30th 1830. 'London collection', King's College, London.

of money and although he did lecture during Turner's absence in January 1828 he did not like the medical orientation of the chemistry teaching in Edinburgh. By July 1828 some form of financial, or family, crisis had occurred and so Graham returned to Glasgow. One account has it that "his father became impatient at his not preaching, and went to Edinburgh to see what his son was doing, where to his indignation he found his lodgings full, not of ponderous volumes of 'the father' and theological works, but of chemical and philosophical apparatus. Promptly breaking these to pieces James Graham cast his son off without a penny, and forbade him to enter his house. Thrown thus upon his own resources, Thomas Graham wisely consulted his old friend and teacher Dr. Meikleham, Professor of Natural Philosophy at Glasgow University and by his advice and help supported himself by giving lessons in mathematics and chemistry." ¹⁶

Meikleham wanted his students to possess a knowledge of mathematics so that they could properly follow his natural philosophy course and so he was able to secure employment for Graham as a mathematics tutor. It is also worth noting that mathematics had become a requirement for the M.A. degree at Glasgow University in 1826. Towards the end of 1828 Graham began teaching practical chemistry privately in a laboratory which he had set up in Portland Street Medical School, Glasgow and he continued to work at this laboratory until at least September 1830. Graham stated in a letter of application for a teaching post that he began teaching chemistry publicly at Glasgow in February 1829. He gave six successive scientific courses of chemistry each of three months duration to classes of increasing size; these courses lasted at least until July 1830. In the winter of 1829-30 he also gave a popular course of chemistry and natural philosophy at Glasgow Mechanics Institute. This course was attended by 260 pupils. At the same time he gave a similar course to a comparable number of students at the Andersonian Institution. ¹⁷

18. 'Thomas Graham', A Biographical Dictionary of Eminent Scotsmen edited by Robert Chambers and continued by the Rev. Thomas Thomson. Half-volume 6 (1875) 615-620. See p 616.
19. MS letter from Graham, July 30th 1830 op.cit. (17).
20. *ibid.*
21. Additional Testimonials in Favour of Thomas Graham A.M. (Glasgow, 1830) (See testimonial from John Leslie). The Wheatstone Collection, small items, biography, obituaries and testimonials, King's College, London.

It is recorded that Graham attended the anatomy and chemistry classes at Glasgow University in the 1828-9 session. He took chemistry again in 1829-30 and in addition he made a formal attendance at the six medical classes.¹⁸ Graham admitted that he had studied medicine "solely with a view to qualify himself as a teacher of chemistry."¹⁹ On July 30th 1830 he applied for the new Chair of Chemistry in King's College, London. In his letter of application Graham stated that he was "at present in the course of being admitted as a member of the Faculty of Physicians and Surgeons of Glasgow. He is also qualified for the degree of M.D. which he would take before leaving Scotland."²⁰ Graham was unsuccessful in his application; the Chair was given to J. F. Daniell. However, Graham did receive strong support in the form of an interesting testimonial written for him by John Leslie.

Leslie wrote "I have great satisfaction in testifying the high estimation I have formed of the uncommon merit of my young friend, Mr. Graham, as a philosophical chemist. The specimens he has already produced in chemical analysis, not only mark accurate and patient investigation, but display ingenuity and inventive talents, which, when matured by experience, promise the happiest results. Mr. Graham possesses a decided advantage over most of his compeers, in being acquainted with the powers of mathematical investigation, which illuminate every part of physics, while the habits he has acquired in the art of teaching, qualify him to hold a distinguished place in a metropolitan seminary."²¹

Finally, in September 1830, Graham achieved a secure teaching appointment when Andrew Ure resigned from his Chair of Chemistry at the Andersonian University, Glasgow and Graham was appointed in his place. He was now able to achieve a reconciliation with his father and this was consolidated as his reputation as a chemical researcher grew. Graham's ambition to succeed as a chemical researcher and teacher continued. For, he wrote to Liebig in October 1837 to tell him about his new appointment as Professor of Chemistry in University College, London: "You are

22. MS letter from Graham to Liebig, October 17th 1837. Liebigiana 58, Bayerische Staatsbibliothek, Munich.
23. Hope attended Black's lectures between 1782 and 1787; Thomson attended Black's lectures from 1795 to 1796.
24. Joseph Black, Lectures on the Elements of Chemistry 1 (Edinburgh, 1803) pp 11-12 edited by John Robison.
25. Thomas Thomson, System of Chemistry 1 (5th edn. London, 1817) p 2.
26. Crosbie Smith, 'Mechanical Philosophy' and the emergence of physics in Britain 1800-1850, Annals of Science 33 (1976) 3-29.
27. T. Thomson, Edinburgh Review 50 (October 1829) 256-276. see p 262.

at present in a very different scientific circle from what we boast of in England, but I trust that we shall yet see better things on our side of the channel. I can do little, but my ambition and the object of my life will be to raise something like a chemical school in London, and your example and success is my most efficient stimulus." ²²

Before examining Graham's early researches it will be useful to consider the views of his teachers concerning the nature of chemistry and then to see what Graham himself taught on this fundamental topic. Both Thomas Thomson and Thomas Charles Hope had learned their chemistry in Edinburgh from Joseph Black.²³ Black, according to Robison, regarded chemistry as the study of "the effects produced by heat and mixture, in all bodies, or in mixtures of bodies, natural or artificial with a view to the improvement of arts and the knowledge of nature." ²⁴

Thomas Thomson and Thomas Charles Hope accepted and taught Lavoisier's anti-phlogistic chemistry. Likewise, they both followed Black in emphasising the importance of heat in chemistry. Thomson drew on the ideas of his Edinburgh teacher of natural philosophy when he wrote that chemistry was that "science which treats of those events or changes in natural bodies which are not accompanied by sensible motions." ²⁵ Sensible motions formed a separate study in the branch of natural philosophy which was known in Scotland as 'mechanical philosophy'. But chemistry was the study of insensible motions. The distinction between chemistry and mechanical philosophy was made by a number of Scottish natural philosophers including: John Robison, John Playfair and Graham's teacher of natural philosophy, William Meikleham.²⁶

In 1829, Thomson gave a more precise description of the objects of chemistry when he wrote that they were two-fold "first to investigate all the effects of heat, and, if possible to ascertain the nature of this powerful, but mysterious agent. Second, to determine the constituents of all the simple bodies which enter into their composition." ²⁷ He expressed this last object more precisely in 1830 as the determination of

28. T. Thomson, 'Chemistry' Edinburgh Encyclopaedia (edited by David Brewster, Edinburgh, 1830 in 18 vols.) Vol. 6 p 1.
29. T. C. Hope, MSS. of chemistry lecture notes. Gen.268-272. The lecture notes are kept in numbered packets in five boxes. These notes were written by Hope between 1790 and 1842. They were presented to the University by his nephew, James Hope in 1902.
Hope MSS. Gen. 271 packet 122.
30. Hope, *ibid.*
31. T. C. Hope, *ibid.* MSS.Gen 271 packet 135 'Chemical action'

"the laws by which the simple atoms of matter unite together and form compounds." ²⁸ Thomson was actively engaged, during Graham's student days, in carrying out a research programme to determine atomic weights. He hoped to be able to provide evidence in support of Dalton's atomic theory and also to be able to substantiate Prout's hypothesis that atomic weights were really integral multiples of the atomic weight of hydrogen.

Hope, on the other hand, regarded chemistry as a study of the changes arising from the mutual action of particles. This consisted of "an alteration in composition and nature, and the kind of effect produced is a change of properties and qualities." ²⁹ These changes took place "between the minute component parts or atoms; when these atoms are brought into the nearest possible contact. These actions are chemical and the investigation of them forms the principal object of chemistry." ³⁰ Hope acknowledged his intellectual debt to Newton when he examined the detailed nature of the constitution of matter. Thus, Hope wrote in his lecture notes that "all bodies are formed of a congeries or aggregation of very small parts or particles Newton was of the opinion that all material objects, that every species of matter, ultimately consisted of atoms of the same nature in short, there existed in nature atoms of one description only. That these atoms of inappreciable smallness were solid, impenetrable, extended, indivisible and immutable actuated by powers of attraction and repulsion. That these atoms by being joined together into groups, give birth to the elementary particles of bodies and that the differences among the elementary particles depended upon the number of atoms, or the size, or the figure, or the density of the particles generated.

According to this view, the elementary particles of iron and of sulphur consist of similar atoms; but they differ widely in their qualities from each other, by reason of their containing a different number of these atoms, or of their having them grouped together in a different manner." ³¹

32. Graham, Wellcome MSS.2579. Notes and drafts for his lectures on Chemistry at University College, London 15411. London 1838-1848. The notes referred to here were probably written in 1838 or 1840.

33. Graham, *ibid.*

Although the above opinion was, according to Hope, 'sufficiently probable', it could only be considered as an ingenious hypothesis. At this stage in his notes Hope wrote the name 'Boscovich' in pencil. From the writing it seems to be a late addition and presumably he intended to mention Boscovich's theory at this juncture. Thomson also wrote of primary matter and as we shall see the notion of primary matter or the atoms of Newton was to be an important component in Graham's speculations on the nature of matter. Indeed Graham said in his University College lectures that: "the ultimate composition of bodies, the materials of which bodies are composed, form the objects of chemical science."³²

Both Thomson and Hope supported a material theory of heat. They gave a detailed account of heat in their chemistry lectures and devoted a lot of attention to the phenomenon of latent heat which had been identified by their mentor, Black. It is therefore not surprising to find Graham defending the material theory of heat in his early writings. Likewise, he emphasised the important role of latent heat in changes of state.

In his chemistry lectures Graham insisted that chemistry and natural philosophy although closely allied should be distinguished from one another because their objects were different. He explained that the chemical changes which formed part of the study of chemistry always altered the nature of the bodies involved or destroyed their individuality. Indeed the essence of changes in chemistry was the loss of identity by substances. Such changes included, according to Graham, the phenomena: of solution, of combination, decomposition, and of chemical affinity in general. On the contrary, attractions and repulsions among masses of matter; the phenomena of motion; and elasticity; pressure etc. resulting from mechanical forces were physical and not chemical phenomena because they were all transitory changes which did not imply any permanent changes in the constitution of bodies. Graham concluded that the essential distinction between physical and chemical phenomena was whether the changes produced, deeply affected the nature of the bodies involved.³³

34. John Herschel, A Preliminary Discourse on the Study of Natural Philosophy (The Cabinet Cyclopaedia London, 1830) pp 299-300. Herschel wrote that the theories of chemistry are "for the most part, of that generally intelligible and readily applicable kind, which demand no intense concentration of thought [Graham did not accept this latter point], and lead to no profound mathematical researches. The simple process of inductive generalisation, grounded on the examination of numerous facts....has sufficed.... to lead, by a clear and direct road, to its highest laws yet known."
35. Graham, op.cit. (33)
36. H. Davy, 'On the electrical phenomena exhibited in vacuo' read December 20th 1821. Phil.Trans. 112 (1822) 64-75 or Davy's Collected Works. 6 (1839-40) 245-256, see p 245.
37. Graham, Wellcome MSS. 2551. op.cit. (8).
38. Robert Hare, 'An essay on the question, whether there be two electrical fluids according to Du Faye, or one according to Franklin,' Phil.Mag. 1 Ser. 62 (July 1823)1-9.

On the theories of chemistry, Graham seems to have echoed the words of Sir John Herschel.³⁴ In his University College lecture notes, Graham wrote that "Chemistry is a completely experimental science and its theories are generally intelligible and of a readily applicable kind involving no abstruse mathematical consideration and [yet] surely demanding intense concentration of thought for their full comprehension."³⁵ It would seem that Graham's view of chemistry was more closely related to that put forward by Hope.

Let us now examine Graham's early research work. These researches were concerned with the fundamental problems of the nature of heat and electricity, and with changes of state particularly those concerned with liquids.

In 1822, Humphry Davy had asked the fundamental questions about heat and electricity when he wrote: "is electricity a subtle elastic fluid? - or are electrical effects merely the exhibition of attractive powers of particles of bodies? Are heat and light elements of electricity, or merely the effects of its action?"³⁶ It appears that Graham's attention was particularly drawn to the problem of the nature of electricity as a result of the offer of a prize by Glasgow University for the best essay on the question: 'Whether is the theory of electricity of Dr. Franklin or that of Dufay the more probable?'³⁷ This title was probably taken from a similar one used by Robert Hare in 1823.³⁸

Amongst the Wellcome manuscripts there is a set of notes on this question written by Graham probably in 1825. He began his notes by describing the phenomenon of the attraction of bits of paper for a rubbed glass tube or a piece of amber. A new property was undoubtedly developed upon these bodies by friction: this was electricity. He described the familiar observation of the appearance of bluish sparks when a glass tube was rubbed with silk in a darkened room. In addition, he mentioned the tickling sensation, and peculiar smell produced, when this glass tube was brought near to the face. Then, surprisingly, he wrote "such are the

39. Graham, Wellcome MSS. 2551. op.cit. (8).

fundamental phenomena of electricity. What is the nature of the principle which produces all the phenomena? How does it exist in bodies? In what manner is its action induced by friction are questions to which we can give no answer." ³⁹ However, in the following year, 1826, Graham was able to put forward a possible solution to these questions based on material caloric.

Before examining Graham's explanation of static electricity it will be useful to try and understand the nature of the problem and to see what opinions were held by his teachers and contemporaries on the nature of electricity. Two theories of electricity had been proposed in the eighteenth century. Firstly, in 1733, du Fay had introduced a two-fluid theory of electricity. He had observed that two electricities could be generated by rubbing together two bodies; the one electric fluid was resinous or like amber, and the other was vitreous or like glass. When two bodies had been charged with the same electricity they were found to repel one another. But if one body was charged with vitreous electricity and the other with resinous electricity then the two bodies were seen to be mutually attractive. Secondly, an alternative one-fluid theory of electricity was favoured, particularly by Benjamin Franklin. He assumed that only one electric fluid existed. Although the particles of this fluid were themselves self-repulsive they were attracted to particles of matter. This electric fluid existed in all matter and friction simply altered its distribution in bodies. An excess or surplus of electric fluid was called positive or plus electricity. This was analogous to vitreous electricity. A deficit of electricity was described as minus or negative electricity and was analogous to resinous electricity. Therefore, on the one electric fluid theory, Franklin ascribed attraction and repulsion simply to a surplus or deficit of one fluid rather than to two different fluids.

Thomas Thomson appears to have vacillated in his views on electricity. In 1815 he gave his comments on Davy's view of chemical affinity. Davy,

- 39a. T. Thomson, 'Sketch of the latest improvements in the physical sciences' Ann.Phil. 5 (1815) 3-4.
40. T. Thomson, 'Remarks on the phenomena of galvanism,' Ann.Phil. 5 (1815) 431-439.
41. T. Thomson, System of Chemistry 1 (5th edn. London, 1817) pp 168-169:-
"The electric fluid, then, supposing it to exist is imponderable. Dufay's original opinion that there exist two kinds of electric fluids, the vitreous and resinous seems to me to correspond better with all the phenomena, and to lead to fewer perplexing consequences than the theory afterwards substituted for it by Dr. Franklin....the recent discoveries made with the Voltaic pile seem to me to agree better with the theory of Dufay than with that of Franklin".
See also T. Thomson, An Outline of the Sciences of Heat and Electricity (London, 1830) pp 530-531 and also see T. Thomson, System of Chemistry 3 (5th edn. London, 1817) pp 19-20 for an attack on the electrical theories of affinity of Davy and Berzelius and an argument in favour of the two-fluid theory of electricity with a possible analogy existing between caloric and electricity.
42. T. Thomson, System of Chemistry 1 (5th edn. London, 1817) pp 155-160.

like Volta, had argued that the affinity between two bodies was caused by electrical differences; one body being electrically positive and the other negative. Thomson wrote: "if it [Davy's view of affinity] be correct, I conceive that the theory of electricity which at present prevails, will not be able to stand its ground. If negative and positive electricity be qualities inherent in bodies, and continuing in them after they unite together, I cannot for my part conceive the one to consist in a deficiency of electric matter, and the other in an excess of it. Neither can I conceive with M. Dufay, the Abbé Häuy, and some other French electricians, that negative electricity consists in one fluid and positive electricity in another, which have an attraction for each other and neutralize each other when they come in contact. But I can conceive negative and positive electricity to be two attractions inherent in different bodies, which make them unite with each other and keep them united."^{39a} And yet, later in 1815, we find Thomson proposing an entirely different view. After considering the effects of galvanism he gave, as a probable explanation of galvanism, a two-fluid theory of electric or galvanic fluids. He believed that it would be difficult to explain both the observed transfer of alkali to the negative pole and of acid to the positive pole⁴⁰ without a two-fluid theory of electricity.

He suggested that two galvanic fluids were generated by the action of a voltaic battery. Both fluids consisted of a large portion of caloric joined to a particular base. The positive fluid contained a base which possessed an oxygen nature and the negative fluid contained a base with a hydrogen character. This conjecture that electricity consisted of two fluids largely made up of caloric was not discussed again by Thomson, but he did retain a preference in his later writings for a two-fluid theory of electricity.⁴¹ In 1817 he again referred to electricity in his discussion of the caloric produced by friction.⁴² This discussion probably influenced Graham's own speculations on static electricity which appear to be an extension of Thomson's own conjectures.

43. Thomson, *ibid.* p 160.

44. Robert Hare, 'A new theory of galvanism supported by some experiments and observations made by means of the calorimeter, a new galvanic instrument,' Phil.Mag. 1 Ser 54 (1819) 206-215.

45. John Leslie, 'Observations on electrical theories,' Edin.Phil.J. 11 (1824) 393-401.

Thomson stated that the caloric generated by friction was not caused by compression. Likewise, it was not due to changes in specific heat or to possible decompositions of oxygen or air. Indeed, he admitted that no satisfactory explanation had been given of the heat produced by friction. He was however quite certain that Rumford was incorrect when he rejected material caloric and replaced it by a peculiar kind of motion in his account of frictional heat. Instead Thomson argued that there was a fundamental analogy between caloric and electricity. Both of these imponderable substances diffused themselves equally; they also expanded bodies; melted metals; and kindled combustible bodies. Now electricity was very often concerned in the heating of bodies and therefore it might well be involved in the generation of the heat produced by friction. He then speculated: "supposing that electricity is actually a substance, and taking it for granted that it is different from caloric, does it not in all probability contain caloric as well as all other bodies? Has it not a tendency to accumulate in all bodies by friction, whether conductors or non-conductors? May it not part with some of its caloric to these bodies, and may not this be the source of the caloric which appears during friction?" ⁴³

In 1819, in a somewhat similar vein, Robert Hare had argued that the galvanic fluid was simply a combination of caloric and electricity. ⁴⁴ However, unlike Thomson, Hare preferred a single Franklinian fluid.

A complete rejection of all fluid theories was urged by John Leslie in his paper on electricity which was belatedly published in 1824. In this paper, originally written in 1791, ⁴⁵ Leslie also developed the analogy between heat and electricity. He explained the transfer of 'electric virtue' to the air, by analogy with heat, as a convection process. Likewise he described the passage of electricity through solids as a transfer of electricity from a region of high to low electrification. This was analogous to the flow of heat down a temperature gradient.

46. John Leslie, 'Observations on electrical theories,'
Edin. Phil. J. 11 (1824) 393-401.

47. Graham, op. cit. (8), had copied out pages 567 to 582
from: John Murray, System of Chemistry 2nd edn. vol. 1
(Edinburgh, 1809). T.C. Hope commented about Du Fay's two
fluid theory in his lecture notes:- "This hypothesis has
many supporters of much note. [The] hypothesis of Dr.
Franklin is a more simple one. Electricians at present
seem equally divided between Du Fay and Franklin; the
Franklinian terms are however most used in Britain."
Hope MSS. 269 packet 49.

The writings of John Murray, the Edinburgh extra-mural lecturer in Chemistry, also appear to have had an important influence on Graham's views about the connection between electricity and caloric. This is evident from an examination of Graham's notes of 1825. After the short introduction Graham continued with a discussion of galvanism. This was simply copied directly from Volume 1 of Murray's System of Chemistry (Edinburgh, 1809).⁴⁶ In his textbook Murray stated that galvanic and electric fluids were probably identical. He preferred the one-fluid theory of electricity because of its greater simplicity. Concerning galvanism, he believed that Volta's 'contact theory' provided an essentially-correct explanation of the phenomena, although he admitted that chemical action seemed to play a subordinate role in galvanism. Volta had stated that when two metals were placed in direct contact with one another the electric equilibrium was disturbed. This gave rise to two different electrical states in which one metal became positive and the other negative. Alternatively, other chemists had argued that electricity was produced by the chemical action of air, or of a liquid on zinc; this was called the 'chemical theory.' Murray also pointed out the similarity between the effects of galvanism and caloric. He wrote that galvanism "has an intimate relation with caloric, or is capable of producing in high intensity the phenomena of heat."⁴⁷ Again, when he discussed the excitement of electricity by friction, Murray wrote: "we conceive the phenomena to be produced nearly in the mode which I have supposed with respect to the generation of caloric. By the vibrations excited by friction in the electric body, the peculiar fluid which gives rise to the phenomena of electricity is forced out, doubtless by the particles being approximated by the vibration. Now the phenomena of electricity show that the fluid thus forced out is not all reabsorbed in the corresponding retrocession of the particles, but that it forms an atmosphere round the electric body, or is carried off by others, while a new portion is received from the matter immediately in

48. Murray, *ibid.* pp 424-425. Murray repeated this argument in the 1817 edition of his System; see Volume 1 p 183.

49. Graham, 'On the heat of friction,' Ann.Phil. 12 (October 1826) 260-262 or Researches pp 626-629.

Note:- For convenience the book

Thomas Graham, Chemical and Physical Researches (Edinburgh, 1876), with a preface and analytical contents by Robert Angus Smith, is referred to as Researches throughout my thesis.

50. Graham, *ibid.*, Researches p 628. He continued: "that heat, possessed of a substantial existence, should be found alone, uncombined with matter, and this combination, of a most elementary kind, should, at all times, be brought about by the calorific principle, impinging with force upon the material body, are not hard postulates."

contact with the electric substance, and in this manner from the earth itself. Thus a perpetual evolution of electricity is kept up. Caloric may follow the same law." ⁴⁸

In October 1826 Graham published what he considered to be an important speculative paper on the heat of friction. ⁴⁹ Undoubtedly ambitious, he wanted to establish a scientific reputation. His resolve at the age of twenty was probably strengthened by his father's opposition to his chosen career of Chemistry. Graham introduced the novel idea that caloric might exist uncombined with matter and without any motive power. He called this form of caloric, 'superficial heat', and stated that it was the electric fluid. Like Murray, he preferred a one-fluid or Franklinian theory of static electricity. As we have seen, Thomson, Hare, Leslie and Murray either recognised analogies between heat and electricity or regarded caloric as a component of electricity. However, they did not make the bold assertion that the electric fluid could be identified with superficial heat. It would seem that Graham was developing the hints thrown out by Thomson and extending them along the lines suggested by Murray.

Graham explained that superficial heat contained particles which powerfully repelled one another. These particles were spread over the surfaces of all bodies because they were attracted to matter without actually combining with it. To convert superficial heat into detectable sensible heat it was only necessary to project superficial heat with sufficient velocity. This could be achieved by rubbing together two surfaces to produce a very close contact. The self-repulsive particles of superficial heat were then forced close to one another producing thereby a powerful force of repulsion which expelled some of these particles as radiant heat. The superficial heat which escaped was replenished by a new supply from the earth. He wrote that "the simplicity of this theory is its chief recommendation." ⁵⁰ He argued that it was not a hard postulate to accept that heat, possessing a substantial existence,

51. Graham, *ibid.* Researches p 628.

52. Graham, 'Galvanism and organic action,' MS. Essays of Glasgow Medical Society (unpublished) Volume 19 (1831-2). This essay was written out by Graham; it is eight pages long (being fifteen sides in all). It is kept in the Library of the Faculty of Physicians and Surgeons of Glasgow.

52a. Graham, *ibid.* p 1.

should be found alone, uncombined with matter. He continued by saying that "most material substances, however strong their affinities for each other, require peculiarly favourable circumstances to enable these affinities to act, otherwise the bodies appear to a certain extent repulsive of each other. Moreover, when we attribute to the matter of heat diffused over the surface of bodies, an attraction for these substances which yet does not amount to the production of combination we are but extending to heat properties which all other material substances evince, in adhesion, capillary attraction etc." ⁵¹

Although Graham expressed his intention of applying the theory of superficial heat to galvanism, he did not do so, presumably because there was insufficient response to his initial theory. Graham did, however, read an essay on galvanism and organic action to the Glasgow Medical Society in 1832 and a manuscript of this essay still exists.⁵² In this essay Graham does not mention his earlier work on the production of electricity by friction except to add a passing allusion to it. He wrote that the frictional electricity produced by electrical machine depended upon "the configuration of their (rubbing) surfaces and other accidental properties, which are little understood, but known to be wholly unconnected with the chemical composition of the touching bodies."^{52a}

Graham commenced his 1832 essay by supposing that a substantial principle existed called 'electricity', whose properties varied in some essential features according to its source. He restricted himself to a discussion of galvanic electricity saying that there were two possible sources of galvanism. Either galvanism was produced by contact between different metals or by chemical reactions involving one of the two different metals. Thus, Graham used both of the prevailing theories which had been proposed to explain galvanism. Volta had argued that when two different metals were brought together, then, mere contact induced them to assume different electrical states. Thus zinc became positive and copper became negative on contact. This was the 'contact

53. W. H. Wollaston, 'Experiments on the chemical production and agency of electricity' Phil.Mag. 1 Ser 11 (1801) 206-211.

54. Graham, op.cit. (52) p 1.

55. Graham, op.cit. (52) p 2.

theory of galvanism.' In the voltaic pile the liquid between the plates simply acted as a conductor of the influence of this contact phenomenon. On the contrary, Ritter, Wollaston, and others, had argued that the development of galvanic electricity was the result of a chemical attack on the more reactive metal. In this 'chemical theory of galvanism', Wollaston maintained that the origin of galvanism in a voltaic pile, consisting of zinc and copper plates, was the oxidation of the zinc plate.⁵³

The first example of galvanism which Graham discussed was that arising from the contact of two different bodies unaccompanied by any chemical change. He wrote "thus, on the theory of two opposite fluids of electricity which neutralise each other when combined and exhibit the appearance of electricity when separated, when zinc and copper are brought into contact, positive or vitreous electricity is evolved on the surface of the first of these metals, and negative or resinous electricity on the other in a corresponding measure."⁵⁴ He added that metals were not alone in possessing electricity because Davy had shown previously that dry acids and alkalis released different electricities when they were thrown on to a copper plate. Indeed, Graham explained that "different metals and chemical bodies are believed to possess an excess of one or other of the two species of electricity, which is natural to them and inseparable. This assumption affords a consistent explanation of the chemical affinities and attractions, subsisting between those bodies which are most strikingly positively electrical, and those which are most strikingly negatively electrical on contact."⁵⁵ Here Graham appears to be following the views of Berzelius on the electrical polarities of atoms in which there was an excess of one of the two electricities in a given atom.

Graham then gave an example of an arrangement for developing this galvanism by contact. It was the dry pile of De Luc in which dry paste-board separated pairs of different metallic plates. The electricity from

56. Graham, op.cit. (52) p 3.

contact could be accumulated by using a series of touching pairs of plates in which the positive and negative electricity moved in opposite directions. Although some experimenters had explained the operation of this pile by the chemical action of moisture Graham believed that the action of moisture had not yet been confirmed. In support of this view he mentioned that Berzelius had not found any tarnishing of the more easily-oxidisable plates over a number of years. The electricity, evolved from such a dry pile, affected the nerves and muscles producing electric shocks, but Graham insisted that, in contrast to ordinary galvanic electricity, the electricity from a dry pile was incapable of producing any chemical action.

Graham considered that there was one important principle to be recognised clearly. It was that electricity capable of producing chemical changes must itself be produced by chemical action. He supposed that the chemical action, which produced electricity in a galvanic apparatus, was generally oxidation. He then gave as an example of a means of making electricity by chemical action: a pile with zinc and copper plates dipping in a dilute acid. He pointed out that two circumstances were essential for the efficiency of this pile. They were: "that the electrical fluid should be disengaged, and that it be confined and carried forward in one direction, so as to be concentrated at the end of the apparatus. The first object is fulfilled by the oxidation of the zinc, the second is effected by the attraction of the next copper plate for electricity. The hydrogen and positive electricity both go to the surface of this plate, but here they separate; the hydrogen being disengaged in the state of gas, and the electricity conveyed onwards to the next zinc plate. Here, being in some degree accumulated, it is extricated in larger quantity, and in a more concentrated quantity, than before." ⁵⁶ By a succession of these events in a series of plates, the electric fluid could be produced at the zinc end of the pile in any assignable degree of force. This galvanism from chemical action was capable of producing

57. John Bostock, 'Theory of the action of the galvanic apparatus' Nicholson's Journal NS 3 (1802) pp 9-13. See also Bostock, 'Remarks on the hypothesis of galvanism.' Ann.Phil. 3 (1814) 32-42, 85-92.
58. It is perhaps possible to assume that Graham used the term 'positive electricity' in the Franklinian sense of a surplus of electric fluid which would mean that he might have been using a one-fluid theory of electricity here. It is not easy to decide which view is correct.
59. T. Thomson, 'On digestion' Glasgow Medical J. 2 (May 1829) 113-119. Thomson advocated the use of galvanism as a treatment for cholera patients in 1832. He was impressed by Wilson Philip's experiment in which the ends of the nerves to the stomach were cut so that respiration and digestion were impeded but they were restored again by using galvanic electricity passed through the severed nerves. See, Thomson, 'Chemical analysis of the blood of cholera patients,' Phil.Mag. 2 Ser 11 (1832) 347-358, particularly pp 357-8.
60. W. Prout, 'On the nature of the acid and saline matters usually existing in the stomachs of animals,' read December 11th 1823. Phil.Trans. 114 (1824) 45-49.
61. W. Prout, Bridgewater Treatise 7, Chemistry, Meteorology and the Function of Digestion, 1st.edn. (London, 1834) pp 496-497.

chemical decompositions although it often possessed little power to produce electric shocks. The force of decomposition was in proportion to the quantity of electricity which had been accumulated from a succession of pairs of plates.

Graham's chemical theory of galvanism for the ordinary voltaic pile resembled that which had been proposed by John Bostock in 1802.⁵⁷ The only difference being that Bostock had assumed the existence of an electric fluid travelling with the hydrogen whereas Graham specifically states that 'positive' electricity moves with the hydrogen. Essentially both these chemical theories involved the movement of one electric fluid, but Graham appears to have agreed with Thomson in favouring a two-fluid theory of electricity.⁵⁸

Having discussed galvanism produced both by contact and chemical action, Graham turned^{to} the organic action produced by galvanic actions inside the living body. In 1829 Thomas Thomson had argued that the nerves of the stomach acted, in the same way as a galvanic current did, by decomposing common salt in the stomach to produce hydrochloric acid and soda.⁵⁹ The weak solution of hydrochloric acid, which was formed, acted as a solvent on the food converting it into chyme. He was less certain about what happened to the soda but he did note that soda was present in blood, bile and most secretions with the exception of urine. He therefore supposed that the soda in these secretions probably came from the galvanic decomposition of salt. Prout extended this view in 1834. As early as 1823, Prout had discovered that hydrochloric acid was present in the stomach and this observation had been confirmed in 1826 by Tiedemann and Gmelin.⁶⁰ In 1834 Prout assumed that the mucous membrane of the stomach, or of the intestinal canal generally, was the positive pole of a kind of galvanic apparatus with the liver being the negative pole.⁶¹ He then explained that galvanic decomposition of salt gave hydrochloric acid in the stomach and soda in the bile and blood. Thus Prout was extending Thomson's earlier theory of the role of salt in digestion.

62. W. Prout, 'Inquiry into the origins and properties of blood,' Ann.Med. and Surg. 1 (1816) p 156. I have taken this reference from W. H. Brock, Ph.D. Thesis: 'The Chemical Career of William Prout' Leicester University (1966) p 157. See also W. Prout, 'On the phenomena of sanguinification, and on the blood in general', Ann.Phil. 13 (1819) 12-25, 265-279.

63. Graham, op.cit. (52) p 5.

64. Graham, op.cit. (52) p 4.

Galvanism had been discussed previously by Prout when he discussed respiration. He believed that respiration converted chyle into blood. This was achieved by removing unwanted carbon by its oxidation into carbon dioxide in the lungs. Indeed he supposed that respiration activated the electrical powers of an organism. He expressed this view in 1816 when he wrote "we may even go so far as to suppose that the colouring principle represents the most oxydisable metal, in the galvanic battery and that the carbonic acid represents the metallic oxide formed during its action." ⁶² In a similar way we find Graham introducing galvanism into a living organism via respiration. He wrote that "we know so little of animal electricity, as to be unable to point out a proper organ or apparatus in the animal economy for its direction; it is in our power to instance a preliminary oxidation which might produce it. I refer to the grand function of respiration. The blood or its particles may acquire electricity at the same time that it is oxygenated; an acquisition on which the vitality of the blood may depend." ⁶³

Graham agreed with Thomson that common salt was decomposed by galvanism. No chemical action could decompose a stable compound like salt into hydrochloric acid and soda, but galvanism was able to bring about this decomposition. On the other hand, a chemical decomposition would necessarily produce a combination with either the soda or the hydrochloric acid instead of giving two free compounds. Graham believed that soda was retained in the blood but he did not think that digestion of food was solely due to the solvent power of 'acetic and muriatic acids.' Thus he concluded: "we may suppose that the food is in a great measure decomposed by the same galvanic action, to which the muriate of soda itself yields. If digestion were merely the solution of the food there would be no reason for the action being confined so strictly to the surface of the stomach as we find to be the case." ⁶⁴

When Faraday identified the different forms of electricity in 1833 and denied the existence of electric fluids, Graham was forced to make a

65. Davy wrote that "heat....may be defined as a peculiar motion, probably a vibration, of the corpuscles of bodies tending to separate them. It may with propriety be called the repulsive motion." H. Davy, Collected Works. Vol. 2 (1839) p 14. This quotation is taken from 'An essay on heat, light and the combinations of light', written by Davy in 1799. The well-known experiment of rubbing blocks of ice together in a vacuum appears in this essay on pp 11-12. Here Davy denied that caloric existed as such and claimed that heat was motion. Similarly Rumford believed that heat was motion; it was caused by the vibrations of an ether which pervaded all space and matter. This wave theory of heat involved interactions between the vibrations of particles and those of the ether. See Davy, Collected Works. (1839) Vol.2 p 390 for an account of Rumford's theory and also:- S. J. Goldfarb, 'Rumford's theory of heat - a reassessment,' B.J.H.S. 10 (1977) 25-36. Rumford had noticed the large amount of heat released during the boring of a cannon and regarded this heat to be motion.
66. Graham, 'On the heat of friction ' Ann.Phil. 12 (October 1826) 260-262 or Researches pp 626-629 see page 626. This paper is dated September 7th 1826.

radical revision of his theories of the voltaic pile. This change in his opinions had definitely occurred, as we shall see, by 1839.

For Graham, as for his teachers Thomson and Hope, the material theory of heat or caloric derived from Joseph Black's teaching was much more convincing than the alternative vibratory theories of heat put forward by Davy and Rumford. Davy thought that heat was the motion of vibration or rotation of particles, whereas Rumford believed that heat was produced by the vibration of particles which in turn caused an elastic ether to undulate or vibrate. Both Davy and Rumford denied the existence of material caloric and in support of their view they cited the phenomenon of the heat of friction.⁶⁵

Like Thomson, Graham admitted that it was generally believed that the heat released in friction was inexplicable upon the material theory of heat. Graham wanted to defend the material or caloric theory which he claimed, was "involved in the principal doctrines of chemistry, while the simplicity and easy application of the theory render its establishment exceedingly desirable."⁶⁶ By the introduction of the concept of superficial heat he believed that he could explain both the production of heat in friction and the electric fluid.

To obtain a clear understanding of Graham's views concerning caloric, in 1826, it is important to examine his detailed discussion of heat. He wrote that: "heat is observed by us, either radiant in motion, and possessed of great velocity; or in union with matter, and capable of regaining this velocity. Probably this velocity is necessary to its entering into bodies and uniting with them; at least we never observe heat do so without it. For, when communicated by radiation, this is evident; and in conduction, which in close contact supplies the place of radiation, it is evident that heat is communicated with a force. Indeed conduction may be reduced with considerable plausibility to an internal radiation. It appears that this motive power, which is essential to the communication of heat and our perception of it, is really never annihilated. It

67. Graham, 'On the heat of friction,' Researches pp 626-627.

68. T. Thomson, A System of Chemistry, Vol. 1 (Edinburgh, 1810)
4th edn. p 457.

disappears when heat passes into a body, but it is merely overpowered for a time, and not altogether lost; for upon reduction of temperature, the heat emanates from the body, evincing its pristine velocity. We may compare the heat in union with matter to that of a bent spring, or a compressed elastic substance, the attraction of the matter for heat being the restraining force. Sensible heat, therefore, we never find destitute of this motive power, nor to lose it - at least heat is never so divested of it as to be incapable of resuming it." ⁶⁷

Therefore Graham accepted that heat in motion could be absorbed by forming a definite union with matter. The motion of this heat was not entirely lost, it was only restrained. He did not describe what kind of motion was retained by caloric particles when they were joined to matter. But it seems evident that some degree of motion was still retained in this caloric-matter complex. However it is important to distinguish this caloric in motion, about the particles of matter, from the Davy-Rumford vibrational theories which denied the existence of material caloric.

The views which Graham expressed on caloric were innovatory but their origins can be recognised in part in the works of Thomson and Leslie. Thomson believed that hot bodies like the sun emitted rays of caloric which differed from light rays. Solid particles could absorb caloric because there was an affinity between caloric and matter which led to the formation of a matter-caloric compound. The affinity of this combination acted as a restraint on the passage of heat through conductors. ⁶⁸ On the contrary, Leslie regarded heat as a combination between particles of light and matter. The light particles held by matter tended to cause expansion due to the force of repulsion operating between the neighbouring light particles. If the attractive powers of matter for light were exactly equal to the repulsive powers between the light particles then a body would be able to absorb any quantity of heat in the form of light. But Leslie recognised that: "after a certain accumulation of heat, the balance is destroyed; and as nature admits only gentle transitions, we

69. J. Leslie, 'On heat and climate' Ann.Phil. 14 (1819) pp 11-12.
70. Richard Olson, 'The reception of Boscovich's ideas in Scotland', Isis 60 (1969) 91-105, see pp 101-102.
71. M. D. Swords, Ph.D. Thesis 'The chemical philosophy of Thomas Graham,' Case Western Reserve University (1973) pp 40-47.
72. Just before this time there were a number of unexplained examples of particulate motion. In 1827 Robert Brown had observed the random motion of burst pollen grains and in 1829 he extended these observations to include the random motions of small particles of inorganic matter. Graham's friend David Brewster in 1829 reviewed this work and wrote, "why should not the molecules of the hardest solids have their orbits, their centres of attraction and the same varied movements which are observed in planets and nebulous matter like in microscopic molecules?" Brewster: 'Observations on the motions of molecules of bodies' Edin.J.Sci. 10 (1829) 216-219, see p 219.

may reasonably conclude, that the attractive power increases regularly at a slower rate than the repulsive. The attraction of the particles of matter to each other, which is the third force necessary to the general quiescence, appears, in all ordinary cases, to be exactly proportional to the quantity of dilatation."⁶⁹ Olson has recently given an ingenious interpretation of Leslie's treatment of expansion in terms of Boscovich's theory of point atoms and force curves.⁷⁰ Whether Graham or Thomson conceived matter-caloric combinations in these terms is uncertain from the available evidence.

In his recent Ph.D. thesis Michael Swords has argued that, in 1826, Graham probably envisaged an atom as a material core surrounded by caloric particles.⁷¹ The caloric particles were invested with an inalienable primordial motion and they moved about the core somehow inexplicably attracted to the core. The core itself also possessed a primordial inalienable motion which attracted other matter to itself. The motion of the core differed quantitatively for each element and determined the most basic properties of the element. This view is founded on an extrapolation backwards from Graham's mature speculations of 1863. Swords has assumed that Graham's vision was essentially unchanged by the introduction of the kinetic theory of gases and the motion theory of heat. Unfortunately there is no clear evidence to decide on the validity of these assumptions. Graham said nothing in 1826, on the identity of all matter when at rest, or on the motion of atomic cores. He did, however, hint at the possibility of caloric particles possessing motion when they were in union with matter, therefore I think that Swords' reconstruction of Graham's view of caloric is probably correct. But I think it is more likely that Graham's belief in the inalienable motion of atomic cores which distinguished all the elements made up of the same primary matter would be more likely to date from about 1830 when Graham possessed the results from his researches on gaseous diffusion.⁷² In 1830 Graham admitted the inadequacy of the prevailing theories of diffusion but he

73. Graham, 'On the law of the diffusion of gases,' (December 1831) Researches pp 44-70. "...diffusion takes place between the ultimate particles of gases, and not between sensible masses, and therefore diffusion cannot be an accident." p 68

The law of diffusion of gases was stated thus: "The diffusion or spontaneous intermixture of two gases in contact is effected by an interchange in position of indefinitely minute volumes of the gases, which volumes are not necessarily of equal magnitude, being in the case of each gas, inversely proportional to the square root of the density of that gas." p 44

and he concluded: "The law at which we have arrived is certainly not provided for in the corpuscular philosophy of the day, and is altogether so extraordinary that I may be excused for not speculating further upon its cause, till its various bearings, and certain collateral subjects be fully investigated." p 69.

74. Graham, Wellcome MS. 2579 'Notes and drafts for his lectures on Chemistry at University College, London.' Author's Holograph MS. 154 ll. London (1838-1848). These notes seem to date from 1838 in this case.

75. F. J. Furnivall, Manuscript Notebooks of Thomas Graham's Lectures on Chemistry at University College, London. The notebooks are kept in the London Collection at King's College, London.
Lecture 17 October 26th 1841.

"Heat or caloric is very different from our ordinary conceptions of matter. It has been presumed that it is not material and this theory is supported first by its never being found alone and second by its adding nothing to the weight of matter. Notwithstanding this, the material theory of heat is more generally adopted and is more convenient and has brought to view latent heat and several other of its properties. All the facts connected with the theory of heat suggest the idea of its being substantial. In the science of chemistry convenience is looked for rather than absolute truth and it is therefore more liable to change than other parts of physics. Chemists are obliged to form theories on very slight grounds and can state all the effects, though the theory is not exactly true. The material theory of heat not only explains its results but also brings to light new facts and for this reason is still adopted and supported by chemists though it is not physically true. The mechanical properties of heat and light are referred to the undulatory theory which is borrowed from that of sound."

avoided any attempt to commit himself to any speculative explanation. He admitted only that diffusion was a process which took place between ultimate particles and that it was subject to a fixed law.⁷³ He recognised that for each gas there was a different and unalterable diffusive motion at constant temperature. This would seem to be an appropriate time for him to speculate on quantitatively different motions of atomic cores for each element but here, again, regrettably, we lack conclusive documentary evidence.

The attitude of Graham to caloric as a material substance is in the tradition of Joseph Black and of his Scottish descendants who taught Graham: Thomson and Hope. The explanation of electricity as superficial heat extended an analogy between caloric and electricity which had been previously suggested by Scottish chemists. Graham's concept of heat as material caloric became gradually modified as more was learned about heat until he definitely adopted a view of heat as motion. His decreasing confidence in the real existence of material caloric can be seen from an examination of his University College lecture notes.

In 1838 he wrote an apologia for the acceptance of material caloric: "Owing to the rapid advance [in Chemistry, more] than in any other branch of Science - [such a] rapid advancement enlarging our views - we think less of the absolute truth of theories than of the assistance they give in leading to new discoveries. The scaffolding of Science is only valuable in erecting the fabric - the means and not the end. I maintain that the material theory has been a most useful one. It has led to many useful results and is likely to lead to more. While other theories which would refer heat to vibrations of particles or some form of motion have proved barren hypotheses in the hands of chemists and have led to nothing."⁷⁴ By 1841 Graham said that "the material theory of heat is still adopted and supported by chemists though perhaps it is not physically true."⁷⁵ These comments show that Graham regarded a theory as only a useful guide to experiment. A theory could be used to help

76. Graham, op.cit. (74).

77. Graham, op.cit. (74) "Grand objection to material theory. One of the sources, the production of heat by the friction of bodies Rumford..., Davy..., Haldat.... Repulsive property." Furnivall op.cit. (75) noted that Graham said in his lecture of October 27th 1841 that "The production of heat by friction is a difficulty which cannot be got over by the material theory of heat. When two pieces of wood are rubbed together heat is produced, where does the heat come from? If heat is immaterial it is possible that this phenomenon may be accounted for, but if heat be material, it is impossible. The undulatory theory of heat is still more defective than that of light, which may perhaps arise from chemists not using it but only the material theory."

78. A. Haldat, 'Inquiries concerning the heat produced by friction,' Nicholson's J. N.S. 26 (1810) 30-39.

discover new experimental facts which might eventually lead to experimental laws. It is probably for this reason that he rarely gave details of the tentative theories which led to his experiments. Thus, in print, he would speculate on experiments rather than present tests of preconceived theories.

Having admitted his belief that the material theory of heat was the most suitable one for explaining "all the phenomena of the accumulation of heat with which chemists were concerned"⁷⁶ he did admit in his 1838 lecture notes that mechanical phenomena such as radiant heat could be equally well explained by an undulatory theory of heat. A hot radiant body could originate undulations in an ether which would spread out like waves analogous to those produced by sound. The analogy between radiant heat and the wave theory of light was, however, less perfect because heat waves could be degraded from high to low intensity. This change would be comparable to an alteration of the wavelength, or colour, of light which did not occur. An even more difficult problem for the wave theory of heat was the conversion of heat from low intensity to high intensity. This occurred in two phenomena: the rapid compression of air or steam, which resulted in a marked rise in temperature, and the phenomena of friction. Therefore Graham concluded that the undulatory theory of heat was even more defective than the undulatory theory of light and so chemists only used the latter.

In his 1838 lecture notes Graham stated a number of objections to the material theory of heat.⁷⁷ There was the problem of the heat of friction. This had been pointed out by Rumford, Davy and Haldat.⁷⁸ In friction, heat of low intensity was converted into heat of high intensity. Interestingly Graham did not refer here, or in his textbook, to his earlier speculations of 1826 on this subject. The other difficulty encountered with the material theory was the repulsive property of heat. This repulsive property had been inferred to exist from a number of experiments. Saigey had found that when he finely suspended a needle of lead from a heated copper bar the number of oscillations of the needle could be varied.

79. J. F. Saigey, 'On some unusual phenomena,' Qu.J.Sci. N.S. 2 (1827) 455-456.
80. Baden-Powell, 'On the repulsive power of heat,' Phil.Trans. 124 (1834) 485-488.
81. Graham, Wellcome MSS. 'Miscellaneous notes and oddments on chemistry' etc. Graham's holograph MSS. No.2580. Unbound in pamphlet case. Item (6) 'On liquid condition of matter.'
82. Letter from Graham to Thomas Andrews, Nov. 25th 1856, Andrews' Papers, Queen's University, Belfast.
83. Graham, 'On the absorption of gases by liquids,' Ann.Phil. 12 (July 1826) 69-74, Researches 1-6.

As the needle was moved away from the hot copper bar there were fewer oscillations per second. He attributed this to the repulsive power of heat which was most noticeable near to the copper bar.⁷⁹ Likewise, Baden-Powell had pressed two slightly-curved glass discs together and observed colours like oil on water. On heating, these colours descended in the scale and vanished. Baden-Powell assumed that this was evidence for the repulsive power of heat causing a slight separation of the glass discs.⁸⁰

By the 1850's, when Graham was studying liquid diffusion and osmosis, he had become converted to the opinion that heat was motion. This is evident from his notes for his 1854 evening lecture to the Chemical Society⁸¹ and is confirmed by a letter which he wrote to Thomas Andrews in November 1856. Graham said in this letter: "I have long been of the opinion that diffusion, transpiration of both gases and liquids will never have an explanation except from the motion theory of heat."⁸² This change of opinion necessitated a reappraisal of his views of matter and its motion. For Graham the motion of all matter was a continuing pre-occupation and his final thoughts on this subject were given in 1863 in his speculative ideas paper. In this paper he publicly acknowledged two beliefs firstly in the motion theory of heat and secondly that all elements were constructed from primary matter and were distinguished only by the inalienable amounts of motion possessed by this matter.

Whilst Graham was speculating on caloric and superficial heat he was also discussing changes of state and liquidity. These topics were intimately connected with both caloric and Black's latent heat. His early writings on the liquid state reveal his fertile powers of imagination. The first paper which he wrote on the subject was entitled 'On the absorption of gases by liquids.' It appeared in the Annals of Philosophy for July 1826.⁸³ T. E. Thorpe has recalled that Graham was supposed to have remarked to his teacher Thomas Thomson: "Don't you think, Doctor, that when liquids absorb gases, the gases might themselves

84. T. E. Thorpe, Essays in Historical Chemistry, (London 1894),
A lecture (with additions), delivered in the Yorkshire College,
Leeds, Introductory to the evening class session 1877-8,
Thomas Graham, pp 160-217, see p 160.
85. M. Faraday, 'On fluid chlorine,' read March 13th 1823, Phil. Trans. 113
(1823) 160-165, 'On the condensation of several gases into liquids,'
April 10th 1823, Phil. Trans. 113 (1823) 189-198, 'Historical statement
respecting the liquefaction of gases,' Quarterly J. of Sci. 16
(January 1824) 229-240.
86. Graham, op.cit. (83), Researches p 2.

become liquids?"⁸⁴ This remark undoubtedly impressed Thomson and it became the central theme of Graham's paper. Once again this early paper was entirely speculative. Unlike many of his later papers, it contained no new experimental results. This is understandable, however, because he did not have the facilities for performing experiments in 1826.

He began by admitting that liquid mixtures such as alcohol and water were often close to 'chemical union'. The evidence for this view was that the volatility of alcohol was reduced by the addition of water. Indeed he argued that it was generally true that the more volatile liquid in a mixture was made less volatile by the affinity which it possessed for the more fixed liquid. Referring to Faraday's work on the liquefaction of gases, under great pressure and low temperature,⁸⁵ he concluded that gases were merely volatilised liquids. There was no permanency in a given physical state and interconversion was demonstrably possible. Thus, in the absorption of gases by a liquid, the gases were first liquefied and then retained by the mutual attraction existing between these two liquids. Graham wrote: "the mere injection into our absorbing liquid of such gases, in their elastic state, will occasion their liquefaction, and consequently bring into play the affinities of liquids, and the concomitant diminution of volatility."⁸⁶ He confidently predicted that when both concentrated sulphuric acid and steam were in contact, even at 600°F, just below the boiling point of the former liquid, liquefaction of the steam would ensue. The affinity of the liquid-liquid interaction would be sufficiently strong to overcome the elasticity of steam at 600°F thereby producing its liquefaction.

The evidence for liquefaction of gases during absorption could be seen from Faraday's liquefaction experiments. Graham pointed out that the most easily-liquefied gases, for example sulphur dioxide, ammonia, and hydrogen chloride, were also those gases which were most easily-absorbed by liquids. Indeed, Graham claimed that the specific gravities of liquid-liquid mixtures were in close agreement with the specific gravities of solutions of gases.

87. J. Dalton, 'On the absorption of gases by water and other liquids,' read to Manchester Lit. and Phil. Soc. October 1803, Phil.Mag. 1 Ser 24 (1806) 15-24.
88. Berthollet, Essai de Statique Chimique, (Paris, 1803) Vol. 1 pp 273-275.
T. de Saussure, 'On the absorption of gases by different bodies,' read in Geneva, 1812, Ann.Phil. 6 (1815) 241-255, 331-347, see pp 338-347 for Saussure's account of the absorption of gases by liquids.
T. Thomson, A System of Chemistry 5th edn. Vol. 3 (1817) pp 62-67.
J. Murray, System of Chemistry 2nd edn. Vol. 2 (Edinburgh, 1809) pp 142-146, and also,
A. Ure, A Dictionary of Chemistry, (London, 1821) See article on 'gases.'
89. Saussure, *ibid.* pp 340-344.
90. T. Thomson, 'Improvements in physical science during the year 1816,' Ann.Phil. 9 (1817) 12-13.
91. W. Henry, 'Experiments on the quantity of gases absorbed by water, at different temperatures, and under different pressures,' Phil. Trans. 93 (1803) 29-42, 274-276.
"under equal circumstances of temperature, water takes up, in all cases, the same volume of condensed gas as of gas under ordinary pressure." p 41.
92. Edward Turner exhibited (at the Royal Society of Edinburgh on May 16th 1824) the experiments of condensing gases into liquids by their own pressure. Ed.J.Sci. 3 (1825) 175.

Graham regarded his chemical theory of gaseous absorption as an extension of the theories of Berthollet, Thomson, and Saussure. It was, however, in direct opposition to Dalton's mechanical theory of gas absorption. Dalton had suggested that gas particles dissolved by occupying the gaps between liquid particles. This process was a purely mechanical one in which a gas was retained inside a liquid by the pressure of the same gas above the liquid. In the mechanical theory, the dissolved gas particles were spread out in the liquid by their mutual repulsion and not by their affinity for liquid molecules.⁸⁷

On the contrary Berthollet, Saussure, J. Murray, Hope and Thomson had all argued that there must be some form of attraction between a liquid solvent and the dissolved gas.⁸⁸ Saussure had demonstrated that there were variations in the absorption of gases by different solvents and also he had found that the order of increasing absorption of different gases varied from one solvent to another.⁸⁹ This had led Thomson to criticise Dalton's mechanical theory.⁹⁰ Indeed, Graham was adopting the prevailing opinion amongst the Scottish chemists: Thomson, Murray, Hope and Ure when he opposed Dalton's explanation of absorption. But he added a new dimension to this criticism with his mechanism involving initial liquefaction of gases and the resultant affinity which existed between the volatile liquefied gas and the solvent. Graham also questioned the validity of Henry's law,⁹¹ arguing that Henry would never have discovered his law if he had experimented with hydrogen chloride gas. The law was at best, a restricted one, only applying to gases which were absorbed with difficulty.

What led Graham to his theory that liquefaction was required for the solution of gases? Faraday's experiments on the liquefaction of a number of gases in 1823 were obviously influential as Graham himself conceded. Faraday had demonstrated by the liquefaction of gases that there was no permanence to the gaseous state and his experiments were soon repeated in Scotland by Edward Turner in 1824.⁹² At the same time

93. J. Perkins, Ann.Phil., 6 (July 1823) 66; for Faraday's comment see Qu.J.Sci. 16 (1824) 240.
94. A. Bussy, 'Note sur la liquéfaction de l'acide sulfureux' Ann. de Ch. 2 Ser 26 (1824) 63-66.
95. Cagniard de Le Tour, 'Account of some results obtained by the combined action of heat and pressure on certain liquids such as water, alcohol, sulphuric ether and essence of rectified petrol,' Ann. de Ch. 2 Ser 21 (1822) 127-132, 178-182. See also Phil.Mag. 1 Ser 61 (1823) 58-61 or Ann.Phil. 5 (1823) 290-294.
96. T. Thomson, MS. lecture notes taken by R. D. Thomson at Thomas Thomson's chemistry lectures (1828-9), Chemical Society, London. See lecture given on January 5th 1829.
97. Saussure had shown that alcohol and water dissolved very different quantities of the same gas and that the order of increasing absorption in different liquids varied. For example ethylene was more soluble in naphtha than carbon dioxide, but carbon dioxide was more soluble in olive oil than ethylene. Thus Saussure concluded that chemical affinity must play a part in the solubility of gases. See Saussure op.cit. (88).
98. L. Pearce Williams, Michael Faraday, (London, 1965) pp 129-131.

Perkins claimed that he had liquefied air itself, by using great pressure, although Faraday questioned the validity of his results.⁹³ Also, in 1824, in France, Bussy had liquefied a number of gases by cooling alone.⁹⁴ The interconversion of gases and liquids was also confirmed by Cagniard de La Tour's experiments of 1822. He had shown that liquids heated under pressure in sealed tubes above their normal boiling points, did eventually vaporise. On cooling, their vapours condensed giving a thick cloud followed by liquefaction.⁹⁵ There is therefore abundant evidence that the liquefaction of gases was a subject of considerable interest when Graham speculated on absorption. In his University lectures, Thomas Thomson said that Faraday had refuted Dalton's opinion that particles of different gases did not repel one another "by showing that gases may be rendered fluid by pressure."⁹⁶ Thomson like Graham was convinced that chemical affinity was involved in all cases of gaseous absorption by liquids and he believed furthermore that Saussure had proved this point experimentally.⁹⁷

To understand Graham's conception of the absorption of gases it is necessary to consider his views on changes of state. Presumably a gas molecule would collide with the surface liquid molecules. The pressure of the liquid molecules would overcome the calorific repulsion; heat would be lost and the gas molecule would become liquefied. The molecule of liquefied gas would not escape immediately because it was held inside the liquid by the attractive force of the surrounding liquid molecules. Graham pointed out that heat was evolved both in the compression of vapours and in the mixture of liquids. Therefore, the observed increase in temperature, when gases were absorbed, was to be expected and was accounted for by the latent heat released when a gas was liquefied.

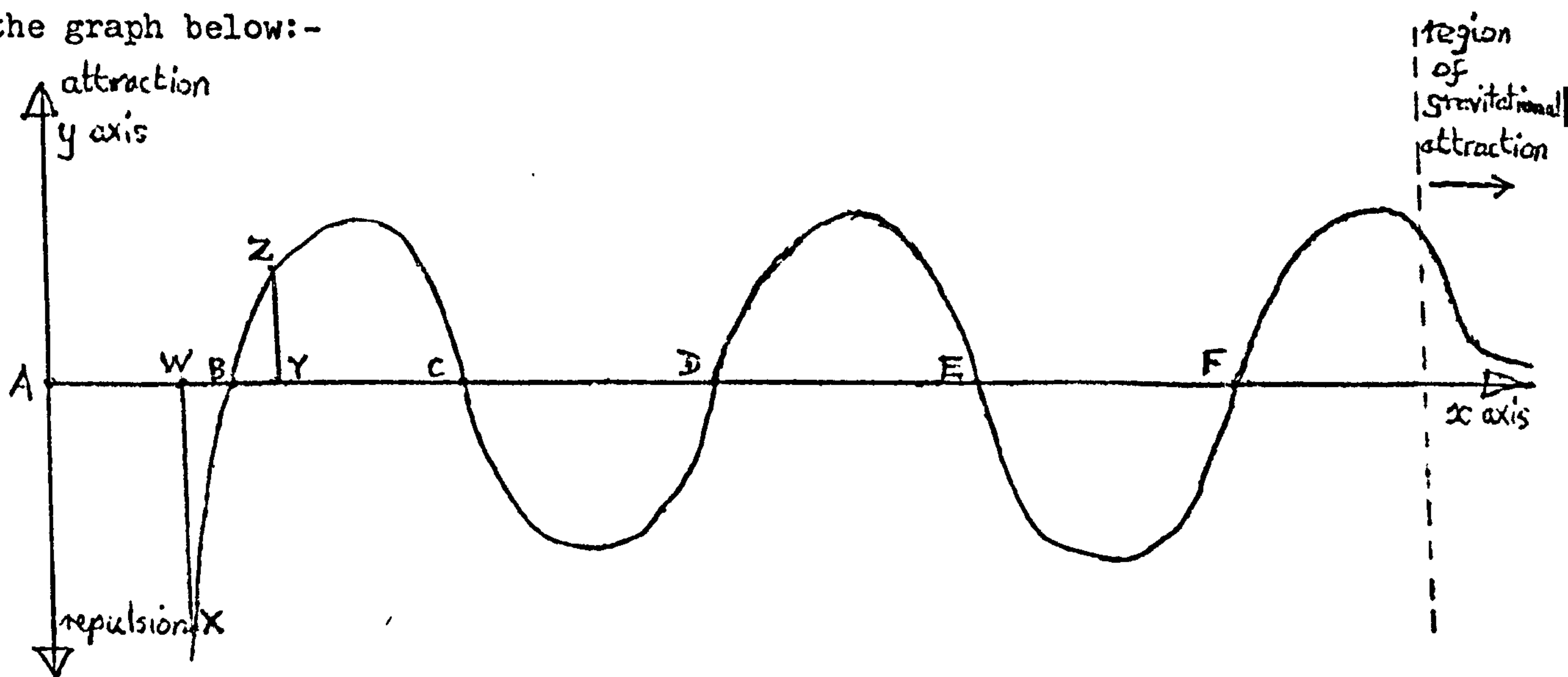
In his explanation of Faraday's liquefaction experiments L. Pearce Williams has suggested that a sensible interpretation of them can be achieved by considering the process in terms of Boscovich's theory.⁹⁸ We might ask whether Graham could have been thinking along similar lines?

99. The three textbooks mentioned are:
John Leslie, An Experimental Inquiry into the Nature and Propagation of Heat, (London, 1804) see pp 515-516.
John Robison, A System of Mechanical Philosophy, (Edinburgh, 1822) in 4 volumes, Volume 1 contains 100 pages devoted to Boscovich's theory: pp 267-368.
T. Thomson, A System of Chemistry, 5th edn. (London, 1817) in 4 vols. see vol. 3 83-84, 114-116.
100. R. J. Boscovich, Theoria Philosophiae Naturalis (Venice, 1763). This work was translated by J. M. Child, A Theory of Natural Philosophy, (Chicago, 1922). A copy of the 1763 edition is kept in the library of St. Andrews University; it bears the bookplate of John Robison dated 1786 and after his death it was purchased by John Leslie and then by James David Forbes.
101. John Robison, A System of Mechanical Philosophy, edited by D. Brewster (Edinburgh, 1822) Vol. 1 pp 267-286 and John Robison, Article 'Boscovich' in Encyclopaedia Britannica, 3rd edn. Supplement Vol. 1 (Edinburgh, 1801) 92-107.

There is no direct evidence in support of this conjecture for Graham did not mention Boscovich in his writings. And yet his teachers and friends were influenced by Boscovich's theory and it is certain that Graham would have been introduced to this theory through the lectures of Thomson, Leslie and possibly Hope. Furthermore, Graham possessed in his library three works in which Boscovich's theory was discussed and these works might have formed part of his reading whilst he was a student at Glasgow.⁹⁹

The mid-eighteenth century philosopher Boscovich viewed matter as a set of identical point atoms surrounded by attractive and repulsive forces.¹⁰⁰ When two point atoms were very close together a strong repulsive force existed which prevented contact and penetration. At sensible distances the force of gravitational attraction operated and it varied according to the inverse square law of Newton. In the region between strong repulsion and gravitational attraction there were alternating forces of attraction and repulsion. A force curve was drawn by Boscovich to represent these changes in accordance with the law of continuity.

This force curve was considered in detail by John Robison in his textbook¹⁰¹ and Robison, it is to be remembered, taught Graham's mentors: Thomson and Leslie. Consider a point atom placed at the position A on the graph below:-



All the points where the curve cuts the x-axis were positions between attraction and repulsion or of zero force. If one atom was placed at A

102. Richard Olson, 'The reception of Boscovich's ideas in Scotland,' Isis 60 (1969) 91-105.
103. J. Robison, A System of Mechanical Philosophy, (Edinburgh, 1822) Vol.1. Robison wrote about Boscovich's theory: "I am by no means certain that this inextension of an atom [i.e. a point atom] is indisputably requisite in a theory which maintains the discrete constitution of matter....neither can I....conceive those powers to have no substance to which they belong, or to which they are related intrinsically or extrinsically." p 299.
104. T. Thomson wrote "with respect to the nature of the ultimate elements of bodies, we have no means of obtaining accurate information; but it is the general opinion that they consist of atoms, or minute solids, incapable of further division. That these atoms are mere mathematical points surrounded with spheres of attraction and repulsion, as Boscovich supposed, appears to me incomprehensible. They must, I think, be physical points, as minute as you will, but still possessed of length, breadth and thickness. This opinion, I say, is generally received by philosophers; and I cannot, for my part, conceive any other. It is taken for granted, as the foundation of the Daltonian theory; and, I presume, will be readily admitted by everyone without hesitation."
'On the Daltonian Theory of definite proportions in chemical combinations,' Ann.Phil. 2 (1813) pp 33-34.
105. John Leslie, An Experimental Inquiry into the Nature and Propagation of Heat, (London, 1804) pp 122-124, 515-516, and also for the same view: Leslie, Elements of Natural Philosophy, Vol.1 (Edinburgh, 1829, 2nd edn.) pp 35-38.

and a second atom at B then a stable equilibrium was achieved. With a small disturbing force, the atom at B could be moved nearer to the atom at A, that is by movement to W; this atom would then experience a force of repulsion proportional to the distance WZ driving the atom back to B. Likewise if the atom at B was drawn to Y it would be attracted back to B with a force proportional to YZ. Boscovich called the stable positions B, D and F the 'limits of cohesion'.

In order to bring about a change of state, a particle must move from one limit of cohesion to another. For example to change a liquid into a solid, an atom might be moved from D to B. This would require a compressing force so that the atom was pushed beyond C, over the repulsive arc CD. Beyond C the atom would be attracted and so it moved to the stable position B.

As Richard Olson has pointed out, Scottish scientists, brought up in the tradition of common sense philosophy were prepared to accept the parts of Boscovich's theory which could be obtained by induction from observed phenomena but they rejected what they regarded as metaphysical principles.¹⁰² Thus the force curve was acceptable but point atoms were unacceptable. Point atoms were metaphysical entities. Robison,¹⁰³ Thomson,¹⁰⁴ and Leslie¹⁰⁵ latterly, all insisted on a physical atom from which the force field emanated. An atom possessed a real size and was not just a point. With similar eclecticism Thomson and Leslie rejected Boscovich's ideas on heat. Boscovich regarded heat like Boyle and Boerhaave before him as a motion of fire particles, whereas Thomson considered heat to be a matter-caloric combination and Leslie considered it as a matter-light combination.

Thomas Thomson probably exerted a significant influence on Graham's early chemical studies. Indeed, he had encouraged Graham to take up Chemistry. During Graham's student days Thomson was extending and developing Dalton's atomic theory. This work culminated in 1825 with Thomson's publication of his controversial book: An attempt to establish

106. T. Thomson, An Attempt to Establish the First Principles of Chemistry, in 2 volumes (London, 1825).
107. T. Thomson, *ibid.* Vol. 1 p 30.
108. T. Thomson, A System of Chemistry 5th edn. (London, 1817) Vol. 3, p 114.
109. T. Thomson, *ibid.* Vol. 3 p 84 "we may conceive with Boscovich, that the atoms of liquids are placed in the limit between attraction and repulsion. Their atoms cannot be forced nearer each other without experiencing an attraction from the diminished action of the combined heat, compared with that of the attracting particles. The distances of the atoms are so regulated, that the attraction and repulsion by which they are at once activated just balance one another; while their form is such, that they can move freely among each other without altering these distances. It is this which seems to constitute the real cause of fluidity."
110. R. Angus Smith, The Life and Works of Thomas Graham, (Glasgow, 1884), p 15, letter of Graham to his mother, January 29th 1827.
111. J. Leslie, 'On heat and climate,' Ann.Phil. 14 (1819) 5-27 read to the Royal Society of London in February or March 1793. See p 10 "All matter is, therefore, essentially the same; ... particles of matter are endued with certain attractive and repulsive powers ... they [the particles] are only mathematical points, to which certain powers are directed. A physical particle is only a cluster of primeval points, whose attractions and repulsions, sometimes conspiring, and sometimes counteracting each other, will form a compound action varying extremely according to the figure of the arrangement.... Such is the substance of the ingenious and profound theory of the late Abbé Boscovich.... A mature reflection will convince us of the solidity as well as the beauty of the system."
112. Leslie, *ibid.* p 12.
113. Leslie, An Experimental Inquiry into the Nature and Propagation of Heat, (London, 1804) p 123.

the first principles of Chemistry.¹⁰⁶ This work contained the results of his researches into the atomic theory and also included an account of Boscovich's theory which he described as the "latest and most ingenious [atomic theory] which has been offered to the public."¹⁰⁷ Thomson was not prepared to speculate on the proposition that all atoms were identical although he did remark that most of the known elements were probably truly compounds. Indeed it was even possible, he said, that there were only two ultimate elements, presumably he meant by this: hydrogen and oxygen. In his textbook, A System of Chemistry, 5th edition (1817), Thomson suggested that Boscovich had given the best explanation of the nature of cohesion.¹⁰⁸ He remarked that this was the most beautiful and satisfactory part of the theory. Liquids contained particles placed at Boscovich's limits of cohesion and the combined heat would resist any displacement from these positions. The globular form of liquid particles allowed them a freedom of movement, provided that the particles were retained at distances corresponding to their limits of cohesion. He felt that this was the true cause of liquidity.¹⁰⁹

Early in 1827 Leslie invited Graham to attend his lectures and laboratory whenever he wanted.¹¹⁰ These two men shared common scientific interests concerning the nature of heat and matter. Leslie was committed to Boscovich's theory. He first indicated this in an essay 'On heat and climate' written for the Royal Society of London in 1793. The Royal Society rejected the paper and so it was not published until 1819.¹¹¹ By 1804 Leslie had replaced point atoms by physical atoms but he retained Boscovichean force curves. His decision to accept that atoms had a finite size came from his observation of the discrete modes of vibration in strings. Thus he replaced his earlier statement of 1793 that "nature admits only gentle transitions,"¹¹² by "nature presented always individual objects and proceeded by finite steps or differences - absolutely continuous shades exist only in our modes of conception."¹¹³ The latter revision dates from 1804 and he repeated this latter opinion in his text-

114. Leslie, op. cit. (105).

115. D. F. Larder, 'Prout's hypothesis - a reconsideration,' Centaurus 16 (1970) 44-51.

116. Graham, Elements of Chemistry part 1 1st.edn. (London, 1837) pp 65-66.
Laplace, Traité de Mécanique Céleste, Volume 5 (Paris, 1825), 'De l'attraction et de la répulsion des sphères et des lois de l'équilibre et du mouvement des fluides élastiques' pp 99-132.
See particularly pp 104-106 for Laplace's discussion of the three states of matter.

117. T. Thomson, op.cit. (96) lecture of April 6th 1829 "Mr. Graham conceives that the gas is converted to a liquid previous to absorption."

118. T. Thomson, An Outline of the Sciences of Heat and Electricity, (London, 1830) p 239 "Graham has suggested that these gases before they can be absorbed by or combine with water, in all probability assume the liquid form. If this conjecture be admitted, it is clear that the quantity of each absorbed must bear some relation to its elasticity. It may not be in the inverse ratio exactly, because the amount of the affinity between the gases and water may and probably does differ considerably."

119. W. T. Brande, 'On the solution of gases in water,' Qu.J.Sci. 22 1 (October 1826) p 204. "Mr. Graham...has brought forward several ingenious arguments, to show that when gases appear to be absorbed by liquids they are simply reduced to that liquid and comparatively in-elastic form which otherwise (by cold or pressure) they might be compelled to assume."

book of 1829, where he redrew Boscovich's force curves with many small but discrete steps.¹¹⁴

Finally T. C. Hope might be mentioned in connection with Boscovich. D. F. Larder has recently stated that Hope in his lecture notes considered matter to be made up of a congeries of atoms or particles all of which were identical on the authority of Newton. Boscovich was pencilled in over these notes and therefore Hope may have mentioned his theory during his lectures.¹¹⁵

Is it possible, therefore, that Graham was thinking in terms of a Boscovichean force curve? - so that when a gas particle dissolved, it was moved by the attraction of the liquid particles, from a repulsive position on the force curve to an equilibrium position between attraction and repulsion? We cannot be certain here, for it is equally possible that Graham was thinking more generally along the lines of the Laplacian caloric theory. In this theory three forces were necessary to explain the different states of matter. They were the force of attraction of particles for one another; the force of attraction of particles for the caloric which surrounded neighbouring particles; and finally the force of repulsion which occurred between adjacent caloric particles. In the liquid state the dominant force was the attraction of particles for the caloric surrounding neighbouring particles which allowed particles to move freely among themselves. Gaseous particles in contact with a liquid would be attracted by liquid particles and liquefied by the loss of some of their combined caloric.¹¹⁶

The response to Graham's paper on gaseous absorption was generally favourable. Thomson quoted Graham's views in his lectures of 1829¹¹⁷ and in his textbook: Heat and Electricity published in 1830.¹¹⁸ In London, William Brande mentioned Graham's 'ingenious arguments' favourably.¹¹⁹ William Henry in his textbook admitted that the solution of gases was a controversial field. Most chemists adopted a theory of chemical affinity whereas he and Dalton preferred chiefly, if not wholly,

120. W. Henry, Elements of Chemistry, 11th edn. (London, 1829) Vol.1 p 153. "The principles on which gases are absorbed and retained by liquids has been a subject of controversy. By Berthollet, Thomson, Saussure and the generality of chemists, it is ascribed, in all cases to the exertion of chemical affinity between the gas and the liquid, but it is contended by Mr. Dalton and myself that the effect in most cases is chiefly, if not wholly, mechanical." This statement also appears in the 9th edn. of Henry's Elements of Chemistry (London, 1823) p 144.
121. Berzelius, Traité de Chimie, translated by A.J.L. Jourdain (Paris, 1829) Vol.1 pp 472-480.
122. Berzelius, Jahresbericht 8 (1829) pp 66-67.
123. Graham, 'Notice of the singular inflation of a bladder,' (October 1829), Researches 40-41; 'On the diffusion of liquids,' (1849), Researches 446-447; 'On the absorption and dialytic separation of gases by colloid septa,' (1866), Researches 235-239, 253-4, 272; 'On the occlusion of hydrogen gases by metals,' (1868), Researches 288-290.
124. H. Colquhoun, 'Notice of a new form of carbon supposed to be the pure metallic basis of the substance; and also of several other interesting aggregations of carbon, especially in so far as they elucidate the history of certain carbonaceous products found in coal gas manufactures,' Ann.Phil. 12 (July 1826) 1-13.

a mechanical theory. Nevertheless, he advised that Graham's essay was "deserving of the reader's attention."¹²⁰ On the continent, Berzelius accepted two classes of absorption of gases by water. In the first class there was a true combination between a gas and water with a release of caloric, for example this class included the gases: hydrogen chloride and ammonia. In the second class there was a simple mechanical absorption, for example this occurred with the gases carbonic acid, hydrogen and nitrogen. In the second class the amount of gas absorbed was either equal to, or below, the volume of water used and no caloric was released.¹²¹ Reviewing Graham's paper in the Jahresbericht of 1829 Berzelius considered that the suggestion that gases were liquefied during absorption was an attempt by Graham to overturn Dalton's opinion of mechanical absorption.¹²² Berzelius remained uncertain about absorption himself. But, he admitted that both the absorption of gases by water and the solution of solids, or salts, in water might be similar phenomena although he was reluctant to accept chemical combination.

The explanation of gaseous absorption by liquefaction was a recurrent theme in Graham's work. He used this concept: to explain the passage of carbon dioxide through a moist bladder; in liquid diffusion; in the dialytic separation of a mixture of gases and even in the occlusion of gases by solids.¹²³

One writer on Science who made immediate use of Graham's views was E. W. Brayley, who attempted to explain the formation of carbon fibres in steel-making. In May 1826, Thomas Thomson's nephew and assistant, Hugh Colquhoun noticed that carbon fibres were produced in steel-making. He had seen iron, heated in a current of carburetted hydrogen, deposit remarkable long fibrous strands of carbon. They had a bright metallic black appearance. He assumed that they were formed either from a state of fusion or more probably by the aggregation of gaseous carbon particles resulting from their natural polarity.¹²⁴ In July 1826, Brayley argued that there was evidence for the partial melting of carbon at high

125. E. W. Brayley, 'On the rationale of the formation of the filamentous and mamillary deposits of carbon; and on the probable existence of but two distinct states of aggregation in ponderable matter.' Ann. Phil. 12 (September 1826) 192-201 (in a letter to Richard Phillips dated July 7th 1826).
Edward William Brayley (the younger 1802-1870) was a student of the London and Royal Institutions. He attended Brande's Chemistry lectures and later became a writer on Science being one of the editors of Ann.Phil., Phil.Mag. and Zoological Journal between 1822 and 1845. He lectured at the London Institution during the 1830's. In 1834 he prepared the last edition of Samuel Parke's Chemical Catechism. He helped W. R. Grove with his book Correlations of the Physical Forces. Along with Faraday and Gassiot he witnessed Grove's decomposition of water by heat. D.N.B.
Graham recorded in a letter to his mother, dated 21st September 1826, that "My essay in the Annals seems to have had some effect as will appear from a quotation...from...the present month, p 100 - the author is a Mr. Bailey, and he is criticising Dr. Hugh Colquhoun's paper" R. A. Smith, Life and Works of Thomas Graham, (Glasgow 1884) p 12. It is apparent that Smith made two errors in transcribing this letter. Firstly the author was Mr. Brayley not Bailey and secondly the page referred to should have been p 196 not p 100.
126. E. W. Brayley, *ibid.* p 196.
127. Graham, *op.cit.* (125).
128. Graham, 'On the great weight of charcoal,' Chalmer's Journal of Useful Knowledge and Monthly Miscellany of Arts and Sciences (Edinburgh, 1827) Vol. 1 (March 1827) pp 25-26. Graham wrote:
"we may safely hazard the opinion, that the matter of charcoal is precisely of the same weight as the diamond, which chemistry has shown to resemble it exactly in composition. Charcoal, therefore, should be of the specific weight 3.5 (that of the diamond) instead of 0.441, which is generally given it." p 25. Here Graham was allowing for pores and vacuities in charcoal. He continued
"Professor Leslie lately proposed a new method of ascertaining the specific weight of substances as are not compact; and by that method he derived for charcoal a specific weight greater than that of diamond. But this method, although in general susceptible of greater accuracy, is liable to great error in the case of charcoal, and that error is unfortunately on the side of excess." p 25.
129. John Leslie, 'An apparatus for the specific gravity of powders,' Quart.J.Sci. 21 (1826) 374-376 or Ann.Phil. 11 (April 1826) 313-315. Leslie quoted a figure of 0.5 for the specific gravity of charcoal as the one then in use but he found it to be more than 3.6 by experiment.
130. Graham, *op.cit.* (128) p 26.

temperatures.¹²⁵ He assumed that carbon separated out from carburetted hydrogen as a gas, and this gas then passed into a liquid form and finally solidified rapidly. Once the gaseous carbon particles were aligned, liquefaction would occur to form fibres. He remarked that the experiments of Faraday, Perkins, and Cagniard de La Tour had shown that there was no real distinction or line of demarcation between vapours and liquids. They passed imperceptibly by degrees in a perfectly continuous manner into one another. Cold and pressure condensed gases with the passage of latent heat into sensible heat. As evidence for his views Brayley wrote that: "the accurate reasoning of Mr. Graham, in his observations on the absorption of gases by liquids,, as well as the experimental evidence he cites, is entirely favourable to this view of solidity and fluidity being the only distinct physical forms, or states of aggregation of ponderable matter; the gaseous and liquid states being merely continuous degrees of one and the same form."¹²⁶ This reference pleased Graham and gave him confidence to extend his researches.¹²⁷

Interestingly Graham also studied carbon fibres when he was examining the specific weight of charcoal in 1827.¹²⁸ He was critical of the accuracy of Leslie's method for the determination of the specific gravity of charcoal.¹²⁹ Graham had made his own estimate of the value. He decomposed olefiant gas by volatilising sulphur through it. Glossy filaments of carbon or charcoal were deposited. As he expected the specific weight of charcoal was much below Leslie's value. Leslie had found that the density of charcoal was over 3.5 or even greater than that of diamond. Although Graham reasoned that the density of charcoal would be similar to diamond, if the vacuities were allowed for, he did not accept a higher figure than that of diamond itself. He showed that charcoal filaments sank in concentrated sulphuric acid and therefore he concluded that the density of this form of charcoal must be at least 1.85.¹³⁰

A practical extension to his theory of gaseous absorption was given

131. Graham, 'Experiments on the absorption of vapours by liquids,' read before the Royal Society of Edinburgh on March 3rd 1828. Edin.J.Sci. 8 (1828) 326-335 or Researches 17-24. For previous work on the boiling points of solutions see: Thomas Griffiths, Quart.J.Sci. 18 (1824) 89; Faraday, Ann.de.Ch. 20 (1822) 320; Faraday and Gay Lussac, Ann.Phil. 5 (1823) 74-75. (In the latter article Faraday agreed with Gay Lussac that vapour was at the same temperature as the boiling solution).
132. Graham 'On the finite extent of the atmosphere' dated December 14th 1826. Phil.Mag and Ann.Phil. 2 Ser 1 (February 1827) 107-109 or Researches 6-9.
133. W. H. Wollaston, 'On the finite extent of the atmosphere,' from Phil.Trans. for 1822, Ann.Phil. NS.4 (1822) 251-256.

by Graham in a paper on the absorption of vapours read to the Royal Society of Edinburgh in March 1828.¹³¹ He placed different solutions in glass basins and supported them over pure water in a closed box. He found that these solutions absorbed water vapour because they released less vapour than did pure water. Generalising his results he argued that the absorbing power of a solution was inversely proportional to the evaporating power of the solution. As a measure of the absorbing power he used the boiling point of the solution. He found that a greater quantity of water vapour was absorbed by solutions with higher boiling points. Next he examined the absorbing powers of pairs of different liquids. As he anticipated, the less volatile liquid absorbed the vapour of the more volatile liquid. He confirmed this experimentally with: alcohol and sulphuric acid; alcohol and water; ether and alcohol. A remarkable example of this absorbing power was shown by the solids: mercury chloride, or camphor, which deliquesced when they were supported over alcohol. This study can be seen as an early attempt to establish a connection between the vapour pressure of a solution and its boiling point; this property of solutions was developed by later workers in their studies of colligative properties.

Graham's concern with change of state in chemical problems can be seen in another imaginative paper which he wrote in December 1826. This was a speculative paper entitled 'On the finite extent of the atmosphere'.¹³² It was based on Wollaston's suggestion that the atmosphere was limited in its extent and therefore not infinite.¹³³ In 1822, Wollaston had argued that if a limited atmosphere existed it would consist of ultimate atoms which were no longer divisible. On the other hand if there was no limit to ^{the} divisibility of matter, the atmosphere would be spread throughout space and it would be collected around the sun and the planets. Here was an experimental test for the existence of atoms. Observe the sun and the planets and see if they had atmospheres. If they did not, then the earth's atmosphere would be limited. Observations of the passage of

134. Wollaston, *ibid.* p 251.

135. Graham, *op.cit.* (132) Researches p 7. Leslie had estimated a cooling of the air of 1^oF for every 300 feet ascent. See Leslie's 'On heat and climate,' Ann.Phil. 14 (1819) 5-27. (footnote on p 26.)

136. J. A. Buchner, 'Light produced during crystallisation of benzoic acid,' [1824] Edin.J.Sci. 3 (October 1825) pp 368-369 from Schweigger's J. 41 (1824) 222-232. Buchner heated impure dry benzoic acid with a little charcoal powder at a moderate temperature for several days. He placed a cylinder over the mixture to observe crystallisation. When the crystals began to form, Buchner raised the temperature and observed flashes of light in the cylinder. These flashes did not continue after the crystals had been deposited. Buchner supposed the light was produced by neutralisation of electricity. In the same volume J. Foggo reported seeing iridescent clouds in Britain like those observed by Humboldt in South America.

137. Graham, *op.cit.* (132) Researches p 8.

Venus close to the sun, and of the satellites of Jupiter, appeared to indicate that neither the sun, nor Jupiter, had an atmosphere. So the earth must have a finite atmosphere composed of ultimate particles or atoms. To explain the limited height of the atmosphere Wollaston suggested that there was a balance at the limit of the atmosphere between two opposing forces: the force of expansion of the atmosphere, caused by the repulsion between its constituent particles, and the force of gravity acting downwards on each particle. He estimated that the earth's atmosphere was about forty miles high.¹³⁴

On the contrary Graham argued that the atmosphere could be limited without reference to divisibility and the existence of atoms. The cooling of the atmosphere with increasing height would be sufficient to liquefy or solidify air thus limiting its extent. He pointed out that, assuming Gay-Lussac's figure, air would contract by $\frac{1}{480}$ th part of its volume at 32°F, for a one degree fall in the temperature.¹³⁵ Thus a cooling of 480°F would give air of negligible volume. To avoid absurdity he argued that gases must be condensed to give liquids or solids. Accepting that the atmosphere cooled regularly, by 1°F for an ascent of 300 feet, Graham fixed the height of the atmosphere at 27.27 miles. At this height gaseous air would solidify with a considerable release of latent heat. He chose a solid boundary for the atmosphere because liquids would continue to evaporate and so they could not impose a limit. Latent heat was evolved during solidification and this appeared in the form of light. Graham mentioned that this phenomenon had recently been demonstrated. For, in 1824, Buchner had shown that when benzoic acid was sublimed it gave out light as it condensed.¹³⁶ Furthermore, Graham added that this light was the cause of the observed luminosity of the upper regions of the atmosphere. Referring to this luminosity he wrote that it "has induced Professor Leslie, with that daring originality which frequently characterises his beautiful speculations, to attribute to them a phosphorescent property."¹³⁷ Now this light would be at its lowest and

138. John Leslie, Treatises on Various Subjects of Natural and Chemical Philosophy (Edinburgh, 1838), This book includes Leslie's articles on 'Meteorology' and 'Climate' which were taken from the 4th edn. of Encyclopaedia Britannica Supplement (Edinburgh, 1815-24). See in the Treatises, 'Climate' pp 261-340 in which Leslie deduces his formula for the decrease in temperature with increasing height and 'Meteorology' pp 402-410. Leslie gives his value for the height of the atmosphere on p 410. See also Richard Olson, 'Count Rumford, Sir John Leslie and the study of the nature and propagation of heat at the beginning of the nineteenth century.' Ann.Sci. 26 (1970) 273-304, see p 299.

139. Leslie, *ibid.* 'Climate' p 410.

most magnificent at the poles and it could spread out from them. Was this, Graham asked, the explanation of the Aurora Borealis and the prevailing atmospheric circulation?

This imaginative paper was again concerned with the condensation of gases. The expansion of the air caused its particles to absorb latent heat as they rose with consequent cooling. When the temperature was low enough the particles would attract one another so that eventually they could unite to form a solid. The latent heat would then be thrown out in the form of light or heat. Again it is conceivable that Graham might have considered particles being forced from a repulsive position on a Boscovichian force curve to a limit of cohesion corresponding to the solid state; or on Laplace's caloric theory, when attraction between matter particles predominated, solidification would occur with a loss of latent heat.

Apart from the admitted influence of Wollaston's paper on Graham's speculations it is probable that the researches of Leslie, James Ivory, and certainly those of Faraday all played a part in Graham's thoughts on the limitation of the atmosphere. The problem of the extent of the atmosphere had been raised by Leslie in 1815.¹³⁸ He had published a formula for the fall in temperature as the atmosphere was ascended which indicated a more rapid fall in temperature at greater heights. Also he had used an alternative suggestion drawn from Kepler's work on twilight to calculate the height of the atmosphere. He worked in a quite different way to that chosen later by either Wollaston or Graham. Leslie's calculations did not assume a strict limit to the atmosphere provided that it was so thin above that rays of light were not noticeably reflected by it. He obtained a value of 1,638 miles for the height of the atmosphere.¹³⁹ This figure was much greater than that deduced by later workers but Leslie must be given credit for drawing attention to the possible limitation of the height of the atmosphere.

In 1821, the Scots mathematician, James Ivory, explained that the cooling of the air by its own expansion would check the elastic force by

140. James Ivory, 'Remarks on the gradation of heat in the atmosphere,'
Phil.Mag. 1 Ser 58 (1821) 24-31.
See also James Ivory, 'On the constitution of the atmosphere;'
Phil.Mag. 1 Ser 66 (1825) 81-93, 241-250, for a detailed discussion
of Leslie's formula.

141. Graham, op.cit. (132) Researches p 6.

142. Faraday, 'On the existence of a limit to vaporization,' read to the
Royal Society on June 15th 1826. Ann.Phil. 12 (December 1826)
436-441.

143. L. Pearce Williams, Michael Faraday, (London, 1965) pp 125-127.

144. Graham, Elements of Chemistry, 1st edn. part 1 (London, 1837) p 65.

which it tended to fly off from the earth.¹⁴⁰ With this fall in temperature, operating along with gravity, he concluded that the fluid of the atmosphere would cling to the earth. This imposed a limited boundary to the atmosphere. There is a definite similarity between the arguments of Ivory and those used subsequently by Graham except that Ivory did not postulate a solidification mechanism to limit the atmosphere.

At the beginning of his atmosphere paper Graham referred to Faraday's endeavour to find examples of the "equilibrium between the expansive power of gaseous matter and its clogging gravity."¹⁴¹ This was an allusion to Faraday's paper 'On the existence of a limit to vaporisation'.¹⁴² Acknowledging his debt to Wollaston's paper, Faraday argued that there was a temperature below which bodies ceased to produce vapour. He believed that, by a sufficient lowering of temperature, the elasticity of a vapour could be reduced sufficiently to be entirely overcome by the stronger force of gravity or cohesion. As a result the vapour would condense and the body would no longer be able to emit vapour. In his biography of Faraday, Pearce Williams has accounted for this lack of continuity by suggesting that the repulsive force loses the necessary 'exaltation' needed to cross the hump of a Boscovichean force curve so that the forces of attraction and repulsion would then be balanced. A further lowering of temperature would push the particles into an attractive arch forming a solid with no vapour below a certain temperature.¹⁴³ Later Graham expressed his reservations about the abrupt cessation of vapour, arguing that a continuous reduction would be more likely. This opinion was expressed in 1837 and it shows Graham's belief in the property of continuity in nature which is a recurrent theme in his work.¹⁴⁴

Graham's paper did not go un-noticed; Berzelius mentioned it in his Jahresbericht of 1829 but he dismissed it, arguing that the emission of light did not occur in this way and so presumably condensation itself did not take place. He explained that the Northern Lights were simply caused by the close approach of phosphorescent clouds to the earth, and so, he

145. Berzelius, Jahresbericht., 8 (1829) 15.

146. E. Turner, Elements of Chemistry 2nd edn. (1828) pp 206-208, 3rd edn. (1831) pp 227-228: "I do not think much weight can be given to this [Wollaston's] argument even admitting solar observations for proving by inference that the atmosphere of the earth is limited, Wollaston has only considered pressure in the reduction of elasticity of gases and he has ignored the temperature reduction, which tends to deprive gases of their elastic form. Therefore it appears to me that the extreme cold which is admitted to exist in the higher regions of the air, may of itself, be a condition sufficient to put a limit to the extent of the atmosphere. Some very ingenious remarks have been made on the subject by Graham." Turner, Elements.(1828) p 207.

147. J. B. Dumas, Leçons sur la Philosophie Chimique, (Paris, 1837) pp 235-242.

148. C. Daubeny, An Introduction to the Atomic Theory, 2nd.edn. (London, 1850) p 131. See pp 125-135 for Daubeny's defence of atomism.

149. W. Whewell, 'Remarks on Dr. Wollaston's argument respecting the infinite divisibility of matter, drawn from the finite extent of the atmosphere' B.A.Report (Birmingham, 1839) Transactions p 26. Whewell maintained that it was impossible to specify the height of an atmosphere.

150. D. C. Goodman, 'Wollaston and the atomic theory of Dalton' Historical Studies in the Physical Sciences 1 (1969) 37-59. See pp 53-58, particularly pp 57-58.

151. G. Wilson, 'On Wollaston's argument from the limitation of the atmosphere, as to the finite divisibility of matter,' read April 21st 1845, Trans.R.S.Edinburgh 16 (1849) 79-86.

rejected Graham's only piece of evidence for a solidification mechanism.¹⁴⁵ On the other hand, Graham's colleague in Edinburgh, Edward Turner, indicated that he preferred Graham's explanation to that given by Wollaston. He expressed this opinion in his influential textbook, Elements of Chemistry, in 1828, and repeated it in successive editions until 1834.¹⁴⁶

Similar views to those of Graham were put forward in 1836 by J. B. Dumas. They were apparently worked out from Faraday's arguments on vaporisation.¹⁴⁷ It is not surprising that Dumas should have opposed Wollaston's argument because it was seen as a support for simple atomism, and by 1836 Dumas had rejected this view. Instead, Dumas proposed the alternative view that the outer regions of the air might become liquid or solid because Faraday had shown that mercury did not vaporise at all near to 0°F. For example a gold leaf suspended over mercury at this temperature failed to amalgamate. Therefore it might well be possible for oxygen and nitrogen to become liquids and solids when deprived of pressure. Referring to Poisson's calculations, he supposed that there was a sufficient temperature reduction at the extremities of the atmosphere to produce liquefaction or congelation of the very rarefied air, thus limiting the atmosphere.

In England, Charles Daubeny rejected the notion that there was a liquid or solid boundary to the atmosphere because it would be, as he said, "a palpable barrier to the transmissions of heat and light."¹⁴⁸ And by reference to different calculations, made by Fourier, Daubeny argued that the temperature of space was not much below polar temperatures. Therefore he considered that Dumas's views were incorrect and it can be inferred that Daubeny would also have rejected Graham's explanation. Daubeny accepted Wollaston's explanation, (despite later criticism by Whewell,¹⁴⁹) as evidence for simple atomism, in which he believed. As D. C. Goodman has recently pointed out¹⁵⁰ these discussions were concluded when George Wilson, Graham's student, stressed that it was quite possible to suppose that air was composed of molecules instead of atoms.¹⁵¹ There

152. Graham, Elements of Chemistry, 1st.edn. (London, 1839) part 3, p 273.
153. Graham, 'On the influence of the air in determining the crystallisation of saline solutions,' read to the R.S.E. on December 17th 1827. Trans.R.S.Edin. 11 (1831) 114-118 or Researches 24-27.
154. Gay-Lussac, 'On the influence of the pressure of the atmosphere on the crystallisation of salts,' Ann.de Ch. 1 Ser 87 (1813) 225-236 or Phil.Mag. 1 Ser 44 (1814) 44-48.
155. Thomas Thomson had also investigated the crystallisation of Glauber's salt in 1822. Thomson concluded that "the water of crystallisation of the salt which crystallises gives out its latent heat, and this evolution is the cause of the augmentation of temperature observed." Thomson 'On certain saline solutions which may be cooled without crystallisation; but deposit crystals when agitated,' Ann.Phil. N.S. 3 (1822) 169-174 see p 174. Thomson did not comment on the details of how crystallisation began although he did refer to removing the cork from flasks and agitating the solutions.

was no necessity to link a belief in atomism to the finite extent of the atmosphere. Wilson rightly commented that this alternative solution to the problem had been missed by all the earlier workers, including Graham. Although it is relevant to stress that Graham did not discuss simple atomism in his paper instead he was simply providing an alternative explanation of the finite extent of the atmosphere. Nevertheless, if Graham's opinion had been widely-adopted, it would have removed an apparent experimental support for simple atomism. Clearly, Graham did not persuade Daubeny of the correctness of his explanation. Interestingly, Graham appears later to have been rather diffident about his own views. For he wrote in 1839 that the atmosphere "is certainly limited, but whether by the cold prevailing in its higher regions, which may liquefy or even solidify the aerial particles, or from their expansibility having a natural limit, is uncertain."¹⁵²

In 1827 Graham again discussed the problems of change of state, using his concept of liquefaction during gaseous absorption in rather a surprising context. This was in a paper entitled: 'On the influence of the air in determining the crystallisation of saline solutions.'¹⁵³ In 1813, Gay-Lussac had shown that hot supersaturated solutions of Glauber's salt did not crystallise on cooling in a vacuum.¹⁵⁴ However, when a bubble of air was added, crystallisation did commence. He had also observed that hydrogen, carbon dioxide, or nitrous gas (nitric oxide), all had the same effect as air in promoting crystallisation. The absorption of air by boiled water was a slow process and so Gay-Lussac assumed that even a little dissolved air would precipitate out a small amount of Glauber's salt thus beginning the crystallisation process. He explained that the difficulty of crystallising Glauber's salt was caused by the figure and arrangement of the molecules which strongly resisted the change of state needed to produce crystals under certain circumstances.¹⁵⁵

In a similar way to Gay-Lussac, Graham confined a tube containing a hot, supersaturated solution of Glauber's salt over hot mercury.

156. Graham, 'An account of M. Longchamp's theory of nitrification, with an extension of it,' Phil.Mag. 2 Ser 1 (March 1827) 172-180 or Researches 9-17, see p 14.

157. Graham, op.cit. (154) Researches p 26.

Crystallisation was started when an air bubble was blown up into the tube. However, crystallisation did not occur when a glass bead was thrown into the solution of Glauber's salt. Thus it did not appear to be a mechanical effect as Gay-Lussac had inferred. Was it perhaps a manifestation of chemical affinity? Other gases were tried: carbon dioxide worked instantly, producing crystals in solutions where air had failed to give this effect. Using weaker solutions of Glauber's salt, both air and carbon dioxide failed to give crystals, but ammonia and sulphur dioxide were both immediately effective. The latter two gases, unlike air, often gave tracks of crystals. Now sulphur dioxide and ammonia were both very soluble gases which were easily-liquefied. To Graham it was apparent that chemical affinity was indeed involved in this phenomenon. As he had previously remarked in a different context: "all bodies, when in the liquid state possess their powers of combination most energetically."¹⁵⁶ As a test of his belief that the chemical affinity between liquids was the underlying cause of this phenomenon Graham used hydrogen gas which was less soluble than air. As expected, he found it was indeed less effective than air. Furthermore, he showed that the miscible liquid, alcohol, was just as effective as the soluble gases in causing the crystallisation of Glauber's salt.

Graham concluded that when gases were dissolved in water they gave a shock to the feeble power holding the excess salt in solution. The dissolved gases were themselves present in the liquid state when they had been absorbed and therefore the chemical affinity, or attraction, between water and the liquefied gas was sufficient to overcome the weak force holding Glauber's salt in solution.¹⁵⁷ Again it is possible to interpret Graham's explanation in this paper, either in terms of Boscovichian force curves or equally well in Laplacian terms. The attraction of the liquefied gas for water withdrew the water particles from the Glauber's salt. This removal of water forced or compressed the particles of Glauber's salt closer together causing crystallisation.

158. Graham, 'On the influence of the air in determining the crystallisation of saline solutions,' Phil.Mag. 2 Ser 4 (September 1828) 214-218, see p 218.
159. Graham, 'On the diffusion of liquids,' (1849) Researches 444-544, see p 470.
160. E. Turner, Elements of Chemistry 2nd.edn. (London, 1828) p 547.
"the influence of air may be ascribed to its uniting chemically with water; for Graham has proved that gases which are more freely absorbed than air, act more rapidly, in producing crystallisation. Indeed the rapidity of crystallisation occasioned by contact with gaseous matter, seems to be proportional to the degree of affinity for water."
161. W. T. Brande, Manual of Chemistry 4th.edn. (London, 1836) p 112.

The originality of Graham's theoretical explanation was, as he later admitted, not to be insisted upon because Gay-Lussac "had distinctly thrown out the same theory as a conjecture, although the circumstance is not noticed by any systematic chemical writer. But as M. Gay-Lussac brings forward no experimental illustration of the theory, and indeed adduces one experiment unfavourable to it, the experimental confirmation of the theory is novel and was certainly required." ¹⁵⁸

At a later period, during his researches into liquid diffusion in 1849, Graham deftly developed the analogy between liquefaction of gases and crystallisation of solutions. This analogy, as we shall see, had been noticed first by Gay-Lussac and it proved to be useful in explaining the diffusion of salts in water. Graham wrote: "on approaching the degree of pressure which occasions the liquefaction of a gas, an attraction appears, which impairs the elasticity of a gas; also on approaching the point of saturation of a salt an attraction of the salt molecules for each other occurs tending to produce crystallisation." ¹⁵⁹

Graham's explanation of the crystallisation of supersaturated solutions was quoted favourably by Edward Turner in 1828; ¹⁶⁰ likewise, Brande also included it in his textbook. ¹⁶¹ Brande did not make any comment on Graham's work except to say that the phenomenon of crystallisation of strong solutions was connected with latent heat, and was as yet, imperfectly investigated.

During these early years of difficulty Graham had attempted to work assiduously to establish himself as a chemical researcher. He had shown an imaginative and original approach in his attempt to explain the origin of static electricity. But, of greater significance, in Graham's subsequent career, are his considerations of the caloric theory of heat and of the changes of state which occurred when gases were liquefied, or solidified. In these researches Graham illuminated problems as diverse as the solution of gases in liquids and the limited extent of the earth's atmosphere. In the next chapter we will consider his studies of the

gaseous state which were based on the motion of gases. The examination of the inherent motion of matter was a necessary preliminary study to the basic question of the ultimate constitution of matter itself.

Chapter 3

GRAHAM'S WORK ON THE MOTION OF GASES

1. J. Clerk Maxwell, 'Diffusion of gases through absorbing substances'
This was a review by Maxwell of the book with this title written by
Dr. Sigmund Wroblewski. Nature 14 (May 11th 1876) 24-25.

GRAHAM'S WORK ON THE MOTION OF GASES

"The importance of the exact study of the motion of gases, not only as a method of distinguishing one gas from another, but also as likely to increase our knowledge of the dynamical theory of gases, was pointed out by Thomas Graham. Graham, himself, studied the most important phenomena, and distinguished from each other those, in which the principal effect is due to different properties of gases." ¹ In this statement Maxwell admitted Graham's important contribution to the study of the motion of gases. Graham's experiments on the movement of gases began with diffusion. His investigations extended over forty years and throughout he performed careful and well-designed experiments to reveal the nature of the motion of gases. His own understanding of the nature of this motion through various different barriers evolved gradually. Graham's early discovery and development of the diffusion law raised problems which forced him to question the prevailing views of the gaseous state. The actual ways in which gases passed through different materials had to be carefully distinguished from one another. For example, he found that the motion of a gas passing under pressure into a vacuum was not the same as a simple diffusion process. Eventually Graham demonstrated that the passage through partitions of gases under pressure was either an effusion or a transpiration process. Although he was unable to formulate a coherent theory for transpiration, he did define the essential conditions for its occurrence. And with masterly precision he established the effusion law and correctly distinguished between the very different processes of diffusion and effusion.

Graham's work on gas motion was criticised by both Herapath and Bunsen. This probably explains why Graham's diffusion law was not used as an experimental foundation for the dynamical or kinetic theory of gases. In 1863, Graham finally replied to his critics with further investigations which were conclusive. He distinguished clearly between the three different modes of gas motion, which are still recognised today.

2. H. Cavendish had also found that a mixture of hydrogen and air did not separate out on standing. This is recorded in an unpublished note of 1784. See the Cavendish Papers edited by E. Thorpe (Cambridge, 1921) 2 317 and the B.A. Report (Birmingham, 1839) pp 67-68.

He also presented a remarkable hypothesis on the nature of matter in which he fused together the concept of primary matter and molecular motion. It is possible that Herapath may have influenced Graham to accept a dynamical view of matter.

The very different materials used by Graham for diffusion, for example stucco, graphite, rubber and metals, reveal his considerable experimental insight and ingenuity in this field.

The final clear grasp of the influence of different materials on the mode of gas motion shows that Graham was not just a distinguished experimenter but that he had a sound theoretical understanding of the different types of gas motion. It can be inferred that he had a consistent vision of both the diffusion and liquefaction of gases from his earliest studies of these phenomena.

Graham's initial researches on the motion of gases were devoted to a study of diffusion in a piece of work which was remarkable for its experimental innovation and precision. Previous studies of gas diffusion had not been quantitative, but they are nevertheless important because they are central to early discussions of the nature of gases. It will be helpful to examine these earlier researches on gas diffusion so that Graham's work can be more clearly appreciated. In this way the magnitude of his achievement in obtaining a quantitative law of diffusion can best be assessed.

In the latter half of the eighteenth century, the different gases had been distinguished from one another, notably by Priestley. In 1777, Priestley tried to find out whether different gases would separate out after mixture. He chose pairs of gases with different specific gravities, for example nitrous air and common air; carbon dioxide and nitrous air; carbon dioxide and common air. He found that mixed gases did not seem to separate out into distinct strata;² instead they remained uniformly diffused through one another. However, Priestley added one note of caution to this conclusion, pointing out that if two gases were placed

3. J. Priestley, Experiments and Observations on Different Kinds of Air 3 (London, 1777) 301-305. See p 305.

4. J. Priestley, 'Experiments relating to phlogiston and the [seeming] conversion of water into air' read 26th June 1783, Phil.Trans. 73 (1783) 398-434 and also in Experiments and Observations Relating to the Various Branches of Natural Philosophy (London, 1786) 3 29-69.

The true explanation of Priestley's supposed conversion of water into air had been suggested to him by Josiah Wedgwood in a letter, dated 23rd January 1783, in which he wrote "if water passes through the retort outwards, may not air pass inwards?" See J. R. Partington History of Chemistry 3 (London, 1962) 345-351.

5. J. Priestley, Experiments and Observations, 3 (London, 1786) 64-67 for his later interpretation.

6. J. Priestley, Experiments and Observations, 3 (London 1786) 377.

carefully in a vessel without any mixture then:- "they might continue separate, as with the same care water and wine may be made to do; but that, ^{when} once they have been mixed, they will continue to be so, like wine and water, after having been shaken together." ³ These reservations were later rejected by Dalton. Further important examples of gaseous exchange and diffusion were also observed by Priestley. In 1783 he examined a suggestion made by Watt that it might be possible to make 'permanent' steam by converting the latent heat of steam entirely into sensible heat. Priestley heated wet lime in a clay retort but found that the evolved gas, which he collected over mercury, was not steam but common air; the steam had apparently been exchanged for common air via the pores of the heated clay retort. ⁴ Initially, Priestley suggested that the air outside the hot retort had been condensed or combined with the clay. This condensed air was then transferred from one part of the clay to another until it reached the inside of the vessel and regained its aerial form. This explanation was similar to that used at a much later date, by Graham, to explain the passage of gases through impermeable barriers, such as water films, bladders, rubber and metals.

However, Priestley did not retain this explanation, ⁵ because he discovered that clay retorts were not entirely air-tight. Although air could not be blown through the retorts, it was possible to draw air through them using an air pump. Consequently, he argued that the air entered by capillary attraction and so the loss of aerial form was unnecessary. Yet Priestley could not explain why this mutual exchange of gases occurred, and he did not have (as he admitted) any clear conception of how the capillary power acted so that steam could escape at the same time as air entered. Dalton and Graham would later comment on these experiments and clarify the explanation in terms of diffusion.

In 1786, Priestley observed the exchange of gases through the walls of a wet bladder. ⁶ When a bladder of nitrous air was suspended in ordinary air for a few days it shrank to one quarter of its original

7. J. Priestley, 'Experiments relating to the change of place of different kinds of air through several interposing substances.' (This paper was read in 1800). Trans.Amer.Phil.Soc. 5 (1802) 14-20, 43-50.

volume and it then contained only phlogisticated air (nitrogen). Likewise hydrogen was shown to pass out through the walls of a bladder into pure oxygen, whilst at the same time oxygen entered the bladder. Then, in 1800, Priestley performed a more-controlled experiment on the diffusion of gases through the walls of a wet bladder. He left a bladder containing pure oxygen inside a jar full of hydrogen for one month; afterwards the contents of the bladder and the jar were found to be identical mixtures of hydrogen and oxygen both of which could be exploded by ignition. This experiment demonstrated that diffusion through a bladder was a two-way process which produced a uniform mixture of gases both inside and outside the bladder. In 1829 Graham also examined the diffusion of gases through the walls of a bladder; in contrast to Priestley, he was able to develop a theory for the diffusion of gases through wet bladders.

Priestley concluded his researches on diffusion in 1800,⁷ when he discovered that gases exchanged places with one another regardless of affinity. The best way he had found to demonstrate this process was to enclose a gas in an inverted earthenware tube, one end of which was sealed, the other being placed in water. He heated the top end of the tube and found that hydrogen, oxygen, or nitrous air could be exchanged for the common air outside. In these exchanges he noticed that there was usually a change in volume; but this significant feature of diffusion was not commented upon adequately until Graham published his researches. It is probable that Graham had not read Priestley's 1800 paper on diffusion before 1830. The evidence for this is that Graham did not mention that Priestley had anticipated Doebereiner's observations on the escape of gases from cracked vessels. Priestley had noticed that broken vessels, repaired with paint or cement, allowed an exchange of gases with the outer air and that cracked vessels themselves were not entirely impervious.

8. J. Priestley, *ibid.* p 17.

9. J. Dalton, Meteorological Observations and Essays (Kendal, 1793)

10. J. R. Partington, History of Chemistry 3 (London, 1962) 761-767 and A. Thackray, John Dalton, Critical Assessments of His Life and Work (Harvard, 1972) 66-69. T. C. Hope wrote in his lecture notes: "I hold that evaporation is a solution of the substance [water] in the air of the atmosphere" Hope MSS 268 packet 36.

The later work of both Deville and Graham was also partly anticipated by Priestley in his last diffusion paper, when he examined the escape of gases from red hot tubes. He found that when the two-to-one explosive mixture of hydrogen and oxygen was kept in red hot tubes such as gun barrels; copper, silver, or gold tubes; then it lost its power to explode. Furthermore, gases could be exchanged when they were passed through hot metallic tubes, for example hydrogen could be exchanged for air. More particularly, when hydrogen was heated in a silver tube and then cooled, he showed that air had entered the tube. These observations were noticed again, apparently independently, by both Deville and Graham.

Although Priestley had observed the diffusion of gases into one another with resultant volume changes he was unable to explain the nature of diffusion. He realised that it did not depend upon affinity and he commented on the change in volume: "there was always however some change in the quantity, but on what principle this change was made, I could not satisfy myself." ⁸

Dalton was the first to attempt an explanation of diffusion in his Meteorological Observations ⁹ published in 1793. In this work he challenged two of the prevailing opinions concerning the atmosphere. Firstly, he argued that the air was not a compound of nitrogen and oxygen but rather it was a mechanical mixture of these gases. Secondly, he suggested that water vapour was itself diffused mechanically within the rest of the air, a view, which was similar to that put forward by De Luc in 1792. De Luc had suggested that water vapour was mixed or diffused in the air by the repulsive force of heat. Most scientists were opposed to this mechanical theory of the atmosphere; instead they advocated a chemical theory of the atmosphere. They believed that water vapour was dissolved in the air by a weak force of chemical affinity. This theory of chemical solution had been put forward by Halley and Le Roy, and was accepted by Franklin, Saussure, Berthollet, Hope, and John Murray. ¹⁰

11. J. Dalton, 'On the constitution of mixed gases', read 2nd October 1801, Manchester Memoirs V ii 535-549.

12. I Newton, Principia (London, 1687) Book 2, proposition 23, (from the translation by Cajori in 1934, p 300) "If for a fluid composed of mutually repulsive particles the density is proportional to the pressure, the centrifugal forces of the particles are inversely proportional to the distances between their centres. And conversely, particles, the repulsive forces between which are inversely proportional to the distances between their centres, compose an elastic fluid the density of which is proportional to the compressing force Whether elastic fluids do really consist of particles repelling one another is a physical question. We have demonstrated here mathematically the properties of fluids constituted of such particles so that philosophers may take occasion to discuss the question."
Newton had shown that a gas with these repulsive forces would obey Boyle's law, but he did not insist on his view and he did not say whether he imagined gas particles to be at rest or in motion.

13. T. Thomson, A System of Chemistry 1st edition (Edinburgh, 1802) 3 270-271.

14. J. Dalton 'New theory of the constitution of mixed gases', Phil.Mag. 14 (1802) 169-173.

15. J. Dalton, 'On the tendency of elastic fluids to diffusion', read on January 28th 1803, Mancs.Mem. 2 Ser 1 (1805) 259-270 or Phil.Mag. 24 (1806) 8-14.

To support his view of the atmosphere, Dalton put forward his first theory of mixed gases in 1801.¹¹ If two gases, A and B, were mixed together then the particles of gas A repelled only those of their own kind, but they did not repel particles of gas B; indeed particles of gas A were inelastic to those of gas B. Newton had suggested in 1687 that gases might possibly contain particles which repelled one another with a force inversely proportional to their distance apart;¹² but he had not postulated the selective forces of repulsion which Dalton now added. With this static theory of mixed gases, Dalton could explain how particles of water vapour could spread out into the air or into a vacuum. The weakness of this theory was the necessity of proposing a different kind of repulsion for each gas, and Dalton later recognised this problem. He then suggested a second theory of mixed gases probably in reply to the considerable criticism which had been voiced against this first theory.

An early critic of Dalton's first theory of mixed gases was Graham's teacher, Thomas Thomson. In 1802, Thomson had argued that, on Dalton's theory, different gases ought to separate into layers according to their specific gravities.¹³ Dalton quickly replied saying that Thomson had not understood his ideas clearly,¹⁴ which was true. But Thomson's criticism may have been useful because Dalton began his studies on gas diffusion at this time. The results of these studies were presented to the Manchester Literary and Philosophical Society in January 1803.¹⁵ Dalton began by examining Priestley's earliest suggestion that gases of very different specific gravity might stratify when they were placed together if care was taken to avoid any mixture. He connected together two glass flasks containing different gases by using an adjoining glass tube. All the gases mixed uniformly regardless of their specific gravity or affinity. Priestley had come close to this discovery in his final paper on diffusion but Dalton's simpler method clearly demonstrated the point. With the lighter gas hydrogen in the upper flask and the heavier carbon dioxide in the lower flask, Dalton obtained uniform diffusion in thirty minutes.

16. T. C. Hope was Professor of Chemistry at Edinburgh University and Graham attended some of his lectures between 1826 and 1827. Roscoe and Harden in their book: A New View of Dalton's Atomic Theory (London, 1896) quoted Hope's letters to Dalton. See pages 130-134. e.g. Hope wrote to Dalton about diffusion on November 4th 1803: "Suppose a bottle were filled with sand and the atmospheric air were extracted from the interstitial spaces by an air pump and a communication [was] then established between the interior of the bottle either of hydrogen or carbonic acid gas. Don't you imagine that in much less than an hour, that in a few seconds the gas would make its way between the particles of the sand, though the interstices between them must be incomparably smaller than those between the particles of another gas?"
17. T. C. Hope, *ibid.*, letter from Hope to Dalton (undated - early 1804?)
18. C. L. Berthollet, Statique Chimique (Paris, 1803) 1 483-489.
19. J. Murray, A System of Chemistry 2nd edn. (Edinburgh 1809) 2 48-53 and notes.

These experiments effectively disposed of Thomson's criticism. Dalton also explained the exchange of steam and air through the pores of an earthenware vessel. He rejected Priestley's explanation that the exchange occurred by capillary attraction; instead he suggested that the pores were analogous to the glass tube which connected the two flasks of gas together and so the exchange was simply a diffusion process.

Dalton's experiments were an important advance in the study of the movement of gases. They established clearly the spontaneous process of diffusion. But his explanation of the diffusion process in terms of the first theory of mixed gases was widely-criticised especially by the Scottish scientists. T. C. Hope argued that, if Dalton was correct, diffusion should occur in a few seconds but it invariably took much longer.¹⁶ To overcome this difficulty Dalton argued that the caloric atmospheres surrounding gas particles caused the slow intermixture. But Hope replied that this was the strongest argument against the first theory of mixed gases; he wrote that "this [heat] atmosphere I deem the essential cause of the elasticity and repulsion among the particles of the gas, and I cannot conceive that this atmosphere as it surrounds a particle of oxygen should repel the atmosphere that surrounds another particle of oxygen and should not repel the atmosphere that envelopes a particle of azote, hydrogen, or any other gas."¹⁷

This went to the heart of the matter, as Dalton later conceded. Further criticism caused Dalton to re-examine the problem of the speed of diffusion of gases which had not been discussed before. In 1803 Berthollet also rejected Dalton's mechanical theory and argued for the alternative chemical solution theory¹⁸ in which gases dissolved one another by a weak force of affinity. This force was supposed to be too weak to produce chemical combination, but capable of causing air to draw out vapours from liquids. This view was supported by the Edinburgh lecturer John Murray¹⁹ and more particularly by T. C. Hope and Thomas Thomson, who insisted that the constant composition of the air indicated

20. T. Thomson, A System of Chemistry 2nd edn. (Edinburgh, 1804) 3 314-317.

21. J. Dalton, 'On the supposed chemical affinity of the Elements of Atmospheric air: with remarks upon Dr. Thomson's observations on this subject.' See p 80 "but if it be found that any one gas diffuses itself in any other with nearly the same celerity, it will be a presumption in favour of my hypothesis if otherwise, it may be argued that the quicker diffusion is owing to the stronger affinity. I have made a great number of experiments on this head, but could not find any remarkable difference in the time and circumstances of diffusion of the same gas." Phil.Mag. 19 (1804) 79-83.

22. The timing of Dalton's second theory of mixed gases has been controversial; but he stated in his lectures of 1810 that the theory was developed in 1805 (See Roscoe and Harden, p.16 and A. Thackray, *op. cit.*(10), Chapter 5) Thomas Thomson had again criticised Dalton's first theory of mixed gases in the third edition of his system in 1807. Like Berthollet, he pointed out that gases should diffuse into one another as rapidly as they pass into a vacuum if Dalton was correct, and Thomson also asked the question, why, if there was no repulsion between particles of hydrogen and oxygen, did they not combine when the particles met? See T. Thomson, A System of Chemistry, 3rd edn. (Edinburgh, 1807) 3 440.

23. J. Dalton, A New System of Chemical Philosophy (Manchester, 1808) 1 187-192.

24. Wilson L. Scott has suggested that Dalton introduced atoms of different sizes to overcome the objections of John Gough. Gough had argued that when two different gases with different specific gravities were placed apart, the force of buoyancy would prevent their mixture. This criticism may have persuaded Dalton to vary the size of the particles of different gases, so that the specific gravities of different gases were effectively equalised and a mixture of gases was possible.
See Wilson L. Scott, The Conflict Between Atomism and Conservation Theory, (London, 1970) Chapter 9 pp 195-198.

that air was held together by chemical affinity.²⁰

In reply Dalton suggested an experimental test; if gases diffused into one another with nearly the same speed then the mechanical theory would be favoured, but if there were different speeds then affinity must be involved and a chemical theory of diffusion would be favoured. Curiously, Dalton did not notice any significant differences in his experiments on the speed of diffusion of the same gas into a number of other gases. He found that, when a narrow tube (12" x $\frac{1}{4}$ ") was filled with hydrogen, the loss of gas was unaffected by position. The same volume of gas escaped in a given time whether the tube was pointing upwards, downwards or horizontally.²¹ These experiments in support of the mechanical theory did not convince his critics. With more care Dalton might have discovered some relationship between diffusion speed and specific gravity. However, it must be admitted that he used techniques in these experiments which were not sufficiently sensitive to reveal different speeds of diffusion.

The next significant development for Dalton came when he acknowledged the views of his critics and proposed a different theory of mixed gases. This second theory²² was published in his New System of Chemical Philosophy in 1808.²³ He now accepted that all gas particles repelled one another because each gas particle consisted of an "impenetrable nucleus, together with a surrounding repulsive atmosphere of heat."²³ He no longer postulated selective forces of repulsion. Instead there was a single force of repulsion: caloric. All the particles in the same gas were identical in size but these particles were different in size to those of other gases.²⁴ He regarded a gas as an ordered, statical arrangement of particles held apart by calorific repulsion. This was analogous to a pile of shot: "the particles [of which] must be disposed into horizontal strata, each four particles forming a square: in a superior stratum, each particle rests upon four particles below, the points of its contact with all four being 45° above the horizontal

25. J. Dalton, op.cit. (23) pp 189-190.

26. Dalton, *ibid.* p 190.

27. In February 1810, Dalton gave a series of lectures at the Royal Institution in London. In Lecture 17, Dalton described the development of his mechanical theories of the constitution of gases and he admitted the weakness of his first theory: "We were to suppose as many distinct kinds of repulsive powers, as of gases; and moreover, to suppose that heat was not the repulsive power in any one case; positions certainly not very probable. Besides, I found from a train of experiments, ..., that the diffusion of gases through each other was a slow process, and appeared to be a work of considerable effort." He continued by considering the possibility that gaseous particles might have different sizes:- "By size I mean the hard particle at the centre and the atmosphere of heat taken together ... And if the sizes be different then on the supposition that the repulsive power is heat, no equilibrium can be established by particles of unequal sizes pressing against each other." From Roscoe and Harden, op.cit. (16) p.16.

The table of diameters of gaseous particles appeared in the second part of the New System published in November 1810, p.560; hydrogen, carbonic acid, carburetted hydrogen, sulphuretted hydrogen and phosphuretted hydrogen all had a diameter of 1 relative to hydrogen. The diameter was calculated, by Dalton, by taking the cube root of, the atomic weight divided by the relative density of the gas. See Roscoe and Harden, op.cit. (16) pp 24-25.

28. T. Thomson, A System of Chemistry, 4th edn. (Edinburgh, 1810) 3
461-2.

plane On this account the pressure is steady and uniform throughout." ²⁵

To explain the diffusion of gases he argued that when two gas surfaces met, the particles of the different gases were of different sizes, so there could be no stable geometrical arrangement or equilibrium. Therefore he said that: "an intestine motion must arise from this inequality, and the particles of one kind be propelled amongst those of the other no equilibrium can ever take place amongst the heterogeneous particles. The intestine motion must therefore continue till the particles arrive at the opposite surface of the vessel against any point of which they can rest with stability, and the equilibrium at length is acquired when each gas is uniformly diffused through the other."²⁶

This interpretation resembled Graham's early views on gas motion and diffusion. However, there were difficulties with this new theory. Dalton found that five gases at least contained particles with an identical diameter. He did not comment on this problem but it may explain why he did not publicise his second theory of mixed gases after 1810,²⁷ and why he reverted to the first theory in 1826.

Thomas Thomson was attracted towards Dalton's new theory, although he had certain reservations. He argued that intestine motions in mixed gases did not necessarily follow from the probable differences in particle size. He wrote: "to ascertain the motions which will be produced when gases whose particles differ in size, are brought into contact, is a problem of some difficulty. It is very possible that Mr. Dalton's conclusion may be correct; but I own I have some doubts on the subject. If Mr. Dalton will produce a mathematical demonstration of his position, all doubts will be removed and the mutual mixture of gases [will be] explained in a satisfactory manner."²⁸

Dalton did not respond to this challenge, presumably because he recognised that his theory had foundered on the problem of particle size. In 1809, Dalton learned that Berthollet had repeated his diffusion

29. C. Berthollet, 'On the reciprocal mixture of gases,' Mémoires d'Arcueil 2 (Paris, 1809) pp 463-470.

30. Roscoe and Harden, op.cit. (16) pp 146-150. Letter from Thomas Thomson to J. Dalton, 13th November 1809.

31. Thomas Thomson, A System of Chemistry, 5th edn. (London, 1817) 3 31-37.

experiments. Both Berthollet and Thomson had raised the same objection to Dalton's first theory, that diffusion was a slow process. If, on Dalton's theory, two gases were brought into contact then diffusion should have been virtually instantaneous because the particles of the two gases were inelastic. The diffusion of hydrogen into oxygen should be almost as fast as the diffusion of hydrogen or oxygen into a vacuum. Berthollet's experiments on the speed and extent of diffusion were made with great care. He used two flasks of gas linked by a connecting tube and placed them in still air at a constant temperature.²⁹ Thomson informed Dalton of these experiments: "The gases were always uniformly mixed in 24 hours if one of them was hydrogen (as hydrogen + carbonic acid, hydrogen + oxygen, oxygen + carbonic acid); but other gases did not mix uniformly in that time - (as air + carbonic acid, oxygen + nitrogen, nitrogen + carbonic acid, oxygen + carbonic acid). Air and carbonic acid did not mix uniformly in 17 days. In the highest globe there were 42 [measures] of carbonic acid and in the lowest 50 [measures]. These experiments are rather adverse to your peculiar opinion respecting gases."³⁰

By 1817 Thomson had rejected not only Dalton's first theory, but Berthollet's chemical solution theory as well. The slowness of diffusion could not be reconciled with gases behaving towards each other like vacua; rather it lent support to the view that gases were mutually elastic and not inelastic. Furthermore, Thomson asked why particles of hydrogen and oxygen did not combine on collision if they were supposed to be mutually inelastic. As a result he argued that the particles of different gases must be mutually elastic. The origin of this elasticity was the heat which surrounded all atoms. This elasticity would prevent gas particles approaching one another too closely and so combination between hydrogen and oxygen would not occur at room temperature and atmospheric pressure.³¹

Although Thomson had previously supported Berthollet's theory that there was a weak affinity between different gases which caused diffusion,

32. In 1810 Thomson had accepted Berthollet's chemical solution theory. See T. Thomson, A System of Chemistry, 4th edn. (Edinburgh, 1810) 3 461.
33. It is curious that although Thomson had rejected Berthollet's theory for the diffusion of gases he continued to refer to air as a compound of nitrogen and oxygen. See Thomson, A System of Chemistry 5th edn. (London, 1817) 3 p.174. "Air, then, is a compound of oxygen and azotic gas."
34. J. Dalton, 'On the constitution of the atmosphere' (February 14th 1826) Phil. Trans. 116 (1826) 174 - 182. Dalton could only explain the repulsion between like gas particles, by using an analogy with a magnetic repulsion, which was indifferent to other kinds of gas particles. This idea had been mentioned formerly in his New System.

he decided to reject this view in 1817.³² He explained that chemical combination however weak always involved a change in specific gravity but when gases were mixed the specific gravity was always found to be the mean, of that of the gases before mixture. There was no evidence for such a change in specific gravity and hence there was no evidence for affinity, or chemical solution, when gases were mixed.³³

The only explanation which Thomson could offer for diffusion was that gases were mutually elastic. The gradual interpenetration of gases resulted from their elasticity which was caused by the repulsion between the adjacent caloric atmospheres surrounding atoms. When two gas surfaces met there was a mechanical obstacle which made diffusion a slow process. Thomson had partly-adopted Dalton's second theory in this explanation of diffusion but he did not actually say that there was an intestine motion when two gases came into contact. The exact details of the diffusion process were not described by Thomson, but he generally subscribed to Dalton's view that repulsion between the caloric atmospheres of adjacent atoms was responsible for diffusion. The problem of the considerable differences in the times of diffusion which had been noticed by Berthollet was left unexplained by Thomson. It was to provide Graham with a topic for research.

Whilst Graham was a student at Glasgow from 1819 to 1826 he must have been made aware of Thomson's views on gaseous diffusion. The reluctance of Scottish chemists to accept Dalton's first theory of mixed gases might well have influenced Graham's earliest thoughts on diffusion. Graham's attention might also have been drawn towards diffusion by Dalton's paper on the constitution of the atmosphere which was read to the Royal Society in 1826.³⁴

Significantly, in this paper Dalton had reverted to his first theory of mixed gases and he did not even refer to his second theory. This shift in his opinions may have stimulated further discussions in Scotland about the problems of diffusion and intermixture of gases.

35. J. Dalton, 'Sequel to an essay on the constitution of the atmosphere.'
Phil.Mag. 3 Ser 12 (1838) 156-168, 397-406.

36. The Life and Works of Thomas Graham, collected together by R.A.Smith
and edited by J.J.Coleman (Glasgow, 1884) p 64.
This notebook has since disappeared along with the 64 letters which
were quoted by Smith.

Dalton argued that in a static atmosphere there would be less oxygen at higher altitudes because the height of an individual gas atmosphere was dependent upon the specific gravity of the gas. In an attempt to confirm this prediction, he continued to perform experiments on the atmosphere. He recognised that the atmosphere was not really static and later on, he found that there was very little variation in the atmospheric composition at different heights.³⁵

Graham's first recorded thoughts on diffusion were quoted by R. A. Smith. In a passage, taken from page 144 of Graham's laboratory notebook written between 1827 and 1828, Graham wrote that "Dalton's theory of the tendency of gases to mix with each other, that they are vacua to each other, is faulty as it would occasion an instantaneous and complete mixture, which certainly does not take place and I have shown previously that cold should be produced on a mixture as a necessary effect of Dalton's supposition, which I have found on trial not to be the case. The gases must, therefore, actually press against each other. Aqueous vapour in the atmosphere must be pressed upon, and be really as dense as the atmosphere. Suppose a vacuum be made in the receiver of an air pump, as nearly perfect as possible. Admit a little water, the vacuum would be filled completely with aqueous vapour of light tension; upon admitting air into the vacuum, the first effect would be to drive the aqueous vapour before it, compress and condense it. If the bottom of the receiver was not dry, aqueous vapours would rise without the artificial introduction of water, and it is probably the condensation of such vapours which occasions the haziness often observed on the entrance of air. This of course is quite contrary to Mr. Dalton's theory of vacua."³⁶

Smith commented that Dalton would have accepted that a gas under pressure could drive back another gas, but Dalton was never able to express clearly the 'mystical relationship' between identical gas particles. He then said that Graham had not made clear the distinction between specific gravity and tension. Graham's first point about the

37. Graham, 'A short account of experimental researches on the diffusion of gases through each other, and their separation by mechanical means', Quart. Journal of Science N.S. 2 (September, 1829) 74-83.

38. *ibid.* Researches. p 28.

time taken for diffusion was not new but his second point on temperature changes had not been made before. If gases expanded into one another as into a vacuum then they would absorb caloric and the temperature would decrease as a consequence. This was a significant criticism. Diffusion occurred between gases when they were mixed at normal pressures. Graham suggested that a similar process should occur when air at normal pressure was admitted into water vapour at low pressure or tension. If gases were vacua to one another this would follow. Graham was arguing here that gases must be pressing against one another and therefore they were not inelastic. Smith was wrong to suggest that Graham had confused pressure and specific gravity. The specific gravity or relative density of air ~~or~~ water vapour was only relevant to the speed of diffusion, but Graham was pointing out that instantaneous diffusion did not occur. Gases were elastic to one another so compression was observed in practice before the slow process of diffusion could occur.

In 1829, Graham published his first paper on the diffusion of gases. He began with a brief review of the earlier studies made by Dalton and Berthollet. They had shown that, when different gases were brought into contact, they did not arrange themselves in layers according to density, but that they spontaneously diffused through each other until a uniform mixture was obtained.³⁷ He thought that Berthollet had not added much more to Dalton's experiments on diffusion: "unless perhaps that hydrogen is much more penetrating and diffusive than any of the other gases. It is sufficiently evident that in cases of gaseous mixture which are exactly similar, corresponding results may be expected, or that the diffusion is not accidental, but subject to fixed laws."³⁸

Graham followed up this suggestion with his own experiments on the diffusion of different gases into the air. The apparatus which he used was characteristically simple. It consisted of a graduated test tube containing a ground-glass stopper fitted with a short right-angled exit tube. Gases were allowed to diffuse out of this tube for a fixed time

39. *ibid.* Researches. p 29.

40. Graham, 'On the molecular mobility of gases,' (1863) Researches
pp 210-234, see p 224.

and then the residual gases in the tube were analysed. As much hydrogen escaped in two hours as carbonic acid did in ten hours. From this he concluded: "it is evident that the diffusiveness of the gases is inversely as some function of their density - apparently the square root of their density."³⁹ This was the earliest statement of the law of diffusion. Graham verified this provisional statement in his next published paper on diffusion.

Other aspects of diffusion were also examined in his 1829 paper. He asked whether mixtures of gases, such as hydrogen and olefiant gas, diffused independently of one another. He found the surprising result that the more diffusive gas left the tube in a greater proportion than might be predicted from single gas diffusion. For example with pure gases:-

75 parts of pure hydrogen would lose 70.85 parts to the air in 10 hours and 75 parts of pure olefiant gas would lose 36.25 parts to the air in 10 hours,

but with a mixture of 75 parts hydrogen and 75 parts of olefiant gas in a test tube, he found that:-

the 75 parts of hydrogen, in the mixture, would lose 71.5 parts to the air in 10 hours

and 75 parts of olefiant gas, in the mixture, would lose 18.4 parts to the air in 10 hours.

Why did the lighter component of a mixture escape more rapidly from a mixture than it did when pure? and why did the heavier component of a mixture escape more slowly than the pure gas? This behaviour would be hard to predict from any of the previous theories of diffusion and it would be difficult to explain. Graham did not give any explanations in this short paper but he did comment on his discoveries in later papers. However, he did point out that the diffusion of gas mixtures could be used to separate the components in the mixture. This idea was an anticipation of the technique of atmolysis which he developed later in 1863.⁴⁰

41. John Leslie, An Experimental Inquiry into the Nature and Propagation of Heat, (London, 1804) p 500.
Humphry Davy, following Leslie's example, compared the cooling power of different gases in 1817. H. Davy 'Some new researches on flame,' Collected Works (London, 1840) 6 pp 66-67.
42. Dalton, A New System of Chemical Philosophy, Part 1 (Manchester, 1808) pp 117-123.
43. Thomas Thomson, A System of Chemistry, 5th edn. (London, 1817) 3 p 40.

He found that the diffusion of gases into vapours appeared to be analogous to the interdiffusion of gases. For example, hydrogen gas expanded four times more rapidly than air in the vapour from ether. Similarly gaseous mixtures diffused unequally into vapours. He demonstrated this by adding ether to a tube containing a 2-to-1 mixture of hydrogen and oxygen kept over water. He collected the first bubble of gas to escape from the tube and washed it to remove ether. After sparking, over half of the gas remained, and this was pure hydrogen. Therefore the bubble was relatively richer in hydrogen showing that hydrogen diffused more rapidly than oxygen into ether.

Another property, which was dependent upon the density of gases, was the cooling power or mobility of a gas. Graham noted that both Leslie⁴¹ and Dalton⁴² had found that solids cooled more quickly in the lighter gases. This was an important observation; here Graham had linked the two processes: of diffusion and cooling power, both of which involved gaseous expansion. Gases of lower density diffused more rapidly and so removed the heat from solid surfaces more rapidly. Therefore these two processes were indeed related.

Graham's vision of diffusion was certainly not a static picture. Lighter gas particles moved more rapidly than heavier ones. In consequence any explanation of diffusion must be based on the motion of gas particles. Different gases therefore contained particles which possessed quantitatively different motions.

Like Dalton, Graham recognised that Priestley's experiments on the exchange of gases through the pores of heated porcelain tubes were examples of diffusion. He corrected Thomson's erroneous interpretation of them.⁴³ The speed of diffusion was definitely increased by raising the temperature. But this was not caused by an expansion of the porcelain pores which was a trivial effect even in the most intense heat. Rather the speed of diffusion, being inversely proportional to the density of a gas, was greatly increased by rarefaction, either by a rise

44. Graham, op.cit. (37) p 35.

44a. W. Henry, Elements of Chemistry, 11th edn. (London, 1829) 2
Addenda pp 715-718.

45. Graham, 'Notice of the singular inflation of a bladder'
Quart.Journ.of Sci.^{ns2}(October, 1829) 88-89 or Researches 40-41.

in temperature, or a reduction in pressure.

He concluded his 1829 paper by examining diffusion through barriers. When water and alcohol were placed in a jar, covered with paper, water vapour was more diffusible than alcohol vapour. Furthermore, weak alcohol could be concentrated by placing it inside a bladder; but differences in diffusive power were insufficient to account for this. He supposed that "imperceptible pores, or orifices of excessive minuteness, may be altogether impassable (by diffusion) by gases of low diffusive power, that is, by dense gases, and passable only by gases of a certain diffusive energy."⁴⁴

This significant paper showed that diffusion was a spontaneous process governed by a fixed law. Tentatively Graham had established his diffusion law but more detailed experiments were needed to confirm the accuracy of the diffusion law. William Henry immediately included details of this paper in his textbook and commented that Graham "has judiciously refrained, in the present state of inquiry, from drawing conclusions in favour either of the mechanical or chemical theory of the constitution of mixed gases; but every attentive reader will, I think, perceive that the tendency of the facts, so far as yet appears, is much in favour of the mechanical explanation,"^{44a} that is by Dalton's first theory of mixed gases.

Simple diffusion of gases did not occur through all barriers. Graham pointed this out in a short note of 1829⁴⁵ in which he considered the behaviour of gases in bladders. A moist bladder two-thirds full of coal gas was suspended over water in a bell-jar containing carbon dioxide. After twelve hours the bladder had expanded so much that it was ready to burst. The contents of the bladder were examined at the end. Now the gas mixture contained 35% carbon dioxide but, surprisingly, hardly any coal gas had escaped from the bladder. This was not a simple exchange process. Did coal gas attract carbon dioxide inwards?, Graham wondered; so he suspended a bladder half-full of air in carbon dioxide.

46. Graham, 'On the absorption of gases by liquids' Ann.Phil. 12 (July, 1826) 69-74.
47. R.J.H.Dutrochet, L'Agent Immédiat du Mouvement Vitale, Dévoilé dans sa Nature et dans sa Mode d'Action Chez les Végétaux et Chez les Animaux, (Paris, 1826) see p 114 etc. and Bulletin des Sciences Naturelles 9 (1826) pp 336-337. For a detailed account of Dutrochet's work on endosmosis see Chapter 7 of the Ph.D. Thesis by J.V.Pickstone: The Origins of General Physiology in France with Special Emphasis on the Work of R.J.H.Dutrochet, London, Chelsea College, 1973; and J. and T. Schiller, Henri Dutrochet (Henri du Trochet 1776-1847) (Paris, 1975) Chapter 6.
48. Graham, For references to the starting point of Graham's investigations on diffusion, see his papers 'On the law of diffusion of gases' (1831) Researches p 44 and 'On the molecular mobility of gases' (1863) Researches p 227 in which he refers to the paper by J. W. Doebereiner, 'Sur l'action capillaire des fissures etc.' Ann.de Ch. 2 Ser 24 (1823) 332-334.

Again the bladder became fully-inflated. However, with a bladder containing coal gas, there was no inflation in either air or water. Therefore, attraction was not involved in the exchange of gases through the walls of a moist bladder. He explained the phenomenon by using some ideas on the absorption of gases which he had put forward previously in 1826.⁴⁶ Carbon dioxide gas had dissolved in the water in the walls of the moist bladder forming liquid carbon dioxide. This liquid was then transferred to the inside of the bladder. Here the liquid carbon dioxide escaped and expanded into the coal gas unless it was prevented from so-doing by a pre-existing atmosphere of carbon dioxide within the bladder. Less soluble gases such as air or coal gas were much less easily-liquefied and so they were not easily transferred across a bladder. Graham admitted that an alternative explanation might have been possible in terms of an endosmose of gases. This would be analogous to Dulong's endosmose of liquids which had been introduced in 1826.⁴⁷ But Graham said he preferred not to introduce a "new power" into his explanation.

In the next stage of his inquiry into diffusion Graham wanted to estimate the force with which two gases penetrate each other. He set out on this study by taking note of an unusual observation made by J. W. Döbereiner in 1823.⁴⁸ Whilst Döbereiner had been collecting large quantities of hydrogen for his experiments with spongy platinum he had noticed that the water level in one of the jars had risen by a third. On examination he found that this jar contained an extremely minute fissure. Further investigation showed that the water level rose by $1\frac{1}{2}$ " in 12 hours and by $2\frac{2}{3}$ " in 24 hours. The phenomenon did not occur either when the cracked jar was covered with an outer bell-jar or when the gas in the cracked jar was air, oxygen, or nitrogen instead of hydrogen. To explain this Döbereiner suggested that hydrogen had escaped through the fissure by capillary attraction. Only hydrogen atoms could escape because they were small enough to penetrate the fissure; he stated that hydrogen possessed the smallest solid atoms although they were surrounded by the largest atmospheres of heat.

49. G. Magnus, 'Sur quelques phénomènes de capillarité' Pogg. Ann. 10 (1827) 153-168 or Ann. de Ch. 2 Ser 51 (1832) 166-182, see 166-173.

50. Graham, On the Tendency of Air and the Different Gases to Mutual Penetration (Glasgow, 1830). ~~This is an~~ 18-page probationary essay submitted by Graham to the Faculty of Physicians and Surgeons, Glasgow. This essay is not well-known generally. It is probable that Graham needed to become a member of the Faculty so that he could obtain a chemical lectureship in the Medical Faculty of a Scottish University. He was appointed to a lectureship in Chemistry in 1830 at the Andersonian University, Glasgow (now Strathclyde University).

This interesting observation was taken up first by Magnus in 1827⁴⁹ and then by Graham in 1830. Initially Magnus thought that oxygen from the outer air penetrated the fissure whilst at the same time hydrogen entered it and the two gases condensed to form water. The water created, could evaporate endlessly, resulting in the removal of hydrogen followed by the elevation of the water level in the cracked jar. To test this hypothesis, Magnus confined hydrogen in a cracked jar over mercury and placed a large bell-jar of air over the whole apparatus. As expected the mercury rose inside the inner jar as hydrogen escaped but there was no evidence on the outside of any water formation. The total gas volume remained unchanged because the outer mercury level fell by an amount equal to its rise in the inner jar. The experiment was also repeated with the positions of the gases reversed. Finally, he found that hydrogen could escape into an outer atmosphere of carbon dioxide instead of air. Magnus concluded that hydrogen escaped by evaporation into the air, the process being assisted by the affinity between hydrogen and oxygen from the air. Like Döbereiner he assumed that only hydrogen contained small enough particles to penetrate the minute openings in the crack. Essentially, he conceded that the explanation given by Döbereiner was correct except that Magnus preferred to consider the process as one of evaporation assisted by chemical affinity rather than an example of capillary attraction.

In 1830, Graham presented an essay on diffusion to the Glasgow faculty of physicians and surgeons in which he examined Döbereiner's observations.⁵⁰ This is an important document because it reveals Graham's early opinions on the prevailing theories of diffusion and it shows the gradual process by which he came to understand diffusion.

He began by rejecting Dalton's views on the constitution of the atmosphere. Unlike Thomson, Graham accepted that the atmosphere was a mixture of gases whose composition did not vary with height. His evidence for the constant composition of air was experimental. He had

50a. *ibid.* p 11.

50b. *ibid.* pp 4-5.

50c. *ibid.* p 11.

allowed a closed glass tube of air, which was several feet long, to stand for some months. The air at the top and the bottom of the tube was then analysed and found to be identical in its composition.

Graham then reviewed the current theories of diffusion. Berthollet had supposed that diffusion was induced by a chemical attraction between the particles of different gases. Graham rejected this view arguing that "it is extremely unlikely that the intensity of that attraction, and the consequent rapidity of the diffusion, should depend entirely on the density of the gas, as we have found to be the case." ^{50a} On the other hand he said that "this disposition of different gases to intermix, appeared to Mr. Dalton so decided and strong, as to justify the inference that gases afford no resistance to each other; but that one gas spreads or expands into the space occupied by another gas, as it would rush into a vacuum. At least, that the resistance which the particles of one gas offer to those of another is of a very imperfect kind, to be compared to the resistance which stones in the channel of a stream oppose to the flow of water." ^{50b}

After giving details of his previous diffusion experiments Graham commented:- "The experiments appear compatible, however, with the mechanical theory of Dalton. On Dalton's theory, gases should mutually press through each other, with a force equal to that of the pressure of the atmosphere - they are passing into vacua. ... At first sight, there seems to be no evident method of ascertaining the amount of this force." ^{50c} This statement shows that Graham was not prepared to reject Dalton's first theory of mixed gases at this stage in his inquiries, but further puzzling experiments led him to do so in 1831.

There was a third alternative theory which Graham also rejected: "Some chemical writers, however, have been disposed to overlook both the chemical theory of Berthollet and the mechanical explanation of Dalton, and to view the intermixture of gases ..., as sufficiently accounted for by the action of external disturbing causes operating upon their elasticity

50d. *ibid.* p 5.

51. H. Davy, 'On the composition of the atmosphere' (a course of lectures of 1807) Collected Works edited by J. Davy 8 (1840) 252-255. See also H. Davy, Elements of Chemical Philosophy (London, 1812) p 233.

52. See the useful evaluation of Graham's diffusion experiments by E. A. Mason, 'Thomas Graham and the kinetic theory of gases.' Phil. Journ. 7 (1970) pp 99-115 and also E. A. Mason and R. B. Evans, 'Graham's laws,' J.Chem.Ed. 46 (1969) pp 358-364. E. A. Mason and Barbara Kronstadt, 'Graham's laws of diffusion and effusion.' J.Chem.Ed. 44 (1967) pp 740-744. A. D. Kirk, 'The range of validity of Graham's laws' J.Chem.Ed. 44 (1967) pp 745-750.

and extreme mobility. Upon entering on this enquiry, I very soon found that the last supposition is altogether inadmissible, and that the diffusion of gases is not of an accidental nature, but subject to fixed laws." 50d

It is possible that Davy was being criticised in this statement. Davy had suggested that both Dalton and Berthollet were incorrect in their theories of the atmosphere. He regarded the atmosphere as a mechanical mixture which remained uniformly mixed by the continuous agitation produced by winds.⁵¹

The experiments of Doebereiner provided Graham with an opportunity to measure the force of diffusion. Graham suggested that Doebereiner's own explanation of his experiments was improbable because Saussure had found that hydrogen was the most difficult gas to absorb and condense. Furthermore, there was no reason to suppose that hydrogen particles were necessarily smaller than those of other gases. Graham re-examined these experiments. He found that there was an unequal exchange of hydrogen and air, by diffusion through a fissure, because hydrogen diffused three or four times more rapidly than air. The process was complicated, however, by the inequality of the inner and outer water levels which caused a pressure flow in addition to diffusion. To prove this, Graham used hydrogen in a cracked jar and kept the inner water level below the outer level by using weights on the jar. Then, four or five times as much hydrogen left compared with the air which entered. Therefore Doebereiner had observed the mutual exchange of hydrogen and air by diffusion assisted by a mechanical flow caused by pressure differences. Graham here established the important experimental condition that simple diffusion processes must be studied at constant pressure.⁵²

With gases which were lighter than air in a cracked jar, for example methane or coal gas, the water level rose in the jar; with olefiant gas which had the same density as air there was no change in water level; and with carbon dioxide, which was heavier than air, there was a slight

52a. Graham, op.cit. (50) p 10.

53. Graham, 'On the law of diffusion of gases', read Dec. 19th 1831; an appendix was added to this paper which was dated Sept. 7th 1832, Phil.Mag. 3 Ser 2 (1833)(March 1833)175-190,(April 1833)269-276, (May 1833)351-358, also found in Edin.Royal Soc.Trans. 12 (1834) 222-258 and in Researches 44-70.

54. Graham, ibid. Researches 44.

55. It is possible that Graham was led to try stucco plugs from an account of some experiments mentioned by W. F. Edwards in his book: On the Influence of Physical Agents on Life, (Paris, 1824 - translated into English in 1832). Graham might well have read the review of this book in Edin.Med.Surg.J 18 (October 1824) 332-366. This review reported on page 335 that Edwards had found that if a tube was closed at one end with plaster and filled with mercury and inverted in a trough of mercury then air entered rapidly. In consequence animals could respire in glass vessels closed with plaster. A similar experiment had been reported to the French Academy in 1771. Three toads were kept in a box covered with plaster. The toads were able to breathe through the plaster and two out of the three toads survived after 18 months. It is certain that Graham was interested in the relation between respiration and diffusion from his discussion of this topic in his 'diffusion law' paper.

fall in the water level. Finally, Graham pointed out that Wedgwood stoneware tubes closed at one end were more suitable for demonstrating diffusion than cracked jars. These tubes needed to be unglazed and slightly damp for the best results. He showed that they were sufficiently porous for true diffusion to occur through them without any condensation or absorption of gases.

In this faculty paper Graham did not mention either his experiments with stucco diffusion tubes or his experiments on the diffusion of gases into a vacuum. Therefore it is probable that these experiments were carried out between the latter half of 1830 and December 1831. For they were included in his next paper: 'On the law of diffusion of gases' which was read to the Royal Society of Edinburgh on December 19th 1831.

With regard to Graham's thoughts on the mechanism of diffusion, ^{as found} in his faculty paper we find that he only commented that the "diffusion of a gas into air, does not take place in sensible masses, but in ultimate particles; otherwise mixed gases could not diffuse unequally." ^{52a}

The aim of the diffusion law paper of 1831 was to establish the numerical exactness of the diffusion law. ⁵³ Graham stated his law at the outset: "the diffusion or spontaneous intermixture of two gases in contact, is effected by an interchange in position of indefinitely minute volumes of the gases, which volumes are not necessarily of equal magnitude, being in the case of each gas inversely proportional to the square root of the density of the gas." ⁵⁴ He had devised a new method for determining the speed of gaseous diffusion using a 'diffusion tube'. This was an elegantly simple and efficient development from the stoneware tubes. He used an open glass tube, $\frac{1}{2}$ " wide, and 6" to 14" long, with a dense stucco plug about $\frac{1}{5}$ " thick fixed in one end of the glass tube. The stucco plug was made from slaked Paris plaster. ⁵⁵ It was dried either by exposure to dry air for one day, or by heating it to 200°F for a few hours. The diffusion tube was then filled with water using a syphon, taking care not to wet the stucco. A damp filter paper was tied

56. Later experimenters, for example Loschmidt in his interdiffusion experiments, did not perform their experiments under constant pressure and so their results were less accurate than those of Graham.

57. Graham's table of diffusion volumes ^{is taken} from Researches, p 64.

$$(\text{Air} = 1). \text{ Diffusion volume} = \frac{\text{Volume of gas which escaped}}{\text{Volume of air which entered}} = \frac{G}{A} ;$$

$$\left(\frac{A}{G}\right)^2 = \frac{\text{Density of gas}}{\left(\frac{\text{diffusion}}{\text{volume}}\right)^2} = \frac{1}{\left(\frac{\text{diffusion}}{\text{volume}}\right)^2}$$

<u>Gas</u>	<u>Diffusion volume (air being 1)</u>	
	<u>Experiment</u>	<u>Theory</u>
Hydrogen	3.83	3.7949
Carburetted hydrogen	1.344	1.3414
Olefiant gas	1.0191	1.0140
Carbonic oxide	1.0149	1.0140
Nitrogen	1.0143	1.0140
Oxygen	0.9487	0.9487
Sulphuretted hydrogen	0.95	0.9204
Protoxide of nitrogen	0.82	0.8091
Carbonic acid	0.812	0.8091
Sulphurous acid	0.68	0.6708

58. Thomas Thomson had been criticised between 1822 and 1826 for his inaccurate determination of the specific gravity of hydrogen by the Glasgow physician Harry Rainy. See W. H. Brock, Ph.D. Thesis: The Chemical Career of William Prout (Leicester University, 1966) pp 316-325.

In 1831 the Chemical Committee of the newly-formed British Association for the Advancement of Science recommended that it was important to determine accurately the relative weights or specific gravities of hydrogen, oxygen and nitrogen (B.A.A.S. Report 1 (1831) p 53). Also in 1831, Daubeny informed Prout, that Dalton wanted the specific gravity of hydrogen and other fundamental points of the atomic theory settled by a sort of chemical committee. See Brock Ph.D. Thesis p 337. Was Graham hoping that he might be asked to determine the specific gravities of certain gases by diffusion?

around the outside of the tube to ensure that the external air was saturated with water vapour. Hydrogen was passed into the diffusion tube; from where it escaped through the plug by diffusion and was replaced by the incoming air. During the exchange of gases, the level of the tube was altered so that the inner and outer water levels were always kept the same. This gave constant pressure diffusion.

The experimental results were not much influenced by gas absorption. Graham checked this and found that stucco had a very low absorbent power for gases. Provided that the above conditions were carefully followed, excellent results could be obtained in diffusion experiments. Regrettably some later workers,⁵⁶ like Bunsen, failed to attend to these details and so they were unable to confirm the diffusion law. Graham's own results established the diffusion law with great accuracy. He determined the 'diffusion volume' for several gases; this was the ratio of the volume of gas which escaped, to the volume of air which entered to replace the gas. The diffusive replacement of gases was completed when the water-level in the diffusion tube no longer changed. The diffusion volume of a gas was found to be inversely proportional to the square root of the density of a gas, as Graham's table of results demonstrates.⁵⁷ The careful establishment of the constant-pressure diffusion law was an outstanding achievement for the young Graham, then twenty-five years old. His apparatus for diffusion was ingenious and yet essentially, very simple.

Graham proposed that diffusion experiments could be used to determine the specific gravity of certain gases with greater accuracy than by ordinary means, but it does not appear that his suggestion was taken up.⁵⁸ Inequality of density was not an essential requirement for diffusion as he showed. He connected two open diffusion tubes, dipping into water, with a glass tube containing a stucco diaphragm, $\frac{1}{5}$ " thick, by using caoutchouc adapters. With this apparatus he showed that two gases of the same density, carbon monoxide and nitrogen, interdiffused uniformly at constant pressure after 24 hours.

59. Graham 'On the law of diffusion of gases,' op.cit. (53)
Researches p 56.

60. Graham, *ibid.* p 57.

61. Graham, *ibid.* p 69.

Graham showed considerable reserve and caution about giving any explanation of the diffusion process. A possible reason for this was his discovery of a difficulty, which he was either not prepared, or more probably unable, to explain at this time. The problem arose with the diffusion volume of hydrogen. Dry stucco plugs gave him low values, such as 3.65 and, by contrast, a moist stucco plug gave him a high value of 3.85 compared to the theoretical diffusion law value of 3.79. To explain this Graham suggested that, with dry plugs, the incoming air was expanded by taking up water vapour, whereas with damp plugs, escaping hydrogen, evaporated some of the moisture instead of exchanging with air. He noticed that loose, damp plugs were particularly bad, giving a diffusion volume for hydrogen as high as 4.05. Only hydrogen appeared to give such unusual results and he therefore wondered whether hydrogen possessed some special physical property.

To investigate this he allowed hydrogen, air and other gases to flow into a vacuum through a stucco plug under the influence of mechanical pressure. A small bell-jar was closed with a stucco plug, $\frac{1}{2}$ " thick, and covered with a brass cap and stopcock. This jar was placed on the plate of an air pump and evacuated. Different gases were then allowed to enter and the time was noted for an attached mercury gauge to fall from 29" to 27". His results were most surprising:

Gas:	Air	Moist Air	Carbonic Acid	Nitrogen	Oxygen	Carbon Monoxide	Olefiant Gas	Coal Gas	Hydrogen
Entry time in minutes (\pm 10 or 20 seconds)	10'	10'	10'	10'	10'	9'30"	7'50"	7'	4'

The velocity of carbonic acid was almost identical to that of air. This was certainly not the case in simple diffusion experiments. Hydrogen gas entered the vacuum 2.5, or more precisely 2.408, times more rapidly

59. Graham 'On the law of diffusion of gases,' op.cit. (53)
Researches p 56.

60. Graham, *ibid.* p 57.

61. Graham, *ibid.* p 69.

than air. Yet in diffusion hydrogen passed 3.8 times more rapidly than air, or as Graham stated it after further trials: "... a certain quantity of hydrogen passed through the same porous plug, by the pressure of the atmosphere into a vacuum in 15 minutes; by spontaneous diffusion into air in 60 minutes; or the velocity of diffusion was one-fourth the velocity of mechanical pressure." ⁵⁹

These experiments showed that Dalton's hypothesis that air was a vacuum to hydrogen (or vice-versa) was false or as Graham expressed it: "hydrogen passes 2.4 times more swiftly, [than air under mechanical pressure] and not 3.8 times, as in diffusion experiments." ⁶⁰ His subsequent rejection of Dalton's view that gases behaved to each other as vacua clearly reversed the position which he had held in 1830. He was left without an adequate theory to explain his diffusion law. Therefore he concluded that "the law at which we have arrived is certainly not provided for in the corpuscular philosophy of the day, and is altogether so extraordinary that I may be excused for not speculating further upon its cause, till its various bearings, and certain collateral subjects, be fully investigated." ⁶¹

The reason why gases did not flow into a vacuum in the same time as they diffused into air, became apparent to Graham at a later date. The problem was, that the flow of gases into a vacuum was a mixed phenomenon, partly diffusion and partly transpiration or viscous flow; whereas the passage of gases through thin, dense, stucco plugs into air was essentially a simple process of constant pressure diffusion. In a supplement to his paper, added in 1832, Graham correctly suggested that frictional resistance was involved whenever gases moved through stucco under mechanical pressure.

What was Graham's conception of the process of diffusion at this date? The answer to this can only be conjectural, because there is no documentary evidence available. Nevertheless, certain deductions can be made about Graham's views in 1831. First, it is to be noted that in his

62. Graham, 'On the law of diffusion of gases,' Researches pp 66-67.

63. Graham, Elements of Chemistry 1st.edn. (London, 1842) pp 65-66.

64. Berzelius, Traité de Chimie. Vol. 1 (translated by A.J.L. Jourdan, Paris, 1829) p 85.

65. P. S. Laplace, 'Sur l'attraction des corps sphériques, et sur la répulsion des fluides élastiques,' Ann. de Ch. 2 Ser 18 (1821) 181-190, 273-280.

paper confirming the diffusion law, he stressed that diffusion was a process which took place between ultimate particles and was subject to a fixed law. He emphasised the exchange of position of particles in his comments on evaporation in his 1831 paper. He wrote that: "evaporation or the elevation of vapour from a liquid into air, or any other gas, comes now to be explained on the principles of diffusion. The powerful disposition of the particles of different gaseous bodies to exchange positions may as effectually induce the first separation of vapour from the surface of a liquid, as a vacuum would do. Once elevated the vapour will be propagated to any distance by exchanging positions with a train of particles of air, according to the law of diffusion. The length to which this diffusion proceeds in a confined portion of air is limited by the property of vapour, namely that the particles of a vapour condense when they are within a certain distance." ⁶²

The corpuscular philosophy of the day which Graham suggested was inadequate to explain gas diffusion had been developed from the Newtonian static model of gases. Newton had explained the pressure-volume relations in a gas by assuming that hard inelastic particles repelled one another with a force inversely proportional to the distance between their centres. In the eighteenth century the caloric theory of heat was developed and this led Dalton ultimately to envisage gas particles as hard bodies surrounded by an elastic atmosphere of caloric. In his first theory of mixed gases Dalton had postulated the existence of a repulsive force which acted only between like particles. This idea was followed by his second theory of mixed gases in which he supposed that the elastic atmospheres of caloric were responsible for the repulsive force.

Graham referred to Laplace, ⁶³ as did Berzelius, ⁶⁴ in his explanation of the states of matter. According to Laplace's corpuscular theory of matter ⁶⁵ the particular state of matter depended upon the mutual relations of three forces. Graham explained that these were: "firstly the attraction of each particle for the other particles which surround it, which

66. Graham, Elements of Chemistry 1st.edn. (London, 1842) pp 65-66.
67. In his lecture notes of 1838, Graham referred to the diffusion of gases as a process in which: "a new law of their constitution is observed, which is highly characteristic of the gaseous state. A forcible tendency to intermix or diffuse themselves through each other - a property which illustrates in a very striking way the inherent activity of matter."
See Wellcome Manuscripts: 'Notes and drafts for University College lectures (1838-1848)' 154 ll. Ref. No. 2579 (old no. 3202).
68. Graham, 'On the heat of friction,' Ann.Phil. N.S. 12 (October, 1826) 260-262 or Researches pp 626-630. See pp 626-627.

induces them to approach as near to one another as possible, secondly the attraction of each particle for heat which surrounds other particles in its neighbourhood and thirdly the repulsion between the heat which surrounds each particle and that which surrounds the neighbouring particles of bodies.... When the heat increases to such a degree that the reciprocal repulsive force prevails over the force of attraction of the particles for one another, the particles disperse in all directions as long as they meet no obstacle and the body assumes the gaseous form." ⁶⁶

This was essentially a static model of gas particles, held apart, by the repulsion between their caloric atmospheres. Now, such a theory was inadequate to explain diffusion convincingly as Graham had pointed out.

An alternative view was developed by Graham based on motion. ⁶⁷ But it was not the disordered rectilinear motion of the later kinetic theory. In diffusion, gas particles 'exchanged positions.' How did this occur? Graham envisaged an atom to be a solid nucleus surrounded by an atmosphere of caloric particles. The caloric particles were not at rest. This can be deduced from the comments which he made in his 1826 paper on the heat of friction. In this paper Graham avowed his support for the material, or caloric, theory of heat. Thus he wrote:- "It appears that this motive power, which is essential to the communication of heat and our perception of it, is never really annihilated. It disappears when heat passes into a body, but it is merely overpowered for a time and not altogether lost; for upon reduction of the temperature, the heat emanates from the body, evincing its pristine velocity. We may compare the state of heat in union with matter to that of a bent spring, or a compressed elastic substance, the attraction of the matter for heat being the restraining force. Sensible heat, therefore, we never find destitute of this motive power, nor to lose it - at least heat is never so divested of it as to be incapable of resuming it." ⁶⁸

It is possible that Graham believed that caloric particles were vibrating or rotating about the solid atomic nucleus and that each atom

69. M. D. Swords, The Chemical Philosophy of Thomas Graham, Ph.D.Thesis
Case Western Reserve University, 1973.

70. Graham, 'Speculative ideas respecting the constitution of matter,'
Proc. R. S. 12 (1863) p 620. Researches 299-302.

71. R. A. Smith, 'Graham and other atomists,' the preface to Graham,
Chemical and Physical Researches (Edinburgh, 1876) v-xxi, *See*
especially xvi.

had a characteristic nuclear motion. When two atoms collided, they would be pushed apart by the repulsive force exerted between neighbouring caloric atmospheres. Graham had emphasised that diffusion was not accidental but it was governed by a fixed law. Thus, the repulsive nature of caloric atmospheres surrounding atoms would be insufficient to explain diffusive motion. The atoms themselves must be in motion. Swords⁶⁹ has assumed that Graham had worked out a detailed view of nuclear motion by 1826, but Graham only gave a detailed account of this in 1863, by which time he had rejected the caloric theory of heat.

In 1863 we find that Graham had stated his belief in the concept of primary matter.⁷⁰ He realised, then, that if the ultimate atoms of the different elements were at rest they would be identical. In order to distinguish the atoms of different elements, Graham gave them an unalterable and quantitatively-different motion. This characteristic nuclear motion swept out a constant volume for an atom and this motion of an atom determined its specific gravity, for the specific gravity was inversely proportional to the volume. Also a faster-moving nuclear core gave a greater diffusive velocity. Therefore the velocity of diffusion was inverseley proportional to the specific gravity. Both these properties were related to, and ultimately depended upon, the nuclear or atomic motion. Swords has suggested that the motion of the nucleus was probably revolutionary. Graham hinted at this in his use of a solar system analogy and R. A. Smith also inferred that this kind of motion was envisaged in his essay on Graham.⁷¹

Swords has shown how diffusive velocity can be explained from these ideas: "As the nuclear core revolved about its point in space, the caloric cloud moved with it, creating an oscillating, vibrating atomic complex capable of colliding with atoms as it turned about. Such a collision amounted to a penetration or an intermingling of the respective caloric envelopes until the caloric idio-repulsion threw the atoms apart. This 'throwing apart' constituted the diffusive, rectilinear motion of

72. M. D. Swords, op.cit. (69) Ph.D.Thesis pp 45-46.

73. E. Mendoza, 'A critical examination of Herapath's dynamical theory of gases.' B.J.H.S. 8 No.29 (1975) 155-165.

74. Mendoza, *ibid.*

gaseous atoms. Greater primordial velocities would cause more intimate and frequent collisions and greater consequent repulsions. In the final result, the primordial nuclear velocities determined relative diffusive velocities." ⁷²

This seems to be a sensible interpretation of Graham's view of diffusive velocity. Unfortunately there is no surviving evidence for the details. Did Graham have a clear idea of the motion of atoms in 1831? Did he already in 1831 view these atoms as made up of primary matter? We do not know. Certainly if he had developed these views he would have been able to explain diffusion. However, Graham was reluctant to commit himself to speculative theories; he preferred to determine experimental laws. He wanted to delay any revelation of his thoughts on diffusion until he had completed his researches in this field.

It is possible that the earlier speculations of John Herapath might have influenced Graham's thoughts on diffusion in 1831. But Graham would not have accepted Herapath's views in their entirety because Graham had not yet rejected caloric from gases.

Mendoza has argued convincingly that Herapath modified Dalton's static model of a gas by removing caloric from the gas particles.⁷³ Dalton had explained diffusion using his second theory of mixed gases. It was an orderly interpenetration of two lattices of gas particles. Each gas possessed globular particles which varied in size from one gas to another. Herapath reinterpreted gaseous diffusion in terms of the momenta and collisions of gas particles. He rejected explanations based on the repulsive force between the sheaths of caloric which surrounded gas particles. Mendoza says that: "Herapath's version substitutes the oscillation of the particles which do not match from one gas to the other because the spacings are different among other things." ⁷⁴

Herapath began by dismissing explanations of diffusion based on affinity, suggesting that diffusion followed easily from his theory as follows: "suppose that portions of the surfaces of two media are exposed

75. J. Herapath, 'A mathematical inquiry into the causes, laws and principal phenomena of heat, gases, gravitation etc.' Ann.Phil. 2 Ser 1 (1821) 273-293, 340-351, 401-416, see p 402 for the quotation. By the word 'numeratom' Herapath meant the number of particles in unit volume.

to each other, and that parallel to these portions the media are divided into strata. Then because a difference in the 'numeratoms', a difference in the motions of the particles of the two strata, or a cornered irregular figure in the particles, would render it impossible for the particles of one stratum to be so reflected by the particles of the other, that each stratum would retain its particles entire and unmixed with those of the other, the two strata would intermix; and would not arrive at a state of equilibrium action, until the particles were uniformly and equally disposed in each stratum. For the same reasons, these newly compounded strata would mix with the next; and thus it would go on, stratum intermixing with stratum, until an equilibrium action throughout was restored, by equal and uniform intermixture of the two gases." ⁷⁵ Thus, Herapath's theory of diffusion was probably a modification of Dalton's second theory as given in his New System of Chemical Philosophy.

Herapath's theory of gases differed from that of Dalton in more respects than the absence of caloric. Both Herapath and Thomas Thomson had suggested that it was probable that only one kind of matter existed. They did allow, however, that the primitive particles of this matter could vary in size, figure, and also in their arrangement. Here we have the possible origin of Graham's notion that primary matter could be differentiated by its degree of motion or volume, that is by size and figure. Herapath had admitted that there might be a difference in the motions of particles found in two different gases.

Graham's view of diffusion in 1831 probably resembled that of Herapath in many respects except that Graham would have attributed the force of repulsion both to caloric particles and to nuclear motion. He would not have explained repulsion by nuclear motion alone because he accepted the existence of caloric. Would Graham have accepted primary matter in 1831? I think that it is likely that he would have done. His early researches could have been influenced by Boscovich's theory in which primary matter was assumed. Graham's teacher, Thomas Thomson was

76. Thomas Thomson, System of Chemistry, 4th.edn. (Edinburgh, 1810) Vol.1 p 631 - a similar statement occurs in the earlier versions of this same work, for example 1st.edn. (1802, Edinburgh) 1 386, 2nd.edn. (Edinburgh, 1804) and in the 3rd.edn. (Edinburgh, 1807) See J. Herapath, Ann.Phil. 2 Ser 1 p 281 for a similar statement:- "one of the sublimest ideas of the ancients was, that there is but one kind of matter, from the different sizes, figures, and arrangements of whose primary particles, arises all the beautiful variety ... which is observed in the productions of nature."
77. Thomas Thomson, An Attempt to Establish the First Principles of Chemistry, (London, 1825) Vol.1 pp 30-31.

certainly a reductionist with regard to the number of elements. Until 1810 he wrote that decomposition might eventually yield "those really simple and elementary bodies of which all substances are made. When this happens ..., the number of simple substances will probably be much smaller than at present. Indeed, it has been the opinion of many distinguished philosophers in all ages, that there is only one kind of matter; and the difference which we perceive between bodies depends on the varieties in the figure, size, and density of the primary atoms when grouped together. This opinion was adopted by Newton; and Boscovich has built upon it an exceedingly ingenious and instructive theory. But the full demonstration of this theory is perhaps beyond the utmost stretch of human sagacity." ⁷⁶

This was replaced by a more cautious statement in 1825: "with respect to the notion entertained by Boscovich, that the ultimate atoms are homogeneous, we are incapable at present of deciding whether it be well or ill-founded. It is not likely that any of these ultimate elements has come under our inspection. All our simple bodies are most probably compounds. ^{is possible that the ultimate elements of bodies} It may be very few - it is even conceivable that they may be reduced to two; but in what way all the variety of bodies with which we are acquainted, could be produced from one single kind of elementary body or atom, I cannot, for my own part, form any conception." ⁷⁷

At the time of Graham's researches on diffusion, there was considerable uncertainty about atomic weights. Debates on the atomic theory were centred on the integral multiples hypothesis of Prout and on the determination of accurate atomic weight values, instead of being preoccupied with the more difficult problem of primary matter. But it is to be remembered that Davy, Prout, and Thomson had all speculated on the likely-existence of primary matter, and undoubtedly this would have familiarised Graham with the subject. However, it would have been an inopportune time for Graham to speculate on this problem. He wanted to establish a scientific reputation and he must have been aware that Thomson's own

78. Herapath was actively involved in a conflict with the Royal Society at the time of Graham's first researches. This conflict arose because the Royal Society refused to publish Herapath's papers. Herapath wrote to The Times in 1826 complaining about his treatment. See S. G. Brush, 'The Royal Society's first rejection of the kinetic theory of gases (1821), John Herapath versus Humphry Davy,' Notes and Records of the R.S. 18 (1963) 161-180.

79. John Kearsley Mitchell (1793-1858) was the son of a Scots physician who had emigrated to America. Thus Mitchell studied at Edinburgh and Pennsylvania Universities. In 1819 he graduated as an M.D. He lectured in medicine and physiology at the Philadelphia Medical Institute from 1824 to 1833 and in Chemistry at the Franklin Institute from 1833 to 1838. His early interests were in osmosis (as a result of Dutrochet's research work) and in the liquefaction of carbon dioxide. He held the Chair of Medicine at Jefferson Medical College from 1841 until his death.

80. J. K. Mitchell, 'On the penetrativeness of fluids,' Amer.J.Med.Sci. 7 (1830) 36-67 and also in the Journal of the R.I. 2 (1831) 101-118, 307-321.

80a. J. K. Mitchell, ibid. Journal of the R.I. 2 (1831) pp 107-108.

researches into atomic theory had aroused considerable controversy. Graham presumably felt that it would be wiser to avoid premature speculations on primary matter. Likewise, he made no explicit reference to Herapath's work presumably again to avoid possible controversy. But it is likely that both of these considerations were in Graham's mind at this time⁷⁸ and together they would have provided a basis for his conception of the diffusion process.

The scientific community certainly took note of Graham's researches on diffusion and his work became the subject of considerable comment. The first response to Graham's work came from two American physiologists, J. K. Mitchell and E. Faust. They were interested in the passage of gases through membranes particularly with reference to respiration.

J. K. Mitchell⁷⁹ described his investigations of the passage of gases through membranes in a paper which appeared in November 1830.⁸⁰ He reviewed Graham's short 1829 paper 'On the singular inflation of a bladder' and criticised him for failing to investigate fully the principle of the experiment. Mitchell wrote: "content with a single additional experiment, he [Graham] comes in the ancient method, to immediate conjectural explanation, and has thus lost an easy opportunity of making a beautiful, and perhaps extensively useful discovery In what manner the power of 'rising into the air' was given [i.e. the escape of liquefied carbon dioxide from the membrane into coal gas inside the bladder], and whether it was dependent on the force of water, or some other cause does not and could not be made to appear from the single fact, as presented by Mr. Graham."^{80a}

In fairness to Graham this observation was only incidental to his researches on diffusion. Graham recognised that the passage of gases through a bladder was not a simple diffusion process. It depended upon the liquefaction of gases in the water present in the membrane followed by the evaporation of this volatile liquid on the other side of the membrane.

In 1829 Mitchell had observed that a gum elastic balloon filled with

81. Mitchell's results for the times of permeation of equal volumes of different gases were:-

Gas	ammonia,	sulphuretted hydrogen,	cyanogen,	carbonic acid,
Permeation time:	1'	2½'	¾'	5½'

Gas:	nitrous oxide,	arseniuretted hydrogen,	olefiant gas,
Permeation time:	6½'	27½'	28'

Gas:	hydrogen,	oxygen,	carbonic oxide,	nitrogen
Permeation time:	37½'	113'	160'	even slower.

82. Graham, 'On the absorption and dialytic separation of gases by colloid septa' (June 20th 1866) Researches pp 235-244.

hydrogen rose up to the ceiling and after a time it descended. To investigate this phenomenon further, he covered a bottle of hydrogen with a thin elastic membrane. The membrane became concave and then burst because hydrogen had escaped. There was no change in the weight of the membrane and the experiment could be reversed by putting air into the bottle and then placing it in an atmosphere of hydrogen, so that the bladder became convex. Similar phenomena were observed with heavier gases, such as carbon dioxide or nitrous oxide, in the bottle and air outside, except that the process was more rapid. He realised that these gases were exchanged for air across the membrane. To compare the permeation times of equal volumes of different gases, Mitchell enclosed air in a glass syphon between mercury and a gum-elastic membrane. The time was then noted for different gases to enter the membrane. The results showed clearly that the permeation of gases through membrane was not a simple diffusion process, because the permeation times were not related to the gas densities. Ammonia passed through the membrane most rapidly and nitrogen least rapidly; hydrogen was about six times slower in its passage than carbon dioxide.⁸¹ Interestingly, gases penetrated the membrane with considerable force. A force of over two atmospheres could not prevent the penetration of membranes by gases.

One of Mitchell's experiments was taken up later by Graham in his researches on the dialytic separation of gases.⁸² This experiment was the placing of a bladder full of nitrogen in an atmosphere of oxygen. Mitchell found that, after one night, the gas inside the bladder allowed a taper to burn more brightly than in ordinary air.

Mitchell explained the penetration of gases through organic membranes by suggesting that some form of attraction occurred between the gas and the membrane. He argued that this attraction was not chemical although it did take place between dissimilar substances. Both gum elastic and moist bladder were shown to absorb carbon dioxide. Gases did not just penetrate membranes but they penetrated one another with considerable

83. John Murray may possibly have been Mitchell's teacher at Edinburgh. In August 1830, Edwin Faust, an American physician from Columbia, S. Carolina, published a paper in which he mentioned Graham's bladder experiment. Faust showed that a nitrogen-filled bladder became inflated after one day in an atmosphere of hydrogen. Also bladders containing air or hydrogen placed in carbon dioxide burst in two and eight hours respectively. He accepted Graham's view that gases became liquefied in membranes or blood. He suggested that the exchange of gases was analogous to the endosmose and exosmose of liquids. For example in respiration there was an endosmose of oxygen and exosmose of carbon dioxide; See:- E. Faust, 'On the endosmose and exosmose of gases etc.' Amer.J.Med.Sci. 7 (Nov.1830) 23-26. This paper was reviewed along with Mitchell's first paper in Edin.Med.Surg.J. 36 (1831) 211-213. Later in 1832 William Stevens, a London doctor, wrote, in his book, Observations on the Healthy and Diseased Properties of Blood (London, 1832), that he was the first to suggest the bladder experiments to Mitchell and Faust. Whilst in the W. Indies, in 1827, Stevens showed that carbon dioxide escaped more rapidly from a tumbler covered with a bladder than air could enter. Stevens thought that oxygen in the air attracted carbon dioxide causing the bladder to become concave. He argued that there must be a force of 'latent attraction' to explain the lifting of gases through membranes. He also pointed out that Dalton's theory of mutual vacua could not account for this. Stevens accused Mitchell of plagiarism, saying that he had informed Mitchell that oxygen attracted carbon dioxide through a membrane before Mitchell began his experiments. He maintained that this information was the basis for Mitchell's work.—It was not the balloon experiment or Graham's observations which led to Mitchell's investigations. (See pp 45-46, 53, 89-105, 111 of Stevens' book).
84. J. K. Mitchell, 'On the penetration of gases,' Amer.J.Med.Sci. 13 (1833) 100-112, see pp 100-101. This paper is generally less well-known than Mitchell's former paper. It is interesting to note Mitchell's use of the word 'effused' for the escape of gas; on page 102 of this paper. Graham used the word 'effusion' later for the escape of gases through very small holes in a thin piece of foil.
85. Graham, Wellcome Manuscripts: 'Notes and drafts for University College lectures' 154 ll. (1838-1848) MS. No. 2579 (old no. 3202).
86. Graham, Elements of Chemistry 1st.edn. (London, 1842) 76-77.

force. Mitchell implied that Dalton's theory of mutual vacua was inadequate to explain this process. It seemed that the penetration of one gas by another was controlled by the presence of suitable gaps between the gas particles. It was like a process of solution, which occurred with a greater mechanical force than did mere mixture. Mitchell was closer to adopting the chemical solution theory of gaseous mixture which Berthollet and Murray had favoured.⁸³ He did not accept Graham's suggestion that membranes caused the liquefaction of gases.

In 1833 Mitchell wrote a second paper in which he discussed Graham's diffusion law and extended his own experiments. He began with a criticism: "Mr. Graham of Glasgow, a chemist of growing reputation, has in the course of an experimental investigation of the transmission of gases through stucco plugs and other inorganic substances, confounded together two very different actions, and has thus thrown some obscurity over the whole subject."⁸⁴ He conceded that Graham had established his diffusion law with stucco plugs. But Mitchell argued that diffusion phenomena would only take place when the pores of the barrier were easily penetrated by gases. The quantity of gas presented at the outer surface of the barrier must be greater than the diffusive power could carry away. This was the case with Graham's stucco plugs. On the other hand if the penetration of the barrier was less than the diffusive power then he argued that the action of the barrier would be estimated and not the penetration or diffusion. This was what happened when organic membranes like gum elastic and bladder were used. To increase the penetration of the barrier by a gas he suggested the use of an air current or a vacuum which would greatly increase the amount of gas 'effused'.

Mitchell was correct to distinguish between the diffusion of gases through plugs of fine porosity and the passage of gases through membranes. But Graham had made this distinction quite clearly in 1829 and he repeated it in his lecture notes⁸⁵ and textbook.⁸⁶ Graham argued that in Mitchell's experiments with organic membranes, a new action came into operation. This

87. J. Dalton, A New System of Chemical Philosophy, part 1 (Manchester, 1808) p 203.

88. Graham, op.cit. (53) Researches p 56.

Graham, himself, regarded his paper on the singular inflation of closed bladder as "the basis of the researches on the permeability of animal membranes by gases, published afterwards by Drs. Mitchell and Faust, and Dr. Stevens" See: Testimonials in Favour of Thomas Graham ... Candidate for the Vacant Chair of Chemistry in University College, London (Glasgow, 1837) p 41.

Also Edward Turner wrote: "It appears from the essays of Drs. Faust and Mitchell that their attention was awakened to the permeability of membranes to gases by the endosmose and exosmose of liquids described by Dutrochet, by an insulated example of a similar phenomenon in gases observed by Mr. Graham, and by some facts of a like kind noticed long ago by Priestley." Turner, Elements of Chemistry 5th.edn. (London, 1834) p 980.

was the liquefaction of gases in the membrane. However, the liquefaction of gases did not occur in stucco diffusion and so the two processes were quite distinct. To explain the order of the speeds of passage of gases through membranes, Graham suggested, quite reasonably, that the most easily-liquefied gases passed with greatest rapidity. For example carbon dioxide was readily liquefied to give a volatile liquid which passed through the membrane and evaporated rapidly into the air inside the membrane. Indeed he pointed out that Dalton had observed this phenomenon in its simplest form. Dalton had taken a jar half-full of carbon dioxide over water and added air to it. An air bubble had formed and separated accidentally. Dalton then noticed that this bubble expanded.⁸⁷ Graham interpreted this observation by saying that, carbon dioxide entered the water film by liquefaction, followed by evaporation of carbon dioxide inside, thus expanding the bubble. He emphasised the fact that, even the thinnest film of water was impermeable to gases, unless liquefaction occurred. Therefore the passage of gases through liquids and membranes was not a simple process of gas diffusion.

The only weakness which Mitchell could find in Graham's work was a minor point. Graham had shown correctly that dry bladder was twenty times less-easily penetrated by hydrogen than 1" thick stucco. But he then suggested erroneously that dry bladder would become more permeable under pressure.⁸⁸ Mitchell showed by experiment that dry bladder was almost impermeable under pressure. He used two tubes one sealed with 1" of stucco and the other sealed with dry bladder. Both tubes were filled with mercury and put into a trough of mercury. The mercury level in the stucco tube fell to the trough level in three minutes but the dry bladder held up the mercury for twelve hours and only a small bubble of air had entered in that time.

Undoubtedly Mitchell's work helped to make a clear distinction between the passage of gases through stucco and their passage through membranes. Graham had only examined membranes in a limited way but he had appreciated

unambiguously the difference between the transmission of gases through wet membranes and through stucco. Mitchell's experiments on the passage of gases through membranes were useful additions to the knowledge of this subject but his work cannot be compared with the discovery of the diffusion law.

Mitchell in 1833 corrected some of his earlier experimental results. For example he observed that ammonia was less penetrable than he had found previously. His new results showed the order of penetration of gases through: gum elastic, wet or dry bladder, was, starting with the most rapidly penetrating gas: cyanogen; carbon dioxide; and hydrogen. This order was the reverse of Graham's order for the speeds of diffusion of these gases. To investigate this problem Mitchell allowed compressed gases to escape through different-sized apertures and noted the time taken for the barometer gauge to fall from four atmospheres to one atmosphere. His results were:

Time of passage	of	air,	hydrogen,	carbon dioxide
Theoretical diffusion time (for comparison)		3.795	1	4.690
A visible aperture.		-	1	3.163
A smaller aperture (just visible).		2.344	1	2.688
Uncompressed $\frac{1}{4}$ " stucco.		2.18	1	2.005
Compressed 1" stucco.		1.727	1	1.626

Mitchell interpreted his results incorrectly saying that the time of passage, compressed gases approached Graham's diffusion law when larger orifices were used and he noted that lighter gases escaped with relatively less ease through smaller pores. He even predicted that hydrogen and carbon dioxide might pass through very small pores at the same speed. Indeed it seemed that pores might exist which would reverse the order of escape of these two gases, for example those in gum elastic. Further, ^{more,} he remarked that if the size of the orifice could be determined then it might

- 88a. The Keith Prize was awarded to Graham in April 1833 for his work on the diffusion of gases. The prize was awarded every two years for the most important discovery communicated to the Royal Society of Edinburgh. The prize was a gold medal and a piece of plate. This was presented to Graham from the Chair on December 2nd 1833. The award of this prize was the result of a report made on Graham's diffusion researches by James Forbes. See the letter from J. D. Forbes to Graham, April 6th 1837, Forbes Collection, St. Andrews University.
89. J. C. Poggendorff, 'On the law of diffusion of gases,' Pogg. Ann. 28 (June, 1833) 331-358.
90. J. J. Berzelius, Jahresbericht 14 (1835) 80-84.
91. Other comments on Graham's diffusion law were, in brief:- Faraday mentioned in November 1833 that there were some curious retardation effects of gaseous impurities on a platinum surface during gas reactions. He thought this might be related to the unusual properties of the passage of gases through narrow tubes at low pressure. Here he was referring to his own earlier studies of gas motion. He also suggested that this surface action would probably influence "the highly-interesting phenomenon of diffusion as studied by Graham and Mitchell." He added that it was probable that if spongy platinum had been used, in place of stucco, Graham would have discovered another law of diffusion. See M. Faraday, Experimental Researches in Electricity, Volume 1 (London, 1839) paragraph 659. Daniell must have tried this out, for he said that when a diffusion tube was stopped with finely-divided or spongy platinum, tightly-hammered into a brass column, the diffusion process went on with greatest advantage. He referred to the 'beautifully' determined diffusion law of Graham and accepted T. S. Thomson's explanation of Graham's law. See J. F. Daniell, An Introduction to the Study of Chemical Philosophy, (London, 1839) pp 65-66. Edward Turner also gave details of Graham's law in 1834 and he noted the recent "very clever paper" by T. S. Thomson. Turner accepted that diffusion was a mechanical process and not a chemical process. He realised that Dalton's theory was inadequate but ^{said} it was generally applicable. E. Turner, Elements of Chemistry 5th. edn. (London, 1834) pp 271-273.

be possible to understand the variations in penetration times or even to find the volumes of penetrant atoms.

The motion of compressed gases was not, however, related to the law of constant pressure diffusion. Instead, it was an example of viscous flow or transpiration in which friction was an important influence. Mitchell was correct, however, to point out that differences in the size of pores influenced the process of transmission of gases under pressure. Graham had experienced similar problems when he had allowed gases to pass under mechanical pressure into a vacuum. The times of passage did not agree with diffusion times. Graham realised that friction was involved but he did not examine the problem in detail until the years 1846-9 when he carried out an extensive experimental investigation into transpiration. Finally, after Mitchell's death, Graham turned his attention to the study of the passage of gases through membranes. This was in 1866.

Graham's paper on the diffusion law was, however, favourably received by most of his contemporaries. In April 1833 he was awarded the Keith Prize by the Royal Society of Edinburgh for the most important piece of research presented to the Society over a two year period.^{88a} The paper was translated into German in 1833 by Poggendorff⁸⁹ and it was then reviewed by Berzelius in his Jahresbericht.⁹⁰ Berzelius accepted that there was a good agreement between the experimental and theoretical diffusion law. He advised Graham that his experiments could be further improved to give a greater accuracy. He referred to an intrinsic source of error caused by the presence of the small air bubble trapped under the stucco. The introduction of this air bubble was necessary, however, to avoid wetting the stucco. Berzelius said Graham had corrected for this error 'reasonably for informal experiments' but he had stated his figures too accurately in light of this error. He thought that an accuracy of 0.01 parts in 1 volume would have been more realistic than Graham's implied accuracy of 0.0001 parts in 1 volume, for diffusion volumes. Berzelius's praise was grudging as was often the case when he reviewed Graham's work.⁹¹

92. Thomas Starkie Thomson (1811-1847) is not to be confused with Graham's teacher Thomas Thomson. T. S. Thomson came from Primrose, near Clitheroe, Lancashire. He studied for a year at Edinburgh when he became a favoured pupil of John Leslie. He continued his studies at University College, London and in 1830 he gained the top prize for Natural Philosophy. He worked as a calico printer in Lancashire and his only published papers were on Graham's diffusion law. This first paper was published in both Philosophical Magazine and Annales de Chimie et de Physique. See T. S. Thomson, 'Observations on Mr. Graham's law of diffusion,' Phil.Mag. 3 Ser. 4 (May, 1834) 321-6 (dated April 12th 1834).
93. See letter from T. S. Thomson to J. Dalton dated May 10th 1834 in Roscoe and Harden, A New View of the Origin of Dalton's Atomic Theory (London, 1896) p 189.
94. See: Thomas Webster, Principles of Hydrostatics (London, 1835) 66-69. Webster mentioned Graham's work on diffusion and gave T. S. Thomson's derivation of the diffusion law.

In 1834, Thomas Starkie Thomson attempted to reconcile Graham's law of diffusion with Dalton's theory that gases were mutual vacua.⁹² Apparently Dalton accepted that Thomson's view was sound and free from objection. This is hardly surprising because Thomson was defending Dalton's favoured first theory of mixed gases.⁹³ Thomson praised Graham's work and said that it was a 'striking confirmation of Dalton's hypothesis.' He disagreed with Graham's view that his experiments depended upon some 'newly-discovered property of gases', which was inexplicable on any existing theory. Rather the diffusive velocity was directly proportional to the relative velocity of escape of a gas into a vacuum and in turn this was, from gaseous mechanics, inversely proportional to the square root of the density. Then, by assuming that the momentum of a gas diffusing into a vacuum was identical to that of a gas diffusing into another gas, Thomson was able to deduce Graham's law.⁹⁴ Thomson had to admit that Graham's own experiments on the flow of gases into a vacuum were at variance with this theory. But he argued that the law was so rigorous that either Graham had made inaccurate observations or perhaps his experimental technique was faulty. He favoured the latter suggestion because there was some agreement between Graham's results and the diffusion law, for example hydrogen had flowed into a vacuum more rapidly than air. But, if Dalton's hypothesis was valid, Graham's results on the flow of nitrogen, oxygen and carbon dioxide into a vacuum had to be incorrect. Finally, Thomson pointed out that insufficient attention had been paid to the flow of gases under pressure, and he mentioned that both Leslie and Faraday had obtained different results to Graham. To explain Graham's vacuum results he suggested that angular irregularities in the stucco channels had caused more obstruction for faster moving gases than for slower ones. On the other hand, the relatively slow process of interdiffusion was not subject to the same difficulty, which arose with the rapid entry of gases into a vacuum under mechanical pressure. He urged further research into this problem and Graham took up this challenge later in his paper 'On the motion of gases'.

95. H. Davy, Elements of Chemical Philosophy, (London, 1812) pp 95-96. See also W. H. Brock, Ph.D.Thesis, op.cit. (58) Chapter 8. Brock has noticed that Berzelius sought to explain the gaseous state in terms of mutually rotating atoms with analogous poles which would repel one another; but Berzelius realised that it would be necessary to explain how their axes could be retained in a position so that their poles would cause repulsion. For Berzelius, see his books: Essai sur la Théorie des Proportions Chimiques (Paris, 1819) pp 108-109 or Traité de Chimie by Berzelius translated by Esslinger, 4 (Paris, 1831) p 589.

96. W. Prout, Chemistry, Meteorology and the Function of Digestion. The eighth Bridgewater Treatise, 1st.edn. (London, 1834) p 563.

Further support for Dalton's first theory of mixed gases came from William Prout in his Bridgewater Treatise on Chemistry in 1834. Prout supposed that matter was composed of spherical molecules which revolved about their axes. The axial motion of a pair of molecules, rotating in the same direction, gave rise to a force of repulsion between the molecules. This repulsion counteracted the gravitating force of attraction existing between molecules. These views may have been a development of Davy's dynamical theory of matter, in which fluids contained particles rotating about their axes and also possessing a vibratory motion.⁹⁵ However, Prout went further than Davy and suggested that the velocity of the axial rotation was inversely proportional to the mass of the molecule. This last view appears to be similar to that which Graham proposed in 1863. Graham was not explicit on the type of motion which atoms possessed. But he went further than either Davy or Prout when he argued that although all atoms had the same primary mass, they could be distinguished from one another by the possession of different unalterable degrees of motion.

Unlike Davy, Prout retained a material theory of heat. Prout also explained how polarity occurred in molecules. He supposed that the motions of two adjacent molecules gave rise to polarity. He assumed that there was both an electric and a magnetic polarity. The rotation of two molecules in the same direction gave rise to magnetic repulsion, provided that the electric poles of these two molecules were in opposition. This model gave rise to the self-repulsive gas molecules which Dalton had postulated in 1801. Consequently, Prout's explanation of gaseous diffusion was in accordance with Dalton's first theory of mixed gases. He explained that: "a single row of self-repulsive molecules of a gas passing through the minute apertures of a porous vessel into a vacuum; or what is analogous into another gas having different self-repulsive powers; may be compared to a row of bullets urged by an elastic fluid, in quick succession through a gun-barrel; but with this difference, that the gaseous molecules propel each other; instead of being propelled by a foreign agency."⁹⁶

97. John William Draper (1811-1882) studied Chemistry at University College, London under Edward Turner. In 1832, Draper emigrated to America and took a medical degree under J. K. Mitchell at the University of Pennsylvania in 1836. His thesis was on glandular action which reflected Mitchell's own interests in Dutrochet's work on endosmosis. From 1836-9, Draper was Professor of Chemistry and Natural Philosophy at Hampden Sidney College and from 1839 he was Professor of Chemistry at New York.
98. J. W. Draper, 'On the interstitial movements which take place among the particles of bodies,' March 1836, J. Franklin Inst. reprinted in the Appendix to:-
J. W. Draper, Treatise on the Forces which Produce the Organisation of Plants, (New York, 1844) Appendix pp 13-23.
99. J. W. Draper, 'On the great mechanical forces generated by the capillary attraction of cellular tissue' Am. J. Med. Sci. (1838), reprinted in Draper, Treatise on the Forces which Produce the Organisation of Plants (New York, 1844) Appendix pp 42-57.

The problem of how the particles of one gas repelled only particles of their own kind and not others, was not explained by Prout in his account of Graham's diffusion law.

In America, the subject of gaseous penetration was examined again by John William Draper,⁹⁷ a pupil of J. K. Mitchell. In 1836, Draper suggested that the pores in stucco through which gases passed could be likened to capillary tubes.⁹⁸ Following up this idea, Draper examined the passage of gases through glass tubes covered with india rubber. Observing that oxygen passed more quickly through rubber than nitrogen, he wondered whether it was possible to obtain pure oxygen by forcing air through india rubber or through a gum elastic bag. Draper was unsuccessful; the excess pressure forced unchanged air through the bag. However Graham was successful when he took up this idea in 1865 and used better techniques. In an attempt to achieve his objective, Draper had examined air-filled soap bubbles which were of a closer texture than rubber. He found that oxygen did escape more rapidly from the bubble than nitrogen. He stressed that for gases to pass through a water film an initial absorption must occur. Likewise he argued that absorption was involved in Mitchell's experiments with membranes and therefore he believed they should be distinguished from the diffusion of gases through stucco.

By May 1838 Draper had accepted T. S. Thomson's explanation of Graham's diffusion experiments.⁹⁹ Gases were vacua to each other and the force which impelled the particles of one gas into the interstices of another did not exceed one atmosphere. He explained that the apparent exceptions observed by Mitchell, where gases appeared to penetrate membranes at pressures greater than one atmosphere, were due to the action of the barrier. With a membrane, or india rubber, gases were often absorbed in a very compressed state and this could alter markedly the volume of gas transmitted from that of the diffusion volume, whereas with stucco there was no condensing action. Stucco was merely a mechanical impediment to the motion of gases, like a temporary valve, so that the volumes of gases

100. J. W. Draper, 'Remarks on the constitution of the atmosphere addressed to John Dalton' Phil.Mag. 3 Ser. 13 (October, 1838) 241-252.
101. Graham, op.cit. (45) 'Notice on the singular inflation of a bladder' (1829)
102. Graham, Wellcome Manuscripts 'Notes and drafts for University College lectures' 1838-1848 (154 11). MS. no. 2579 (old no.3202). Most of these notes appear to have been written in 1838.
103. Graham, op.cit. (102).
104. Graham, Elements of Chemistry 1st.edn. part 1 (London, 1837) p 75.
105. Graham, op.cit. (102).

exchanged were inversely proportional to the square root of the gas densities as Graham had found. Draper pointed out correctly that Mitchell had failed to appreciate this distinction. Indeed he noted that Graham had successfully explained small deviations during stucco diffusion in terms of absorption. It seemed to Draper that if allowance was made for absorption then the results of Mitchell and Graham could be shown to agree.

In October 1838 Draper addressed Dalton through the Philosophical Magazine.¹⁰⁰ Again he emphasised the importance of the absorbing power of barriers in diffusion. There was considerable absorption if the barrier was water or rubber. These latter barriers absorbed gases and so increased the gas density and elasticity. After passing through the barrier, these condensed gases would escape from the attractive force of the barrier and then expand freely as into a vacuum.

Thus, Draper made a clear distinction between barriers like stucco and rubber, but he did not go as far as Graham. Although Graham accepted that absorption occurred in rubber or bladder he also believed that liquefaction must take place. Gases did not pass through membranes even in a compressed state; only liquids could pass through these barriers.¹⁰¹ Graham drew attention to the fact that in Mitchell's experiments the more easily-liquefied gases passed most readily.¹⁰² Likewise with caoutchouc, the chemically-related gases such as hydrogen and olefiant gas were transmitted more rapidly than the unrelated gases such as oxygen and carbonic acid. Graham grouped water films, membranes, and rubber, into a class of barriers which were impermeable to gases, as such; only liquids penetrated these barriers. They were clearly distinct from stucco. Graham consistently expressed this opinion throughout his life and it seems to be reasonably correct.

In his lecture notes¹⁰³ and textbook¹⁰⁴, Graham referred to his friend T. S. Thomson's explanation of the diffusion law. He called it "a dynamical confirmation of Dr. Dalton's theory that gases are mutually inelastic."¹⁰⁵ However, Graham was reluctant to accept Thomson's view as "a true

105a. Graham, op.cit. (104).

106. J. B. Dumas and J. D. Boussingault, 'Recherches sur la véritable constitution de l'air atmosphérique,' Ann.de Ch. 3 Ser. 3 (1841) 257-305.

107. Graham, op.cit. (102). He used the last two arguments in his textbook.

representation of the phenomenon although it afforded a convenient mode of expressing it." ^{105a} He saw some advantages in Thomson's arguments.

They accounted for the force of diffusion by which hydrogen diffused four times more rapidly than air. Also they led to a particular view of the constitution of the atmosphere in which there was less oxygen at greater heights. Interestingly this last advantage was soon to be brought into question by the work of Dumas and Boussingault on the constitution of the atmosphere. ¹⁰⁶

These researchers found that there was no appreciable variation in the composition of the atmosphere at different heights. Thus Dalton's first theory of mixed gases was once again rejected as inconsistent with experiment. Consequently T. S. Thomson's explanation of Graham's law, based on Dalton's first theory, was also shown to be inadequate.

In his lecture notes Graham pointed out a number of disadvantages which arose from Thomson's explanation. Firstly, the observed velocity or time of flow of different gases into a vacuum was inconsistent with the diffusion law. The flow times were: air and carbonic acid, the same 10'; carbonic oxide 9', olefiant gas $7\frac{1}{2}'$ and hydrogen 4'. Hydrogen only passed $2\frac{1}{2}$ times more quickly than air, on passing into a vacuum and not 4 times more quickly as in diffusion. Secondly, the gases which passed most easily into a vacuum, hydrogen, olefiant gas, coal gas, and carburetted hydrogen, were those which deviated from the diffusion law as a result of frictional resistance. Thirdly, if gases were supposed to expand into each other as they would do into a vacuum then a fall in temperature of 40 to 45°F should be produced but no change of temperature had been noticed. Finally, air entered different gases with varying speeds; for example air entered hydrogen, carbonic acid and chlorine at speeds proportional to the numbers 1277, 623 and 302 respectively. Now, if air was entering a vacuum in each case, why was not the velocity the same? ¹⁰⁷

Still Graham was not to be drawn on diffusion theory. Obviously he was not satisfied with Thomson's attempted explanations. However, in 1838,

108. Graham, op.cit. (102).

109. T. S. Thomson, 'Observations on the diffusion of gases' and 'Additions to a former communication on the diffusion of gases' Phil.Mag. 3 Ser. 25 (1844) 51-55, 282-283.

110. W. Onion, 'On the diffusion of gases' The Chemist Vol. 5 II New Series (1844) pp 112-114.

Onion had rejected Dalton's theory that gases were mutual vacua because the atmosphere did not contain different proportions of oxygen at different altitudes. Likewise, he rejected the view that the atmosphere was a compound. Instead, he suggested that gaseous diffusion was caused by a weak force of chemical affinity analogous to that between sulphuric acid and water. This was a return to the earlier views of Berthollet concerning the constitution of the atmosphere. Onion also rejected Donovan's arguments in favour of a compound atmosphere. For an interesting criticism, of Dalton's first theory of mixed gases, based on affinity, see M. Donovan, A Treatise on Chemistry, Lardner's Cabinet cyclopaedia (London, 1832) pp 145-151.

Graham did add one tantalising comment on the nature of diffusion in his own lecture notes: "Diffusion is a property which illustrates in a very striking way the inherent activity of matter." ¹⁰⁸

In 1844, T. S. Thomson discussed the last two criticisms, which Graham had raised. It is to be noted that these criticisms had been repeated in Graham's textbook. ¹⁰⁹ Thomson accepted that a fall in temperature would occur when air rushed into a vacuum. He added that Dalton had observed a fall of 40-45°F, but the interdiffusion of gases was a much slower process so any temperature change would not be noticeable. He maintained that Graham's final criticism was a misunderstanding. Thomson claimed that he had not suggested that air entered other gases with the same velocity. Instead he had argued that the moving force of the two currents was equal. He accepted that air would pass more rapidly into hydrogen than into carbon dioxide, because hydrogen and carbon dioxide rushed into a vacuum in 4' and 10' respectively.

T. S. Thomson then proposed a different explanation of diffusion, presumably because he recognised that studies of the atmosphere had persuaded scientists of the inadequacy of Dalton's opinion that gases were mutual vacua. ¹¹⁰ Certainly, Thomson had discussed the problem of the nature of the atmosphere and diffusion with the Scottish mathematician James Ivory in 1842. At this time Ivory was writing a mathematical paper on the presence of water vapour in the atmosphere. He was critical of Dalton's view that gases were mutually inelastic. But he believed that Graham's experiments were 'very ingenious' although he thought that they did not explain diffusion. Ivory examined Thomson's new explanation of diffusion and judged it to be 'unobjectionable'. Thomson had abandoned the idea that gases were mutually inelastic. Instead he supposed that a chemical attractive force existed between the particles of different gases. With this force he was able to account for diffusion. For example, when hydrogen diffused into oxygen, the heat surrounding an oxygen particle would repel the heat around a hydrogen particle, but beyond this heat atmosphere there was an

111. Graham, 'On the diffusion of liquids' November 16th 1849 Phil.Trans. 140 (1850) pp 1-46, 805-836 and 141 (1851) 483-494. See also Researches 445-446 for this reference.
112. Graham, Wellcome MS notebook No.14 (MS number 2565) Entry dated October 17th 1844. Initially Graham examined the diffusion of gas mixtures. He confirmed his earlier experimental views that there was unequal diffusion in the first few moments of the diffusion process, that is, the lighter gas escaped more rapidly than would be expected from its diffusion volume.
113. Graham, 'On the motion of gases' 18th June 1846 with an appendix dated November 1846, Part 1. Phil.Trans. 136 (1846) 576-632, or Researches 88-161. The MS of this paper in the Royal Society was originally entitled 'On the movement of gases' but this was crossed out and the above title was substituted. Royal Society MS 31.8.

incipient attractive force between hydrogen and oxygen particles. This attractive force was not strong enough to produce chemical combination but it was capable of causing the gradual diffusion of hydrogen into oxygen. Thus, like-particles of gases receded, and unlike-particles approached one another. By Newton's third law of motion, the same mathematical formulae could be used in this revised model of the gas state and so Graham's diffusion law could be deduced. Essentially Thomson had reverted to the earlier chemical solution theory of Berthollet and Murray.

Therefore when Graham wrote his paper on liquid diffusion in 1849 he included two possible theories for gas diffusion. They were: the chemical theory of T. S. Thomson or alternatively the mechanical theory of Dalton in which different gases were mutual vacua.¹¹¹ It seems that Graham was merely stating the contemporary view that there were two alternative ways of explaining gas diffusion, but it is probable that he was not convinced by either of these explanations.

From his laboratory notebooks it is evident that Graham began to re-examine diffusion in 1844.¹¹² These studies developed into a major research work in which he distinguished for the first time the two newly-recognised forms of gas motion: effusion and transpiration (or viscous flow).¹¹³ Previously these two separate modes of gas motion had been generally confused.

Graham stated that 'effusion' was the passage of gases through an aperture in a thin plate into a vacuum. He found that this process only occurred when the apertures in the plates had no sensible thickness. Having established this fundamental limitation, Graham discovered that effusion was a well-defined process, subject to a fixed law with a similar form to the diffusion law.

'Transpiration' was defined as the passage of gases through a tube into a vacuum. He discovered that transpiration experiments gave regular results provided that there was sufficient resistance to the gas flow. Graham found that this occurred when he used either very long tubes or with shorter tubes

114. J. Leslie, An Experimental Inquiry into the Nature and Propagation of Heat, (London, 1804) Note XXI pp 534-535.

of very narrow diameter. Where short tubes were used, in general, there was a lower resistance to gas flow, and a mixed phenomenon of effusion and transpiration was observed to take place. This was particularly noticeable when hydrogen gas was used. The studies which Graham made on transpiration did not reveal the true nature of the process but they did define the correct conditions for transpiration to occur. His carefully-collected transpiration data were very useful to later researchers, like Maxwell, who could interpret them successfully.

The origins of Graham's work on effusion and transpiration, published between 1845 and 1849, can be traced back to his own earlier work. In 1831 he had obtained both irregular results with hydrogen diffusion and anomalous results for the speeds of passage of gases into a vacuum. These observations clearly needed explaining. Other research workers had studied the flow of gases into a vacuum but as we shall see they had been unable to disentangle the two distinct flow processes of effusion and transpiration.

In 1804, John Leslie had described a method for determining the specific gravity of a gas. It was essentially an effusion-transpiration process.¹¹⁴ He fitted a glass cylinder with a brass cap, stopcock, and a short pipe, $\frac{1}{32}$ " in diameter. The cylinder was then placed in water and the water was sucked up. A large bladder of gas was finally attached to the pipe, and gas was sent into the cylinder by opening the stopcock. The time was noted for the water-level to fall to a pre-determined mark. Leslie explained this flow process by the law of pneumatics which stated that fluids projected from small holes travelled at a speed inversely proportional to the square root of, either the height of the column, or the specific gravity of the fluid. His results were rather inaccurate because this law only applied rigorously to truly-effusive flow, and in his experiments there was considerable viscous flow. Air and hydrogen were compared; they gave a specific gravity ratio of 8.3 to 1 instead of 14.4 to 1. By calculation, this gives a velocity of hydrogen of 2.9,

114a. G. G. Schmidt, 'Experiments on the law by which gaseous fluids flow out of narrow openings of different shapes, and through tubes under pressure,' Ann. der Physik. 66 (1820) 39-83, see pp 78-81. Georg Gottlieb Schmidt (1768-1837) was Professor of Mathematics at Giessen from 1789 and later he became Professor of Physics at Giessen. Like Leslie he used the hydrodynamic law that the velocity of flow of a gas was inversely proportional to the square roots of its specific gravity. He tested this law on impure hydrogen (of measured specific gravity 0.2594) and air. He found that the volumes of these gases which escaped from his apparatus in one minute were: 204.1 c.c. of air, and 400.35 c.c. of hydrogen.

Therefore the ratio of velocities was $\frac{204.1}{400.35} = 0.5097$ and this figure corresponded very well with the inverse ratio of the square roots of their specific gravities, which was $\frac{0.2594}{1} = 0.5093$

With carbon dioxide and air, he found that 47 c.c. of air escaped in the same time as 40 c.c. of carbon dioxide

Ratio of velocities = $\frac{47}{40} = 1.175$, and he took the specific gravity of carbon dioxide as 1.5 and air as 1.

So $\frac{1.5}{1} = 1.225$. The agreement here was less close but Schmidt explained it away by saying that his sample of carbon dioxide was impure.

115. M. Faraday, 'On the escape of gases through capillary tubes' Quart. J. of Sci. 3 (1817) 354-355 also in, Faraday, Experimental Researches in Chemistry and Physics (London, 1859) 5-6.

which is intermediate between the true effusion velocity of 3.8, and the transpiration velocity of 2.4 (using Graham's values and taking the velocity of air as 1). By using a tube, or pipe, rather than an aperture in a thin plate, Leslie had been studying, unwittingly, a mixed-flow phenomenon.

Better results were obtained in 1820 from some effusion experiments made by Georg Gottlieb Schmidt, Professor of Physics and Mathematics at Giessen.^{114a} He compared the flow rates of impure hydrogen and air, and also of carbon dioxide and air. His results showed a reasonably-close agreement with the law, that the flow velocity was inversely proportional to the square root of the specific gravity of a gas. His work may be regarded as an early anticipation of the effusion law. Schmidt's work, however, was not mentioned by Graham.

The passage of gases through capillary tubes had been studied by Faraday in 1817.¹¹⁵ He believed that the mobility of gases depended upon physical properties, such as specific gravity. He suggested that gases with high specific gravities would pass more slowly through capillary tubes because the internal motions of these gases would be more affected in such a flow. He used gases compressed to 4 atmospheres and then allowed them to escape through a thermometer tube (20" long) until the pressure was reduced to $1\frac{1}{4}$ atmospheres. The times of flow showed that the mobility of a gas was inversely proportional to the specific gravity. Indeed, Faraday's results correspond closely to effusion times, with one exception: hydrogen. It can be seen that he came very close to the discovery of the effusion law.

<u>Flow Time</u> (air being taken as 1)	<u>Carbonic</u> <u>Acid</u>	<u>Olefiant</u> <u>Gas</u>	<u>Air</u>	<u>Carbon</u> <u>Monoxide</u>	<u>Hydrogen</u>
Faraday's result	1.223	1.059	1	1.040	0.4453
Effusion time	1.20	1.01	1	0.99	0.28
Transpiration time	0.81	0.57	1	0.9635	0.44

Faraday confirmed the existence of a definite relationship between the mobility and specific gravity of a gas. Anticipating Maxwell's later

116. See J. C. Maxwell 'On the viscosity and internal friction of air and other gases,' Phil.Trans. 156 (1866) 249-268 also in Scientific Papers of J. C. Maxwell 2 1-25 edited by W. D. Niven (Cambridge, 1890).

117. M. Faraday, 'Experimental observations on the passage of gases through tubes,' Quart.J. of Sci. 7 (1819) 106-110 also in Faraday, Experimental Researches in Chemistry and Physics (London, 1859) 6-10.

experiments,¹¹⁶ he used a wheel of vanes which was rotated by a constant force supplied by different gases. The time was noted for the wheel to come to a stop after the constant force had been removed. Again this time was inversely proportional to the specific gravity of the gas. The true effusion law, however, eluded Faraday, for the velocity of gas flow was inversely proportional to: the square root of the specific gravity and not simply to the specific gravity.

When Faraday examined the flow of gases at low pressures he came across a difficult problem. There did not seem to be any simple relation between the mobility and the specific gravity of a gas. Surprisingly, olefiant gas passed as rapidly as hydrogen and twice as rapidly as air. Also carbon monoxide and carbonic acid escaped more rapidly than a number of lighter gases. He wondered whether there was some gain or loss of force in the tube. Similar problems were experienced by Graham in 1831 when he examined the flow of gases through a stucco plug into a vacuum. Returning again to this problem in 1819, Faraday gave details¹¹⁷ of the times of flow of equal volumes of a number of gases under different pressures:-

<u>Gas</u>	<u>Hydrogen</u>	<u>Olefiant Gas</u>	<u>Carbon Monoxide</u>	<u>Carbonic Acid</u>
Time at high pressures	57"	135.5"	133"	156.5"
Time at low pressures	8'15"	8'11"	11'34"	9'56"

A gas which passed most rapidly at high pressure, for example hydrogen, seemed to pass much more slowly at low pressure. This 'low pressure effect' was always observed when fine tubes were used. He also examined the passage of hydrogen and olefiant gas through a platinum foil containing either a set of fine holes or a series of slits. Hydrogen passed through the slits more slowly than olefiant gas. He found that the low-pressure effect was not caused by mechanical obstructions such as paper or powdered glass. Also the effect was common to both glass and metal tubes. It could be increased by using either lower pressures; or longer tubes; or

118. P. S. Girard, 'Sur l'écoulement uniforme de l'air atmosphérique et du gaz hydrogène carboné, dans des tuyaux de conduite' Ann.de Ch. 2 Ser. 16 (1821) 129-152.

tubes of smaller diameter. He thought that a constant influence might be observed by using two different gases with the same specific gravity, such as carbon monoxide and olefiant gas. But he found that this was not true, both gases flowed through tubes in different times.

Faraday was puzzled by his discoveries. At high pressures, there was an approximately-constant ratio between the times of flow of hydrogen and olefiant gas (1 to 2-2.5), but in a longer tube the flow of olefiant gas fell less rapidly than that of hydrogen. Was there some power of expansion, he wondered, peculiar to each gas? He was not prepared to say but he promised to do further work on the problem. However, he published nothing further on the subject.

The problem of gas flow was also taken up in the same year by Girard¹¹⁸ who was interested in the problems of gas distribution. He said that he was unable to deduce any law of gas flow from Faraday's work because insufficient information had been given, for example Faraday had not quoted:- the lengths and diameters of the tubes used; the pressure ranges; or the temperatures. Therefore Girard began his own investigation on the flow of air and carburetted hydrogen through steel tubes. He wanted to find out whether there was any cohesion between, either the gas particles themselves, or the gas particles and the tube. He had correctly assessed the nature of the problem as one concerned with viscosity. He showed that carburetted hydrogen escaped from tubes more rapidly than air, but the relative volumes of these gases were not simply-related to specific gravities. If they had been, they would have given a volume ratio for air to carburetted hydrogen of approximately one to two, but Girard obtained a ratio of 902 to 281. With longer tubes, the gases escaped more slowly. He supposed that there was a greater resistance from the tube walls, caused, either by the adherence of the gas to the wall, or by the roughness of the wall, or by a combination of both effects. This resistance could be transmitted through a mass of gas in motion so that concentric layers of gas would adhere with a certain force. He argued that there was a complete

119. Graham, 'On a new property of gases,' B.A.A.S. Report (Cambridge, 1845) part 2 p 28, Researches pp 84-85. (read June 30th 1845) See also the account of this meeting in the Literary Gazette (1845) p 455 in which the comments of Alexander Bain and Vernon Harcourt are recorded. Bain suggested that Graham's researches could be used to explain the suspension of aqueous vapour in the clouds and other meteorological problems.
120. See W. Vernon Harcourt B.A.A.S. Report (Birmingham, 1839) pp 67-68. Harcourt had given details of some of Henry Cavendish's unpublished manuscript notes. These included some laboratory notes of 1784 in which Cavendish had investigated the rate of efflux of gases. Cavendish had wondered whether the vis inertiae of nitrogen (phlogisticated air) was the same in proportion to its weight as common air. He had timed the passage of gases through a hole in a tin vessel held over water. The tin vessel had been lowered during the escape of the gas to maintain a constant force on the gas. He had found that the time for the escape of air in three experiments was 2'15", 2'12 $\frac{1}{2}$ " and 2'9" whereas for nitrogen (or common air which had been exposed to liver of sulphur to remove the oxygen^{the time}), was 2'7". The nitrogen had a specific gravity which was $\frac{1}{47}$ th less than air and the figures show that nitrogen flowed out of $\frac{1}{47}$ the vessel more rapidly than air. However, Cavendish did not pursue these experiments and they remained unpublished until 1839.
121. Graham 'On the motion of gases' part 1 June 18th 1846 Phil.Trans. 136 (1846) 576-632 or Researches 88-161. (Graham originally called his paper 'On the movement of gases' but this was altered to the above title for Phil.Trans. See original MS of the Paper held by the Royal Society).
122. Graham ibid. Researches 92.
123. J. Robison, A System of Mechanical Philosophy (Edinburgh, 1822) 3 pp 681-684 and Leslie op.cit. (114) who had used the same principle in his earlier study of the problem in 1804. Torricelli's theorem (1641): liquids which issue with violence (from an opening in a vessel) have at the point of issue the same velocity which any heavy body would have, or any drop of the same liquid, if it were to fall from the upper surface of the liquid to the orifice from which it issues. Robison pointed out the analogy between air flowing into a vacuum impelled by its weight and the problem of water flowing out of a vessel through an orifice (p 681). Now the velocity acquired by a falling body varies not directly as the height but as the square root of the height. The height of an atmosphere of uniform density is inversely proportional to its specific gravity. Therefore rate of flow of a gas into a vacuum will be inversely proportional to the square of its specific gravity or density.

analogy between gas flow and the linear motion of incompressible liquids so that the same formulae could be used in both cases. Hence the gas velocity was directly proportional to the pressure differences at the ends of the tube and inversely proportional to the square root of the tube length.

Thus, by 1845, there was a considerable amount of previous work on the problem of gas flow, when Graham announced the results of his first experiments on the effusion and transpiration of gases to a meeting of the British Association at Cambridge.¹¹⁹ In this preliminary paper Graham identified the new property of 'transpiration'. This mode of gas flow occurred when a gas passed through the pores of stucco into a vacuum. He also gave details of the experiments which he had carried out on the effusion of gases. Interestingly, W. Vernon Harcourt commented that some experiments of a similar nature had been performed previously by Cavendish.¹²⁰

Graham extended his researches and reported them in his paper 'On the motion of gases' read to the Royal Society on June 18th 1846.¹²¹ He conceived the basis of this work to be the law concerning the passage of gases in a vacuum: "molecules of a gas rush into a vacuum with the velocity they would acquire by falling from the summit of an atmosphere of the gas of the same density throughout; while the height of such an atmosphere, composed of different gases, is inversely as their specific gravities."¹²²

This pneumatic law had been deduced by John Robison¹²³ from Torricelli's theorem of the velocity of efflux of fluids. The velocity which a gas would acquire when it escaped by effusion into a vacuum was inversely proportional to the square root of the density of the gas. This was analogous to the velocity which a gas would acquire on falling through a uniform atmosphere and it was proportional to the square root of the height or density of the atmosphere.

Earlier work on the flow of gases under pressure was first briefly surveyed by Graham. He admitted that Faraday and Girard had shown that

124. Graham, op.cit. (121) Researches 89.

125. E. A. Mason, 'Thomas Graham and the kinetic theory of gases,'
Phil.Journ. 7 (1970) pp 99-115.

126. Graham, op.cit. (121) Researches p 95.

lighter gases escaped more rapidly than heavier gases but he considered that their results were "a very imperfect support to the theoretical law [of effusion]." ¹²⁴ Some of their results were wholly inconsistent with the law, for example consider the changes in the relative rates of flow of hydrogen and olefiant gas observed by Faraday, when these gases flowed under different pressures through a capillary tube. Graham also referred to his own previous work in which he had observed that air and carbonic acid flowed through stucco into a vacuum at approximately the same speed.

With considerable insight, Graham distinguished two different processes: the flow of gases through an aperture in a thin plate into a vacuum, which he called 'effusion', and the flow of gases through a tube into a vacuum, which he called 'transpiration'. It is remarkable, as E. A. Mason has pointed out recently, ¹²⁵ that Graham could disentangle these two different modes of gas motion experimentally, without a formal mathematical analysis of the problem.

The declared aim of Graham's paper was to determine the coefficients of effusion and transpiration. Let us examine firstly his work on effusion. He allowed equal volumes of different gases to effuse into an evacuated receiver at constant temperature. These gases passed through either a very short glass jet or a minute circular aperture in a very thin brass plate. Alternatively, he observed the time taken for mercury to fall through a given height as gases effused freely into the evacuated receiver. All of these experiments demonstrated beautifully the truth of the law of effusion which Graham stated as follows:-

"Different gases pass through minute apertures into a vacuum in times which are as the square roots of their respective specific gravities; or with velocities which are inversely as the square roots of their specific gravities." ¹²⁶

During publication, Graham inserted his best effusion results. They were obtained in February 1846 by using a thin sheet of platinum foil with a circular aperture in it. He found that the rates of effusion of gas

127. Graham, *ibid.* Researches p 140.

mixtures were correspondingly simple; being the expected averages of the rates for pure gases. This fact differentiated effusion from both diffusion and transpiration. Effusion occurred only with apertures in plates of no sensible thickness. Graham found that with tubes, however short, a mixed phenomenon of effusion and transpiration took place and this was particularly noticeable when hydrogen gas was used.

Transpiration gave regular results when there was sufficient resistance to the flow of gas. This regularity was found either with very long tubes or with shorter tubes of small diameter. He found that the rate of transpiration was independent of the nature of the tube because he obtained similar results by using glass, stucco, and copper tubes. Graham also found, like his predecessors Faraday and Girard, that there was no uniform relation between the rates of transpiration and the density or specific gravity of a gas. He found that both the lighter gas hydrogen and the heavier carbonic acid transpired more rapidly than oxygen. Using equal volumes of air under different pressures there was no variation in the effusion rates for moderate changes in the air pressure. But the transpiration rate did depend on the air pressure. Indeed, it was proportional to the air pressure. Here was another clear distinction between effusion and transpiration.

With tubes of sufficient resistance the relative times of transpiration of gases into a vacuum gave constant results. How was this to be explained? Graham was uncertain. He did say that "the rate of transpiration depends on a constitutional difference in the gases themselves."¹²⁷ He added that the most probable explanation appeared to be that transpiration was a kind of elasticity which depended upon the total quantity of heat in a given volume of gas. This total quantity included both latent and sensible heat. This was an attempt to relate the rate of transpiration to the specific heat of a gas but Graham did not deduce any quantitative relation. His explanation, anyhow, was incorrect. Maxwell later deduced the correct explanation of gaseous transpiration in terms of viscosity.

128. Graham, op.cit. (121) Researches p 152.

129. Graham, 'On the motion of gases' part 2, read to the Royal Society on June 21st 1849, Phil.Trans. 139 (1849) 349-392 or Researches 162-210.

130. J. L. M. Poiseuille, (1799-1869 - a French physicist), 'Experimental researches on the movement of liquids in tubes of very small diameter,' Comptes Rendus 11 (1840) 961-967, 1041-1048, 12 (1841) 112-115 and Ann.de Ch. 3 Ser 7 (January 1843) 50-74.

Poiseuille's equation for the total volume of fluid flowing through a tube per second is $(P_1 - P_2) R^4$

$$\text{Velocity of flow} = \frac{(P_1 - P_2) R^4}{8l\eta}$$

where l = tube length; P_1 and P_2 are the pressures at the ends of the tube; R is the tube radius and η is the viscosity of the fluid. This equation applies to incompressible fluids; it can be used for liquids but not gases. With gases the volume is a strong function of pressure. If the pressure at which the volume is measured is P_0 then the equation for gases is

$$\text{Velocity of flow} = \frac{(P_1^2 - P_2^2) R^4}{16l\eta P_0}$$

In November 1846, Graham added an appendix to his paper in which he recorded a large number of experimental results on the transpiration of gaseous mixtures. Some mixtures, such as: oxygen and nitrogen; oxygen and carbon monoxide; gave rates of flow corresponding to mean transpiration rates; but this was not the case with gas mixtures containing hydrogen. Here, Graham had made a discovery, whose importance was recognised later by Maxwell. The addition of small amounts of hydrogen to other gases did not increase their rates of transpiration as might have been expected because a lighter gas was being added. Significantly, when 5 to 10% of hydrogen was added to methane, the mixture transpired more slowly than either of these gases on their own. This was also observed with mixtures of hydrogen and carbonic acid.¹²⁸ An example of this effect can be seen in the transpiration of hydrogen and methane; the transpiration times in seconds were: for pure methane 389; for 90% methane + 10% hydrogen 398; and for pure hydrogen 310.

In 1849 Graham added a second part to his paper giving further new experiments on transpiration.¹²⁹ He noticed that there was a remarkable constancy in these experiments. He acknowledged that his transpiration rates could be compared with the results found by Poiseuille for the flow of liquids through capillary tubes. In 1840, Poiseuille had worked out his well-known formula for the rate of flow of liquids along capillary tubes.¹³⁰ However, Graham did not use this formula for calculations presumably because he wanted to avoid mathematical complexity and also because the analogy between liquids and gases was not straightforward. Instead he was searching for simpler experimental relationships. Graham was convinced that transpiration was a fundamental property of gases. Therefore some simple relationship must exist like that found between the effusion or diffusion velocity and the specific gravity of a gas, or even, as he speculated, something as simple as the ratios of combining volumes of gases. He stressed the need for further investigations of transpiration: "as the results, too, were entirely novel, and wholly unprovided for in the received view of

131. Graham, op.cit. (129) Researches p 162.

gaseous constitution, of which they prove the incompleteness, it was the more necessary to verify each fact with the greatest care." 131

Once again, he was critical of the accepted view of the constitution of gases, but he did not attempt to speculate further and expound his own views. Thus, the second part of his paper was devoted to achieving three experimental objectives: firstly to determine the resistance and dimensions of tubes which gave normal transpiration; secondly to redetermine and extend the knowledge of transpiration rates; and thirdly to examine the influence of temperature and pressure changes on these rates.

The most important factor controlling the resistance to gas flow in a capillary tube was the tube length. For normal transpiration he found that the length of the tube should be greater than 4000 times its diameter. He found that it was possible to replace the single tubes in his experiments by bundles of capillary tubes which were equally effective. Although he was unable to deduce any simple generalisations, Graham did observe, with some gases, that the transpiration times relative to oxygen were simply related. The times which he found were: oxygen 1, air 0.9010, nitrogen and carbon monoxide 0.8750, hydrogen 0.4375, and carbonic acid 0.7272. Graham noticed that certain pairs of gases, with the same specific gravity, possessed the same transpiration velocity, for example nitrogen and carbon monoxide; nitrous oxide and carbon dioxide; but, on the other hand, hydrogen transpired twice as fast as nitrogen, although the ratio of their specific gravities was one to fourteen.

When gases were made denser by cooling or by increasing the pressure they flowed more rapidly by transpiration. He pointed out that this discovery was relevant to the distribution of coal gas in towns which was an effect of transpiration.

Although Graham could not work out the mathematical relations involved in viscous flow or transpiration of gases, he did clearly define the conditions for transpiration to occur and he produced a lot of data which was to prove useful to Maxwell and O. E. Meyer in their subsequent studies of gas viscosity.

132. John Herapath, (1790-1868), Mathematical Physics (London, 1847)
Volumes 1 and 2.
133. E. Mendoza, 'The surprising history of the kinetic theory of gases,'
Manus.Lit. and Phil.Proc. 105 (1963) 15-28 and more recently,
'A critical examination of Herapath's dynamical theory of gases.'
B.J.H.S. Vol. 8 No.29 (July 1975) pp 155-165. See also S. G. Brush,
'The development of the kinetic theory of gases, 1, J. Herapath,
Ann.Sci. 13 (1957) 188-191.
134. H. Davy, Elements of Chemical Philosophy, (London, 1812) p 95
"It seems possible to account for all the phenomena of heat if it
be supposed that in solids the particles are in a constant state of
vibratory motion, the particles of the hottest bodies moving with
the greatest velocity and through the greatest space; that in fluids
and elastic fluids, besides the vibratory motion, which must be
conceived greatest in the last, the particles have a motion about
their axes, with different velocities, the particles of elastic
fluids moving with the greatest quickness; ..." p 95.
135. Herapath, op.cit. (132) Volume 1 pp 220-221.

One of the first people to comment on Graham's work was John Herapath whose Mathematical Physics appeared in 1847.¹³² This work was based on his earlier papers of 1816 to 1821 and E. Mendoza has suggested that Herapath had merely extended his earlier views.¹³³ Herapath regarded gases as a collection of particles, or atoms, which mutually impinged on one another, and on the sides of their containing vessel. He continued to reject the caloric theory of heat, preferring the view that heat was the vibratory motion of particles or an intestine motion. The temperature of a gas was equal to the average momentum of its particles. This dynamical theory of gases was similar to that proposed by Davy except that Davy explained heat by two kinds of particulate motion: vibration and rotation, whereas Herapath restricted himself to vibrational motion.¹³⁴ The detailed arguments used by Herapath reveal that he had confused the concepts of conservation of momentum and conservation of energy.

Mendoza has argued, convincingly, that Herapath viewed a gas as a regular array of particles, vibrating about their mean positions, colliding with neighbouring particles and being reflected from them or from the walls of the container. Particles did not move randomly in Herapath's vision; rather they oscillated about a particular lattice position, colliding with adjacent particles. The phrase 'flying about in all directions', which Herapath used is ambiguous according to Mendoza.

In essence, Herapath's model of vibrating gas particles, occupying lattice positions, was a development of the caloric theory of gases and not a completely new theory. This can be seen from Herapath's treatment of change of state, in which he argued that there were no sharp divisions between gases, liquids, and solids. The transition from liquid to solid, or from gas to liquid, only involved an aggregation of particles. This increased the mass of the aggregate and brought about a corresponding reduction in the vibration of the particles at a given temperature.¹³⁵ This was because at a fixed temperature the individual particle momentum, or mass multiplied by velocity, remained constant. There is a close

136. Herapath, *ibid.* 1 p 237.

137. Graham, 'Speculative ideas respecting the constitution of matter'
(1863) Researches 299-302.

137a. MS letter from Graham to Andrews, November 25th 1856, Andrews papers, Queen's University, Belfast. He wrote: "I have long been of the opinion that diffusion; transpiration of both gases and liquids will never have an explanation except from the motion theory of heat."

resemblance between these views and Graham's speculations on changes of state.

The explanation of gaseous diffusion which Herapath gave in 1847 was essentially the same as his earlier explanation of 1821. When two gases were in contact, he argued that it would be impossible for the particles of one gas to meet and beat back every particle of another gas. Hence, even if some particles were beaten back, others would pass through, and this process would continue in a stepwise manner until a uniform gaseous mixture was obtained. He believed that gases were "composed of very minute, perfectly hard particles, which, flying about in all directions, and, by their collisions with each other and the sides of the containing vessel, maintain a constant pressure against the sides, as if endeavouring to press them outwards. In what directions these motions are made we do not consider, all that we have to do with is the mean state of the case."¹³⁶

Like Graham, Herapath did not assume that the particles of bodies must be indivisible. A vibrating particle might contain secondary vibrating particles so that the total vibratory motion of a particle could be a compound motion. When Graham speculated on matter in 1863,¹³⁷ he considered that diffusive molecules were made up of ultimate atoms, each atom possessing a characteristic motion. But he went further than Herapath when he added the final concept that the identical primary atoms of different elements were distinguished from one another by possessing different, but unalterable, degrees of motion. It is possible that Herapath's work may have influenced Graham's thoughts on gas motion. The gradual transition from a caloric theory of gases to Herapath's dynamical theory would not have been too radical a step for Graham to have made. It is uncertain when Graham made this transition but it must have been before 1856 because in that year he expressed his belief in the motion theory of heat in a private letter to Thomas Andrews.^{137a}

Graham's acceptance of a motion theory of heat can also be detected in his lecture on the 'liquid condition of matter' delivered to the

138. Graham, Wellcome Manuscripts 2580 (old no.3390)
'Miscellaneous notes' - 'On the liquid conditions of matter' -
undated. [Presumably this is the manuscript of the lecture, with
the same title, read to the Chemical Society on March 6th 1854]
Certainly Graham admitted in a letter to Thomas Andrews in 1856:
"I have long been of the opinion that diffusion; transpiration of
both gases and liquids will never have an explanation except from
the motion theory of heat." Letter from Graham to Thomas Andrews,
November 25th 1856, in the Andrews' papers, Queen's University,
Belfast.

138a. Graham, *ibid.*

139. John Herapath, Mathematical Physics, Volume 2 (London, 1847) p 2.

Chemical Society in 1854.¹³⁸ He wrote that: "the essential characters of a gas are few and striking. Their nature exhibits a severe but grand simplicity. All gases have weight. Indeed the weight or gravitating tendency of matter is not lost or altered by change of state. Another property is diffusibility. When a mass of one gas is placed in contact with another gas, neither gas can remain at rest. They spontaneously mix, the particles of one gas dispersing themselves among the particles of the other till a uniform mixture is produced; which is the only condition of equilibrium (or rest) between different gases in contact. This property carries us at once to the molecular condition of gases. Even when the mass is at rest, the molecules are in motion, exchanging places with each other, a balanced movement which involves no loss of force and may therefore be perpetual.

The force thus at work is the same in a cubic inch of every gas and is measured by the elasticity. But where the gas is light (like hydrogen) the particles are moved more rapidly than where the gas is heavy as in oxygen." ^{138a}

This text shows that Graham had a dynamical view of gas motion at this time, and it is even possible that his views were derived from those of Herapath.

Herapath praised Graham's "very beautiful experiments"¹³⁹ on diffusion which had led to the diffusion law and he remarked that Graham was the only worker he knew of in this field. Herapath deduced an expression for the flow of gases through a small aperture into a vacuum. At constant temperature and elasticity he obtained the following (rearranged) formula:-

$$\frac{\text{Volume of gas}}{\text{time of percolation}} \propto \frac{\text{temperature}}{\sqrt{\text{specific gravity of gas}}}$$

Herapath claimed in his textbook of 1847 that he had drawn up these ideas on March 17-18th 1844 saying that no experiments were then available to test these deductions. Then, in December 1846, he had read the first part of

140. Herapath, *ibid.* p 9.

141. Herapath, *ibid.* p 10.

142. Herapath, *ibid.* p 11.

143. Herapath, *ibid.* pp 349-350.

Herapath did try and lessen the impact of his strictures on Graham's work, when he wrote, in the Introduction to Volume 1 of his Mathematical Physics p XL, "On reviewing one or two expressions since the work has been printed off, I fear they may appear somewhat harsh towards Professor Graham. If they should be thought to be so by others, I can only say that I regret the appearance of what was not intended."

Graham's textbook, Elements of Chemistry (part 1) which had been published on December 13th 1846.¹⁴⁰ Consequently he claimed that he had anticipated Graham's results. Herapath said: "it was my intention to communicate to Mr. Graham the results at which I had arrived, as a guide to him in future experiments, but as he did not think proper to answer some questions I sent him, I did not deem it worthwhile."¹⁴¹

From the above formula, Herapath claimed that it followed that the effusion times of equal volumes of air under different pressures would be the same. Graham had confirmed this result experimentally and Herapath wrote: "this is precisely the law laid down [by me] nearly two years and three quarters before."¹⁴² Then he showed distinctly muddled-thinking by maintaining that there was no difference in the three modes of gas motion, diffusion, effusion, and transpiration, apart from a dependence on friction in the last case. He criticised Graham for attempting to distinguish between effusion and transpiration, suggesting that Graham would be 'wasting his time' if he thought that transpiration was a new constitutional property of gases. There was nothing new in it and he could have told him so in March 1844.

Likewise he regarded with scepticism Graham's correct observation that impure hydrogen always transpired more slowly than pure hydrogen, being an effect which might be used as a test of purity for hydrogen.

In a supplement to his textbook, dated March 6th 1847, Herapath reviewed the first part of Graham's paper: 'On the motion of gases'. He wrote: "as anticipated he has made nothing out of his supposed new property of transpiration he observes that transpiration has no uniform relation to the density of the gases [and he has] not yet succeeded in reconciling transpiration with any physical law."¹⁴³

Herapath attributed the observed differences in the flow of gases through tubes to probable differences in the figures of the gas particles, adding that this had nothing to do with specific gravity. He remarked that transpiration was merely common effusion or flowing of gases affected by

144. Herapath ibid. 2 p 350.

145. Herapath ibid. 2 pp 366-367.

145a. Herapath ibid. 2 p 367.

146. Gasometry: Comprising the Leading Properties of Gases (London, 1857) by Robert Bunsen, translated by H. E. Roscoe from Bunsen's Gasometrische Methoden (Braunschweig, 1857).

147. Wellcome Manuscripts Graham autograph letters and notes. Note dated September 1st [1850?]

friction. It was more probably allied to chemical union than to any other property of gases. Condescendingly, he admitted that "Graham's experiments were not without interest,"¹⁴⁴ for example he had shown that there was a constancy in the relative rates of transpiration with long-enough tubes. He added that Graham was "on the right scent"¹⁴⁵ when he regarded transpiration "to be the effect of friction" but it had "nothing to do with the heat of the gas latent or sensible."^{145a} Herapath's criticism was correct on this last point but like Graham he was unable to work out a detailed explanation of gaseous friction. However Graham was definitely justified in making a clear distinction between effusion and transpiration. Herapath was obviously annoyed that he had been ignored by Graham and so he relished the opportunity to point out the latter's failure to explain transpiration in terms of a constitutional property of gases. Graham did not take up this criticism of his work.

Worse criticism was to follow, however, and this Graham could ill-afford to ignore. In 1857, Bunsen published his important study of gases, Gasometry, which was immediately translated into English by Henry Roscoe,¹⁴⁶ a student of both Bunsen and Graham. Bunsen had included some results from his earlier unfinished and unpublished studies of gas diffusion. He had designed a new apparatus to study diffusion which he called a 'diffusiometer'. This useful apparatus incorporated a lever arrangement to maintain a constant pressure during diffusion. It was used later by Graham in his new studies of gas diffusion. Graham had seen this apparatus before when he had visited Bunsen at Marburg in 1850 and he commented briefly on Bunsen's research in his manuscript notes:- "in gas diffusion [his] mathematical expression [is] complicated in the extreme."¹⁴⁷

Bunsen accepted that gases effused into a vacuum with a velocity inversely proportional to the square root of their density, provided that they escaped through fine openings in a thin plate; but he added that this was not the case when capillary tubes were used. He said that diffusion had been explained by assuming that two gases flowed into one another as

148. Bunsen, op.cit. (146) p 203.

they might effuse into a vacuum. He argued that it was improbable that the flow of gases through a porous diaphragm would follow a law like the effusion law, and yet Graham had developed such a law; the diffusion law, using a stucco plug. Was the diffusion law correct, Bunsen asked?

To examine this he took a stucco plug, 46 mm. thick, and allowed hydrogen and oxygen to pass through separately under pressure into their own atmospheres. The ratio of effusion times should have been oxygen time:hydrogen time = $\sqrt{\text{s.g. hydrogen/s.g. oxygen}}$ = 1 to 4 or even more accurately 1 to 3.995, but Bunsen found by experiment that the ratio was 1 to 2.73. He concluded that stucco diaphragms did not act like fine holes in thin plates; instead they acted as systems of capillary openings. Therefore the theory of diffusion through stucco must be incorrect. He checked the absorption of gases by stucco but, like Graham, he found that there was no attraction between stucco and hydrogen or oxygen.

Bunsen proceeded to examine Graham's diffusion law. He allowed hydrogen to diffuse directly into oxygen. His measured diffusion times in two experiments were in the ratio of 1 to 3.127 or 2.903 respectively. From the diffusion law the ratio should have been 1 to 3.995. To eliminate any possible sources of error Bunsen used a more sensitive liquid, water, in place of mercury, and a larger diffusion tube, 2' long and 1" in diameter. Hydrogen was then allowed to diffuse into air. The ratio of volumes, of hydrogen exchanged for air, was 3.34 to 1 and not 3.80 to 1 as the diffusion law predicted. Therefore Bunsen commented: "from these experiments, we are forced to conclude that the diffusive interchange does not occur in the relation of the inverse square roots of the specific gravities." ¹⁴⁸ In other words, Graham's law of diffusion was incorrect.

This conclusion was not true as Graham proved in 1863. Bunsen had not followed Graham's instructions on the preparation of stucco plugs with sufficient care. However, Bunsen's errors must have encouraged Graham to search for a more suitable material for diffusion experiments and as we shall see he was successful.

149. MS. letter from Graham to J. Liebig, dated 28th October 1857.
Bayerische Staatsbibliothek Handschriften, Munich.
Liebigiana 58.

150. Letter from H. E. Roscoe to W. S. Jevons, dated 1st February 1858,
quoted in Papers and Correspondence of William Stanley Jevons,
edited by R. D. Collison Black, Vol. 2 (London, 1973) 316-317.

Bunsen attempted to determine the 'true relation' between the volume of gases exchanged by examining the volumes of gases in the diffusion tube at successive periods during their diffusion. He found that the volume of oxygen exchanged for hydrogen was in the ratio 1 to 3.345 and not 1 to 3.995 as the diffusion law would suggest. He concluded that the rate of diffusion of a gas depended firstly, on a coefficient of friction related to the nature of gas and the diaphragm, and secondly, on the pressure differences above and below the diaphragm. He then gave a complex mathematical explanation of his results.

Graham realised the seriousness of this attack on his diffusion law. This can be seen from the following extract of a letter which he wrote to Liebig in 1857:- "Bunsen's onslaught upon the law of diffusion of gases will compel me to return to that old subject. I believe that there is a fallacy in Bunsen's experiments - but we shall see by and by. Perfectly dry stucco, which he uses, also failed entirely in my hands as is stated in my first paper." 149

Between 1857 and 1862 Graham investigated these problems and examined gas motion with great care and insight. In 1858 Henry Roscoe wrote to another of Graham's former students, William Stanley Jevons: "... he (Tommy Graham, as he was known to his students) is very busy making experiments on the diffusion of gases - the law of which (inverse square roots of densities) has been impugned by Bunsen in the book on Gasometry, which I translated. Graham says that Bunsen is quite wrong and that the law is still true - as however the experiments are not yet finished, much less published, I am rather inclined to side with Bunsen, whose methods are always precise and delicate and in whose work I have the greatest confidence." 150

In December 1857, Henry Watts, an editor and later librarian for the Chemical Society, completed his supplement to the second volume of Graham's textbook. He considered that the differences between Bunsen's exchange volumes and those calculated from Graham's diffusion law were too great to

151. Graham, Elements of Chemistry, 2nd.edn. Volume 2 - revised by Henry Walls with a new supplement by Watts (London, 1857) supplement pp 624-625. W. Chandler Roberts stated that Graham had suggested that Bunsen's plaster plug caused an actual retention of hydrogen in its pores. W. C. Roberts 'On the apparatus employed by the late Mr. Graham F.R.S. in his researches,' Nature 14 (1876) 511-514, see p 513.

152. MS. letter from Graham to C. F. Schönbein dated January 9th 1862. MS. letter no. 483, Universitäts Bibliothek, Basel.

153. J. C. Maxwell, 'Illustrations of the dynamical theory of gases,' Phil.Mag. 4 Ser. 19 (1860) 19-32 and 4 Ser. 20 (1860) 21-37.

be explained by an error of observation. He drew attention to the marked difference in the thickness of the stucco plugs used by Bunsen and Graham, being 2" and $\frac{1}{5}$ " respectively. Therefore he suggested that a mixed phenomenon of diffusion and transpiration was occurring in Bunsen's experiments. Watts explained that "in the interior of a considerable mass of stucco with hydrogen one side and oxygen on the other, the stucco acts as a vessel, a partial vacuum being formed in its centre. To this point, both oxygen and hydrogen are impelled by pressure [transpiration], in the ratio of 1 to 2.3 instead of 1 to 4 the relation of diffusion!"¹⁵¹ This was a correct interpretation of Bunsen's ratios of 1 to 2.73 under pressure and 1 to 3.345 for diffusion.

By 1862 Graham was confident that he had exposed the true source of Bunsen's error. This can be seen in Graham's letter to Schönbein written in January 1862. Graham wrote: "I have an investigation closed on gas diffusion. Into the last I was led by Bunsen's failure to obtain the [diffusion] law by my old method. After a world of trouble, I hit upon the cause of his failure. His stucco diaphragm was overheated in the drying, which causes a molecular change in the gypsum, destroying entirely the fine porosity upon which the suitability of stucco for the experiment depends. My new results which are numerous, give a more precise determination of the subduplicate ratio [inverse of the square root] than the experiments of my old paper."¹⁵²

Before Graham could publish his new experiments James Clerk Maxwell published his first paper 'On the dynamical theory of gases', in which he considered diffusion of gases.¹⁵³ Maxwell chose to represent gases as sets of hard, elastic spheres, moving in straight lines and colliding with other spherical particles, or with the walls of the container. He established the law of distribution of velocities and then he calculated the mean free path for a particle of air to be $\frac{1}{447,000}$ th of an inch from a consideration of gaseous friction. He looked for a theoretical explanation of gaseous diffusion. His explanation was based on the mean free

153a. Maxwell, ibid. Phil.Mag. 4 Ser 20, p 28.

154. Maxwell wrote to G. G. Stokes on May 30th, 1859 giving details of his investigations into gaseous friction. He wrote:- "The rate of diffusion of gases depends on more particles passing a given plane in one direction than another.... It appears that the mean free path should be the same [?] for all pure gases at the same pressure and temperature, but I have found only a very few experiments by Prof. Graham on diffusion through measurable apertures and these seem to give values of λ much larger than from friction." See: Memoir and Scientific Correspondence of the Late Sir George Gabriel Stokes, by Joseph Larmor, (Cambridge, 1907) Volume 2 pp 8-11. Graham had performed a few experiments on the diffusion of gases contained in glass bulbs, connected by a glass tube; but Maxwell needed, ideally, data on the interdiffusion of gases possessing the same specific gravity, for example: nitrogen and carbon monoxide; or carbonic acid and nitrous oxide. These results were not available.
155. Maxwell recognised later that Graham's transpiration experiments supported his conclusion. This was made clear to him from G. G. Stokes's work. See the letter from Maxwell to H. R. Droop, dated January 28th 1862, in the Life of James Clerk Maxwell by L. Campbell and W. Garnett, (London, 1882) p 332. Maxwell wrote that ... "Stokes has been examining Prof. Graham's experiments on the rate of flow of gases through fine tubes and he finds that the friction if independent of density accounts for Graham's results, but if taken proportional to density, differs from these results very much. This seems a rather curious result and an additional phenomenon, explained by the 'collision of particles' theory of gases."
156. O. E. Meyer, 'On the friction of gases - 2nd. paper: On the passage of gases through capillary tubes' Pogg. Ann. 127 (1866) 253-281, 353-382 and also O. E. Meyer, The Kinetic Theory of Gases (1877 - revised and translated into English by R. E. Baynes in 1899) pp 183-205.

path concept which had been developed by Clausius. On Graham's diffusion law he commented: "our assumptions that the porous plug acts like a system of fixed particles, and that Graham's law is fulfilled more accurately, the more compact the material, are scarcely sufficiently well-verified for the foundation of a theory of gases" ^{153a}

It is probable that Bunsen's criticism of the diffusion law, as a result of his own faulty stucco-plug experiments, had cast doubt on Graham's earlier diffusion experiments in which a stucco diaphragm had been used. Therefore Graham's results were not used by Maxwell to provide an experimental foundation for the dynamical theory of gases. Instead Maxwell used the results of an experiment on diffusion without a stucco plug performed by Graham in 1829:— Olefiant gas had been allowed to diffuse freely from a glass tube into air and in 4 hours, 152 parts of olefiant gas were reduced to 99 parts. From this Maxwell calculated the mean free path of olefiant gas to be $\frac{1}{389,000}$ th of an inch or 0.00000256". This result was similar to that which he had deduced from gaseous friction.

One remarkable result emerged from Maxwell's study of gaseous friction: the coefficient of friction was found to be independent of density. ¹⁵⁴ This important conclusion could only have come from a dynamical theory of gases. A quite different conclusion followed from a static theory of gases, for an increase in density would have caused an increase in gaseous friction. Here was a means of deciding between the statical and dynamical theories of gases by an experimental test. Initially Maxwell assumed that there were no accurate experiments on gaseous friction or viscosity. But he had overlooked Graham's experiments on transpiration, from which he could have confirmed his result, that the coefficient of friction did not depend on the gas density. ¹⁵⁵ This was pointed out later by O. E. Meyer. ¹⁵⁶

It is evident that Graham's researches on diffusion and transpiration could have provided an experimental basis for the dynamical theory of gases, but criticism of the diffusion law, and Graham's failure to give a mathematical account of transpiration, both contributed to a lack of appreciation

157. Graham, 'On the molecular mobility of gases,' read June 18th 1863,
Phil.Trans. 153 (1863) 385-405 and Researches 210-234.

158. Graham, *ibid.* Researches p 211.

158a. Graham, *ibid.* Researches pp 211-212.

of the true significance of his work in 1860.

Eventually, in June 1863, Graham delivered his reply to Bunsen in an important paper: 'On the molecular mobility of gases.'¹⁵⁷ He began by describing an innovation in his experiments. This was the introduction of a new material for diffusion experiments which was superior to stucco as a porous diaphragm. This material was artificially-compressed graphite which was used for making pencil leads. It was sold in London as 2" cubes and he used slices of one to two inches thickness which were further reduced to a thickness of $\frac{1}{2}$ mm. by using a sandstone. Graphite was ideally-suited for diffusion experiments because its pores were so minute that masses of gas could not penetrate them. He laid particular emphasis on this important property saying: "it seems that molecules only can pass; and they may be supposed to pass wholly unimpeded by friction, for the smallest pores that can be imagined to exist in the graphite must be tunnels in magnitude to the ultimate atoms of a gaseous body."¹⁵⁸

At the beginning of his 1863 paper, Graham stated his support for a dynamical or kinetic interpretation of the diffusion process essentially based on Maxwell's dynamical theory. He wrote that: "the sole motive agency appears to be that intestine movement of molecules which is now generally recognised as an essential property of the gaseous condition of matter. According to the hypothesis now generally received ([See the work of] D. Bernoulli, J. Herapath, Joule, Krönig, Clausius, Clerk Maxwell and Cazin. The merit of reviving this hypothesis in recent times, and first applying it to the facts of gaseous diffusion, is fairly due to Mr. Herapath. See Mathematical Physics in two volumes by J. Herapath Esq., 1847), a gas is represented as consisting of solid and perfectly elastic spherical particles or atoms, which move in all directions, and are animated with different degrees of velocity in different gases."^{158a}

Therefore diffusion was due to an unceasing atomic motion which continued without diminution because of the perfect elasticity of particles.

He then stated that there were three different ways in which gases

159. Graham, *ibid.* Researches. p 214 and p 219.

could flow. This particularly important distinction was recognised by Graham with remarkable clarity of thought. The three modes of gas motion were: firstly, effusion, in which a gas passed into a vacuum through a minute aperture in a thin plate, such as platinum foil; here the rate of passage of an effusing gas was inversely proportional to the square root of the density of the gas. Secondly, there was diffusion, which followed the same law as effusion but occurred by an entirely different process. Diffusion occurred when a gas passed through a partition containing minute pores like those found in graphite; diffusive transport involved the motion of individual molecules whereas effusion was the movement of masses of gas. Furthermore, the latter process, effusion, occurred at speeds which were many thousand times greater than those for diffusion. Thirdly, there was capillary transpiration. This was the flow of a mass of gas through tubes possessing sufficient resistance to produce a constant rate of flow. Graham mentioned that Poiseuille had ~~that~~ found the rate of flow of liquids through capillary tubes was proportional to the fourth power of the diameter of the tube, but he admitted that the relation for gases had not yet been observed. Transpiration was also observed when certain porous solids were used. These solids were loosely-packed minerals which resembled a mass of capillaries, for example lime plaster, stucco, baked clay and chalk.

The diffusimeter which Graham had used was then described. It was based on Bunsen's apparatus, except that a $\frac{1}{2}$ mm. graphite plate was used in place of stucco. He described graphite as a 'molecular sieve'. It did not allow masses of gas to pass through it; only molecules could penetrate through the pores of graphite. Thus there was no interference from capillary transpiration. He demonstrated that the passage of equal volumes of gases through graphite, under constant pressure, was certainly a diffusion process. This can be seen clearly from his results:-¹⁵⁹

<u>Gases:</u>	<u>Oxygen</u>	<u>Hydrogen</u>	<u>Carbonic Acid</u>
Time of passage of gases through	1	0.2505	1.1860
graphite at constant pressure	1	0.2472	1.1886
Square root of density (oxygen = 1)	1	0.2502	1.1760
Time for same gases in transpiration experiments	1	0.44	0.72

Therefore Graham had certainly demonstrated the validity of his diffusion law.

In 1831, he had used compressed stucco, 5 mm. thick, to investigate constant pressure diffusion. Now he tried a stucco cylinder, 12 mm. thick, which had been dried over concentrated sulphuric acid. The relative times for the passage of hydrogen into air were 1 to 2.894, at low pressure; and at high pressure, 1 to 2.891. For true diffusion, the time would have been 1 to 3.80, and for transpiration 1 to 2.04. Obviously a mixed-phenomenon occurred when gases were passing through stucco under pressure. To some extent it was the molecular diffusion into a vacuum, which had been observed with a graphite plate, but principally it was the capillary transpiration of a mass of gas.

Graham then prepared stucco in the same way that Bunsen had done by heating the stucco at 60°C for one day. This appeared to alter the porosity of the stucco and the times for the passage of hydrogen into air were 1 to 2.788 at low pressure and 1 to 2.744 at high pressure. Therefore Graham commented that Bunsen had observed a mixed gas motion partly diffusion and partly transpiration. Bunsen's stucco must have been even less dense than that used by Graham, because Bunsen had found the ratio of the times of passage, for hydrogen to oxygen, to be 1 to 2.73, whereas they should have been 1 to 4 for true diffusion, and 1 to 2.27 for transpiration.

Hence Graham had proved that his diffusion law held under the correct conditions of constant pressure and with a porous barrier of sufficiently fine porosity to allow only molecular passage. Bunsen's experiments were correct, but his interpretation of them was incorrect. He was measuring

159a. With a mixture of 50% hydrogen and 50% oxygen, transmitted into a vacuum, atmolysis gave 77% hydrogen and 23% oxygen. Also when air was passed through graphite there was a 1% increase in its nitrogen content.

The word 'atmolysis' is not used in the Wellcome MS. draft copy of Graham's paper: 'On the molecular mobility of gases.'

the flow of gases through stucco under pressure and this was a mixed-flow process of molecular diffusion and capillary transpiration.

Having resolved Bunsen's mistaken interpretation of diffusion, Graham studied the diffusion of gaseous mixtures into a vacuum through his new graphite partition. He discovered that a partial separation of gaseous mixtures occurred for which he eventually proposed the new name 'atmolysis'. Graham first observed atmolysis with a mixture of 95% hydrogen and 5% air. The gases passed through graphite in a shorter time than he had anticipated from the mean diffusion time. This was not caused by transpiration, because transpiration would have taken a longer and not a shorter time. Analysis of the gases which had permeated through the graphite showed that there was more hydrogen and less air present, than in the original mixture.^{159a} Thus, this movement was molecular and each gas was impelled by its own molecular force, hydrogen passing 3.8 times more rapidly than air.

Graham compared the permeation of gases through graphite into a vacuum, with their diffusion into air. He found that there was a close agreement between the two processes. Hydrogen diffused into air at the rate of 1.243 c.c. per minute, whilst hydrogen permeated into a vacuum at the rate of 1.289 c.c. per minute. Therefore both these movements could be called diffusion of gases. He stated that they were caused by the 'inherent mobility of the gaseous molecule.' The speed of diffusion was ultimately caused by the degree of motion of the molecules and not by their specific gravity. Indeed the degree of motion controlled the volume of a gas and hence its specific gravity. Graham extended these views in a theoretical appendix. (See Chapter 7).

To improve the technique of atmolysis Graham designed an 'atmolyser'. This was a porous clay pipe enclosed in a larger glass or metal tube. Gases were passed through the inner clay tube and a vacuum was maintained in the outer tube. The results which he obtained with this atmolyser were quite remarkable. An explosive mixture of 67% hydrogen and 33% oxygen was passed through the clay tube but the mixture which emerged from

the clay tube did not explode. It contained only 9% hydrogen and 91% oxygen, sufficient oxygen for a taper to burn in it without any explosion!

Graham added a valuable final section to his paper on molecular mobility between the reading and publication stages. It concerned the interdiffusion of gases without a partition. Perhaps this was added in response to Maxwell's request for further experiments of this kind. Graham carefully filled a closed cylinder with $\frac{1}{10}$ th of carbon dioxide at the bottom and $\frac{9}{10}$ th of air above. The apparatus was then left for several minutes after which the top $\frac{1}{10}$ th was drawn off. By this method he was able to determine the absolute velocity of molecular movement. He found that carbon dioxide diffused upwards into air at a speed of 73 mm. per minute. In a similar experiment, starting with $\frac{9}{10}$ th of air below and $\frac{1}{10}$ th of hydrogen above, the hydrogen diffused downwards at a speed of 350 mm. per minute, that is 5 times as fast as carbon dioxide diffused upwards. This experiment provided direct evidence for inherent molecular motion. He concluded that in still air, the molecules moved half a metre in 5 to 6 minutes, and in hydrogen, the molecules moved two metres in 6 minutes.

Graham had clarified his views on gas motion in this paper, by distinguishing, unambiguously, between the three modes of gas motion. He had conveyed a more precise idea of the diffusion process and thereby had explained the basis of Bunsen's experiments. He had also developed a new process for separating mixed gases, 'atmolysis', and had introduced an important new material for diffusion experiments, artificially-compressed graphite. Therefore this paper must be seen as a considerable achievement, the flowering of more than thirty years of study on the motion of gases.

Maxwell made use of the final interdiffusion experiments, of Graham's 1863 paper, in his own revised account of diffusion. Also, he at last realised the usefulness of Graham's transpiration results. This can be seen from a letter written by Maxwell to Graham in 1865. He wrote: "I have a few results to compare with your experiments on the transpiration of gases, but I find that my method of observation is more exact than some of

160. Unpublished MS. letter from J. Clark Maxwell to Graham, dated May 1st 1865, Cambridge University Library.

161. J. C. Maxwell, 'On the viscosity or internal friction of air and other gases,' received November 23rd 1865, read February 8th 1866. Phil.Trans. 156 (1866) 249-268.

162. G. G. Stokes, 'On the effect of the internal friction of fluids on the motion of a pendulum' December 9th 1850. Cambridge Phil.Soc. Trans. 9 (1851-6) part 2 pp [8] - [106]

my data, derived from measurements, so that at present I have taken the apparatus down to measure everything and so get results worthy of the troubles. I have tried air at pressures from 30" to 100.7" and from 42°C to 158°C. Friction is the same for all densities but increases with the temperatures, apparently in the same proportion as the air expands. I expected it would be as $\sqrt{T_{\text{abs}}}$ but I think I am wrong. These results agree with yours. I have also tried hydrogen and carbonic acid and find the velocity of hydrogen is 2.16 \times air a little more than yours, but my results are not fully reduced yet Have you got any more results about transpiration velocity of mixed gases especially hydrogen and oxygen or ether vapour and oxygen? I see that you have determined the transpiration of equal volumes of hydrogen and oxygen. If you have also that of 2 volumes of hydrogen and 1 volume of oxygen, it would serve as a test for the theory. I think the absolute value of the friction of a few gases may best be determined by my method, but the comparison of gases and the effect of mixture can best be done by transpiration through tubes by your method. Has anyone but you made such experiments on gases, of course Poiseuille and others have tried liquids I suppose hydrogen particles must either be much bigger than oxygen ones or else they must act on one another at a greater distance though they are 16 \times less in mass." 160

This last comment referred to the transpiration of gas mixtures containing hydrogen. Surprisingly, hydrogen transpired as slowly as any other gas, with which it was mixed, and sometimes caused the mixture to transpire even more slowly than either of the separate constituent gases.

In 1865 Maxwell experimented on gaseous friction or viscosity by suspending glass plates from wires and allowing them to oscillate in different gases.¹⁶¹ He then noted the time taken for these oscillations to die away. This method of experiment had been suggested in 1850 by G. G. Stokes.¹⁶² Maxwell believed that his method of measurement had some advantages over Graham's transpiration experiments. In transpiration,

163. Oskar Emil Meyer (1834-1915) was the younger brother of J. Lothar Meyer. O. E. Meyer was Professor of Physics at Breslau from 1864. His paper was read to the Naturforscher Versammlung on September 23rd 1863 but it was not published until 1865:- 'On the viscosity of gases - 1st paper - On the effect of air on pendulum oscillations' Pogg. Ann. 125 (1865) 177-209, 401-420, 564-599.
164. See the article on Maxwell by C.W.F. Everett in the Dictionary of Scientific Biography (edited by C.C. Gillespie).
165. P. M. Heimann, Ph.D. thesis: James Clerk Maxwell. His sources and influence. (Leeds, 1970) See chapter II pp 38-79, 'Statistical representation and molecular forces'- particularly pp 47-50.

it was difficult to measure the diameter of the small-bore tubes accurately. Also, the transpiration times might possibly be affected by interactions between gas molecules and the tube walls. However, Maxwell accepted that Graham's transpiration method was very convenient especially for comparative measurements. That the viscosity of air did not depend upon its density, was confirmed by Maxwell's experimental results. Indeed, he believed that his results were correct because they agreed with calculations made from Graham's transpiration experiments. Independently of Maxwell, O. E. Meyer reached the same conclusion in 1863.¹⁶³

Maxwell determined the viscosity ratios of gases relative to the air. They were: 0.859 for carbonic acid, and 0.5156 for hydrogen. Graham had found the transpiration ratios for these same gases to be 0.807 and 0.4855 respectively. Maxwell admitted that his higher values were obtained because he was using less pure gas samples than those used by Graham. Indeed he admitted that Graham's method was really more suitable for determining viscosity ratios.

Maxwell's first paper of 1860,¹⁶⁴ on the dynamical theory of gases, contained certain difficulties including the theory of gas diffusion. In 1862 Clausius pointed out that Maxwell's distribution function for the velocities of gas molecules was incorrect. This was because temperature differences affected the motion of gas molecules and so all the directions of motion in a gas were not equally probable. As Heimann has shown,¹⁶⁵ in his thesis, Maxwell planned to derive a more appropriate distribution function, in 1864, for a projected paper on the conduction of heat in gases. However, this paper did not appear because Maxwell found out that the elastic sphere model of gases predicted that gas viscosity was proportional to the square root of the absolute temperature and this was contradicted by experiment. His experiments had shown him that the viscosity (or transpiration rate) of a gas was directly proportional to the absolute temperature and not to its square root.

Thus, in 1866, Maxwell was led to reformulate his dynamical theory of

166. J. C. Maxwell, 'On the dynamical theory of gases' received May 16th 1866, read May 31st 1866. Phil.Trans. 157 (1867) 49-88 or Scientific Papers of James Clerk Maxwell (edited by W. D. Niven, Cambridge, 1890) Vol. 2 pp 26-78.

gases. He chose a Boscovichian force-field model, in which the atom was a point centre, with a repulsive force chosen so that the viscosity of a gas could be proportional to the absolute temperature.¹⁶⁶ In this paper he deduced a diffusion coefficient for carbon dioxide and air using Graham's 1863 interdiffusion figures. He also compared this value with one calculated from some results taken from Graham's first diffusion paper of 1829. The diffusion coefficient calculated from Graham's 1863 results was three times greater than that from the 1829 results. Maxwell attributed this to an inequality in the gas composition, of Graham's earlier experiments, caused by the bend used in the exit piece of the glass tube.

To show that the transpiration velocity of a mixture depended mainly on the slower moving gas Maxwell again relied on Graham's experiments. Here he drew attention to the remarkable results, contained in Graham's experiments, that the viscosity of a gas mixture could be greater than that of either of the component gases taken separately. For example he quoted Graham's figures for the transpiration of a mixture of carbon dioxide and hydrogen; (notice particularly the figures for the transpiration of mixtures containing 25% and 10% hydrogen).

% hydrogen in the mixture	100	97.5	95	90	75
Observed transpiration time (Graham)	0.4321	0.4714	0.5157	0.5722	0.6786
Calculated time (Maxwell)	0.4375	0.4750	0.5089	0.5678	0.6822
% hydrogen in the mixture		50	25	10	0
Observed transpiration time (Graham)		0.7339	<u>0.7535</u>	<u>0.7521</u>	0.7470
Calculated time (Maxwell)		0.7652	0.7468	0.7361	0.7272

Therefore Graham's experimental researches on gas motion became a useful test for the dynamical theory of gases. His results were used by both Maxwell and O. E. Meyer to provide experimental confirmation of their theoretical studies of gas diffusion and viscosity. This practical demonstration of some parts of the dynamical theory of gases inevitably contributed towards its general acceptance.

167. O. E. Meyer, 'On the friction of gases - 2nd. paper: On the passage of gases through capillary tubes' (Breslau November 24th 1865) Pogg. Ann. 127 (1866) 253-281, 353-382. See also O. E. Meyer, The Kinetic Theory of Gases, (first edition 1877) The first English translation was made by R. E. Baynes (London, 1899) See pp 183-205.

168. Graham, 'On the absorption and dialytic separation of gases by colloid septa,' received June 20th 1866, read June 21st 1866, Phil. Trans. 156 (1866) 399-439 and Researches 235-281.

169. J. Herapath, Mathematical Physics (London, 1847) Vol. 2 p 5.

O. E. Meyer made use of Graham's experimental results in both of his papers on the viscosity of gases¹⁶⁷ and in his textbook. He used both the mean value of the viscosity of air and Graham's transpiration coefficient of air to calculate the viscosity coefficient of oxygen. He then used this result, together with Graham's transpiration figures, to calculate, with considerable accuracy, the viscosity coefficients of seventeen other gases. Meyer also attempted to explain Graham's observation that some gases with the same molecular weights possessed the same coefficient of transpiration. He supposed that these gas molecules contained equal numbers of atoms, for example CO_2 and N_2O , and therefore they would have comparable mean free paths and collision frequencies.

In 1866 Graham wrote a paper entitled 'On the absorption and dialytic separation of gases by colloid septa' in which he extended his researches on gas motion.¹⁶⁸ In the first part of this paper, he examined the use of caoutchouc (rubber) for the atmolysis of gases. Porous partitions like graphite, or clay, were unsuitable for separating gas mixtures of similar density, such as oxygen and nitrogen in air. On the other hand, liquid mixtures of a similar density were easier to separate. Now Graham believed that gases were liquefied by a non-porous barrier such as rubber, which was a soft colloid. He had consistently expressed the view, that gases were liquefied when they were absorbed by liquids, since his 1826 paper on the absorption of gases by liquids. He also considered that soft colloid materials, such as rubber, acted like a true liquid towards gases. Graham remained convinced of his explanation even although others, for example, Herapath, had expressed their doubts about 'true liquefaction' occurring in membranes.¹⁶⁹

Graham reviewed the earlier experiments of Mitchell and Draper but he did not give sufficient credit to Draper, who had suggested, in 1836, the use of rubber for separating gaseous mixtures. Draper was not particularly successful in his own experiments but he deserves credit for suggesting the technique which Graham now used for the atmolysis of air. In these

170. Draper had emphasised that absorption must occur when gases penetrated rubber, followed by transmission of gases in a very compressed state, but he did not go as far as Graham, in advocating the true liquefaction of gases by rubber. Matteucci also emphasised the differences in the process of gas transmission through membranes. See C. Matteucci, 'Sur la diffusion des gaz à travers certains corps poreux' Comptes Rendus. 57 (1863) 251-253.

171. Graham, op.cit. (168) Researches. p.236.

172. H. Sprengel (of St. Bartholomew's Hospital, London) 'Researches on the vacuum,' J.Chem.Soc. 18 (1865) 9-21.

earlier experiments, Graham insisted that, insufficient attention had been paid to two essential points needed for a proper understanding of the process, of the passage of gases through india rubber or membrane.¹⁷⁰

They were: that gases must be liquefied inside soft colloids like rubber, and that transmission across the partition was effected by a process of liquid diffusion and not by gas diffusion. These strictures were succinctly expressed by Graham when he wrote: "indeed the complete suspension of the gaseous function during the transit through colloid membrane cannot be kept too much in view."¹⁷¹

Gases were allowed to pass into a vacuum through a film of rubber, supported on a thin stucco plate fixed in the diffusimeter. As he had anticipated the times of passage showed no relation to diffusion times. The initial absorption of gas by the rubber seemed to depend upon a chemical affinity between the gas and rubber, analogous to the attraction between a solute and solvent. The rubber was 'wetted through' with the liquefied gas and this liquid evaporated at the other side either into a vacuum or into another gas. Also the permeability of rubber increased as the temperature was raised, in the same way that the solubility of salts in water usually increases with temperature.

To atmolyse air, Graham left a rubber balloon filled with carbon dioxide in air for four hours. The balloon shrank. Any carbon dioxide left inside the balloon was absorbed using alkali. The balloon was then found to contain 62.9% nitrogen and 37.1% oxygen, sufficient oxygen being present to relight a glowing wooden spill. Thus, air was partially atmolyzed. A better separation of air was achieved by using a thin film of rubber over a thin stucco plate in a diffusimeter. Working at atmospheric pressure, air was passed into a vacuum for one day. This gave a mixture containing 57.4% nitrogen and 42.53% oxygen. Finally, Graham used an improved apparatus incorporating a vacuum pump which had been designed by Hermann Sprengel in 1864.¹⁷² A bag was attached to the side of a long tube, down which a head of mercury was dropped, either to

173. Henri Saint-Claire Deville (1818-1881) obtained his M.D. in 1843 and became Professor at the École Normale from 1851 to 1880. He also substituted for Dumas as a lecturer at the Sorbonne from 1853, becoming a full lecturer from 1866. On Deville see:- R. E. Oesper and P. Lemay, 'Henri Sainte-Claire Deville (1818-1881)' Chymia 3 (1950) 205-221.
174. W. R. Grove, 'On certain phenomena of voltaic ignition and the decomposition of water into its constituent gases by heat,' Phil. Trans. 137 (1847) 1-21.
175. H. St-C. Deville, 'De la dissociation ou décomposition spontanée des corps sous l'influence de la chaleur,' Comptes Rendus 45 (1857) 857-861.
In 1856, Regnault showed that melted silver at 960°C decomposed steam by absorbing oxygen and releasing hydrogen. Deville supposed that steam decomposed in the surrounding porcelain tube, because silver did not have sufficient affinity for oxygen to be able to decompose steam at this temperature.
176. H. St-C. Deville, 'On the decomposition of bodies by heat, and on dissociation,' Phil. Mag. 4 Ser. 20 (1860) 448-458, translated into English by E. Atkinson from the Soc. de Physique et d'Histoire Naturelle de Genève, Mémoires.

evacuate the bag, or to remove gases from the bag. The bag, itself, was made either from a supported piece of sheet rubber, or from some silk or cotton, coated with rubber varnish. With the bag and Sprengel pump, Graham succeeded in partially separating the gases in air to give a mixture containing about 40% oxygen. This should be compared with the usual 21% of oxygen found in ordinary air.

In the second part of his paper, Graham examined the passage of gases through red hot metals. The origins of this work can be traced back to Priestley's experiments on the exchange of gases across the walls of red-hot tubes made of copper, silver, or gold; although Graham, himself, made no reference to them. The immediate influence on Graham's own studies was the work of Henri Saint-Claire Deville.¹⁷³

Deville had set out to explain an observation made by W. R. Grove, in 1847, that water vapour was partially decomposed by hot platinum near to its melting point.¹⁷⁴ In 1857, Deville repeated Grove's experiments and attempted to find the temperature at which water vapour dissociated.¹⁷⁵ Deville had introduced the concept of 'dissociation' in 1860.¹⁷⁶ He explained that all compounds contained a collection of molecules separated by small finite spaces. The force which held adjacent molecules together was cohesion and the force which held elements together inside a molecule was chemical affinity. Now, heat diminished both of these forces. It reduced cohesion to zero separating molecules from one another and probably it also expanded individual molecules by partly reducing the force of chemical affinity. During this expansion an equilibrium point was reached between stability and decomposition; this was the point of dissociation.

With water, the cohesive force holding neighbouring water molecules together was destroyed at 100°C. As the temperature was raised further to 1,000°C, the stability of the molecules of steam was decreased. At 1,000°C the dissociation of steam could occur. The least disturbing influence caused steam to dissociate at a suitable temperature. For example this dissociation could be promoted either, by the solubility of

177. H. St-C. Deville, 'De l'influence qu'exercent les parois de certains vases sur le mouvement et la composition des gaz qui les traversent,' Comptes Rendus. 52 (1861) 524-527.

178. Edmond Becquerel, 'Recherches sur la détermination des hautes températures et l'irradiation des corps incandescents' Ann.de Ch. 3 Ser. 68 (1863) 49-142.

179. H. St-C. Deville et L. Troost, 'De la mesure des températures élevées,' Comptes Rendus. 56 (1863) 977-983.
Deville and Troost showed that when dry carbon dioxide was passed through a platinum tube; and hydrogen was passed through the annular space between the platinum tube and an outer porcelain tube, then the emerging gases from the platinum tube were a mixture of carbon dioxide, carbon monoxide, hydrogen and water vapour.

180. H. St-C. Deville et L. Troost, 'Sur la perméabilité du fer à haute température,' Comptes Rendus. 57 (1863) 965-967.

181. H. St-C. Deville, 'Note sur le passage des gaz au travers des corps solides homogènes,' Comptes Rendus. 59 (1864) 102-107.

oxygen in silver at $1,000^{\circ}\text{C}$, or by the mechanical action of platinum at $2,000^{\circ}\text{C}$. Finally, at a sufficiently high temperature, say $2,500^{\circ}\text{C}$, steam would be completely decomposed.

In 1861, Deville independently rediscovered Priestley's diffusion technique using earthenware tubes.¹⁷⁷ He enclosed an earthenware tube inside a glass tube and passed carbon dioxide into the annular space whilst hydrogen was sent through the earthenware tube. Only the gas which emerged from the annular space was inflammable. Therefore, most of the hydrogen must have passed outwards through the earthenware tube. Graham used this same apparatus for his first atmolyser, of 1863, presumably following Deville's example.

Also, in 1863, Deville and his assistant Troost discovered that both platinum and iron were permeable to gases at red heat. They made use of Edmond Becquerel's application of platinum as a pyrometer¹⁷⁸ and found that dry air lost oxygen when it was passed through a heated platinum tube.¹⁷⁹ A platinum tube was enclosed in a porcelain tube and porcelain fragments were put in the annular space. They found that if a mixture of nitrogen and steam was passed through the platinum tube at $1,100^{\circ}\text{C}$, and at the same time hydrogen was passed through the annular space, then the gas emerging from the platinum tube was a mixture of hydrogen and nitrogen. Therefore platinum walls were permeable to hydrogen at $1,100^{\circ}\text{C}$. On the contrary, if, in the same experiment, carbon monoxide was used as the annular gas in place of hydrogen, there was no penetration of the walls by carbon monoxide.

The next important discovery made by Deville and Troost was that hydrogen could also pass through the walls of an iron tube which had a low carbon-content.¹⁸⁰ They passed hydrogen through an iron tube at high temperatures and then they cut off the supply of hydrogen. But, hydrogen still gradually escaped outwards from the iron tube into the air, leaving a partial vacuum in the tube. To explain the permeability of iron and platinum at high temperatures Deville suggested, like Priestley before him, that these tubes became porous.¹⁸¹ The porosity, according to Deville,

182. Deville, *ibid.* p 107. Deville obtained some results using an iron tube which puzzled him. Nitrogen gas was sealed in the iron tube which was contained in an outer impermeable porcelain tube. Hydrogen gas was passed through the annular space. At low temperatures hydrogen penetrated into the iron tube containing nitrogen and the pressure inside and outside the iron tube was the same; but at 1400°C the pressure of hydrogen inside the iron tube exceeded that outside. This contradicted the law of uniform diffusion. Why was this happening? Deville provided two explanations: Either a mixture of nitrogen and hydrogen might act as one homogeneous gas at high temperature, so more hydrogen would be drawn into the iron tube. He regarded this explanation to be unlikely. Alternatively the gases inside the iron tube were immobile unlike the hydrogen outside. Interestingly, Deville added that if the latter explanation was correct then important conclusions could be drawn in support both of the mechanical theory of heat and of the new ideas on gaseous constitution which would include Graham's hypothesis. Cautiously, Deville refused to speculate further until he had considered these experiments more carefully.

arose from the expansion of intermolecular spaces between the regularly arranged molecules in the metal. At high temperatures these spaces were large enough for gases to enter them and so pass through the metal.

Deville compared these spaces in very hot metals to the pores which existed in Graham's compressed graphite and he wondered if it might be possible to estimate the size of gas molecules at very high temperatures from the size of the intermolecular spaces.¹⁸²

Returning to Graham's researches on red-hot metals: he began by suggesting that there might be an analogy between the passage of gases through rubber and their passage across red-hot metals. The liquefaction of gases in red-hot metals might seem improbable but some degree of absorbing and liquefying power must exist with softened or liquefied metals, like melted silver, which retained up to 20 volumes of oxygen at red heat.

In a similar experiment to that performed by Deville, Graham used a platinum tube kept vacuous with a Sprengel pump. This tube was enclosed in a larger porcelain tube. Hydrogen gas was put into the annular space. No hydrogen passed through into the platinum tube until a dull red heat was reached. But above this temperature hydrogen entered the platinum tube at a rate of $489.2 \text{ c.c. min}^{-1} \text{ m}^{-2}$. This was four times faster than the passage of hydrogen through rubber at room temperature. He tried other gases in this experiment but only hydrogen appeared to pass through red-hot platinum to any noticeable extent.

It then occurred to Graham that if hydrogen was condensed and liquefied in red-hot platinum then it might be possible to trap hydrogen in a platinum plate or wire. A platinum wire was placed in a glazed porcelain tube attached to a Sprengel pump. The tube was first evacuated and heated to redness for one hour, to drive out all gases. Dry hydrogen was then admitted and the temperature was gradually reduced over a period of twenty minutes to just below dull red heat. When the apparatus had cooled, any hydrogen was flushed out with a stream of air or nitrogen, and finally the tube was evacuated. No hydrogen was released during the

183. Graham, op.cit. (168) Researches p.263.

evacuation. The tube was then heated to redness in vacuo and some hydrogen was indeed released. Thus, Graham discovered a new property of platinum which he called 'occlusion'. He defined 'occlusion' as "the power to absorb hydrogen at red heat, and to retain that gas at low temperatures, under redness for an indefinite time." ¹⁸³ After occlusion of hydrogen, the platinum was unchanged in appearance but it was slightly expanded. When the hydrogen gas was driven off by heat the platinum seemed to be whiter in colour.

Graham found that palladium foil showed the property of occlusion to an even greater extent than platinum. Vacuum-ignited palladium foil could occlude large volumes of hydrogen at low temperatures; for example, at 90-97°C, one volume of palladium foil occluded 643.3 volumes of hydrogen. This discovery led him to notice that spongy palladium, containing occluded hydrogen, had an enhanced chemical reactivity. This metal possessed considerable reducing powers. In one day, it reduced dilute solutions of: ferric salts; potassium ferricyanide; and chlorine water even when kept in the dark. Palladium sponge, unlike platinum and iron, preferentially absorbed alcohol to water; it also absorbed hydrogen in preference to all other gases. Graham emphasised that palladium must absorb hydrogen as a volatile liquid, and not as a gas, because palladium was not sufficiently porous to absorb gas molecules. Indeed he extended these views to explain why graphite plates allowed more hydrogen to pass through them than the diffusion law predicted. He suggested that a small proportion of the hydrogen must diffuse through graphite in the liquid state.

In an important extension of his vision of gas motion, Graham stated that there was a progression in the degree of porosity of different substances, which controlled the kind of gas motion which occurred. He wrote: "there appear to be:-

- (1) Pores through which gases pass under pressure or by capillary transpiration, as in dry wood and many minerals,

184. Graham, op.cit. (168) Researches p.272.

185. Royal Society Referee's Report by J. C. Maxwell (R.S.reference 5.138) on Graham's paper 'On the absorption and dialytic separation of gases by colloid septa,' Maxwell's report is dated July 17th 1866. W. A. Miller in his Royal Society Referee's Report on the same paper wrote: "the paper abounds in original and important observations" (R.S. reference 5.137) Report dated July 4th 1866.

186. M. F. Margueritte, 'Recherches sur l'aciération' Ann.de Ch. 4 Ser. 6 (1865) 55-85.

- (2) Pores through which gases do not pass under pressure but pass by their proper movement of diffusion, as in artificial graphite, and
- (3) Pores through which gases pass neither by capillary transpiration nor by their proper diffusive movement, but only after liquefaction, such as the pores of wrought metals and the finest pores of graphite." ¹⁸⁴

Maxwell wrote a referee's report on this paper for the Royal Society. He attempted to explain how Graham's views on the passage of gases through red-hot metals differed from those of Deville. The latter believed that metals were expanded by heat till the gases with the smallest molecules were able to penetrate the intermolecular spaces. In contrast Maxwell wrote: "Mr. Graham's explanation leads him to look for the phenomenon not among 'crystallised masses' of metal having planes of cleavage but among amorphous masses whose molecules may interchange places without any break of continuity. When a portion of such a mass is charged with a substance capable of being absorbed by it, then there is such an interchange of molecules of that substance as to diffuse it through the mass. This diffusion however may not be possible except at high temperature which by increasing the excursion of and the velocity of the molecules enables them to pass from one part of the mass to another I consider Mr. Graham's paper an important contribution to our knowledge of the physical states of matter." ¹⁸⁵

Graham concluded his paper on the absorption and dialytic separation of gases with an examination of the occlusion of gases by iron. This was an important consideration in metallurgy. Graham confirmed Deville's observation that carbon monoxide was released from red-hot iron and he also detected the release of carbon dioxide. He then found that pure iron occluded carbon monoxide at low red heat; one volume of iron occluded 4.15 volumes of carbon monoxide. In 1865 Margueritte had shown that carbon monoxide could convert iron into steel. ¹⁸⁶ He supposed that carbon

187. Graham, 'On the occlusion of hydrogen gas by metals,' read June 11th 1868, Proc.R.S. 16 (1868) 422-427 or Researches 283-290.
188. Graham, 'On the relation of hydrogen to palladium, and on hydrogenium,' read January 14th 1869, Proc.R.S. 17 (1869) 212-220, 500-506 or Researches 290-299.
189. J. Murray, System of Chemistry 2nd.edn. (Edinburgh, 1809) Vol.2 pp 111-112. Murray wrote "hydrogen may be a metal in the aerial form" Also Humphry Davy had suggested that hydrogen might be a common principle joined to an earthy base in all metals. In his lecture notes for May 18th 1838, Faraday wrote: "not impossible that hydrogen a metal" See H. Bence Jones, Life and Letters of Faraday (London, 1870) Vol.2. p 87.
190. W. C. Roberts, 'The Graham lecture,' Glasgow Phil.Soc.Proc. 2 (1879) pp 345-364.
191. Graham, 'On the occlusion of hydrogen gas by meteoric iron,' read on May 16th 1867, Proc.R.S. 15 (1867) 502-503.

monoxide dissociated and decomposed on the outside of hot iron, releasing carbon dioxide, and depositing carbon in the correct proportion to convert iron into steel. In this explanation, carbon monoxide did not spread through the metal; instead carbon penetrated into the iron from the outside. Graham rejected Margueritte's explanation. Instead he thought that carbon monoxide penetrated into the interior of iron where it converted iron into steel. This accounted for the blistering which was often observed in steel-making. Therefore Graham recommended that steel should be made in two steps. Firstly carbon monoxide should be introduced into iron at a low red heat and then at much higher temperatures a second stage would occur; the carbon monoxide would then decompose, supplying carbon to make steel and releasing carbon dioxide gas.

In his final years Graham continued to study the occlusion of gases by metals. In 1868, he showed that hydrogen could be occluded by using an electrolytic method. — He connected palladium or platinum cathodes to a zinc anode and used them to electrolyse dilute sulphuric acid.¹⁸⁷ In 1869, Graham suggested that palladium with occluded hydrogen, should be regarded as an alloy of two metals, the one being palladium and the other, the volatile metal 'hydrogenium'.¹⁸⁸ It had often been suggested, on chemical grounds, that hydrogen was the vapour of a very volatile metal.¹⁸⁹ W. Chandler-Roberts, who assisted Graham in his researches from 1865, has suggested that Graham believed that hydrogen, itself, would eventually be obtained in a metallic form.¹⁹⁰

The remarkable power of certain metals to retain hydrogen by occlusion was demonstrated in an unusual way by Graham in 1867. He carefully showed that gases were occluded in the Lenarto meteorite; hydrogen was the main gaseous constituent along with traces of carbon monoxide and nitrogen. Thus Graham wrote: "this meteorite may be looked upon as holding imprisoned within it, and bearing to us, hydrogen of the stars."¹⁹¹

The occlusion of hydrogen by palladium was analogous to the alloying of a volatile metal with an involatile metal. Graham found that, when

192. Graham, 'Additional observations on hydrogenium' received by R.S. on June 10th 1869, read on June 17th 1869, Phil.Mag. 4 Ser. 38 (December, 1869) 459-465.

193. Published MS. letter from Graham to A. W. Hofmann!- 28th December 1868, J. Chem. Ed. 16 (1939) 497.

palladium wire was charged electrolytically with hydrogen, one volume of palladium occluded 936 volumes of hydrogen. He noticed that the length of the wire was increased by occlusion but the density, strength, and electrical conductivity were all reduced. Graham then predicted the properties of the new metal, 'hydrogenium'. It would be a very light metal with a density of about 1.7 (he later reduced this to 0.854).¹⁹² Hydrogenium would also be magnetic and this could account for the presence of meteoric hydrogen. Indeed, he concluded that it would be a white, lustrous metal with a similar strength and electrical conductivity to other metals.

These bold speculations were made in the last year of Graham's life. They show that his imagination was not extinguished. This can be seen in the letter which he wrote to A. W. Hofmann in 1868:- "there is a communication of mine before the R.S. at present which I believe will amuse you, or at least the hardiesse of the thing will surprise. What do you think of hydrogenium, a white, magnetic metal of the s. g. 2?"¹⁹³

Although solid hydrogen was later shown to be non-metallic, current research suggests that metallic hydrogen might exist. If hydrogen could be exposed to a sufficiently great pressure, metallic hydrogen might be produced and it may even exist in the cores of the outermost planets of the solar system.

Graham had completed forty years of work on the movement of gases. He had discovered the three distinct modes of gas motion and stated the laws of diffusion and effusion; thus adding greatly to the existing knowledge of these phenomena. He had distinguished the different types of barrier through which gases passed, emphasising that variations in porosity could determine the nature of the gas motion. His researches also provided a valuable experimental support for the dynamical or kinetic theory of gases. His speculations on the nature of matter were derived largely from his study of gases and diffusion. In 1863 he accepted that all atoms were identical primary matter. To distinguish the atoms of one element from those of another, he suggested that different degrees of

motion were possessed by atoms of different elements; the motion of these primary atoms was unalterable. The primary atoms were grouped together to form the molecules involved in gaseous diffusion. These diffusive molecules were able to change their speeds as the temperature was altered. The characteristic differences in their diffusive velocities were retained when the diffusion speeds of the gaseous molecules of different elements were compared at the same temperature. The motion of diffusive gas molecules constituted the phenomenon of heat. This was Graham's final view of heat. He adopted this view after he had rejected his earlier support for a material theory of heat. Graham's unique experimental contribution in the field of gas motion was undoubtedly a significant achievement leading as it did to the development of a better understanding of the nature of gases in the nineteenth century.

Chapter 4

THE ROLE OF WATER IN THE CONSTITUTION OF ACIDS AND SALTS

1. MS. letter (University College, London) of application for the Chair of Chemistry at University College, London. Letter from Thomas Graham to the Council of University College, dated February 25th 1837.

THE ROLE OF WATER IN THE
CONSTITUTION OF ACIDS AND SALTS

"The first portion of my enquiries respecting the chemical constitution of salts was contained in a memoir, on the arseniates, phosphates and modifications of phosphoric acid, in the London Philosophical Transactions for 1833. In this paper a principle was first established of extensive application, namely, the interference, in a most essential manner, of water in the constitution of salts and hydrated acids.

An explanation was thus afforded of those difficulties, for which Chemists had recourse to the startling doctrine of Isomerism, or that two or more bodies might exist identical in composition and constitution, but differing in properties. These researches were continued in a memoir upon water as a constituent of sulphates (Edinburgh Transactions, 1835), in which the derivation and constitution of super-sulphates and double sulphates were explained. The most recent results of my labours, in this department, are contained in a memoir, on the constitution of various classes of salts, read before the Royal Society of London in December last...." ¹

In this letter of application for the Chair of Chemistry at University College, London, Graham emphasised the importance of the role of water in the constitution of both acids and salts. He realised that it was necessary to consider the function of water in salts in order to understand their true nature. It will be shown that by paying careful attention to the role of water in these compounds Graham was able to establish the concept of the polybasicity of acids. This idea led chemists to reconsider the nature of acids and salts in both organic and inorganic chemistry. This was an essential prelude to the researches of Liebig on organic acids; to the re-evaluation of the Berzelian views on the nature of acids and salts; and to the later extensions of these ideas made by Gerhardt, Williamson and Odling in which the electrochemical theory of Berzelius was questioned.

2. G. F. Stahl (1660-1734), Traité des Sels ... (Paris, 1771) translated from the original work of 1723, p 287.
3. C. N. Neumann (1683-1737), Chemical Work of Caspar Neumann, by W. Lewis (London, 1759) p 247.
4. E. Swedenborg, Some Specimens of a Work on the Principles of Chemistry etc., translated by C. E. Strutt from three small treatises published in 1721 (London, 1847) pp xix, 3-73.
5. G. F. Rouelle (1703-1770), 'Sur les sels neutres', Mémoires d l'Académie Royale (June 3rd 1744) 353-364, see p 353.

Graham's researches played a significant part in refining the concept of isomerism. He questioned the application of this idea in Chemistry and thereby clarified the discussion of isomerism particularly in the inorganic domain. It will be shown that Graham also made important contributions in the studies of complex salts and co-ordination chemistry.

The history of the essential role of water in salts can be traced back to the beginning of the eighteenth century at least. Stahl noted that salts contained an earthy element and water.² Under the heading of salts he included acids and alkalis. Neumann recorded that many hard crystalline salts contained water, for example green vitriol and alum.³

One of the most interesting accounts of the nature of salts was given by Swedenborg.⁴ He explained that salts originated in the primeval ocean. Common salt was formed in the interstices which existed in between the neighbouring rounded water particles. A salt particle was therefore pointed and surrounded by six neighbouring water particles. Crystallisation occurred when the number of water particles surrounding a salt particle was reduced below six. Swedenborg found that some water was still retained even inside a solid salt because he noticed that distillation of the solid salt produced both a phlegm and a spirit. If the sharp points of a salt particle were broken off then he suggested that an acid would be generated and it could then be distilled. Undoubtedly, Swedenborg had recognised that water was an essential constituent of salts.

The presence of water in salt crystals was emphasised by G. F. Rouelle in 1744 when he introduced the term 'water of crystallisation'. For Rouelle, neutral salts included "all salts formed by the union of some acid, either mineral or vegetable with a fixed or volatile alkali, or an absorbent earth, a metallic substance or an oil."⁵ Crystals of salts contained both saline molecules and water. Rouelle added that the water was not essential to the nature of these salts because it could be

6. *ibid.* p 356.

7. Anonymous article entitled 'Crystallisation', Encyclopaedia Britannica 3rd.edn. (Edinburgh, 1797) 5 579-588, see p 587.
8. T. Bergman (1735-1784), Physical and Chemical Essays, translated by E. Cullen Volume 1 (London, 1784) 177-
9. R. Kirwan (1733-1812), Elements of Mineralogy (London, 1784) 174-202.
10. R. Kirwan 'Of the strengths of acids and the proportions of ingredients in neutral salts', Trans.R.Irish Acad. iv (1790) 66.
11. L. J. Proust (1756-1826) 'Recherches sur le cuivre' Ann.de Ch. 1 Ser. 32 (1799) 26-54, see pp 41-45.
12. J. J. Berzelius, 'An attempt to determine the definite and simple proportions, in which the constituent parts of inorganic substances are united with each other.'
Phil.Mag. 1 Ser 41 (1813) 1-8, 81-90, 193-205, 275-284, 334-346, 401-415;
Phil.Mag. 1 Ser 42 (1813) 40-44, 135-142, 171-182, 265-276, 371-386, 440-463;
Phil.Mag. 1 Ser 43 (1814) 42-54, 88-101, 161-175, 245-249.

removed without destroying the salt; but he thought that water was essential to the structure of salt crystals, because crystals were destroyed when all the water was removed. He wrote: "I call this water which enters thus into the formation of crystals, 'water of crystallisation' in order to distinguish it from the water which is lost by evaporation, to which I give the name 'superabundant water of crystallisation' or 'water of dissolution', for it is this latter water which is properly the instrument of solution."⁶

By the end of the eighteenth century the presence of water in crystals of salts was clearly recognised. This can be seen from an article on water of crystallisation written in 1797:- "The crystals of every kind of salt contain water as an essential to their composition and if deprived of this, they lose their crystalline form entirely and fall into powder. It is plain therefore that the saline particles attract not only one another, but some part of the water which dissolves them....."⁷ Although the concept of essential water in salts was not new, Graham was to bring out its significance as we shall see presently.

After Lavoisier had developed his oxygen theory it was possible to formulate salts as compounds of a metallic oxide, an acidic oxide and water of crystallisation. The determination of the accurate composition of salts was therefore a necessary prerequisite for any theory which considered the detailed role of water in salts. Some important early contributions to the determination of the water-content of salts were made by Bergman⁸ and Kirwan⁹. Interestingly, Kirwan remarked that water might be essential in acids to develop their characteristic properties.¹⁰ In 1799, hydrates of metallic oxides were recognised by Proust when he made a precise distinction between copper oxide and the hydrate of copper oxide (copper hydroxide).¹¹ Thus it could be inferred that water had a role in acids and bases as well as in salts.

The most significant study of the water-content of salts was made by Berzelius between 1810 and 1816.¹² In his important investigations on

13. *ibid.* 1 Ser 43 (1814) 100-101.

14. *ibid.* 1 Ser 43 (1814) 95.

15. *ibid.* 1 Ser 43 (1814) 162.

16. *ibid.* 1 Ser 43 (1814) 246.

17. Berzelius 'Sur la composition des acides phosphoriques et phosphoreux, et sur leurs combinaisons avec les salifiables.' Ann.de Ch. 2 Ser 2 (1816) 151-177, 217-241, 329-339. In 1816 Berzelius would have written the formula of neutral phosphate of soda as $\text{NaO}_2, \text{PO}_5$. This formula was printed in ~~the~~ table in his Essai sur la Théorie des Proportions Chimiques (Paris, 1819), Table of atomic weights p.70. Berzelius later revised his atomic weights in light of the work of Dulong and Petit on specific heats and of Mitscherlich on isomorphism. In 1826 Berzelius gave the formula $2\text{NaO}, \text{P}_2\text{O}_5$. He had halved the atomic weights of P and Na between 1819 and 1826. In 1819 he gave his atomic weights as follows O = 100, P = 392.30, Na = 581.84 so $\text{NaO}_2, \text{PO}_5 = 1674.14$ and in 1826 he gave his new atomic weights as O = 100, 2P = 392.285, 2Na = 581.794 so $2\text{NaO}, \text{P}_2\text{O}_5 = 1674.079$. Berzelius, Traité de Chimie 5 (Esslinger translation, Paris 1831, from German edition of 1826) p 16 of table of atomic weights.

the law of definite proportions Berzelius demonstrated that "the oxygen of the water of crystallisation is always an integral multiple, or, as in the case of citric acid an integral sub-multiple, of the oxygen of the base;" ¹³ for example in $\text{FeO} \cdot \text{SO}_3 + 7\text{H}_2\text{O}$ the oxygen ratio of water to base was 7 to 1. Berzelius accepted the possibility that in salts, water could be present as a base. For example he found that the acid tartrate of potash contained water of crystallisation with exactly as much as oxygen as in the base potash, "but since this water can only be expelled by the addition of a second base,, this salt may be considered as a double salt, of which water is the second base." ¹⁴ This was an anticipation of Graham's later view of the basic role of water in the phosphoric acids and phosphates.

To define neutral salts was not easy, since some 'neutral' salts had acidic and alkaline reactions. Berzelius suggested that all examples of earthy and metallic salts should be considered as neutral, in which the acid was united with as much oxygen in the base, as is found in another decidedly neutral combination of the same acid, with an alkali or an alkaline earth. He wrote: "thus I consider as neutral all those sulphates, in which the base contains one-third as much oxygen as the acid....," ¹⁵ for example $\text{MgO} \cdot \text{SO}_3$. Salts with an excess of acid he called supersalts [acid salts] and salts with an excess of base he called subsalts [basic salts]. Double salts were simply combinations of two neutral salts which were obtained either by mixing together solutions of the two salts and crystallising them or by displacing the water in an acid salt by a second base.

Berzelius thought that he had discovered a simple rule that "the oxygen of the acid [in neutral salts] is a multiple by 2,3,4,5,6,7 or 8 of the base," ¹⁶ but he soon discovered that there were exceptions to this rule. In 1816 he examined the composition of phosphoric and phosphorous acids ¹⁷ and he discovered that the neutral phosphate of soda had a formula which he later wrote as: $2\text{NaO}, \text{P}_2\text{O}_5$. This gave an oxygen ratio

18. Berzelius op.cit. (12) Phil.Mag. 1 Ser 43 (1814) p 246.

of acid to base of 5 to 2, or $2\frac{1}{2}$ to 1, which was a non-integral multiple. The application of this rule together with the concept of a neutral salt was to cause difficulty for Berzelius when he was called upon to consider polybasic acids. He was unable to accept Graham's view that there were three different phosphoric acids, distinguished by their different basicities. The converse of this rule also raised problems for Berzelius with organic acids, for example when their atomic weights were multiplied to reveal their possible polybasic natures. For Berzelius, the atomic weight of an organic acid was fixed as the weight of acid which would combine with one atom of a base, such as soda. He believed that it was not possible for both phosphoric acid and metaphosphoric acid to form neutral salts by combining with different weights of soda. Likewise, Berzelius could not accept that different phosphoric acids were combined with different amounts of water, which acted as a base in these acids.

Despite these problems, Berzelius defined hydrates in the same sense as Graham. For example Berzelius explained that in the hydrates of acids: "the water takes completely the place of the base; the acid takes up a quantity of it [water] which contains exactly as much oxygen as any other base with which it would be saturated: and this water is totally distinct from the water of crystallisation contained by some of the acids." ¹⁸ Graham called this water in hydrated acids 'basic water' and he extended its role from acids to salts. The water combined with bases was also distinguished from water of crystallisation by both Berzelius and Graham who regarded this water as a substitute for an acid.

The role assigned to water in hydrated acids and bases by Berzelius was developed by Graham in his later researches; here Graham was following the lead given by Berzelius rather than that of his teacher Thomas Thomson. Although Thomson accepted the term hydrate, he could not accept the extension given to its meaning. He expressed this opinion when he wrote in 1817: "the hydrates indeed have been considered by some modern chemists [Berzelius?] as likewise saline combinations. But this

19. T. Thomson, System of Chemistry, 5th.edn. (London, 1817) 2. 699
See also 2 17 in which Thomson pointed out that "the compounds called hydrates deserve attention"

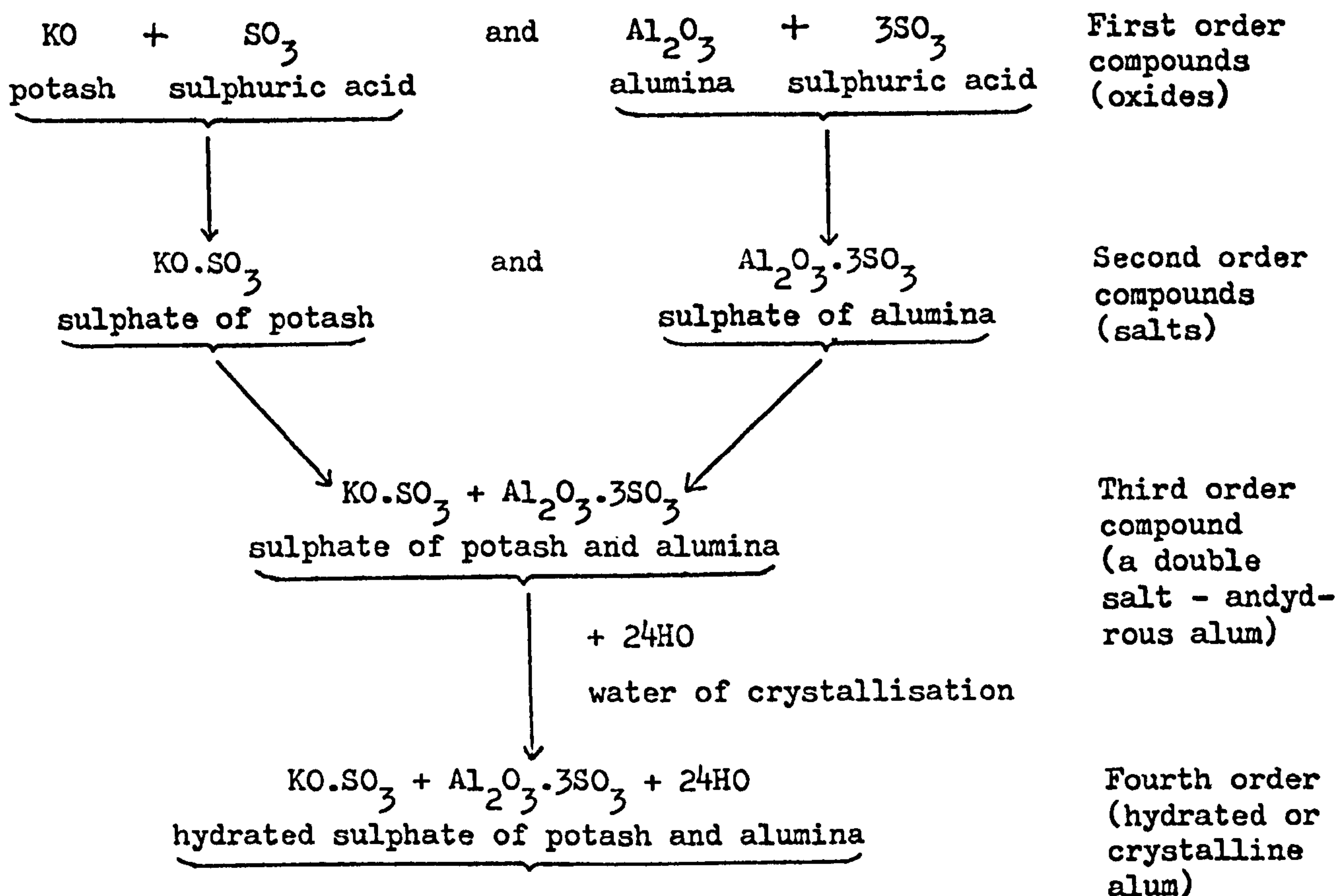
20. Thomson *ibid.* 3 p 20; and Ann.Phil. 5 (1815) 8. See also
T. H. Levere, Affinity and Matter (Oxford, 1971) pp 107-111.

name cannot be applied to them without extending the meaning of the terms acid and base as far as to render them useless. For in the hydrates we must consider the water sometimes acting the part of an acid and sometimes that of a base. While in crystallised salts as in sulphate of soda it would be impossible to apply the term acid or base to the water without impropriety. It seems much better therefore to consider hydrates as a species of compound quite different from salts. The water is capable equally of uniting with acids, bases and salts. It does not deprive them of their characteristic properties or neutralise them as the bases do the acids." ¹⁹

These differences of opinion between Thomson and Berzelius might be attributed to Thomson's known distaste for electrical interpretations of chemical affinity.²⁰ Berzelius had developed a comprehensive theory of electrochemical dualism according to which atoms possessed both positive and negative electricity, but one kind of electricity prevailed to give a 'specific unipolarity', so that if positive electricity predominated the atom would be electropositive and vice-versa. Combination between atoms occurred when the opposite poles touched, discharging their electricities with the evolution of heat. It was possible for two electronegative atoms to combine, for example sulphur and oxygen, but clearly there was no neutralisation of the electric charges so a residual electronegative character remained after combination. Indeed the dualistic combination of polar atoms frequently left a residual quantity of positive or negative electricity in a compound, for example when a metallic oxide was formed, the positive pole of the metal predominated. Berzelius did not have a clear appreciation of the distinction between the electric charge and its intensity. Nonetheless the dualistic theory was very influential in the thoughts of contemporary chemists. Graham was influenced by the dualistic theory in his later speculations on polar molecules and molecular theory, and to a certain extent in his conception of the constitution of acids and salts.

21. In this reconstruction I have used Graham's formulae for the different oxides. The example I have given was adapted from Partington, A History of Chemistry 4 (London, 1964) 172. See also C. A. Russell 'The electrochemical theory of Berzelius,' Ann.Sci. 19 (1963) 117-145 and the introduction to ^{the} reprint of: Berzelius, Essai ... Johnson reprint (1972) v-xlix by C. A. Russell.
22. Berzelius, Essai Sur la Théorie des Proportions Chimiques (Paris, 1819) p 174.
23. Gay-Lussac, 'Sur l'acidité et sur l'alkalinité' Ann.de Ch. 91 (1814) 130-160.

A useful summary of ^{the} electrochemical dualism of Berzelius can be seen by examining the construction of crystalline alum from its constituent oxides.²¹ At each stage of the successive combinations, leading to the formation of alum, there was a residual electropositive or electronegative character.



With regard to the nature of acid hydrates, Berzelius commented that water "combines with the acids in the same way as oxides of iron or potassium, but neutralising infinitely less their acid qualities, it is necessary to consider the water as playing the role of an electropositive body, that is to say as a base."²² This was a role which Thomson did not accept for water.

An alternative approach to hydrated acids like sulphuric acid, $\text{HO} \cdot \text{SO}_3$, was to regard them as hydrogen acids or hydracids, for example $\text{H} \cdot \text{SO}_4$. In 1814 Gay-Lussac proposed that there should be two classes of acids: oxyacids and hydracids.²³ Oxyacids contained oxygen as the acidifying principle combined to another element. Examples of oxyacids were: chloric, sulphuric, carbonic, nitric, phosphoric and boric acids.

24. Gay-Lussac, 'Researches on prussic acid' Ann.de Ch. 95 (1815)
136-232, see pp 155, 161.
25. Berzelius, 'Mémoire sur les sulfo-sels', Ann.de Ch. 2 Ser 32 (1826)
pp 62-65.
26. H. Davy, Collected Works edited by J. Davy (London, 1839) 5 502
'Some experiments on a solid compound of iodine and oxygen, and on
its chemical agencies' from Phil.Trans. (1815).
27. *ibid.* p 501.
28. *ibid.* p 502.

Hydracids contained hydrogen joined to another body, the latter being the acidifying principle, for example HI, HBr, H₂S; to these hydracids Gay-Lussac added the further example, in 1815, of prussic acid.²⁴ This view of acids introduced an artificial division in the family of acids dividing them into two classes. It was retained however by Berzelius who extended it to salts: salts of oxyacids he called amphigen salts and salts of hydracids, haloid salts.²⁵ Davy, on the contrary, was moving in an opposite direction towards a theory which would incorporate all acids. This theory was later identified as the hydrogen theory of acids. Davy clearly distinguished between hydrated acids or acids in water, and anhydrous acids; indeed he wanted to restrict the term 'acid' to the former group of compounds: "I am desirous of marking the acid character of oxyiodine [iodine pentoxide] combined with water, without applying the name to the anhydrous solid."²⁶

He had noticed that when metal iodates were heated they decomposed to become binary compounds: "though they lose all their oxygen, their neutral and saline character remains unaltered, which is not the case with any other known class of bodies, except the hyperoxymuriates [perchlorates]."²⁷ Iodic acid and hydriodic acid were shown by Davy to be distinctly acidic in sharp contrast to the metallic iodates and iodides. What was the origin of this acidity? Davy wrote: "It is not at all improbable that the action of hydrogen in the combined water is connected with acid properties of the compound; for this acid [iodic]acid may be regarded as a triple combination of iodine, hydrogen and oxygen, an oxyide [iodate] of hydrogen, and it is possible that hydrogen may act the same part in giving character, that potassium, sodium or the metallic bases perform in the oxyiodes [iodates]; and as hydrogen combined with iodine forms a very strong acid, and as this acid would remain, supposing all the oxygen to be taken away from the oxyiodic acid [iodic acid], it is a fair supposition that its elements must have an influence in producing the acidity of the substance."²⁸

29. op.cit. (24) p 155.

30. Davy, Collected Works 5 p 513.
'On the analogies between the undecomposed substances, and on the constitution of acids' from J.Sci.Arts 1 (1816) article xviii.

31. ibid. 514-516.

32. P. L. Dulong, Mémoires de l'Institut de France (1815) cxcvi-cc
a summary of the memoirs of 1815 by Baron Cuvier.

This cautious statement shows that Davy was prepared to accept that hydrogen might play a part in determining acidity; but he was not prepared to go as far as Gay-Lussac in assigning a specific role for hydrogen. Gay-Lussac had suggested that hydrogen was an alkalising principle in prussic acid²⁹ but Davy objected to this 'occult quality' commenting: "it is strange that it [hydrogen] should form some of the strongest acids by uniting to bodies not in themselves acid."³⁰

Davy further criticised Gay-Lussac's view of the acidity of chloric acid.³¹ Davy found when he prepared an oxide of chlorine $[\text{ClO}_2]$ that it had no acidic properties and yet Gay-Lussac had explained the acidity of chloric acid $[\text{ClO}_5]$ by assuming the acidification of chlorine by oxygen. Now, according to Davy, chloric acid contained two proportions of hydrogen, one of chlorine and six of oxygen, so he thought it was probable that the acidity of chloric acid was due to the combined hydrogen. His evidence was that the corresponding metallic chlorates which contained one proportion of metal, one of chlorine and six of oxygen were neutral. Thus Davy could not accept that acidity was caused by a hypothetical oxide ClO_5 . He also recognised that both nitric and sulphuric acids were hydrated and contained hydrogen in their composition which he implied must be involved in the development of their acidity. Although Davy did not extend these comments to produce a full theory of hydrogen acids, he did demonstrate that hydrogen must be considered as an important component in the development of acidity.

A more complete theory of hydrogen acids was introduced by Dulong, although he does not appear to have published the details of his theory, which arose out of his study of oxalates.³² Dulong found that the oxalates of zinc and lead did not contain any water when they were dry; but on the other hand the dry oxalates of copper, silver and mercury did contain water. Now oxalic acid could be considered either as a hydrated acid $[\text{H}_2\text{O} + \text{C}_2\text{O}_3]$ or as a hydrogen acid $[\text{H}_2 + \text{C}_2\text{O}_4]$ and Dulong favoured the latter view. He suggested that the water lost from oxalates by

33. Gay-Lussac, 'Sur les combinaisons formées par l'iode et par le chlore'
Ann.de Ch. 2 Ser 1 (1816) 157-173.
34. T. Thomson, An Attempt to Establish the First Principles of Chemistry
by Experiment (London, 1825) 1 27.
35. T. Thomson, System of Chemistry 5th.edn. (London, 1817) 2 393.
36. op.cit. (34) Vol.2 467-468. Thomson added that except for "phosphate of magnesia, all the salts which contain 7 atoms of water are either sulphates or nitrates. The metalline sulphates seem to affect 7 atoms of water. No salt of barytes, strontian, iron, manganese, bismuth, or mercury, contains 6 atoms of water; and only 14 simple salts occur containing that quantity of water. The other five are compound salts etc."

drying or heating came from the reaction between the oxygen extracted from the metallic oxide and the hydrogen of the acid. Thus dry lead oxalate could be considered as a metallic salt $[Pb + C_2O_4]$ which was derived from a hydrogen acid. He concluded that ordinary acids and hydracids could be united as one single class of hydrogen acids. It will be seen later that Dulong's theory of hydrogen acids and the reduction of metallic oxides by these acids formed an important part of Liebig's vision of the constitution of both organic and phosphoric acids, as hydrogen acids.

Gay-Lussac did not accept the views of either Davy or Dulong on acidity. He was convinced that water was neutral in both acids and alkalis. Therefore he saw no need either to distinguish anhydrous acids from hydrated acids or to suggest that hydrogen could develop acidity.³³

Thomson shared Gay-Lussac's opinion that water was neutral in its combinations. Between 1819 and 1825 Thomson was engaged in researches on the determination of atomic weights. This research included the determination of the composition of a considerable number of salts and also an attempt to see "whether any law would develop (sic) itself respecting the quantity of water of crystallisation which these bodies frequently contain. With this view a great number of salts were subjected to experiment; but the only obvious result is that the number of atoms of water in salts, depends more upon the base than upon the acid; for the same base, in general affects nearly the same number of atoms of water in its salts. But to this law there are many exceptions."³⁴ Thomson had already commented that Berzelius's generalisation on the oxygen ratio of water to base in salts was essentially correct. But he maintained that it was a rule of less significance than Berzelius believed because it was self-evident if the base was a metallic protoxide.³⁵ And yet, the examination of 307 salts by Thomson and his students did not provide any general law with respect to the number of atoms of water of crystallisation. The conclusions which Thomson drew from his experiments were merely statistical³⁶; he found that the water of crystallisation in 307 salts was as

37. Berzelius, Jahresbericht, trans. by F. Wöhler 6 (1827) 77, 179-181 and Anon. Phil.Mag. 4 (1828) 450.
38. Obituary notice of Graham by Lord Neaves, R.S. of Edinburgh Proc. (1872) 16-17.
39. MS. letter of application for the Chair of Chemistry at King's College, London. Letter to the Secretary of the Council from Graham July 30th 1830.
40. A Biographical Notice by E. Walford (December 1856) repeated in John Timbs, The Year-book of Facts in Science and Art (London, 1857) p 3.
41. R. A. Smith, Life and Works of Thomas Graham (Glasgow, 1884) p 65.

follows:-

Number of water atoms	Anhydrous	1HO	2HO	3HO	4HO	5HO	6HO	7HO	8HO	9HO	10HO	11HO	12HO
Total number of salts of this type	80	31	50	27	18	12	19	18	10	4	6	0	2

Compound salts like alums contained still more water.

These apparently sterile conclusions show that Thomson was unable to advance any further than Berzelius, despite his implied criticism of Berzelius's rule. Without a leading role for the water found in salts it was difficult for Thomson to deduce much from his results. Furthermore, the experimental basis for his researches was shown to be faulty by Berzelius in 1827.³⁷ In contrast, Graham assumed like Berzelius that water could assume a basic role in salts and he was therefore able to draw more fruitful conclusions from his researches. Whilst studying under Thomson, Graham is reputed to have suggested that water might play an important part in the constitution of acids and salts; as a result Thomson was "struck by the ideas of his young pupil, and encouraged him to continue his investigations on this subject."³⁸

Did Graham assist Thomson in his researches before or after^{his} (Graham's) graduation on April 28th 1824? We do not know; but it would seem to be unlikely that Graham actually assisted Thomson with his research work. It is certain that Graham studied Chemistry under Thomson from 1823 to 1824.³⁹ Then for the next two years Graham is said to have remained at Glasgow University, chiefly devoting himself to the study of mathematics and physical science.⁴⁰ This was followed by two more years at Edinburgh University from 1826 to 1828. Thomson must have inspired Graham to take an interest in the water-content of salts. This influence can be detected in the contents of one of Graham's early notebooks (regrettably lost), which included notes on phosphates, alcohates, salts of magnesia, atomic weights and combining proportions, the absorption of salts from solutions, water of crystallisation "a subject on which he spent much time."⁴¹

42. Graham, 'On exceptions to the law that salts are more soluble in hot than in cold water; with a new instance'. Phil.Mag. 2 (July, 1827) 20-26 and Researches 303-309. W. T. Brande wrote of this paper: "Mr. Graham has added one to the few facts of this kind with which we were acquainted, and has accompanied its description with some very interesting considerations." Qu.J.Sci. 2 (July - December, 1827) p 202.
43. Dalton, A New System of Chemical Philosophy, part 2 (London, 1810) 509-510.
44. Gay-Lussac, 'On the solubility of salts in water' Ann.Phil. 15 (1820) 1-12, see pp 10-11,-a translation made from Ann.de Ch. 2 Ser 11 (1819) 296-315.
45. Thomson, 'On anhydrous sulphate of soda' Ann.Phil. 12 (1826) 401-403 and in System of Chemistry 7th edn. (London, 1831) Vol.2 444-445.
46. Faraday, 'Composition of crystals of sulphate of soda.' Quarterly J. Sci. 19 (1825) 153 also in Experimental Researches in Chemistry and Physics (London, 1859) 153-154.
47. W. K. Haidinger, 'A comparative view of the series of crystallisation of Epidote and of Glauber's Salt' Ed.Phil.J. 10 (1824) 305-316, see pp 314-315, also see: F. Mohs. Treatise on Mineralogy translated by Haidinger Vol.2 (1825)(Edinburgh) 33.
 Wilhelm Karl Haidinger (1795-1871) was born near Vienna. He assisted Mohs in 1812. He moved to Edinburgh in 1823 to arrange the mineral collection of Thomas Allan. Between 1823 and 1827 he published a number of papers on the determination of mineral species. In 1827 he went to work in a china factory at Elbogen.

In 1827 Graham wrote his first paper on the role of water in compounds. It contained a discussion of the anomalous solubility of salts in water and introduced a new example: magnesium phosphate.⁴² Firstly, he referred to previously observed cases of anomalous solubility. For example, in 1810, Dalton had mentioned that the solubility of lime, or hydrate of lime, diminished as the temperature was raised.⁴³ Also, Gay-Lussac discovered, in 1819, that the solubility of Glauber's salt was anomalous. He noticed that the solubility of both anhydrous and hydrated sulphate of soda increased as the temperature was raised to 33°C; but above this temperature the solubility began to decrease.⁴⁴ Gay-Lussac did not attempt to interpret his observations but he did say that he was unable to determine the solubility of hydrated sulphate of soda above 50°C because it retained less water than at lower temperatures. In 1826, Thomson demonstrated that a boiling solution of Glauber's salt deposited anhydrous sulphate of soda⁴⁵ and Faraday observed that a boiling, supersaturated solution of Glauber's salt deposited crystals on cooling which contained 8 parts of water rather than the usual 10 parts.⁴⁶ The first correct interpretation of Gay-Lussac's results was given by Haidinger in 1824. He explained that salts which were crystallised at different temperatures contained differing quantities of water of crystallisation. At ordinary temperatures he found that sulphate of soda crystallised with a fixed amount of water, but above 33°C this salt crystallised without water.⁴⁷

In 1821, Richard Phillips discussed Dalton's observations on the unusual changes in solubility of lime at different temperatures. He checked Dalton's experiments and found that they were correct. When a solution of lime water was heated and then cooled, crystals of lime were indeed deposited. But what was the cause? Phillips supposed that heating increased the force of cohesion or aggregation of the lime particles. He gave a lucid description of the different affinities which were involved in the changes of solubility with increasing temperature.

48. R. Phillips, 'On the solution and crystallisation of lime' Ann.Phil.
1 (1821) 107-111. See p 109.

49. *ibid.* p 109.

They were "the attraction of aggregation of the particles of lime for each other, the attraction of the lime to form a hydrate with a small portion of water, and the mutual affinity existing between the hydrate and the water of solution." ⁴⁸

Phillips gave another example of the aggregating power of heat. He wrote that "if some peracetate of iron be decomposed by ammonia, the oxide is quickly redissolved by acetic acid; but if the oxide of iron be boiled in the solution from which it is precipitated, the acetic acid is incapable of dissolving it, on account of the cohesion which the oxide of iron has suffered by heating. As crystallisation is but a modification of cohesive affinity, we may, I think consider, that the cohesive or crystalline affinity excited by the heat, increased by the affinity of the lime for a definite portion of water, is so much greater than the affinity of the hydrate of lime for the water of solution as to occasion crystallisation." ⁴⁹

Graham did not agree with Phillips' explanation of the changes in solubility and reactivity of the oxide of iron or the oxides of tin, chromium and aluminium. He discussed this problem in greater detail later when he examined the phenomenon of isomerism. Graham believed that the reduced solubility of oxide of iron after boiling was due to a loss of combined water and not to an increase of cohesion. He came to this conclusion from his observation that the efflorescent crystals of hydrated magnesium phosphate became less soluble in water as the temperature was raised. In addition he found that anhydrous magnesium phosphate was thrown out from the solution on heating. He explained that, with efflorescent salt hydrates, there was a weak force of affinity between the salt and water at room temperature. This affinity was reduced still further in solution by a small rise in temperature and so it might eventually overcome and even counteract the increasing solvent power. Thus Graham was able to account for the decreasing solubility of efflorescent salt hydrates as the temperature was raised: a temperature would be reached

50. Graham, op.cit. (42) Researches p 308.

when the salt hydrate would lose its water of crystallisation. He further believed that salt hydrates were always more soluble than the corresponding anhydrous salts.

Graham then insisted that hydrates were of different types. This was an important distinction which led him to study the role of water in compounds. Unlike most of his contemporaries Graham did not dismiss the water in hydrates simply as water of crystallisation. Water was combined differently in the hydrates of: alkalies; earths and metallic oxides; and especially salts. There was ^a subtle difference in his explanation of the loss of solubility of hydrates of oxides and earths with increasing temperature. He wrote that it "arises from the loss of water with which they were previously combined if we examine the solubility of these bodies, we shall find that at no time is the simple substance itself dissolved, but always an original and intimate compound of the substance with water. These compounds are of a higher order than the common hydrates, and frequently require peculiar circumstances for their formation. Silica is a good instance. Dried and destitute of water it is altogether insoluble and cannot be made again to form a solid combination with water, but in a state of intimate combination with water it is soluble." ⁵⁰ Similarly the alkalies were hydrated when in solution. Lime water was a solution of hydrate of lime and not just lime. This water appeared to be more closely united to lime than say water of crystallisation was in efflorescent salts. This emphasis on the importance of the existence of combined water in solutions of alkalies, silica and salts was significant for Graham's later studies of the phosphates, and the role of water in their constitution.

As we shall see, Graham developed his views on the loss of solubility of hydrated oxides at a later date. He thought that the solubility reduction was caused by a loss of combined water from the hydrate followed by a polymerisation of the anhydrous material.

In the same year, 1827, E. Mitscherlich discussed changes in the

51. E. Mitscherlich, 'On the changes of crystalline forms which are produced by different degrees of temperature in sulphates and seleniates', Ann.de Ch. 2 Ser. 37 (1828) 202-211.
52. W. Haidinger, 'Notice respecting Professor Mitscherlich's observation on the dimorphism of hydrous sulphate of zinc and hydrous sulphate of magnesia,' Edinburgh J.Sci. 4 (1826) 301-302.
53. Mitscherlich's brother analysed the two crystalline sulphates and found that the octahedral forms contained a little less water than the prismatic forms, but this did not alter E. Mitscherlich's opinion that the isolated particles inside solids are mobile with regard to one another and can change position without becoming fluid. See E. Mitscherlich, 'On the crystalline forms and composition of sulphates, seleniates and arseniates,' Ann.de Ch. 2 Ser. 38 (1828) 54-66, particularly p 59.

crystal form as the temperature was altered.⁵¹ He correctly attributed to Haidinger, the first observation that a salt retained different quantities of water, when crystallised at different temperatures. Haidinger had found that sulphate of soda crystallised with a definite amount of water below 33°C , but above this temperature anhydrous crystals were formed. In 1824 Haidinger had informed Mitscherlich that the sulphates of zinc and of magnesia both crystallised in different forms when they were made at higher temperatures.⁵² Mitscherlich investigated this phenomenon and found that the sulphates of zinc, nickel, and magnesia all produced isomorphous prismatic crystals at 15°C . And yet between 15°C and 20°C the sulphate of nickel gave octahedral crystals. This change from prismatic to octahedral crystals occurred, without liquefaction, when the crystals were exposed to light.⁵³ This type of change was first seen by Mitscherlich when he warmed the sulphates of zinc and magnesia in alcohol. Without melting the crystals lost their transparency and changed crystal form. Did these observations influence Graham to study salts in alcohol? It is possible as we shall see. Mitscherlich concluded by mentioning that the phosphates and arseniates of soda could also crystallise with different quantities of water depending on the temperature used. Here, he was taking an example from the work of Graham's friend Thomas Clark and from Haidinger's crystallography. These experiments were a confirmation for Mitscherlich of his ideas that changes in crystal form were caused, either by differences in the arrangement of the atoms in the solid crystal, or by an alteration in the quantity of water of crystallisation which was retained.

Graham consistently adhered to the view that changes in the crystal form and reduction in the solubility of hydrated salts as the temperature was raised were related to changes in the degree of hydration. In a comment on Graham's anomalous solubility paper, Berzelius expressed his own uncertainty when he wrote that: "the property of losing solubility when a solution is heated to the boiling point is in some way connected

54. Berzelius, Jahresbericht. 8 (1829) p 173.

55. R. A. Smith op.cit. (41) See letter from Graham to Johnston, 4th October 1827 and the reply from Johnston to Graham on 7th October 1827, pp 23-28.

56. *ibid.* p 24.

57. J. F. W. Johnston, 'On the combination of chlorine with prussiate of potash and the presence of such a compound as an impurity in Prussian blue.' (read January 7th 1828) Trans.R.S.Edin. xi (1831) 210-222. He concluded wrongly that potassium ferricyanide contained chlorine.

with the property of ignition at higher temperatures and to the property of being far less affected by aqueous chemical reagents after the glowing or ignition." ⁵⁴

The careful attention which Graham gave to water of crystallisation can be seen in his correspondence with J.F.W. Johnston during 1827.⁵⁵ Johnston had written a paper on potassium ferricyanide and sent it to Graham for his comments. Johnston claimed that the composition of potassium ferricyanide was as follows:-

2 atoms of potassium K, 1 atom of iron Fe, $\frac{1}{2}$ atom of chlorine Cl, and 3 atoms of cyanogen CN_2 .

To which Graham added the comment "and of these elements (mark) alone, no water, no hydrogen or oxygen present." By the action of heat on these crystals, Johnston said he had obtained ammonia and hydrogen cyanide at low temperatures but no water; and at higher temperatures he had obtained potash and peroxide of iron as a residue.

Graham saw that the stated composition was quite inconsistent with the experimental observation obtained from the action of heat. Therefore he wrote: "here we have oxygen and hydrogen in abundance in a body which contains not an atom of either. An analogous result of the igneous decomposition of the old ferrocyanide of potassium did not disturb Porrett or Berzelius (and perhaps misled you?); but why? Because they allowed 3 atoms of water in their salt, the decomposition of which accounted for the disengaged oxygen and hydrogen which appeared. Now unfortunately your theory is expressly founded on the supposition that these 3 atoms of water are got rid of." ⁵⁶ He advised Johnston either to give up the theory of the composition of potassium ferricyanide or to give up his experiments on the decomposition of the salt by heat. Accordingly Johnston omitted the experiments of decomposition by heat when he read his paper to the Royal Society of Edinburgh.⁵⁷

In December 1827 Graham read a paper on alcohols to the same society. In this he suggested a new method for dehydrating alcohol and introduced

58. Graham, 'An account of the formation of alcoates definite compounds of salts and alcohol analogous to the hydrates' (read December 17th 1827) Trans.R.S.Edin. xi (1831) 175-193 also in Researches pp 309-321. Also see the brief note referring to Gay-Lussac's suggestion of the use of quicklime as a drying agent in distillation. Ann.Phil. 4 (1814) 230.

59. Berzelius, Jahresbericht 8 (1829) 258.

60. T. Thomson, System of Chemistry 7th.edn. (London, 1831) Vol.2 p 288.

a new class of salts which contained alcohol of crystallisation instead of water of crystallisation.⁵⁸ Graham removed water from alcohol, by standing a basin of aqueous alcohol over quicklime in an evacuated receiver. Gay-Lussac had previously suggested the use of quicklime or barytes as substitutes for calcium chloride in the concentration of alcohol by distillation. Graham found that pure alcohol was produced in a few days by his method; Hope tried it out and was most impressed with the result.

The action of alcohol vapour on a number of substances was then discussed by Graham. Alcohol vapour was absorbed by water; quicklime; concentrated sulphuric acid and particularly by calcium chloride which even deliquesced in alcohol vapour. Now the deliquescence of salts by absorption of water vapour occurred by the formation of hydrates. This suggested to Graham that analogous compounds might occur containing combined alcohol instead of water. He found that this was indeed correct. He prepared a number of these new compounds which he called 'alcoates'. They contained salts joined in definite proportions to alcohol of crystallisation. The alcoates of calcium chloride; calcium or magnesium nitrate; manganese or zinc chloride were soft, indistinct and transparent crystals. Berzelius referred to this research and stated that it deserved to be extended and enlarged.⁵⁹ Likewise in 1831, Thomson made the prophetic statement that: "when the crystalline shape of the alcoates comes to be more accurately studied than it has hitherto been, we may expect additional information respecting the part which water plays in saline combinations - a branch of chemistry hitherto very little examined."⁶⁰

So far, in these early papers, Graham had considered the role of water in salts and its influence on solubility; the differences between the attachment of water to salts and alkalies and metallic oxides; and the analogues of water of crystallisation. He now widened his research programme on the water-content of compounds in one of his most important

61. See appendix 1 for an explanation of the symbols used by Graham in this paper and in his notebooks and the summary chart of the more important reactions of the phosphates which Graham deduced.

62. Berzelius, 'Sur la composition des acides phosphorique et phosphoreux, et sur leurs combinaisons avec les salifiables' Ann. de Ch. 2 Ser. 2 (1816) 151-177, 217-241, 329-339.
As mentioned previously (op.cit. 17) Berzelius wrote the formula of anhydrous phosphoric acid as PO_5 between 1816 and 1826. It was only from 1826 that he halved his atomic weight of phosphorus and wrote P_2O_5 . Likewise, neutral phosphate of soda was written as NaO_2, PO_5 (O=100, Na=581.84 and P=392.30) in 1819 and as $2NaO, P_2O_5$ in 1826 (O=100, 2Na=581.794, 2P=392.285). The sesquiphosphate of silver was written as $3AgO_2, 2PO_5$ in 1819 (Ag=2703.21) and as $3AgO, P_2O_5$ in 1826 (Ag=1351.607). The acid phosphate of soda was written $NaO, 2PO_5$ in 1819 and as NaO, P_2O_5 in 1826. In this chapter, I have used for Berzelius's work his 1826 atomic weights and formulae; likewise for Mitscherlich's formulae, which were given as atomic ratios rather than printed formulae in his paper on isomorphism.

63. E. Mitscherlich, 'On the relation which exists between crystalline form and chemical proportions' Ann. de Ch. 19 (1822) 350-419 or Qu. J. Sci. 14 (1823) 198-206, 415-418.

studies: the role of water in arseniates, phosphates and modifications of phosphoric acid.⁶¹ This was the field in which Graham established his reputation as a chemist of the first rank. It is therefore important to begin with a summary of the background to this work.

Phosphoric acid and its salts had been carefully studied before Graham began his own researches. In 1816 Berzelius had established the correct composition of anhydrous phosphoric acid. He expressed its formula later as two atoms phosphorus joined to five of oxygen or P_2O_5 .⁶² Neutralisation of this acid by soda gave him the neutral phosphate of soda. Berzelius formulated this later as $2NaO, P_2O_5$ which correctly represented the ratio of base to acid. This allowed him to define neutral phosphates as those in which the ratio of oxygen in the base to that of the acid as 2 to 5. Salts like the yellow silver salt $3AgO, P_2O_5$ with an oxygen ratio of 3 to 5 he considered to be basic or subsalts; and salts like the acid phosphate of soda NaO, P_2O_5 with an oxygen ratio of 1 to 5, he called acid salts or bisalts.

Berzelius would not accept that it was possible for an acid to be polybasic; only one salt of soda was considered to be neutral: this was common phosphate of soda $2NaO, P_2O_5$. Although Berzelius often determined the water-content of phosphates he regarded this water simply as water of crystallisation. He failed to appreciate that water could play a significant role in the constitution of phosphates. This failure caused confusion and obscured the true nature of the phosphoric acids and their salts. It was not until Graham emphasised the essential differences between basic water and water of crystallisation and then introduced the concept of polybasicity that this confusion could be removed.

The analytical achievements of Berzelius led to important results in the hands of his student Mitscherlich. In 1820, Mitscherlich observed that analogous arseniates and phosphates often crystallised in identical forms.⁶³ The relation between identity of crystalline form and similar chemical composition led Mitscherlich to deduce the principle of

63a. Berzelius had given 61.89% water and Mitscherlich took this as $24\text{H}_2\text{O}$ ($24\text{H}_2\text{O}$ would be equivalent to 60.18% water; $25\text{H}_2\text{O}$ would be equivalent to 62.69% water). Graham found the water content was 62.90% in September 1832.

64. J. F. Engelhart, 'On the colouring matter of the blood' - a prize essay on the nature of the colouring matter of the blood being the successful dissertation for the prize question of the Göttingen Medical faculty, for 1825, Ed. Med. and Surg. J. 27 (1827) 95-101.

65. Engelhart and Berzelius, 'Manière singulière dont se comporte l'acide phosphorique avec l'albumine' Ann. de Ch. 2 Ser. 36 (1827) 110-111.

isomorphism. He calculated the oxygen ratios of base to acid, and of base to water, and thereby focussed attention on the water-content of phosphates and arseniates, but he continued to consider the water simply as water of crystallisation. He was the first to deduce fully the correct formula of biphosphate of soda: $\text{NaO},\text{P}_2\text{O}_5 + 4\text{H}_2\text{O}$; a result which was important for Graham. The formula which Mitscherlich gave for common phosphate of soda was incorrectly stated because he gave the water content as $24\text{H}_2\text{O}$; apparently this resulted from a mis-reading of the analysis quoted by Berzelius. [Berzelius repeated this mistake in his atomic weights of 1826.] The correct formula should have been stated as $2\text{NaO},\text{P}_2\text{O}_5 + 25\text{H}_2\text{O}$.^{63a}

The ensuing discoveries concerning the phosphoric acids were difficult to interpret whilst the misconceptions of Berzelius were adhered to. The first serious difficulty arose in 1825 when Engelhart stated, in a report on blood serum, that phosphoric acid gave a white precipitate with serous albumen.⁶⁴ Berzelius was unable to confirm this test and so he invited Engelhart to investigate the problem along with himself. They found that only freshly-prepared phosphoric acid gave the albumen test, that is, phosphorus freshly burned and added to water.⁶⁵ On standing, the phosphoric acid no longer gave the test. The cause of this anomaly was puzzling. The only suggestion which they could offer was that perhaps phosphoric acid combined with water after a period of time. Indeed this interpretation was essentially correct but its true significance was missed by Berzelius because he made no real distinction between anhydrous and hydrated acids. The significant point was that Engelhart had discovered metaphosphoric acid. Furthermore he had found a distinctive test for it, using albumen, but he had failed to recognise the significance of his discovery. On standing, the metaphosphoric acid was hydrolysed and no longer gave the albumen test because it had been converted into pyrophosphoric or common phosphoric acid. Later Graham was able to clarify this problem when he identified the constitution of Engelhart's

66. T. Clark, 'On pyrophosphate of soda; a new species of salt, formed by the action of heat on the phosphate of soda.'
Edin.J.Sci. 7 (1827) 298-316 and Ann.de Ch. 41 (1829) 276-290.
 On Clark, see J.H.S.Green, 'Thomas Clark (1801-1867) a biographical study.' Ann.Sci. 13 (1957) 164-178.
 Clark and Graham were rival candidates for a lectureship in Chemistry at the Glasgow Mechanics Institute in 1826; Clark was appointed. He resigned his post in 1829 and Graham took over lecturing at the Mechanics Institute until 1830 when he became Andersonian Professor of Chemistry. Meanwhile Clark had entered Glasgow University as a Medical Student qualifying in 1831 as an M.D. (presumably to obtain an appointment as a teacher of Chemistry in a Medical School). Graham was also giving formal attendance at the medical classes at this time and in 1830 he claimed that he was working for his M.D. (See King's College letter of application July 30th 1830 op.cit. (39)). In 1833 Clark was appointed Professor of Chemistry at Marischal College, Aberdeen. Did he advise Graham in his work on phosphates? He must have taken an interest in this work for he was in Glasgow at the time of Graham's researches.
67. A. Ure, A Dictionary of Chemistry on the Basis of Mr. Nicholson's (London, 1821). See the article on Acid (phosphoric).
68. Thomson's analysis of yellow phosphate of silver:
 Silver oxide 482.3 Phosphoric acid 100
 Berzelius's analysis of yellow phosphate of silver:
 Silver oxide 487.38 Phosphoric acid 100.00
 (Thomson, First Principles etc. (1825) 2 408, Berzelius, Ann.de Ch. 2 Ser. 2 (1816) 163. In 1825 Thomson considered phosphoric acid to be PO_2 and silver phosphate to be AgO, PO_2 whereas Berzelius considered that phosphoric acid was P_2O_5 and silver phosphate $3\text{AgO}, \text{P}_2\text{O}_5$.

acid; which he then renamed 'metaphosphoric acid'.

The problem of the composition of phosphates was also pursued at this time by Graham's friend, Thomas Clark.⁶⁶ Both Thomson and Berzelius had expressed different views regarding the composition of phosphates and Clark set out to see which of their views was correct. Thomson had changed his mind on this subject more than once and he was ridiculed by his arch-opponent Andrew Ure because of his very uncertain approach.⁶⁷ As a starting point for his research Clark decided to examine the yellow phosphate of silver, $(3\text{AgO},\text{P}_2\text{O}_5)$. Both Thomson and Berzelius agreed with regard to the composition by weight of this particular compound.⁶⁸ To his surprise, Clark obtained a white silver precipitate, from a solution of common phosphate of soda mixed with silver nitrate, instead of the usual yellow precipitate. He traced the cause to the fact that his sample of phosphate of soda had been heated to redness and then recrystallised before use. This treatment had produced a new salt which Clark named pyrophosphate of soda. How did this change occur? Clark found that common phosphate of soda contained 25 atoms of water (here he corrected Mitscherlich's erroneous figure); and at low heat, 24 out of the 25 atoms of water were lost to give a monohydrate $2\text{NaO},\text{P}_2\text{O}_5 + \text{HO}$, which still gave a yellow silver precipitate. At red heat, the final atom of water was lost creating the new pyrophosphate of soda $2\text{NaO},\text{P}_2\text{O}_5$ which gave a white silver precipitate. The new soda salt was dissolved in water and then crystallised. On analysis it was shown to contain 10 atoms of water of crystallisation. The crystal shape of pyrophosphate of soda differed from that of common phosphate of soda. Clark concluded that the last atom of water, removed by heating from common phosphate of soda $2\text{NaO},\text{P}_2\text{O}_5 + 25\text{HO}$, was in some way different to the rest. He was unable to explain this difference although he offered some interesting speculations. Evidently the last water atom was not simply water of crystallisation. He then speculated by asking: was this water attached to one atom of base as NaO.HO ? or

69. Gay-Lussac, 'Sur l'acide phosphorique', Ann.de Ch. 2 Ser.41 (1829)
332-335.

70. F. Stromeyer, 'Sur l'acide pyrophosphorique et les pyrophosphates'
Ann.de Ch. 2 Ser 43 (1830) 364-379, or Edin.J.Sci.3 (1830) 319-328.
Friedrich Stomeyer (1776-1835) became Professor at Göttingen in 1810.

was the water attached to the acid? or were the H and O in the last water atom separated in the salt? Or was the anhydrous phosphate of soda altered in some way on losing the last atom of water?; perhaps it had decomposed on heating like — sodium sulphite which gave sodium sulphate and sodium sulphide - but if this happened the two parts must remain joined together in the water, to give a single salt with new properties. Clark left the question open for others to attempt to find an answer, remarking that he would be unable to do any further research for some months.

Undoubtedly Clark had made an important step forward in the problem of resolving the constitution of the phosphates. He had highlighted the crucial issue of the water-content of these salts and the differences in the bonding of this water to the salt. Amongst his speculations he had suggested the correct answer: the last atom of water was bonded to the phosphoric acid. His researches encouraged other chemists to attempt to interpret his results and extend them. The challenge which Clark's work posed was taken up with varying degrees of success by Gay-Lussac, Stromeyer, Berzelius and Graham.

In 1829, Gay-Lussac incorrectly attempted to link the researches of Engelhart and Clark and thereby thoroughly confused the issue.⁶⁹ He prepared Engelhart's acid, neutralised it with soda and treated it with silver nitrate. He obtained a white silver precipitate which he wrongly concluded was the same as Clark's white silver precipitate. To complete the false analogy, Gay-Lussac treated pyrophosphate of soda with lead acetate obtaining a precipitate of lead pyrophosphate. He then treated this precipitate with hydrogen sulphide obtaining for the first time a solution of pyrophosphoric acid. This acid, he reported, gave a white precipitate with albumen; this was incorrect as Graham showed later. Regrettably Gay-Lussac's work wrongly appeared to identify Engelhart's acid $[\text{HO}, \text{P}_2\text{O}_5]$ with Clark's acid $[2\text{HO}, \text{P}_2\text{O}_5]$.

The problem was next examined by Friedrich Stromeyer in 1830.⁷⁰

71. Berzelius, 'Composition de l'acide tartrique et de l'acide racémique; poids atomique de l'oxide de plomb, et remarques générales sur les corps qui ont la même composition, et possèdent des propriétés différentes.' Ann.de Ch. 2 Ser.46 (1831) 128-147, see p 136.
From Pogg. Ann. 19 (1830) 305-335.

72. Graham, Elements of Chemistry 1st.edn. (London, 1842) p 154.

He compared Clark's pyrophosphate of soda with common phosphate of soda; certainly they produced different precipitates with a variety of metallic salts. In particular he analysed the yellow phosphate of silver and the white pyrophosphate of silver and found that they differed in composition. Yet common phosphoric acid appeared to have the same atomic weight as pyrophosphoric acid, that is both contained P_2O_5 . How could this be explained? Once again the same error was made:- Stromeyer failed to distinguish between the acids of Clark and Engelhart. As long as the water content was not taken into consideration this was an understandable mistake. Dismissing Clark's sulphite hypothesis, Stromeyer concluded that both common phosphoric acid and pyrophosphoric acid were P_2O_5 . He attributed the differences between the compounds formed from these two acids to the way in which the elements phosphorus and oxygen were joined together. Even although the same elements, phosphorus and oxygen, were joined in the same proportions in P_2O_5 , it was possible to have two different compounds with the same formula. He claimed that this new fact was of great importance because it opened up a new field of research which would be especially valuable in organic chemistry. In the following year Berzelius coined the name 'isomerism' for this phenomenon.

Berzelius defined isomeric bodies as "those which have a similar chemical composition and the same atomic weight but possess different properties." ⁷¹ He gave examples of isomeric bodies which included: the two oxides of tin; fulminic and cyanic acids; phosphate and pyrophosphate of soda; racemic and tartaric acids.

Graham objected to the concept of isomerism arguing that a great physical law must be abandoned if isomerism was admitted namely, "that no change of properties can occur without a change of composition." ⁷² Most of Graham's contemporaries, for example Berzelius, Thomson, Turner and Dumas, accepted that, in simple cases, isomerism could be accounted for by differences in the arrangement of the same atoms. The origin of Graham's opposition to isomerism was probably the discovery made by Clark

73. Berzelius, *op.cit.* (71), see p 139.

that water played a crucial role in determining the differences between phosphates and pyrophosphates. A number of examples of apparent isomerism could be explained by differences in composition if the water content was taken into account. Graham examined the total water content of compounds carefully and realised that water could play different roles in salts, acids and bases. From these studies he recognised that a number of examples of supposed isomerism were false.

Berzelius had failed to appreciate the role of the basic water in common phosphate of soda. Likewise Graham thought he had paid insufficient attention to the differing water-contents of racemic and tartaric acids. Even in cases where it was difficult to identify any differences in water content, Graham suggested that there might be differences in the amount of combined heat in apparent isomers such as the oxides of tin. This suggestion was drawn from Berzelius's observation that, when one isomer was transformed into another, there was sometimes a noticeable glowing or ignition, as heat was released. This was seen with the basic phosphate of magnesia and ammonia, some antimonates, zircon, and the oxides of chromium and iron.⁷³ Thus, Graham believed that differences in composition could be extended to include fixed proportions not only of water but also of combined or latent heat which could be released during an isomeric transformation.

Recently Swords has suggested an alternative hypothesis to account for Graham's rejection of simple isomerism. If it is assumed Graham believed at this time, that atoms possessed an unalterable primordial motion and were surrounded by caloric then Swords argues that "the motion of the atom was, in some unknown way, associated with chemical affinity. When chemical reactions occurred the atoms approached within the caloric spheres, and their resultant motions determined the chemical properties of the new substance. With such a vision of chemical reactions simple unbound atoms could be added to atomic mixes in any order, but, as long as the resultant compounds contained the same atoms, the resultant motion,

74. M. D. Swords, Ph.D. Thesis 'The chemical philosophy of Thomas Graham'
Case Western Reserve University (1973) p 64.

75. Graham, Elements of Chemistry 1st.edn. part 2 (London, 1838) p 155.

76. Berzelius, op.cit. (71) pp 141-146.

Although Berzelius wrote the name 'paraphosphoric acid' for common phosphoric acid, Mitscherlich confusingly wrote: "One gives the name paraphosphoric acid to the modification which has been calcined".

This was what Berzelius wished to call phosphoric acid!

See E. Mitscherlich, Éléments de Chimie (translated by M.B.Valerius, Bruxelles, 1836) 2 p 99.

and the resultant chemical properties of the moving aggregates would always be identical." ⁷⁴

Although this hypothesis could explain Graham's rejection of isomerism, it seems more likely that careful experimental studies, revealing the crucial role of water in salts and acids, led him to question the whole concept of isomerism. In his textbook, Graham wrote that isomerism bodies were found in general to agree: "in the relative proportions of their constituents only, and to differ either in the aggregate number of atoms composing them [for example the polymerism of ethylene to give butylene], or in the mode of arrangement of these atoms [Graham accepted that metamerism could occur, that is isomers might contain different radicals]; and very few cases now remain which do not admit of explanation. That is what was to be expected, for isomerism in the abstract is improbable, a difference in properties between bodies, without a difference in composition, appearing to be an effect without sufficient cause." ⁷⁵

Before examining Graham's work on phosphates it is important to consider the comments made by Berzelius on the same subject in his paper on isomerism. ⁷⁶ Firstly, he proposed a new nomenclature referring to the isomers, pyrophosphoric acid and common phosphoric acid respectively, as phosphoric acid and paraphosphoric acid. Then he criticised Stromeyer's analyses of the silver salts of these acids. Berzelius was rightly convinced that his previous 1816 determination of the composition of the yellow phosphate of silver was correct giving it the formula Ag_3P (or $3\text{AgO}, \text{P}_2\text{O}_5$). He found that the white silver salt was less simple. By following Gay-Lussac and Stromeyer, Berzelius continued to overlook the important differences between metaphosphoric acid and pyrophosphoric acid. But he did discover that there were apparently three silver salts of pyrophosphoric acid. Initially, he mixed calcined phosphoric acid with silver nitrate and obtained a gelatinous, white precipitate which could be coagulated. This precipitate tended to

77. Note Graham wrote $\overset{\text{::}}{\text{P}}$ or PO_5 for an atom of anhydrous phosphoric acid in which phosphorus was taken as a double atom, of atomic weight 62.768 (O=8), whereas Berzelius wrote $\overset{\text{::}}{\text{P}}$ or P_2O_5 , where $\overset{\text{::}}{\text{P}}$ was a double atom or $2\text{P} = 62.768$. Graham wrote the formula of soda as Na or NaO like Berzelius, but he wrote water as H or HO , whereas Berzelius wrote water as H or H_2O (O=8, H=1). See appendix 1.

decompose on washing and he supposed correctly that it was the biphosphate of silver $\overset{\cdot}{\text{Ag}}\overset{\cdot\cdot}{\text{P}}^{\cdot\cdot}$ (or $\text{AgO},\text{P}_2\text{O}_5$ - now called silver metaphosphate). This precipitate decomposed further in boiling water giving a viscous unstable grey mass which he called sesquiphosphate of silver. It had the formula $\overset{\cdot}{\text{Ag}}\overset{\cdot\cdot}{\text{P}}^{\cdot\cdot 2}$ or $\overset{\cdot}{\text{Ag}}\overset{\cdot\cdot}{\text{P}}^{\cdot\cdot 1\frac{1}{2}}$ (that is $3\text{AgO},2\text{P}_2\text{O}_5$ or $1\frac{1}{2}\text{AgO},\text{P}_2\text{O}_5$). Lastly there was the white silver salt prepared from Clark's pyrophosphate of soda and silver nitrate, which Berzelius called the neutral phosphate of silver because it had the formula $\overset{\cdot}{\text{Ag}}\overset{\cdot\cdot}{\text{P}}^{\cdot\cdot 2}$ (or $2\text{AgO},\text{P}_2\text{O}_5$). Berzelius was justified in his criticism of Stromeyer's lack of analytical accuracy, and so he did not accept Stromeyer's opinion that phosphoric acid had different saturation capacities in $\overset{\cdot}{\text{Ag}}\overset{\cdot\cdot}{\text{P}}^{\cdot\cdot 3}$ and in $\overset{\cdot}{\text{Ag}}\overset{\cdot\cdot}{\text{P}}^{\cdot\cdot 2}$. The former salt was, he argued, a basic salt or sub-salt and the latter was a neutral salt because it corresponded to the neutral common phosphate of soda $\overset{\cdot}{\text{Na}}\overset{\cdot\cdot}{\text{P}}^{\cdot\cdot 2}$. Likewise he believed that $\overset{\cdot}{\text{Ag}}\overset{\cdot\cdot}{\text{P}}^{\cdot\cdot 3}$ was an acid salt or a bi-salt.

Graham began his studies on the phosphates and arseniates in 1831 or 1832. He was able to show that water played an important role in the different phosphoric acids and their salts. Thus he was able to give a convincing explanation of the composition of these salts and hence he was led to introduce the concept of the polybasic nature of the phosphoric acids.

It is possible that Graham recognised from the start of his study of phosphates that one out of the twenty-five atoms of water in common phosphate of soda was essentially different because it was basic water. This result might have been partially inferred from Clark's experiment which showed that this last atom of water was not removed easily. Therefore Graham would write the formula of common phosphate of soda as $\overset{\cdot}{\text{Na}}\overset{\cdot\cdot}{\text{HP}}^{\cdot\cdot} + \overset{\cdot}{\text{H}}^{24}$ at a later date.⁷⁷ This formula seemed to indicate that one atom of phosphoric acid was fully saturated by three atoms of base and not two as Berzelius had suggested. Thus we can understand why Graham began his researches by preparing what he called the subsesquiphosphate and subsesquiarseniate of soda which he wrote as $\overset{\cdot}{\text{Na}}\overset{\cdot\cdot}{\text{P}}^{\cdot\cdot 3}$ and $\overset{\cdot}{\text{Na}}\overset{\cdot\cdot}{\text{As}}^{\cdot\cdot 3}$

78. MS. letter from Graham to J.F.W. Johnston, dated 8th September 1832, from a photocopy held in the Royal Academy of Sciences, Stockholm. The original letter is in Leningrad.

(or $3\text{NaO},\text{PO}_5$ and $3\text{NaO},\text{AsO}_5$). As evidence for this view, consider the letter which Graham wrote in 1832 to J.F.W. Johnston who was studying then with Berzelius. "... I have been engaged for some months past on the arseniates and phosphates and have obtained some interesting results chiefly from having formed two fine salts, the subsesquiphosphate and subsesquiarseniate of soda. For this purpose, add an excess of caustic soda to a hot and strong solution of common phosphate or arseniate.

One of these salts gave me an unexceptionable mode of forming the subsesquiarseniate of lead, which by a very careful analysis [this was made on August 15th 1832] consists of Arsenic acid 25.67, Oxide of lead 74.33

Berzelius by theory 25.61, 74.39

a confirmation of the atomic weight of arsenic acid as fixed by Berzelius.

The most curious circumstance is that this subphosphate [$\text{Na}^{\cdot}\overset{\cdot\cdot\cdot}{\text{P}}$] is not convertible into a Pyro salt by heat. Indeed all the pyrophosphates may be reduced to the state of common phosphates by calcining them afresh with an excess of base ... I shall publish on this subject before commencing my winter campaign of four lectures a day. I have also been working on tin and chromium and have a theory of the change which oxide of chromium undergoes by heat, and of the pyrophosphoric acid." 78

At this stage Graham had not distinguished between Engelhart's metaphosphoric acid and Clark's pyrophosphoric acid. It is not clear what Graham meant by his theory of the pyrophosphoric acid. Did he consider that this acid was saturated by two atoms of basic water, $\overset{\cdot\cdot\cdot}{\text{H}}\overset{\cdot\cdot\cdot}{\text{P}}$, like the pyrophosphates of soda or silver, $\overset{\cdot\cdot\cdot}{\text{Na}}\overset{\cdot\cdot\cdot}{\text{P}}$ and $\overset{\cdot\cdot\cdot}{\text{Ag}}\overset{\cdot\cdot\cdot}{\text{P}}$? There is no certain evidence on this point. His notebooks show that he was considering the question of the hydration of salts, acids and bases at this time:-

"saline hydrates We may apportion the 23 atoms of water of the subphosphate [of soda] so

1 atom caustic soda + 8 atoms water

1 atom phosphate soda + 15 atoms water

[Later Graham analysed the water content of subphosphate of soda correctly

79. Graham, MS. Notebook B, (July 1832-August 1834 450 pp) p 39 entry dated August 21st 1832. The Andersonian Library, University of Strathclyde.
80. J. Dalton, 'Experiments and observations on phosphoric acid and on the salts denominated phosphates', read January 22nd 1813 Manchester Memoirs Vol. 3 New Series (Manchester, 1819) p 12. Dalton wrote at a later date that ^{he} had first discovered this salt in 1813 and he insisted erroneously that it contained one atom of soda joined to one atom of phosphoric acid. See Dalton Essay on Arseniates and Phosphates privately printed, (Manchester, 1840) pp 4-6.
81. Graham, op.cit. (79) p 61. Entry dated September 21st 1832.

as 24 not 23 atoms of water. Clark had discovered two varieties of common phosphate of soda which contained 15 and 25 atoms of water respectively and as well, there was the pyrophosphate containing 10 atoms of water.] "Say phosphoric acid carries along with it, water in certain proportions only, or in a certain series of proportions. Common phosphoric acid must have one proportion, it may have 5, 10, 15, 20, 25 proportions. The bases may also combine with certain proportions of water excluding. A salt will contain a proportional quantity of water with its acid and a proportional quantity with its base. Of sulphuric acid we know a 1-hydrate and a 2-hydrate well marked. Of nitric acid a 4-hydrate, perhaps also a 2 and 1. Muriatic acid - a 16-hydrate perhaps also a 12. Acetic acid 1 and perhaps 4." ⁷⁹ The subphosphate of soda had been first described by Dalton in 1819⁸⁰ but Graham was the first to formulate it correctly as $\text{Na}_3\overset{\cdot}{\underset{\cdot\cdot}{\text{P}}}$ and it is clear from these notes that he was attempting to assign a role to the water in salts.

The publication of Graham's researches was delayed until 1833 because of a crucial discovery which he made in September 1832. Graham found that two different acids had been confused under the one name of pyrophosphoric acid. He recognised that, "the albumen test for the phosphoric acid of the pyrophosphate is of no value. I find that a pretty strong solution of the acid from the pyrophosphate of soda which had been crystallised does not affect fresh albumen, although it precipitates silver white. The acid, however, obtained on heating phosphoric acid may I find be treated with excess ammonia, precipitated directly by acetate of lead; decomposed by sulphuretted hydrogen as above and still precipitate albumen. The phosphate of lead was easily decomposed by sulphuretted hydrogen in this case and was not exactly like the above - was gelatinous." ⁸¹ Here was a decisive difference between the two 'pyro' acids, the acids of Engelhart and Clark. This difference allowed Graham to distinguish clearly which acid was present in a given salt, and it led him to a careful examination of the properties of the two pyro acids and their salts.

82. Graham, *op.cit.* (79) p 69.

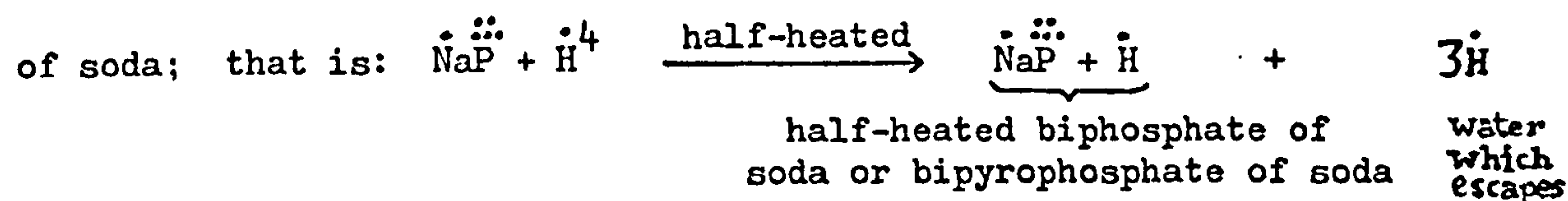
83. Graham, *op.cit.* (79) p 102.

Engelhart's acid precipitated albumen and gave a curdy flaky-white silver precipitate which corresponded as Graham himself noted with the precipitate, Berzelius called, biphosphate of silver $\overset{\cdot}{\text{Ag}}\overset{\cdot\cdot}{\text{P}}$. This acid also gave a gelatinous white precipitate with barium chloride.

Clark's acid gave no precipitate with albumen 'beyond all controversy'; it gave a powdery, white silver precipitate $\overset{\cdot}{\text{Ag}}\overset{\cdot\cdot}{\text{P}}$ but did not affect barium chloride. By boiling, Clark's acid was gradually converted into common phosphoric acid, but this did not proceed via Engelhart's acid.

When Engelhart's acid was evaporated with excess caustic soda there was a 'decisive transition' to common subphosphate of soda, $\overset{\cdot}{\text{Na}}\overset{\cdot\cdot}{\text{P}}$, which in turn gave the yellow silver precipitate $\overset{\cdot}{\text{Ag}}\overset{\cdot\cdot}{\text{P}}$, and an almost neutral solution.⁸²

Next Graham examined biphosphate of soda. He had already observed that this salt lost water in a 'semi-fusion' to give bipyrophosphate of soda. He called this the 'half-heated stage'. It occurred when approximately three-quarters of the water had been removed from the biphosphate of soda; that is:



Then, by preparing and examining the silver salt, he was able to show that Clark's acid was present in the half-heated salt. Further heating of biphosphate of soda resulted first in a complete loss of water followed by a fusion at low red heat. Graham observed the last change in his notes. The salt "swelled up forming large vesicles - suspicious - perhaps passing into E's acid melted at low red heat from a portion, the acid was separated as usual. It coagulated albumen powerfully. In this case the acid was in the state of Engelhart's [acid]." ⁸³ Fusion had thus produced the metaphosphate of soda.

Finally, Graham examined the saturating powers of these acids. Both Clark's acid and common phosphoric acid had the same saturating power with carbonate of soda. This was to be anticipated. If Clark's acid was written as $\overset{\cdot}{\text{H}}\overset{\cdot\cdot}{\text{P}}$, it would be neutralised by two equivalents of soda to give

84. *ibid.* p 121. The simple equivalent for phosphoric acid, $P^{\frac{1}{2}}O^{\frac{2}{2}}$ was neutralised by one atom of soda NaO in common phosphate of soda. The double atom P_2O_5 was neutralised by two atoms of soda 2NaO in the common phosphaté. Thus in the sesquisalt four equivalents of phosphoric acid or $2P_2O_5$ were neutralised by three atoms of soda 3NaO to give the sesquisalt Na_3P^2 or $3NaO, 2P_2O_5$.

85. Letter from Turner to Berzelius, November 16th 1832, ^{Jac.} Berzelius Bref. edited by H.G.Söderbaum Vol. 3 (Uppsala, 1918) pp 284-285.

pyrophosphate of soda $\text{Na}_2\text{P}_2\text{O}_7$. Likewise, common phosphoric acid $\text{H}_3\text{P}_3\text{O}_9$ would be similarly neutralised by soda to give common phosphate of soda Na_2HPO_4 . However, Engelhart's acid had a different saturation capacity. This showed that Berzelius was incorrect to assume that all phosphoric acids had the same saturating power. Surprisingly, Graham found that the saturating power of Engelhart's acid was not straightforward. Engelhart's acid was not neutralised by one atom of soda to form NaP , instead it was neutralised by three-quarters of the amount of soda needed to saturate the common phosphoric acid. Graham suggested this could be explained by assuming that only three parts out of the total of four parts of Engelhart's acid were neutralised to produce a soda salt Na_3P^2 analogous to the silver sesquisalt obtained by Berzelius Ag_3P^2 . Graham wrote that "by the last experiment the portion of E acid which is positive to that which is negative is in proportion nearly 1 to 3." ⁸⁴ Presumably he was considering the possibility that Engelhart's acid was some form of polymer of common phosphoric acid in which one quarter of the acid was in a positive electrical state and so it could not be neutralised by a base which was in the same positive electrical state. The remaining three-quarters of the acid was neutralised by the base because this acid was in a negative electrical state. Graham referred to Engelhart's acid as an 'idiogenic acid' that is a polymer of common phosphoric acid.

Having partly completed his researches, Graham communicated his results to J.F.W. Johnston for inclusion in the 1832 British Association report on the present state of Chemistry. Presumably he also informed his former colleague Edward Turner of his results because Turner wrote to Berzelius on November 16th 1832 saying: "Graham is examining pyrophosphoric acid and has found that two acids very distinct from each other have been included under the same appellation. It would thus seem that phosphorus gives three isomeric acids. The subject is still under examination." ⁸⁵

86. Letter from Berzelius to Wohler, January 8th 1833. Berzelius-Wöhler Letters 1 (Leipzig, 1901) edited by O.Wallach, pp 492-494.
87. See the letter from Berzelius to Dulong, September 1826. Berzelius Letters edited by H.G.Soderbaum Vol.2 (Uppsala, 1915) Part iv 70-71.
- 87a. That Graham did consider the possibility that metaphosphoric acid was a polymer is evident from a report which was given of his paper in Philosophical Magazine. The report includes the following quotation from Graham's paper which appears to have been read in three parts by Edward Turner: "The acid formed by the combustion of phosphorus in air or oxygen, constitutes a third modification of phosphoric acid, distinguished by peculiar properties, and which, from the difference of its saturating power, in relation to that of phosphoric and pyrophosphoric acid, the author considers as a polymeric phosphoric acid; - a term lately applied by Berzelius to bodies of the same composition, but differing in their combining proportions." This account was taken from the meetings of June 6th and 13th 1833 and was reported in Phil.Mag. (December 1833) 3 Ser 3 p 451. In the printed paper, which appeared in Phil.Trans. 123 (1833), this passage, which should have appeared on page 256, is deleted and replaced with the following: "Phosphoric acid, produced in white flakes on burning phosphorus in air or oxygen gas, or the acid heated to redness by itself, constitutes, we shall afterwards find, a third modification of phosphoric acid. This third variety is characterized by alone coagulating albumen; by producing precipitates, even when free, in muriate of barytes, lime, etc." Evidently Graham had decided in favour of the simpler hypothesis, that metaphosphoric acid was HO,PO_5 and not the more complex polymer 3HO,2PO_5 , between the writing of his paper (January 29th 1833) and its final publication in Philosophical Transactions (in September 1833).

Berzelius wrote to Wöhler in January 1833 about the naming of the isomeric phosphoric acids. This subject concerned him because it was to be included in the third German edition of his textbook. "... The more I think of it, the more I tend to the other suggestion a-acid, b-acid etc., the more so, since Turner has just written to me [saying] that Graham thinks he has found no less than three different pyrophosphoric acids. Although I won't dwell on this novelty for long, since Graham belongs to those, who look for the spectacular and who are therefore easily deceived by their wishes; there is still no circumstance which must limit the number of isomeric modifications to merely two, especially with bodies containing three to four constituents It is not easy to find one perfect and suitable nomenclature. Therefore I propose a way out in the interim: the chemical names of the isomeric modifications should be distinguished, like the notes of music, by the letters a, b and c, or as one wants to say, the variations a, b and c. So we obtain the names for the one acid a-phosphoric acid and for the other b-phosphoric acid and [likewise for] their salts." ⁸⁶ Clearly Berzelius did not yet have a high opinion of Graham but this is hardly surprising since Graham was a student of Thomas Thomson, whom Berzelius had already described in his private correspondence as 'a charlatan'. ⁸⁷

In Johnston's report, Graham gave Engelhart's acid the new name of 'metaphosphoric acid'. Interestingly, in this report Graham discussed the saturation capacity of metaphosphoric acid and it is evident that he favoured the view, he finally adopted, that metaphosphoric acid was $\overset{\cdot\cdot}{\text{H}}\overset{\cdot\cdot}{\text{P}}$ or HO,PO_5 , [presumably this was derived from his own analysis of the silver salt as $\overset{\cdot\cdot}{\text{Ag}}\overset{\cdot\cdot}{\text{P}}$] and not the more complex polymer which he appears to have first considered: $3\text{HO},2\text{PO}_5$ or $3\text{HO},4(\frac{1}{2}\text{PO}_5)$. ^{87a} In the final published version of the Royal Society paper Graham omitted to mention, fully, the difficulties of the saturation capacity of metaphosphoric acid, although he did admit that the meta acid tended to unite with alkali to form common phosphate of soda. In Johnston's report, Graham wrote that

88. J.F.W. Johnston, 'Report on the recent progress and present state of chemical science' pp 457-460. British Association for the Advancement of Science Report, 1832 (published in 1833).

metaphosphoric acid "may also be obtained in composition by fusing the biphosphate of soda, dissolving in water and saturating with carbonate of soda. To saturate the common biphosphate, an atom of carbonate of soda is necessary [$\dot{\text{N}}\dot{\text{a}}\dot{\text{H}}\ddot{\text{P}} \rightarrow \dot{\text{N}}\dot{\text{a}}\ddot{\text{H}}\ddot{\text{P}}$]; the fused biphosphate requires for saturation only half an atom and the salt is incrustallisable [$\dot{\text{N}}\dot{\text{a}}\ddot{\text{P}} \rightarrow 1\frac{1}{2}\dot{\text{N}}\dot{\text{a}},\ddot{\text{P}}$]. If the whole acid therefore has undergone a like change, its saturating power has diminished one-fourth, and consequently the weight of an atom of the meta is to that of the common acid as 4 to 3. Such a constitution of the acid if made out, would be sufficiently remarkable." ⁸⁸ The reasoning here can be explained by comparing the acid ratios for the same weights of soda, that is:-

Meta acid	Common acid	
$1\frac{1}{2}\text{NaO} + \text{PO}_5$	$2\text{NaO} + \text{PO}_5$	neutral soda salts
or $3\text{NaO} + 2\text{PO}_5$	$4\text{NaO} + 2\text{PO}_5$	
or $6\text{NaO} + 4\text{PO}_5$	$6\text{NaO} + 3\text{PO}_5$	

Therefore the ratio of meta acid to common acid on this evidence is 4 to 3.

Graham continued, "but the composition of the fused biphosphate after saturation = $\ddot{\text{P}} + 1\frac{1}{2}\dot{\text{S}}\dot{\text{o}}$ or $2\ddot{\text{P}} + 3\dot{\text{S}}\dot{\text{o}}$, may be represented = $(\dot{\text{S}}\dot{\text{o}} + \ddot{\text{P}}) + (2\dot{\text{S}}\dot{\text{o}} + \ddot{\text{P}})$, being a compound of one atom of a biphosphate with two atoms of neutral phosphate. This view obviates the necessity of supposing that there is any change in the saturating power, - a necessity which is not borne out by the known composition of the white biphosphate of silver thrown down by the fused acid [$\dot{\text{A}}\dot{\text{g}}\ddot{\text{P}}$]. If the acid has a less saturating power when combined with soda, it ought to have it also when combined with silver. It is possible, however, that during fusion the free acid in the biphosphate has alone suffered this new change. [that is $2\text{NaO} + 2\text{PO}_5$ or 2 atoms biphosphate on heating gave one atom of common phosphate $2\text{NaO},\text{PO}_5$ + one atom of anhydrous metaphosphoric acid PO_5]. If that change is such as to reduce its saturating power one half, it would at once account for the silver salt containing the elements of two atoms of phosphoric acid [$\text{AgO} + \text{PO}_5$ or $\text{AgO} + 2(\text{P}^{\frac{1}{2}}\text{O}^{\frac{2}{2}})$], and for the fact that half an atom of soda

89. *ibid.* p 460.

90. Graham, *op.cit.* (79) p 132.

Once Graham had recognised the distinction between basic water and water of crystallisation, he was able to recognise the different basicities of the three phosphoric acids which combined with three different proportions of basic water and this almost certainly explains his later comment that: "...on pursuing the investigation a key to the whole mystery of these compounds was discovered by means of which the acids and their salts might, it appeared to me, be explained in a satisfactory manner." Graham, 'Reply to Mr. Phillips' Phil.Mag. 3 Ser.4 (June 1834) 401-404. (April 9th 1834)

91. Graham, *op.cit.* (79) p 132.

is sufficient to saturate the free acid in the salt after fusion

$[\frac{1}{2}\text{NaO} + \text{P}^{\frac{1}{2}}\text{O}^{\frac{2}{2}} \text{ or } \text{NaO} + \text{PO}_5]$." 89 Johnston added that Graham had made him partially acquainted with his results and that he was still working on the subject.

Having clarified his thoughts on the phosphoric acids Graham introduced the concept of water acting as a base and not simply as water of crystallisation. With this idea he was able to impose some order on his results. He first mentioned this idea in his notebooks when discussing the formula of biphosphate of potash. He wrote, "I think it is clear that the formula of biphosphate of potash is $\overset{\cdot\cdot}{\text{P}}\overset{\cdot\cdot}{\text{H}}^2\overset{\cdot}{\text{K}}$ with no water of crystallisation. That of biphosphate of soda is $\overset{\cdot\cdot}{\text{P}}\overset{\cdot\cdot}{\text{H}}^2\overset{\cdot}{\text{Na}} + \overset{\cdot\cdot}{\text{H}}^2$. It is probable that the half-heated, but still soluble biphosphate is $\overset{\cdot\cdot}{\text{P}}\overset{\cdot\cdot}{\text{H}}\overset{\cdot}{\text{Na}}$ or that it contains one atom of water - As there are two atoms of base in the last, the neutral pyrophosphate of silver should fall in precipitation $[\text{Ag}^2\overset{\cdot\cdot}{\text{P}}]$." 90 These ideas were carefully scrutinised by experiment.

Crystalline biphosphate of soda lost half of its water on a water bath and then at 400°F a further atom of water was lost to produce $\overset{\cdot\cdot}{\text{P}}\overset{\cdot\cdot}{\text{H}}\overset{\cdot}{\text{Na}}$, the bipyrophosphate of soda, which gave an acidic solution in water. At higher temperatures, all the water was lost from the bipyrophosphate to give anhydrous biphosphate of soda which was largely insoluble. Finally, at low red heat, fusion occurred to produce metaphosphate of soda which solidified on cooling to produce a soluble glass.

The formula of anhydrous biphosphate of soda raised doubts in Graham's mind and he wondered whether a polymerisation process was involved in the formation of the insoluble material. He wrote: "shall we conclude that the anhydrous biphosphate is insoluble $\overset{\cdot\cdot}{\text{P}}\overset{\cdot\cdot}{\text{Na}}$? or that this is a case of idio-synthesis of the salt (not of the acid) and that its formula is $\overset{\cdot\cdot}{\text{P}}\overset{\cdot\cdot}{\text{Na}} + \overset{\cdot\cdot}{\text{P}}\overset{\cdot\cdot}{\text{Na}}$ or some such? [By idiosynthesis, Graham meant polymer formation; in this case, dimer formation] Query, does the circumstance of the above biphosphate which contains two atoms of basic water dispose it in the act of losing them, to enter into a metidionic compound?" 91

92. *ibid.* p 133.

93. Graham, 'Researches on the arseniates, phosphates and modifications of phosphoric acid' communicated to R.S. by E. Turner - received January 29th 1833 and read in June 1833. Phil. Trans. 123 (1833) 253-284 also in Researches, 321-348, see p 335.

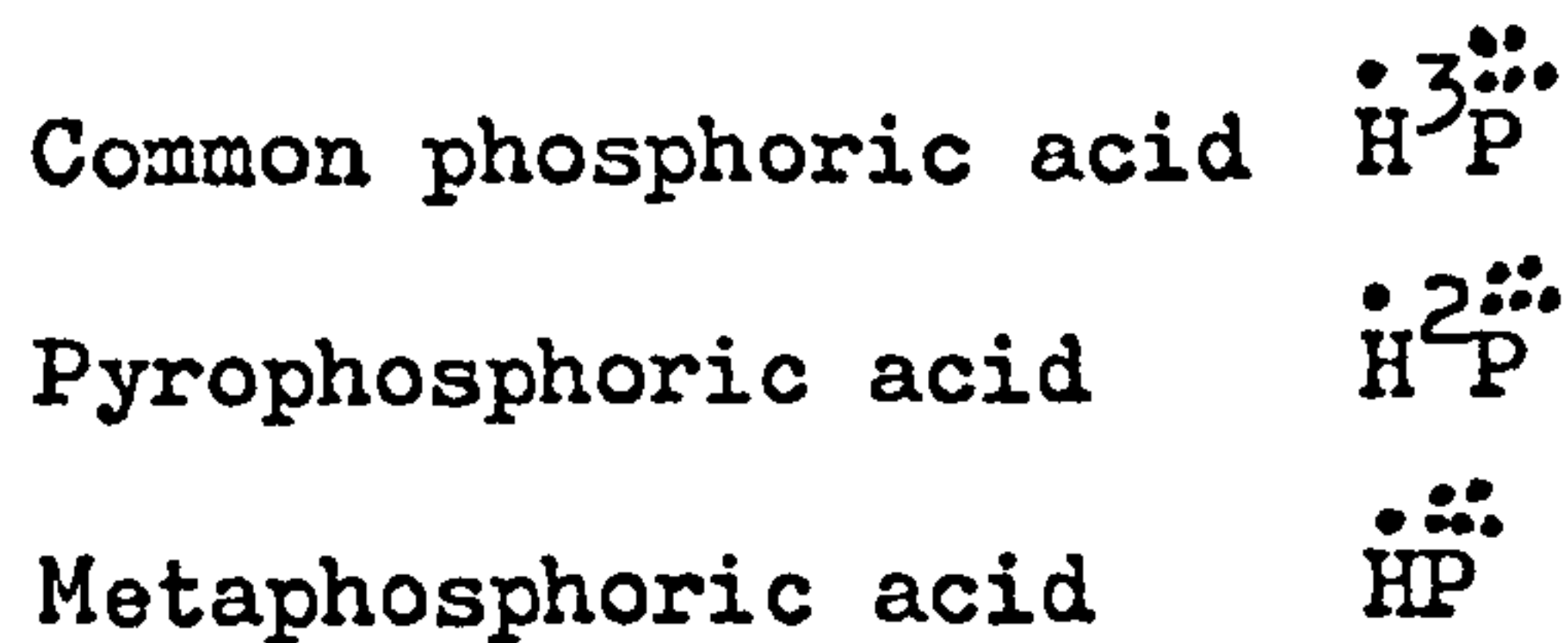
A 'metidionic compound' was one which was made from the same parts but which was transformed in its properties; in this case a polymer was formed which was no longer soluble. He continued: "when the bibasic phosphate of magnesia and ammonia is heated it is said to become luminous and completely insoluble in acids. I believe this is not the case with crystallised phosphate of magnesia itself. Over-dried Paris plaster and anhydrite are probably cases of saline idiosynthesis. There is a native compound of sulphate of soda and sulphate of lime which proves the disposition of the salt to unite. It is also anhydrous and insoluble." ⁹² By loss of water and resultant polymerisation of anhydrous salts there was a change of property, for example a loss of solubility. Graham developed these ideas when he discussed the apparent isomerism of the oxides of tin, chromium and iron as we shall see presently.

To return to the phosphates; in his published paper, Graham emphasised the essential novelty of his views concerning the basic function of water and the polybasic nature of the phosphoric acids. He admitted that Clark had discovered that one atom of water was more difficult to remove from the common phosphate of soda than the other twenty-four, but Graham commented "he did not entertain the idea broached, in this paper, of the basic function of that atom of water in the constitution of the salt. The phosphate of soda contains three atoms of base; namely two atoms of soda and one atom of water; and when added to the earthy or metallic salts, gives precipitates which uniformly contain three atoms of base, namely, three of ... silver, or one atom of water and two atoms of the other oxide, as in phosphate of barytes. These precipitations afford the strongest proof of the basic function of that atom of water which is essential to the phosphate of soda, as they can be accounted for, on the usual laws of double decomposition, [and] on no other supposition. The pyrophosphate of soda, on the other hand, contains only two atoms soda as base, and gives accordingly bibasic precipitates." ⁹³

Graham concluded his researches at the end of January with a clear

94. Graham, op.cit. (79) pp 161-163.

statement of his views on the subject of phosphates and in June 1833, Edward Turner read Graham's paper to the Royal Society. Graham stated in his notebook that "there are probably three compounds of phosphoric acid with three, two and one atom of water. Thus:-



and each of these acids forms a series of salts in which the number of atoms of base is always the same as the atoms of water originally in the acid

<u>1st series</u>	<u>Atoms soda</u>	<u>Atoms water</u>	<u>Atoms acid</u>	<u>Atoms oxygen in acid</u>
Phosphoric acid	0	3	1	5
Superphosphate of soda	1	2	1	5
Phosphate of soda	2	1	1	5
Subphosphate of soda	3	0	1	5
<u>2nd series</u>				
Pyrophosphoric acid	0	2	1	5
Superpyrophosphate of soda	1	1	1	5
Pyrophosphate of soda	2	0	1	5
<u>3rd series</u>				
Metaphosphoric acid	0	1	1	5
Metaphosphate of soda	1	0	1	5

The following table exhibits the quantities of water in the three hydrates of phosphoric acid

Phosphoric acid	100	
One atom water	12.61	
Two atoms water	25.21	
Three atoms water	37.81	" 94

95. Graham, 'Reply to Mr. Phillips,' April 9th 1834, Phil. Mag. 3 Ser. 4
(June, 1834) 404.

96. T. Thomson, System of Chemistry 7th.edn. (London, 1831) Vol. 2
pp 24-25.

97. E. Turner, Elements of Chemistry, 5th.edn. (London, 1834) p 319.

Thus, Graham had recognised that there were three different phosphoric acids each of which had a different basicity. This was caused by the different quantities of basic water in these acids which could be completely replaced by atoms of stronger bases, for example by soda or oxide of silver. In April 1834, he commented on his own researches: "the function of water in the constitution of salts has hitherto been overlooked. I am now prepared to show that its interference is not confined to the phosphates, but that it discharges an equally important function in other classes of salts. It modifies the constitution likewise of many metallic peroxides, for example peroxide of tin, and supplies the explanation of many cases of apparent isomerism." ⁹⁵

Prior to Graham's work the only explanation given for the existence of different phosphoric acids was one involving isomerism. For example in 1831, Thomas Thomson attributed the differences between Clark's pyrophosphoric acid and common phosphoric acid to isomerism, by suggesting that the two atoms of phosphorus and five of oxygen might be arranged in different ways. ⁹⁶ Graham's former teacher made no further comments on this problem.

Edward Turner described Graham's work fully in the fifth edition of his influential textbook published in 1834. He expressed a widely-held opinion when he wrote: "Mr. Graham, indeed, supposes the differences in the three phosphoric acids to arise solely from a disposition to unite in different proportions with water and alkaline bases; but this view scarcely suffices as an explanation, because it does not account for the peculiar disposition which causes their distinctive characters." ⁹⁷ Yet Turner was not entirely convinced by the alternative explanation of isomerism, because the differences in the arrangement of the elements must be, he thought, very slight as these acids were interconvertible.

In contrast, Richard Phillips was critical of Graham's use of Berzelian symbols in a somewhat different sense to that of Berzelius himself. Symbols were not much used in British scientific papers or

98. R. Phillips, 'Observations on the use of chemical symbols' Phil.Mag.
3 Ser.3 (December 1833) 443-445.

99. Graham, 'Reply to Mr. Phillips' observations on the use of chemical
symbols; 16th December 1833, Phil.Mag. 3 Ser.4 (February 1834) pp 106-
107.

textbooks at this time. Turner had only introduced them in 1833 in the fourth edition of his textbook. Phillips declared that he wanted to give an account of Graham's paper but he was in difficulties with the formulae used and therefore he would have to wait until Graham: "has rendered the paper intelligible by explaining the symbols in it." 98

He quoted the formula $\text{Na} \overset{\cdot}{\text{H}} \overset{2\cdot\cdot\cdot}{\text{P}}$ for common phosphate of soda commenting that here was a formula, with its symbolic atomic constitution expressed by Graham, but without: its analysis; atomic weight; atomic weights of acid, alkali or water; or any reference to the author of the system of notation used. Phillips added that Berzelius gave the formula $\text{Na} \overset{\cdot}{\text{P}} + 24\overset{\cdot}{\text{H}}$ for this salt. Now Graham wrote $\overset{\cdot\cdot}{\text{P}}$, not $\overset{\cdot\cdot}{\underline{\text{P}}}$, which Berzelius had used, and $\overset{\cdot}{\text{H}}$ instead of $\underline{\overset{\cdot}{\text{H}}}$. This was not in the original plan of Berzelius, he insisted. Finally, Graham had inserted water between sodium and phosphorus and not at the end. Phillips declared that confusion reigned with symbols. But he, himself, added to this when later in his article he misquoted Graham's formula for the common phosphate of soda, writing it wrongly as $\text{Na} \overset{\cdot}{\text{H}} \overset{2\cdot\cdot\cdot}{\text{P}}$.

On December 16th 1833 Graham replied to this criticism saying that he had used the Berzelian system. He explained the reason why he wrote $\overset{\cdot}{\text{H}}$, where Berzelius would write $\underline{\overset{\cdot}{\text{H}}}$, was that: "... in common with Gay-Lussac and all chemists of this country who have lately published, I consider water as composed of one atom of oxygen and one atom of hydrogen, a constitution expressed by $\overset{\cdot}{\text{H}}$ in the symbolic language of Berzelius. Berzelius, himself, uses the expression $\underline{\overset{\cdot}{\text{H}}}$ because from theoretical considerations, which everybody knows, he halves the combining proportion of hydrogen and therefore makes water to consist of one atom of oxygen united with two atoms of hydrogen." 99

By $\overset{\cdot\cdot}{\text{P}}$, Graham said that he meant one atom of phosphorus joined to five atoms of oxygen; whereas Berzelius wrote anhydrous phosphoric acid as $\overset{\cdot\cdot}{\underline{\text{P}}}$ meaning two atoms of phosphorus joined to five atoms of oxygen. Finally he corrected Phillips on the formula $\text{Na} \overset{\cdot}{\text{H}} \overset{2\cdot\cdot\cdot}{\text{P}}$, saying that: "the formula I would give

100. *ibid.* p 107.

101. R. Phillips, 'Additional observations on the use of chemical symbols' addressed to T. Graham. Phil.Mag. 3 Ser.4 (April 1834) pp 246-251. It must be admitted that Graham was guilty of a certain degree of confusion. He referred in his paper to the double atom of phosphoric acid ($\overset{\cdot\cdot}{\text{P}}$) = 892.3 and then he said in his December 1833 letter that $\overset{\cdot\cdot}{\text{P}}$ is 'one' atom of phosphorus joined to five atoms of oxygen.
102. Graham, 'Reply to Mr. Phillips,' April 9th 1834, Phil.Mag. 3 Ser.4 (June 1834) pp 401-404.
103. Dalton wrote to Graham in April 1837 giving him a testimonial for his application for the Professorship at University College, London. This letter became well-known and was quoted by W.C.Henry: Life of Dalton (London 1854) p 124. Dalton referred to Berzelius's 'horrific symbols ... a young student might as soon learn Hebrew as make himself acquainted with them. They appear like a chaos of atoms ... I am most surprised that such a system of symbols should ever have obtained a footing anywhere.' Dalton never became reconciled to these symbols. In 1839, Dalton attempted to publish an article on phosphates and arseniates in Phil.Trans. but the article was rejected by the Royal Society; this embittered Dalton. Regrettably the paper was couched in old atomic weights and symbols. Phosphoric acid was written incorrectly as PO_2 . Although he made numerous references to Graham and Berzelius, Dalton refused to accept the major achievements of their researches.

Dalton's letter is referred to in a letter, from Augustus de Morgan to Sir Benjamin Brodie dated 19th May 1867, quoted in: The Atomic Debates (Leicester, 1967) edited by W.H.Brock. The letter refers — to Brodie's chemical calculus. Augustus de Morgan writes: "it is well that Dalton has been taken away from the evil to come. He was much against notation; and when he gave a testimonial to Graham for the Chair of Chemistry in University College, it was with a protest against the adoption of symbols."

Dalton wrote in his 1837 testimonial for Graham: "I may say that he is known to me personally and by his writings, and I think he is a gentleman of great promise. His essays on the Diffusion of gases, on the arseniates and phosphates, on water as a constituent of salts and on phosphuretted hydrogen, would do credit to any scientific chemist. I do not, however, approve of his adopting and defending the chemical notation of Berzelius, which appears to me equally to perplex the adepts of the Science and to discourage the learner, as well as to cloud the beauty and simplicity of the Atomic theory." Letter from Dalton, April 11th 1837. See: Supplement to testimonials in favour of Mr. Graham (Glasgow, 1837) Wellcome Library.

is $\overset{\cdot\cdot\cdot}{\text{N}}\overset{\cdot\cdot\cdot}{\text{H}}\overset{\cdot\cdot\cdot}{\text{P}} + \overset{\cdot\cdot\cdot}{\text{H}}\overset{\cdot\cdot\cdot}{\text{O}}\overset{\cdot\cdot\cdot}{\text{O}}\overset{\cdot\cdot\cdot}{\text{O}}$, that is the crystallised salt consists of two atoms of soda and one atom of basic water united to an atom of phosphoric acid, together with 24 atoms of water of crystallisation. In his formulae for salts, Berzelius arranges the symbols so that the most positive ingredient stands first. Now from reasons which are explained in my paper, I presume that besides the soda, one atom of water is positive to the acid and not 24 as you make me say." ¹⁰⁰

Still Phillips was not satisfied. He realised that Graham had made an important contribution to the chemistry of phosphates but he was unhappy about the use of modified Berzelian symbols. Phillips asked for further amplification and drew attention to further inconsistencies in the writings of other chemists, giving examples from the formulae of: Prideaux, Rose, Turner, Johnston and Warington; his comments were finally completed in verse:-

"I must confess that the language of symbols is to me

A Babylonian dialect

Which learned chemists much affect

It is a party-coloured dress

of patched and piebald languages

'T is English cut on Greek and Latin

Like fustian heretofore on satin." ¹⁰¹

This correspondence was concluded on April 9th 1834 with a detailed explanation from Graham. ¹⁰² However the subject of chemical symbols was again raised at the British Association meeting held in September 1834 at Edinburgh and a chemical committee was appointed to review the whole question. This committee included both Phillips and Graham as well as Dalton. In 1835, a majority of the committee reported that they were agreed on the use of the continental [Berzelian] system, although they admitted that there were some differences in detail. Dalton characteristically recommended his own pictorial symbols and issued lithographic copies of these symbols for the British Association meeting held at Dublin in 1835. ¹⁰³

104. Berzelius, Jahresbericht 14 (1835) 111-113, 137-144.

105. Graham, 'On hydrated salts and metallic peroxides; with observations on the doctrine of isomerism'. British Association Report (Sept. 8-13th 1834) 579-582 also in Researches, 349-352 see pp 350-351. This account was also briefly reported in Edin.Phil.J. 17 (1834) 422 and "a long and interesting discussion between Drs. Dalton, Thomson, Turner, Clark and Professor Johnston" was mentioned, regrettably without details.

Berzelius gave a full review of Graham's paper on phosphates in his year-book, of 1835, saying that he considered this to be one of the most important papers of that year. He commented that Graham had carried out his work with great clarity and that his conclusions were acceptable in so far as they were explanations of the facts. He added that there must be a reason why phosphoric acid could take up different amounts of base especially as the observed behaviour of phosphoric acid did not occur for arsenic acid. He thought that it was perhaps to be looked for in the changed relative positions of the atoms of the simple molecule of phosphoric acid $[P_2O_5]$, giving different isomeric modifications of the acid.¹⁰⁴

Graham was determined to oppose any explanations of the different phosphoric acids based on isomerism and his assault on the doctrine of isomerism brought about further disagreement with Berzelius. The important concept of the role of basic water, giving rise to acids of different basicity, was threatened by explanations which involved isomerism.

At the British Association meeting held at Edinburgh in September 1834, Graham fired the first salvo at the doctrine of isomerism and in so doing he precipitated a conflict with Berzelius. Graham discussed the two varieties of peroxide of tin $[SnO_2]$ which had been cited as examples of isomers by Berzelius. Graham argued that this was not a case of isomerism because the two varieties were simply different hydrates of peroxide of tin. He then examined isomerism generally, saying that, "the doctrine of isomerism, or that two bodies may exist of the same composition, but differing in properties has been proposed by Berzelius But the propriety of the inference may be doubted. Most, if not all, cases of apparent isomerism may be explained by reference to one or other of the following properties."¹⁰⁵ He then stated four such properties. Firstly, water was essential to the constitution of many bodies, for example the three phosphoric acids were compounds of anhydrous

106. *ibid.* p 351. Graham was incorrect to single out this example as we now know with hindsight.

107. *ibid.* p 351.

108. Gay-Lussac, 'Observations sur l'oxidation de quelques métaux,' Ann.de Ch. 2 Ser.1 (1816) 32-45, see p 40.

phosphoric acid with three different proportions of water. Secondly, certain compounds on heating, formed a débris, which was not a proper chemical compound of the constituents. For example there was a borate of magnesia and water which on heating to redness lost water and gave a mixture of boracic acid and magnesia. This mixture was not the simple compound, anhydrous borate of magnesia, because the acid could be dissolved out with water. Hydrated peroxide of tin also gave a débris of hydrates on moderate heating and a further example of an imperfect compound was stucco just ready for setting. Thirdly, the true constitution of bodies of similar composition could be widely different because they contained different radicals. Fulminic acid did not contain cyanogen as did its apparent isomer cyanic acid. Graham then rejected the examples, with which Berzelius had introduced his views on isomerism: tartaric and racemic acids. He stated that: "they certainly contain different radicals, and probably have as little relation to each other as any two vegetable acids which could be named. Why, then, associate them as isomeric bodies, and call them the tartaric and paratartaric acids?"¹⁰⁶ Finally a fourth property was quoted which could account for apparent isomerism: "a minute trace of adventitious matter [impurity] may sometimes affect the properties of a chemical body to a surprising degree."¹⁰⁷ This was a reference to his latest discovery that the spontaneously inflammable variety of phosphuretted hydrogen differed from the other form, owing to the presence of an impurity and not because of isomerism.

Graham was here detailing his research programme for 1833-1834 which was aimed at destroying the concept of isomerism. He began by examining the metallic oxides: SnO_2 , Al_2O_3 , Fe_2O_3 and Cr_2O_3 which were known in both soluble and insoluble forms. Two different varieties of peroxide of tin had been discovered by Berzelius in 1811. They were shown by Gay-Lussac, in 1816, to possess the same formula SnO_2 .¹⁰⁸ Berzelius confirmed this in 1817 but he was surprised to discover that the two varieties possessed different properties. The peroxide of tin made by

109. Berzelius, 'Lettre de M. Berzelius à M. Gay-Lussac sur la combinaison de l'oxigène avec le fer, le manganese et l'étain,' Ann.de Ch. 2 Ser.5 (1817) 149-160. (With observations added by Gay-Lussac pp 160-165).
110. Berzelius, op.cit. (71)
111. Graham, op.cit. (79) 173-222. Earlier in 1827 Graham had suggested that the loss in solubility was caused by partial dehydration e.g. the anomalous solubility of magnesium phosphate.
112. Graham, op.cit. (105), Researches p 350.
113. *ibid.*

hydrolysis of stannic chloride was soluble in dilute acids whereas the peroxide of tin prepared by the action of nitric acid on tin was virtually insoluble in acids, although it did combine with hydrochloric acid and sulphuric acid. To distinguish these two peroxides Berzelius called the former, 'peroxide of tin' and the latter 'nitric acid peroxide of tin'.¹⁰⁹ Understandably, he included these two peroxides of tin as examples of isomerism in 1831,¹¹⁰ when he formally introduced the phenomenon of isomerism into Chemistry.

Between 1833 and 1834 Graham examined the two peroxides of tin.¹¹¹ He wanted to demonstrate that they were in fact different hydrates so that it would be possible to deny their isomerism. He checked the water contents many times but his results showed wide disagreements. Reluctantly, he had to conclude that: "the two modifications are merely different hydrates of the peroxide of tin, but it is difficult to ascertain what proportion of water is essential to each."¹¹² When the soluble peroxide was heated on a boiling water bath it was transformed into the almost insoluble peroxide. Further heating to redness completely removed any residual solubility and destroyed the power of both of the peroxides to combine with acids. Graham commented that: "the same is true of many other metallic peroxides; they combine as hydrates only with acids."¹¹³ He also studied the analogous peroxides of chromium, iron and aluminium at this time.

The precise details of the changes, which occurred when these oxides were heated, were not recorded by Graham, but it is possible to reconstruct them from some suggestions which he made in his notebooks. Referring to the coagulation of albumen he wrote: "suppose that there are two hydrates of this principle, a soluble and insoluble one, the first containing most water. Does metaphosphoric acid coagulate by withdrawing water from the fluid hydrate of albumen, while the acid itself becomes at the same time pyrophosphoric [acid]? Alcohol coagulates albumen by taking water? Can the alcohol be washed out? The strong acids also from the same cause?"

114. Graham, op.cit. (79) p 227.

115. Graham, op.cit. (79) p 124.

116. Graham, op.cit. (105), Researches p 350.

Do strong neutral saline solutions coagulate [albumen]? Wash the coagulum." ¹¹⁴ By analogy the soluble peroxide of tin would be more hydrated than the insoluble variety. The conversion of the soluble into the almost insoluble peroxide at 100°C would be the result of a partial dehydration. But this was not all that happened, for he noted that: "alumina and peroxide of iron are largely soluble in acids but they lose a portion of their usual saturating power on boiling which is a proof of their idiogenic combination. We may suppose that it is not alumina in these circumstances which dissolves in the acid, but an idiogenic aluminate, into one integrant particle of which there enter 3, 4 or 5 particles of alumina. The slowness with which the solution takes place favours the idea that it is not a solution merely of alumina in the acid. The excess alumina is not dissolved till an aluminate precipitates where the muriatic acid is supersaturated." ¹¹⁵ Therefore, when a hydrate lost its water, polymerisation began, so that the resultant particles became more difficult to dissolve in acids. Eventually at higher temperatures these polymers reached a sufficient size to become quite insoluble in acids.

Thus, Graham's explanation of the changes which metallic peroxides underwent becomes comprehensible. He said that: "metallic peroxides can be obtained by the application of a moderate heat to their hydrates, in a state in which they are the débris of hydrates, and not neat chemical compounds. Upon heating peroxides in this condition to redness, they generally glow or become spontaneously incandescent at a particular temperature and lose their solubility in acids at the same time. Till they have undergone this change they are not absolute peroxides. Various salts such as phosphates, antimonates etc., exhibit the same phenomenon when heated; but they all had possessed water, which is essential to their first constitution, but not to their second." ¹¹⁶

When Berzelius reviewed Graham's criticism of the doctrine of isomerism in his yearbook, he commented: "Graham's experiments on phosphoric

117. Berzelius, Jahresbericht. 16 (1837) 111-112.

W. T. Brande supported Berzelius's criticism of Graham's work. He argued that Clark's acid and common phosphoric acid were isomeric bodies. Metaphosphoric acid was also mentioned and Brande commented. "In his elaborate essay ... he [Graham] has entered into a variety of details bearing very importantly on the atomic constitution and properties of these acids and their salts ... I cannot adopt his atomic or theoretical views, because they appear discordant with the experimental results of the best analysts, among whom, I especially refer to Berzelius and Dulong." Brande believed that phosphoric acid was $PO_{2.1}$ (P=16, O=8) and that it was neutralised by one atom of base; ^{now} on doubling the atomic weight of phosphoric acid = P_2O_5 it would be neutralised by 2 atoms of base, "which is contrary ^{to} to all analogy." Brande Manual of Chemistry 4th.edn. (London, 1836) 444-5.

118. In 1844, Edmond Frémy (1814-1894) argued that he preferred to regard the water in the different hydrates of SnO_2 as an acid whereas Graham considered that this water acted as a base. Frémy noted that water was easily lost from the two hydrates and that it was difficult to distinguish between hygrometric water and true water of combination. He concluded that the nitric acid peroxide of tin, which he called metastannic acid, was $Sn^{306}, 6H^{20}$ and that stannic acid, the soluble peroxide of tin was $Sn^{306}, 7H^{20}$. Frémy, 'Recherches sur les acides métalliques', Ann.de Ch. 3 Ser.12 (1844) 466-475. Following repeated criticism by Berzelius that the two acids were isomeric, Frémy reconsidered his earlier analyses. Thus, in 1848 he concluded that metastannic acid was $Sn^{5010}, 10H^{20}$ or when dried in vacuo it was $Sn^{5010}, 5H^{20}$ and this latter formula was indeed isomeric with his redetermined formula for stannic acid which he gave as SnO^2, H^{20} . Frémy, Ann.de Ch. 'Researches on hydrates' 3 Ser.23 (1848) 385-404.

acid led him to the idea that isomerism consists of nothing but compounds of the same bodies possessing unequal quantities of water. Referring to this idea, Graham declares that the two isomeric peroxides of tin are compounds with different portions of water, although he does not dare to decide which contains the most water. This kind of scientific philosophy is not to be approved of by any means. As to the assumption that these two oxides and the phosphoric acids have different capacities of saturation, with water playing the role of an additional base in the phosphoric acids, there ought to be a reason for this behaviour. It does not rest in the water, or the bases, but it is to be looked for in the heterogeneous state of the oxide itself, as with the phosphoric acids it is what we call 'isomerism'. Graham has investigated the different effects of isomerism in a most interesting way but he is obviously not right in considering its 'consequences' to be the 'cause'. According to his opinion racemic acid is not to be the same as crystallised tartaric acid, we know however that these two acids are of identical composition and that they form salts of different qualities but with absolutely equal numbers of atoms of base and water. I repeat, my comment of last year, made with regard to Faraday's explanation of the power of platinum to condense hydrogen and oxygen, that there is more scientific clarity in acknowledging, or admitting, that which cannot be explained satisfactorily at present, rather than giving a speculative opinion, when Science has not yet obtained the key." ¹¹⁷

Berzelius was clearly critical of Graham's interpretations of the constitution of compounds in terms of water content rather than isomerism. His comment on the water content of the peroxides of tin was unfair. He knew that this water content was difficult to determine and this was certainly the experience of later workers like Frémy.¹¹⁸ Isomerism applied to inorganic compounds was not a very constructive concept at this period and it had little predictive value because the detailed isomeric arrangements were unknown. On the contrary, Graham's concepts

119. Graham, Elements of Chemistry 1st.edn. (London, 1842) p 154. This part of his book was written in 1838 and first published in August 1838. In 1837 J.F.W. Johnstone had suggested that there was a close analogy between the production of dimorphism and isomerism ... the one change (isomerism) began where the other (dimorphism) ended. "Isomerism like dimorphism is dependent on circumstance, and is developed in certain cases by change of temperature." Johnstone 'On the present state of our knowledge in regard to dimorphous bodies,' B.A. Report (1838) pp 163-215, see pp 209-210. In another context, Richard Phillips argued against Johnstone's proposed changes of atomic weights based on removing anomalies from Dulong and Petit's law. Phillips wrote "Another way round the difficulty ... which did not suggest itself to Johnstone ... if heat combines with bodies in definite proportions, it may in some cases like other elements combine in double proportions; instead of halving the equivalents of these metals, let us suppose they are combined with two equivalents of heat." R. Phillips, 'Observations on Isomorphism..' Phil. Mag. (May 1838) 3 Ser. 12 p 412. Both Phillips and Johnstone appear to be thinking along similar lines to Graham with regard to combined heat as a constituent of compounds.

of the differing amounts and functions of water in compounds was extremely valuable for suggesting further lines of research as will become evident. Possibly in response to this criticism from Berzelius, Graham proposed another hypothesis in 1838 to explain the differences between the two forms of peroxide of tin or alumina. He had noticed, like Berzelius before him, that the transformation of a soluble into an insoluble peroxide was accompanied by a sudden glowing as heat was visibly lost. Generally the loss of water appeared to occur at lower temperatures than this sudden loss of heat, so the presence of combined water was not the only cause of solubility. Therefore, he proposed that these peroxides contained different but definite proportions of combined or latent heat, which was lost during the glowing or ignition. He admitted that there might be a change in the arrangement of the particles at the same time, but, he wrote: "it would be difficult to apply an explanation of this nature to the oxides, such as alumina and peroxide of tin, which contain only two constituents. The loss of heat observed will afford all the explanation necessary if heat be admitted as a constituent of bodies equally essential as their ponderable elements. As the oxide of chromium possesses more combined heat when in the soluble than in the insoluble state, the first may justly be viewed as the higher 'caloruret', and the body in question may have different proportions of this as well as of any other constituent." ¹¹⁹ Thus Graham preserved, what he envisaged to be a fundamental law, that changes of property only occurred with a change in composition. By including combined heat as a constituent of substances he was able to explain cases of dimorphism and to dismiss more apparent examples of isomerism.

In 1841, Graham attempted to deny the isomerism of tartaric and racemic acids more conclusively. He quoted Liebig's formula for racemic acid dried at 100°C: $\text{HO}, \text{C}_4\text{H}_2\text{O}_5$ and he pointed out that it contained only half the number of atoms found in tartaric acid: $2\text{HO}, \text{C}_8\text{H}_4\text{O}_{10}$. Thus, racemic acid was monobasic, whereas tartaric acid was bibasic and so their

120. Graham, Elements of Chemistry 1st.edn. (London 1842) p 950.
See Liebig, Traité de Chimie Organique 3rd.edn. (Bruxelles, 1841)
p 477. "Paratartaric acid does not form a double salt analogous to
Seignette [Rochelle] salt, containing at the same time potash and
soda; this character distinguishes it from tartaric acid and permits
us to consider it as a monobasic acid."
121. Graham Notebooks B and C: Notebook B op.cit. (79) pages 366-371,
378-384, 386-394 and 413-414, continued in Notebook C (252 pp.,
September 2nd 1834 - July 1835, Andersonian Library, Strathclyde
University) pages 1-68.
122. H. Rose, 'Sur la composition de l'hydrogène phosphoré etc. Ann.de Ch.
2 Ser. 51 (1832) 5-56.
123. Graham, 'Observations on the oxidation of phosphorus' from Qu.J.Sci.
ii (October 1829) 83-88 and Researches 36-39.
124. Graham, 'On phosphuretted hydrogen', Phil.Mag. 3 Ser. 5 (December
1834) 401-415 or Researches, 71-84.
125. Liebig, 'On the spontaneous inflammability of phosphuretted hydrogen;
on the remarkable reaction of water in some salts and on stannic
oxide.' Liebig Annalen. 13 (1835) 141-147. The source used by
Liebig for these articles was E. Turner Elements of Chemistry 5th.edn.
(London, 1834) Appendix pp 1037-1040. Berzelius used Liebig's article
for his own review of Graham's researches on the peroxide of tin.
op.cit. (117).

isomerism was accounted for without recourse to differences in atomic arrangement.¹²⁰

Between May and October 1834 Graham examined another reputed example of isomerism.¹²¹ This had been discovered in 1832 by Henry Rose when he showed that spontaneously inflammable and non-spontaneously inflammable phosphuretted hydrogen both had an identical composition, that is, they were isomers.¹²² Graham had previously examined the effect of impurities on combustion reactions in his study of the glow of phosphorus.¹²³ He now examined the spontaneous inflammability of PH_3 and the effect of impurities on this reaction.¹²⁴ In this most interesting piece of research he observed that spontaneous inflammability could be introduced by adding nitrogen peroxide $\overset{\cdot\cdot\cdot}{\text{N}}$, or NO_4 [that is NO_2 ; as it is now formulated]. Conversely, there were several substances which could remove the spontaneous inflammability. By analogy with $\overset{\cdot\cdot\cdot}{\text{N}}$, Graham argued that the impurity causing spontaneous inflammability might be an undiscovered peroxide of phosphorus $\overset{\cdot\cdot\cdot}{\text{P}}$ [now written PO_2] analogous to the corresponding $\overset{\cdot\cdot\cdot}{\text{Cl}}$ [chlorine dioxide ClO_2] discovered by Davy and Stadion. His choice of impurity, PO_2 , was incorrect but it is immaterial to this discussion. He had shown the true nature of the problem. The spontaneous inflammability of phosphuretted hydrogen, prepared from phosphorus and lime, was simply caused by the presence of an impurity. It was not caused by an isomeric modification of the other variety of phosphuretted hydrogen which was prepared from phosphorous acid.

Liebig recorded Graham's views on both the peroxides of tin and phosphuretted hydrogen in his Annalen.¹²⁵ He commented on the latter example, saying that the admixing of an acid impurity $\overset{\cdot\cdot\cdot}{\text{P}}$, which might cause the spontaneous inflammability of phosphuretted hydrogen, would seem to be doubtful, when the self-igniting gas was itself prepared from such an alkaline liquid. But he added that the real cause would not remain hidden for long from such a tireless research worker as Graham. In 1837, W. C. Henry wrote that Graham's memoir on phosphuretted hydrogen

126. Graham, Testimonials in Favour of Thomas Graham ... Candidate for the Vacant Chair of Chemistry in University College, London. Glasgow (1837) 45 pp. Testimonial from Wm. Charles Henry: Manchester, March 28th 1837 p 6. From Wheatstone Collection (Small Biographies, obituaries and Testimonials), King's College, London or from the Wellcome Library copy.
127. *ibid.* Testimonial from J.W. Doebereiner, Jena, 1st March 1837, p 16.
128. M. Leverrier, (a colleague of Dumas), 'Sur les combinaisons du Phosphore avec l'hydrogène' Ann.de Ch. 2 Ser. 60 (1835) 174-194.
129. H. Rose, 'On phosphuretted hydrogen', Pogg. Ann. 46. (1839) 633-639.
130. P. Thenard (son of L.J. Thenard), 'Sur les combinaisons du phosphore avec l'hydrogène', Ann.de Ch. 3 Ser. 14 (1845) 5-40.
131. Berzelius, Jahresbericht. 15 (1836) 90-97.
In 1835 Berzelius wrote to Mulder with regard to the translation of his textbook:- "I am afraid that you have already passed not only phosphuretted hydrogen but also phosphoric acid ... all the article needs to be re-written, since the magnificent experiments of Graham." Berzelius-Mulder correspondence. Söderbaum Vol.2 part 5 p 17. Letter dated 7th April 1835. Similarly Berzelius was complimentary about Graham in his testimonial. He wrote "Your chemical works are distinguished by exact observation as well as by the originality and correctness of the ideas. Your memoir on the three modifications of phosphoric acid is a classical work, that of phosphuretted hydrogen is of major interest. Your researches on the hydrated salts unfold new views on the role which water plays in inorganic combinations." *op.cit.* (126) Letter from Berzelius to Graham, dated March 10th 1837 p 7.
132. Graham, 'On the water of crystallisation of soda alum'. Phil. Mag. 3 Ser. 9 (July 1836) 26-32 or Researches 365-367.
133. R. Phillips added in a footnote to the above paper that Thomas Thomson had already demonstrated Graham's point. This is not strictly true. Thomson had shown that potash alum and soda alum had the same constitution but he had incorrectly suggested that they both contained 25 atoms of water and so the point was lost. Thomson, First Principles etc. (London 1825) Vol. 2 448. Graham's determination was accepted by Johnston in 1837. See:- the published letter dated Sept. 1837 viz. J.F.W. Johnston 'On the received equivalents of potassium, sodium and silver.' Phil. Mag. 3 Ser. 12 (1838) pp 324-9.

could be commended as a fine model of inductive research. He added: "this paper, I was informed by Professor Liebig, had gone far to shake his confidence in the doctrine of isomerism, of which, he had himself, in conjunction with Wöhler previously furnished, in the two cyanic acids, what he then regarded as the most striking example."¹²⁶ Likewise, J. W. Doebereiner wrote to Graham: "the doctrine of isomerism has been powerfully shaken by the result of your researches, and I would that you were inclined to make it still farther the subject of your investigation. The chemists of all Europe would be served by an examination of this subject by one whose talents for observation, and for ingenious experiment are so distinguished."¹²⁷

The impurity responsible for the spontaneous inflammability of phosphuretted hydrogen was correctly identified as the hydride PH_2 [now written as P_2H_4] by Leverrier in 1835.¹²⁸ Despite denials by Henry Rose in 1839,¹²⁹ this fact was confirmed by Paul Thenard in¹³⁰ 1845.

Berzelius reviewed Graham's paper on phosphuretted hydrogen in distinctly complimentary terms describing it as a fine piece of research. Again he noted that Graham considered the conception of isomeric bodies to be a problem. Nevertheless, he believed that Graham's results were of great theoretical importance, not with regard to the question of the existence of the two isomeric forms, which was of secondary importance, but with regard to the effect of impurities on the inflammability of phosphuretted hydrogen.¹³¹ However, Berzelius was far less generous in his next review of the short paper, written by Graham in 1836, on the water of crystallisation in soda alum.¹³²

In this paper, Graham showed that soda alum, the double sulphate of alumina and soda, contained 24 atoms of water, and not 26, as Berzelius had supposed.¹³³ Furthermore, the coincidence of form between potash alum and soda alum appeared to indicate isomorphism, with the possibility that soda and potash might therefore be isomorphous. But Graham admitted that the crystal dimensions had not actually been measured in this experiment.

134. Berzelius, Jahresbericht 17 (1838) 137-139.
In the same year-book, Berzelius reviewed another paper (on pages 63-64) by L.A. Buchner, who had written a prize essay in 1836 for the Munich Philosophy Faculty. Buchner had analysed phosphates and tartrates. He argued that they were not to be considered as isomeric substances but rather that the differences between the phosphoric acids, the oxides of tin and zirconia etc. were due to unequal water-contents. Berzelius noted that this agreed with Graham's views but stressed again that "unequal capacity for water and bases must also have a cause based on unequal states of bodies which combined with unequal quantities of water." He also dismissed a final explanation, given by Buchner, that the cause of these differences was based upon a dynamic process which had as its basis the essence of matter.
135. Letter from Berzelius to Mulder dated 17th February 1843 Berzelius Letters edited by A.G. Söderbaum Vol. 2 (Uppsala, 1915) pp 222-223, and also see Berzelius 'Essay on the allotropy of simple bodies' read before the Academy of Sciences, Stockholm on 13th September 1843 and translated into English in Taylor's Scientific Memoirs iv (London, 1846) 240-252 [from Pogg. Ann. 61 (1844) 1-18.] See also Berzelius, 'On the compounds of phosphorus and sulphur' Pogg. Ann. 59 (1843) 76-94, 463-478, 593-615; particularly pp 76-79.

This paper was reviewed in caustic terms by Berzelius who wrote that: "Graham, who sometime ago, thought he would give the theory of isomeric bodies a fatal blow with his experiments on phosphoric acids, has thought that he could show that isomorphous relations were 'illusory' to use his own term. From one experiment only, which he considers sufficient to prove that the fine theory of isomorphism is illusory. With questions of such great importance one cannot endeavour too much in being peremptory A salt does not lose its clarity by becoming dry. Graham's salt had obviously lost some water and had changed at the surface, that is, it had effloresced." ¹³⁴ But Berzelius was wrong; Graham's analysis proved to be correct although he had only performed one analysis on a crystal which had lost its transparency. What had Graham suggested, which was illusory? certainly not isomorphism; but the particular isomorphism between KO and NaO + 2HO which he correctly suggested was "likely to prove illusory."

We have seen that Berzelius was determined to oppose Graham's theory that the three phosphoric acids possessed different basicities because they contained unequal quantities of basic water. How did Berzelius explain the differences between these acids in terms of isomerism? He did not merely dismiss the problem as insoluble instead he proposed two possible explanations. His first view was an attempt to explain isomerism by using the phenomenon of allotropy, which he had introduced into Chemistry in 1840. Berzelius developed his explanation clearly in a letter to Mulder in 1843 and also in a lecture given in the same year. ¹³⁵ There were two allotropes of phosphorus, the ordinary colourless variety and the red allotrope. Berzelius suggested that the different isomeric states of phosphorus compounds might depend on the allotropic form of phosphorus in the radical. At high temperatures, the oxide of phosphorus became red in colour so pyrophosphoric acid must contain red phosphorus and therefore common phosphoric acid would contain the ordinary colourless phosphorus. Metaphosphates were in his opinion merely pyrophosphates combined in different proportions with anhydrous phosphoric acid.

136. *ibid.* Letter from Berzelius to Mulder p 223.

137. Berzelius, Textbook of Chemistry 2nd French Edition (Paris, 1845)
Vol. 1 514-528, see p 514.

Likewise, spontaneously inflammable PH_3 seemed to contain ordinary phosphorus whereas the non-spontaneously inflammable variety contained red phosphorus. The evidence for this view was that sunlight in the absence of air changed the former compound into the latter, just as sunlight converted ordinary phosphorus into red phosphorus. In conclusion, Berzelius wrote to Mulder:- "These comparisons appear to me to be of great importance, since they rid us of the foolish explanations which Graham has given to us on the different states of phosphorus compounds, and since they show that the cause of isomerism does not always consist of a different order in the position of atoms, which are identical, when the allotropic state of the radical, or of one of the components is different." ¹³⁶

In 1845, Berzelius revised his opinion, saying that it was not possible to decide whether the different properties of the two isomeric phosphoric acids originated from the allotropy of the radical or from the unequal juxtaposition of the atoms. ¹³⁷ He conceded that there were three modifications of phosphoric acid which he designated by the letters a-, b- or c-phosphoric acids, corresponding to metaphosphoric, pyrophosphoric and common phosphoric acids respectively. Only two isomeric modifications existed; one being found in the a- and b-acids, and the other in the c-acid. All three acids were saturated by two atoms of base. Although the a-acid could be written as $\text{H}\ddot{\text{P}}\ddot{\text{P}}$, which would be saturated by one atom of base, Berzelius suggested that it could be considered alternatively as a combination of one atom of b-acid and one atom of anhydrous phosphoric acid $\text{H}^2\ddot{\text{P}} + \ddot{\text{P}}$. Thus this a-acid would then be neutralised by two atoms of soda to give $\text{Na}^2\ddot{\text{P}} + \ddot{\text{P}}$. Both b- and ^{also} c-acids were saturated by two atoms of soda. He did not accept Graham's argument that the c-acid was saturated by three atoms of soda, because he maintained that the soda salt $\text{Na}^3\ddot{\text{P}}$ was so alkaline that it was almost caustic. Berzelius also rejected the argument that the c-acid was tri-basic, because the common phosphate of soda $\text{Na}^2\ddot{\text{H}}\ddot{\text{P}}$ still retained one atom

of water very strongly up to red heat. He countered this by quoting the sulphates which did not give clear evidence for deciding on the basicity of sulphuric acid. He pointed out that sulphate of potash was anhydrous and yet the sulphate of zinc retained one atom of water at high temperature; therefore he asked was sulphuric acid saturated by one or two atoms of base? Berzelius had turned the argument nicely against Graham who had shown that sulphate of zinc retained one water atom at high temperatures. Both chemists agreed that sulphuric acid was saturated by one atom of base and not by two atoms of base. Berzelius was not prepared to compromise on his views. He had ignored the important developments in organic chemistry which were inspired by Graham's theory of polybasic acids, for example the researches of Liebig on organic acids. This failure to accept the need for change in the dualistic electrochemical theory arose from Berzelius's conviction that acids had only one fixed basicity. Thus, he could not accept the idea of polybasic acids containing different amounts of basic water.

Despite the opposition from Berzelius, Graham's views on the phosphates influenced workers in both France and Germany. Initially Dumas supported the ideas of Berzelius on isomerism. In 1831, Dumas put forward the view that the beginnings of the development of isomerism could be recognised by increases in density, cohesion, hardness, or changes in crystal form, for example in arragonite and calcite. These changes in physical properties were the first signs of the development of isomerism which was ultimately caused by molecular movement. A more complete change was brought about by a greater molecular movement. This produced new chemical properties without altering the atomic weight. These changes led to proper isomerism. Dumas suggested that it might be possible to account for the isomerism of phosphoric and pyrophosphoric acids by regarding one as a hydrate and the other as the true hydrophosphoric acid, according to the hydracid theory of Davy and Dulong. Thus the two acids could be written $P^2O^5 + H^2O$ and $P^2O^6 + H^2$. They were simply different

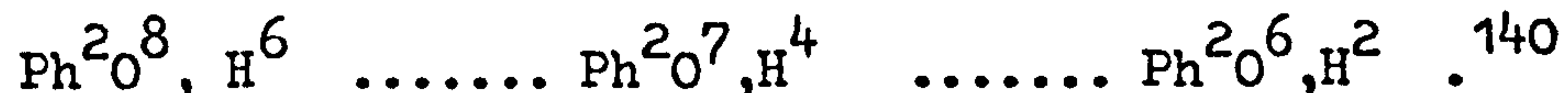
138. 'Lettre de M. Dumas à M. Ampère, sur l'isométrie', Ann.de Ch. 2 Ser.47 (1831) 324-335.
139. Graham's researches appeared in French in 1835. See Graham, 'Sur l'isométrie de l'acide phosphorique', Ann.de Ch. 2 Ser.58 (1835) 88-100.
140. J.B.Dumas, Leçons sur la Philosophie Chimique (Paris, 1836) 342-345. Bineau, who collected together these lectures of Dumas, was reluctant to accept the idea that the three phosphoric acids were isomeric. He rejected isomerism because of the observed interconversion of these acids and suggested that P_2O_5 combined with different proportions of base or water thereby forming molecules which were only changed with difficulty into one another. Therefore there was no need to invoke ideas such as isomerism or dimorphism in these explanations. Bineau put forward these opinions in his Essai de Philosophie Chimique which is found in L.J.Thenard's Traité de Chimie, 6th.edn. (Paris, 1836) Vol.5 pp 478-481, 492-493.
141. Longchamps, 'Theorie des acides hydrogéniques' Ann. de Ch. 2 Ser.61 (1836) 53-66.
142. J.F.Couerbe, 'Some reflections on Chemistry' read to the Académie des Sciences, 15th February 1838, Ann.de Ch. 2 Ser.68 (1838) 160-204.
143. Couerbe claimed that he had previously suggested that water had an alkaline role in sabadilline, in 1833, and therefore deserved priority in this discovery. Sabadilline was an organic base extracted from the seeds of a Mexican plant. See Couerbe: 'Recherches chimiques sur quelques substances quaternaires d'origine organique.' Ann. de Ch. 2 Ser.52 (1833) 352-386, see p 376.

molecular arrangements of the same atoms.¹³⁸

Following Graham's investigation of the phosphoric acids,¹³⁹ Dumas changed his opinion and wrote the three hydrates of phosphoric acid as:-



atively, he suggested that the three acids could be written as hydracids:-



However, he was unhappy about the number of new undiscovered radicals which would be created if the hydracid view was adopted. Also, the hydracid view would presuppose marked changes in the natures of these compounds which would be hard to reconcile with the ease of their inter-conversion. Dumas noted that yet a third view of acids and salts had to be considered. This had been proposed by Longchamps¹⁴¹ who said that acids like sulphuric acid, represented as $\text{SO}^3, \text{H}^2\text{O}$ on the oxyacid theory, or as SO^4, H^2 on the hydracid theory, could alternatively be considered as sulphurous acid combined with oxygenated water: $\text{SO}^2, \text{H}^2\text{O}^2$. Dumas regarded the last view as being even more unlikely than the hydracid theory. Therefore, he supported Graham's representation of the formulae of the three phosphoric acids, and said he was reluctant to take up other theories unless they were seen to be absolutely necessary.

Another view of Graham's researches was given by J. F. Couerbe in 1838.¹⁴² Proust had been the first to use the term 'hydrates' of metallic oxides, and Proust had also compared water to an acid, for example in hydrate of potash. Couerbe maintained that Graham, in his 'superb researches' on the three phosphoric acid hydrates, was incorrect to say water possessed a basic role in acids. On the contrary, water had an acid function in these compounds. Couerbe did not deny that water could possess a basic function; indeed he disputed Graham's priority in this respect.¹⁴³ But he argued that it was inappropriate to suggest that water was basic in the acid hydrates. Alternatively, he suggested that anhydrous phosphoric acid, P^2O^5 , was a compound radical which became acidic, by combination with one atom of water. Water developed these

acidic properties, either by a molecular rearrangement on combination, or by acting as a conductor of acidic properties. Couerbe then developed a rather speculative theory. He said that water reacted with anhydrous phosphoric acid by filling up a single depression or pole of affinity to produce P^2O^5, H^2O which, in turn, could become polarised at another point so that a further one or two water atoms could be attached in a chain. This explained why metaphosphoric acid reacted with more water after a period of time. Only the water atoms directly linked to P^2O^5 were acidic; for example in common phosphoric acid H^2O, P^2O^5, H^2O, H^2O the last water molecule in the chain of two was neutral. Finally, he explained that acid phosphates were produced by substituting one atom of base (RO) for one atom of acidic water, to give RO, P^2O^5, H^2O, H^2O .

These speculations do not appear to have had much influence on other chemists. Couerbe was not convincing in his explanations of the alternative acidic or basic roles of water. But he was aware that Graham's explanations were not entirely satisfactory. Why was it that metaphosphoric and pyrophosphoric acids did not take up water immediately in solution? He was not alone in feeling that Graham's explanations were incomplete.

Before examining these shortcomings, it will be worthwhile to consider the work of another French chemist who was influenced by Graham's researches. Persoz wrote a paper on solubility in 1836 which arose, he said, from conversations he had had with Graham concerning the formation of double salts. This led Persoz to interpret the solubility of salts in terms of their combination with water. Salts tended to be either acidic or basic, and water accordingly took the opposite role. This was essentially the Berzelian conception of double salts in which one salt acted as a base and the other as an acid. Now, he argued that soluble salts were either acidic or basic and therefore they tended to combine with water during solution whereas insoluble salts were neutral and so did not tend to combine with water. When the alkalinity of a salt was

144. J. F. Persoz, 'Note sur la solubilité en général et en particulier sur celles des sels', Ann.de Ch. 2 Ser.63 (1836) 273-281, see p.281.
145. MS. letter from Mary Graham to Liebig, dated 17th September 1869. Graham's sister wrote a personal note to Liebig, rather than sending a formal intimation of her brother's death, saying: "I know you were one of his most esteemed friends."
MS. letters of Graham to Liebig, Bayerische Staatsbibliothek, Munich. Liebigiana 58.
146. Note in Liebig-Berzelius Letters that Liebig said he had been working for 18 months on the analysis of organic acids before March 1838, Berzelius und Liebig, Ihre Briefe von 1831-1845, ed. J. Carrière, (Munich and Leipzig 1893) p.147.
147. 'Extract of some researches made at Giessen by Liebig and Pelouze'. Ann.de Ch. 2 Ser.62 (1836) 438-440.
Graham visited E. Mitscherlich after meeting Liebig and he discussed the role which water played in an acid. Mitscherlich's response impressed Graham. Mitscherlich said that "the base, which may be water, has here manifestly an effect upon the atomic constitution of the acid, if we could figure it out for ourselves. Water may have a similar effect in the metaphosphate of water, which contains one atom of water. The influence of water on the arrangement of the particles composing phosphoric acid may be different from what it was in the other case. This idea of Mitscherlich is, of course altogether hypothetic, and he by no means pressed it, but it is certainly a very little assumption, and we can observe in it the great secret of correct philosophising, namely, to advance by the shortest possible steps." - letter from Graham to his brother, 27th September 1836, quoted in R. A. Smith, The Life and Works of Thomas Graham, (Glasgow, 1884) p.38.
148. Graham, 'Inquiries respecting the constitution of salts. Of oxalates, nitrates, phosphates, sulphates and chlorides.' received June 23rd 1836 and read on November 24th 1836. Phil.Trans.12(1837) 47-74 and Researches.367-397. See also Liebig Annalen.29 (1839) 1-35.

reduced, by adding an acid, the solubility was consequently lowered, for example when carbonate of potash was converted into the less soluble bicarbonate of potash by adding carbonic acid. He gave another example, which had been suggested by Graham. Persoz felt this example was important evidence in support of his view of solubility. It was that of anhydrous boric acid, which was insoluble in alcohol, whereas hydrated boric acid was soluble in alcohol.¹⁴⁴

When Graham left Persoz, he travelled to Giessen, where he met Liebig. He stayed with Liebig for two days in September 1836; it was the beginning of a life-long friendship.¹⁴⁵ Of more significance, is the fact that Liebig's researches on organic acids were begun in September 1836.¹⁴⁶ It is very probable that Graham discussed his own researches on the phosphoric acids and their salts with Liebig at this time. Indeed, there is evidence for this view, in an extract of the chemical researches undertaken by Liebig and Pelouze at Giessen in 1836. They wrote: "we believe that mellitic acid (from the analysis of its compounds with oxide of silver) is a hydracid and our experiments confirm in this respect the views of M. Dulong on oxalic acid. The researches of M. Graham have excited the attention of chemists on the role which water plays in a collection of compounds."¹⁴⁷

Is it possible that Graham's researches were a guide for Liebig in his eighteen-month research programme on the constitution of organic acids? The evidence contained in Liebig's paper published in April 1838 seems to indicate that Graham's researches were indeed very influential.

In June 1836, Graham had just completed his paper on the constitution of salts.¹⁴⁸ In this paper: he discussed oxalic acid and its salts; he classified the phosphates as monobasic, bibasic, or tribasic; and he established a criterion to show that the so-called double phosphates were not true double salts. Double salts contained two separate salts joined together, for example alum was a combination of potassium sulphate and aluminium sulphate. Now alum contained sulphates of two bases,

149. Graham, Elements of Chemistry 1st.edn. (London, 1842) p 476.

150. MS. letter from Graham to Liebig, dated 10th August 1838.
Liebigiana 58, Bayerische Staatsbibliothek, Munich.

potash and alumina, which belonged to quite different families of bases. The double phosphates, on the contrary, contained a single atom of phosphoric acid neutralised by two different bases from the same family not from different families and so they were not double salts; they were polybasic salts. The crucial example of a polybasic salt was the phosphate of soda and ammonia, or microcosmic salt, which had the formula $\text{HO,NaO,NH}_4\text{O,PO}_5 + 8\text{HO}$. Graham admitted later that: "this salt I believe proved the key to the constitution of the bibasic and tribasic organic acids by supplying the canon, founded upon it by myself, that bases of the same family may exist together in the salts of such acids, but not in ordinary double salts, which was happily applied to elucidate the salts of the acids in question by Leibig and Dumas." ¹⁴⁹

Graham made the same point when he wrote to Liebig in 1838 saying: "it was with intense delight that I perused your great paper on the organic acids. Your new principles are most successfully established. I agree with you on the characters by which bibasic and tribasic salts can be established, the combining at once with bases of the same natural family as magnesia and water, potash and soda; and I always considered that as a reason why Seignette salt [Rochelle salt] was likely to be bibasic, as it has proved to be." ¹⁵⁰

The problem with Graham's view of the three phosphoric acids as different hydrates was that it was not clear why metaphosphoric and pyrophosphoric acids or their salts did not immediately take up more water when they were dissolved. Also, why was the neutral phosphate of soda Na^2HP whereas the neutral phosphate of silver was Ag^3P ? By applying the concept of hydrogen acids to the phosphoric acids, Leibig was able to remove some of these difficulties as we shall now see.

Liebig took great pains with his research work. He recognised its importance and he checked his experimental results with great care to avoid mistakes. He wanted to show that the organic acids were hydracids as Dulong had done with oxalic acid. He recognised that this would be a

151. MS. letter from Liebig to Pelouze, 20th November 1837. Letters of Pelouze, Académie des Sciences, Paris.
152. Letter from Liebig to Wöhler, 23rd November 1837. Liebig-Wöhler letters (1829-1873), 2 volumes (Brunswick, 1888). pp 113-117.
153. See letters of Liebig to Berzelius, op.cit. (146), dated: November 26th, December 21st 1837, January 5th, March 7th, April 15th 1838 and the replies from Berzelius: December 19th 1837, February 20th, May 4th 1838, op.cit. (146), pp 121-161. During this period Graham wrote to Berzelius asking him, "as the acknowledged head of our science," for a recommendation to support his application to be Professor of Chemistry at University College, London. (MS. letter from Graham to Berzelius, dated February 22nd 1837, kept in the Royal Academy of Sciences, Stockholm). Berzelius mentioned this to Liebig on December 19th 1837 remarking that Graham was being rather presumptuous because he did not even know him. However, he replied with encouragement adding that Graham "is the most deserving of the English chemists, from his written work, to improve Turner's Professorship." See also the useful article on 'Liebig' by F. L. Holmes in Dictionary of Scientific Biography, 8 (1973) 329-350.
154. *ibid.* letter from Berzelius to Liebig, February 20th 1838, op.cit. (146) pp 144-147.
155. Unpublished letters from Liebig to Pelouze, dated: November 20th, December 9th 1837 and April 18th 1838. Pelouze letters in the Académie des Sciences, Paris.
156. Unpublished letters from Liebig to Dumas, November 29th, December 19th 1837 etc. Dumas letters in the Académie des Sciences, Paris.
157. For details of the unfortunate personal disagreements see the article on 'Liebig' by F. L. Holmes, op.cit. (153). Dumas published his results on citrates and tartrates at a later date: Dumas and Piria, 'Fifth memoir on types' Ann.de Ch. 3 Ser. 5 (1842) 353-395.
158. J. Liebig, 'Sur la constitution des acides organiques', Ann.de Ch. 2 Ser. 68 (1838) 5-93 [or Liebig Annalen. 26 (April 1838) 113-189]

major innovation which would alter not only the constitution of organic acids and their salts but also the generally-accepted dualistic treatment of the constitution of all acids and salts.

He wrote to Pelouze that the organic acids: "are sorted out perfectly by the supposition that they are all hydracids like mellitic acid. I have suspected this for some time."¹⁵¹ Similarly he wrote to Wöhler saying that: "I have been dominated with the absurd idea for years that all the organic acids are hydrogen acids from the well-remembered days of our benzoyl work."¹⁵² Liebig tried to win over the opinions of his colleagues and friends to his view of hydrogen acids. To this end, he wrote several letters to Berzelius, but he was unable to convince him.¹⁵³ He did, however, accept the advice which Berzelius gave to him on the presentation of his paper; it was to publish the facts first and then to present his different views or explanations at the end, in the form of questions, as Newton had previously advised.¹⁵⁴ Liebig also explained his views in detail in his letters to Pelouze,¹⁵⁵ Wöhler and to Dumas.¹⁵⁶ At one period he had intended to work jointly with Dumas on this research but Dumas contributed very little to the work and the joint effort was soon abandoned as a result of personal disagreements.¹⁵⁷

Liebig began his paper with a presentation of the experimental facts and then turned to the theory.¹⁵⁸ He began by criticising the definition of the atomic weight of an acid given by Berzelius, who had defined it as equal to the quantity of acid which combined with one atom of base. Liebig commented that he had discovered nine organic acids which, like phosphoric and arsenic acids, did not follow this rule. Indeed the tribasic acids such as citric, cyanuric, tannic and meconic acids showed a perfect analogy with phosphoric acid. Furthermore, he was able to extend the analogy between the different phosphoric acids and tartaric acid together with its pyroderivatives. He explained that phosphoric acid was the model for much of his work. Taking the salt $\text{Na}^{\cdot}\text{P}^{\ddot{\cdot}\ddot{\cdot}}$ or the acid $\text{H}^{\cdot}\text{P}^{\ddot{\cdot}\ddot{\cdot}}$ ($3\text{NaO}, \text{P}_2\text{O}_5$ or $3\text{H}_2\text{O}, \text{P}_2\text{O}_5$), one atom of base must be joined to,

159. *ibid.* pp.35-36.

160. *ibid.* pp.35-36.

161. *ibid.* pp.37-38.

two-thirds of an atom of phosphorus, and to five-thirds of an atom of oxygen, which he noted: "contradicted the best-founded laws of the atomic theory." 159

Thus, he demolished Berzelius's criterion for the atomic weight of an acid, by arguing that one atom of phosphoric acid was saturated by three atoms of base, for example water or soda. He included the formulae of the common phosphates from the "very meritorious works of Graham." 160 This reference lacked generosity but it is probable that Leibig believed that Graham had not interpreted his work sufficiently because he commented: "This explanation certainly shows us the relation existing between the hydrates and the salts of these acids, but without indicating to us at all why the expulsion of one or two atoms of base changes the properties of the acid in such a striking way, why one of the hydrates contains three atoms of water whilst the others contain only one or two, why the acid of one atom [of water] put in the presence of water does not take up two other atoms [of water] at once." 161

Liebig suggested an alternative view of the composition of the three phosphoric acids. He conceded that this view did not represent the true constitution of these acids but it provided a useful analogy with tartaric acid and its derivatives. If common phosphoric acid could be expressed as $2P + 3Aq$, where $2P$ equalled one atom of anhydrous phosphoric acid P^2O^5 or $2PO^{2\frac{1}{2}}$ and $Aq = H^2O$, then pyrophosphoric acid and metaphosphoric acids could be written with the same saturation capacity. Pyrophosphoric acid was saturated by two atoms of base, that is $P^2O^5 \equiv 2H^2O$ or $PO^{2\frac{1}{2}} \equiv 1H^2O$, or $3PO^{2\frac{1}{2}} \equiv 3H^2O$, so this acid could be written as $3P + 3Aq$. Metaphosphoric acid was saturated by one atom of base or $P^2O^5 \equiv 1H^2O$ which could be written as $6P + 3Aq$. This view allowed Liebig to explain how one could transform, as desired, metaphosphate of soda into the pyrophosphate or common phosphate by a dry fusion with fixed amounts of soda. He explained that phosphoric acid must be a volatile or easily-decomposed acid. It could therefore be removed by combination with caustic soda without any

162. It may be useful to compare Graham's formulae with those of Liebig, op.cit. (158) p.39.

	<u>Graham</u>	<u>Liebig</u>
Common phosphoric acid	$\text{H}^{\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{P}}}}_3$ or $3\text{HO},\text{PO}_5$	$\text{H}^{\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{P}}}}_3$ or $3\text{HO},\text{P}_2\text{O}_5$ or $2\text{P} + 3\text{Aq}$
Pyrophosphoric acid	$\text{H}^{\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{P}}}}_2$ $2\text{HO},\text{PO}_5$	$\text{H}^{\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{P}}}}_3^{3/2}$ $3\text{HO},\text{P}_3\text{O}_{7\frac{1}{2}}$ $3\text{P} + 3\text{Aq}$
Metaphosphoric acid	$\text{HP}^{\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{P}}}}$ HO,PO_5	$\text{H}^{\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{P}}}}_3$ $3\text{HO},\text{P}_6\text{O}_{15}$ $6\text{P} + 3\text{Aq}$

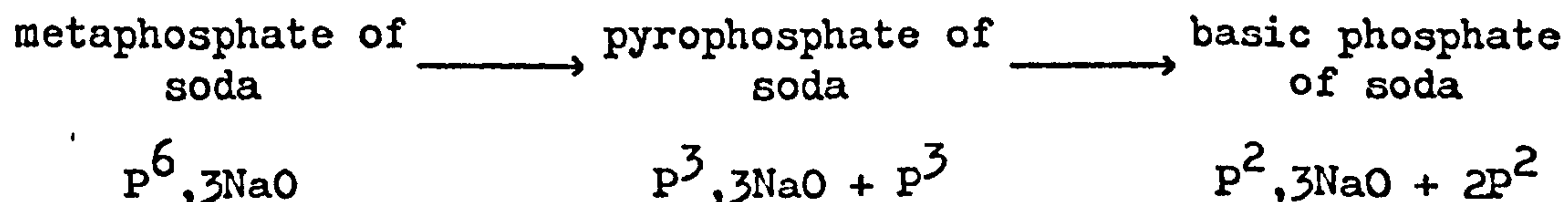
(where
 $2\text{P} = \text{P}_2\text{O}_5$
or
 $\text{P} = \text{PO}_{2\frac{1}{2}}$)

163. Liebig, op.cit. (158) p.55.

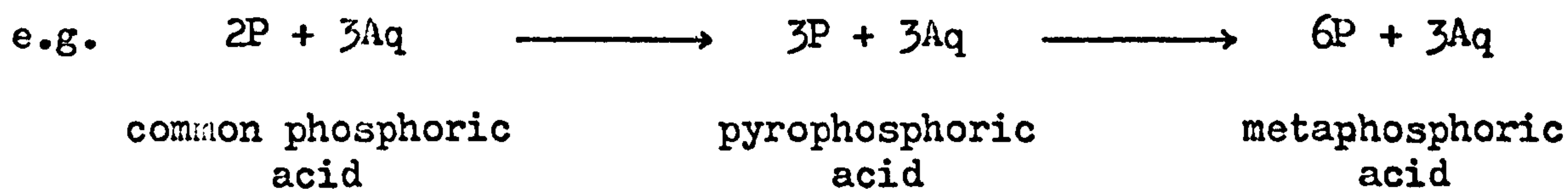
164. Berzelius wrote to Liebig about organic acids and commented:- "You link the phenomena of Graham's work on phosphoric acid with Frémy's present work on tartaric acid. Your parallel is sweet and correct but these phenomena belong to a different order with regard to the water lost by cyanurates, tartrates and citrates. If it was not so, hydrated tartaric acid, by heating, would offer a perfect analogy to tartar emetic on heating, but they are not similar. This confuses the issue. With regard to monobasic, bibasic and tribasic acids, you place great store on the properties of salts to lose water on heating without further decomposition. You assume that this water was contained previously in the compound and this throws out the whole theory." Letter from Berzelius to Liebig, May 4th 1838. (Liebig-Berzelius correspondence op.cit. (146) pp 158-161). Clearly Berzelius was not prepared to accept polybasic acids either in the form of Graham's phosphoric acids or Liebig's organic acids.

165. Liebig, op.cit. (158) pp.40-41.

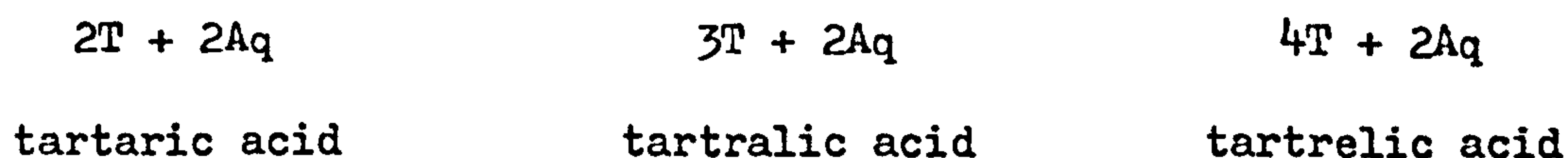
change in the saturation capacity. For example consider the conversions:



where $P^2 = P^2O^5$.¹⁶² The metaphosphate of soda contained all the acid in its radical; the pyrophosphate of soda contained half of the acid in its radical, and half outside; and the basic phosphate of soda contained a phosphate of soda combined with two atoms of anhydrous phosphoric acid outside. He assumed that this outer anhydrous phosphoric acid had no acidic properties. Essentially Liebig was interpreting the phosphoric acids and their salts in terms of isomerism in order to develop an analogy with tartaric acid and its salts. He also explained the reverse transformation of phosphoric acid into the pyro and meta acids. A new quantity of phosphorus and oxygen entered into the radical of the acid, in such a way, that the atomic weight rose without altering the saturation capacity



The comparison with tartaric acid and its pyro-derivatives was as follows:



where $2T = C^8H^8O^{10}$.¹⁶³

To determine the correct constitution of an acid it was important to be able to ascertain the basicity of the acid. This often involved a doubling or tripling of the previous formulae of organic acids, for example tartaric and citric acids, whose formulae were doubled and tripled respectively.¹⁶⁴ Liebig followed Graham's work closely in this assignment. The whole concept of neutrality was imprecise; which one of the salts of phosphoric acid was the neutral salt, Liebig asked? All that could be said was that phosphoric acid could be saturated by one, two, or three atoms of base.¹⁶⁵ Liebig used two guiding principles derived from Graham's researches. Firstly, to find the basicity of an acid, prepare its silver

166. *ibid.* p.68. Liebig had developed his views on reduction of silver oxide and hydracids in his joint work with Pelouze on mellitic acid. See Ann.de Ch. 2 Ser.63 (1836) pp.125-131.

167. Liebig, *op.cit.* (158) p.42.

168. *ibid.* see pp.70-93.

salt; then use the principle that each atom of basic water in the acid would be replaced by one atom of silver oxide. Liebig interpreted this reaction as a reduction process. If acids were considered as hydracids, it was easy to see why silver oxide could replace all the hydrogen in an acid, whereas potash could not. This was because silver oxide, unlike potash, was easily reduced by hydrogen. Secondly, bibasic and tribasic acids could form 'double' salts in which one molecule of acid was joined to two or more bases from the same family. These salts were not resolvable into two separate salts. On the contrary, unibasic acids¹⁶⁶ (this was the term Liebig used) either did not give double salts or, if they did form them, they would be capable of separation into two different salts which crystallised separately. Unfortunately, this latter principle was not wholly reliable. It led Liebig to classify sulphuric acid as unibasic; on the other hand it allowed him to decide correctly that tartaric acid was bibasic from the constitution of Rochelle salt and also that fulminic acid was bibasic from the double fulminate of silver and potash. Liebig emphasised the importance of the principle of 'double salt' formation when he wrote: "I regard this character as decisive for the constitution of these acids and of all those which form similar combinations to those of phosphoric acid."¹⁶⁷

Thus, Liebig extended Graham's concept of polybasicity from the phosphoric acids to all the organic acids, classifying them into three groups: unibasic, bibasic, or tribasic acids, as Graham had done for the phosphates.

Finally, Liebig turned to the theory of hydrogen acids, which he attempted to justify with great care.¹⁶⁸ He recognised that the origins of this theory were to be found in the work of Dulong on oxalic acid and also in the suggestions of Davy on the nature of chloric and iodic acids. On this theory, acids were radicals joined to hydrogen and salts were radicals joined to a metal. This differed from the generally-accepted dualistic view by which acids were represented as anhydrous acids joined

169. *ibid.* pp.84-86.

Liebig used a curious justification for the hydrogen acid theory (*ibid.* pp.74-75). He suggested that sulphocyanic acid was either $\text{H}^2\text{S}, \text{Cy}^2\text{S}$ on the dualistic theory or it was $\text{H}^2 + \text{Cy}^2\text{S}^2$ on the Davy hydrogen acid theory. Now its lead salt, lead sulphocyanide [thiocyanate] would therefore be either $\text{PbS}, \text{Cy}^2\text{S}$ or $\text{Pb} + \text{Cy}^2\text{S}^2$ on the Davy theory. Liebig argued that the latter formula must be correct because, when hydrogen sulphide was bubbled through a solution of this salt, a black lead sulphide precipitate was deposited and this would not happen if PbS already existed in the salt. This obscure example was unsatisfactory because many metallic oxides, which pre-existed in salts, could be precipitated by potash e.g. CuO from $\text{CuO}.\text{SO}_3$. This criticism was made by Alexander Crum Brown in his careful review of this work. See A. Crum Brown, 'On the basicity of acids' 4th Triennial Graham lecture, 5th May 1890, Proc.Phil.Soc.Glasgow 21 (1890) pp.69-91.

It is interesting to see that these theories still caused difficulties until there was a clear appreciation of ions in solution; Crum Brown's argument, however, is a valid criticism which might have been used against Liebig by his contemporaries, but it does not seem to have been raised.

170. MS. letter from Liebig to Pelouze (unpublished), 20th November 1837. *op.cit.* (151).

to water, and salts were anhydrous acids joined to metallic oxides.

Liebig argued that the saturation capacity of an acid was simply explained on the hydracid theory as the number of hydrogen atoms joined to the acid radical. It could be determined by the reduction of silver oxide and it was not related to the oxygen-content of the anhydrous acid as Lavoisier and Berzelius had thought.

On the hydrogen acid theory, the three phosphoric acids were written by Liebig as follows:¹⁶⁹ Phosphoric acid $P_2O_8 + H^6$, pyrophosphoric acid $P_2O_7 + H^4$ and metaphosphoric acid $P_2O_6 + H^2$. Liebig was convinced that the true constitution of the phosphoric acids was obtained by representing them as hydracids. He was carried away in a burst of enthusiasm for his theory of hydracids when he wrote to Pelouze that: "the ordinary definition of phosphoric acids teaches us nothing at all, but $P_2O_8 + 6H$, $P_2O_7 + 4H$ and $P_2O_6 + 2H$ explain all and are mentally satisfying."¹⁷⁰

Liebig had made a valuable contribution towards a better understanding of the constitution of organic acids. There can be little doubt that he drew inspiration and guidance in part from Graham's earlier researches. Although he wrote to Graham describing his own work on organic acids, he did not lay any emphasis on the theory of hydracids; indeed he did not even mention this view! Thus Liebig wrote: "You will see my work on the organic acids in the journal and the work with Wöhler on uric acid. I am very happy that my research concerning the salts of organic acids has been developed by you in your paper. From all this one sees that the present theories have left much unexplained and the [saturation] concept given by Berzelius for the phosphoric acids is positively wrong and that these acids are not a single exception to the rule. For we have just obtained more exceptions to the rule with our experiments than it could permit. I have shown that nine organic acids are similar in their salts to phosphoric and arsenic acids and as a rule which is to be established that the main characteristic of an acid, which is neutralised by one atom of base, is that the double salt, is formed

171. MS. letter from Liebig to Graham, dated 8th August 1838 (unpublished),
Gesellschaft Liebig-Museum, Giessen.

172. Graham, Elements of Chemistry 1st.edn. (London, 1842) p.160.
(probably written in 1838).

173. *ibid.* p.161 (probably written in 1838).

with bases which are not isomorphous to one another and whose compounds with acids contain no saline water." 171

The challenge to Graham's views was now presented by the hydracid interpretation of his work rather than the challenge of isomerism. How did he react to this new challenge? In short, Graham was prepared to accept this new interpretation. He observed that Davy had suggested that salts might be binary compounds and "it is, therefore, deserving of serious consideration." 172 He then compared the formulae of acids and salts on the dualistic theory with those on the hydracid theory. He wrote:-

"old view:

Hydrated sulphuric acid or sulphate of oxide of ... $\text{HO} + \text{SO}_3$

Sulphate of soda or sulphate of oxide of sodium ... $\text{NaO} + \text{SO}_3$

new view:

Sulphatoxide of hydrogen $\text{H} + \text{SO}_4$

Sulphatoxide of sodium $\text{Na} + \text{SO}_4$." 173

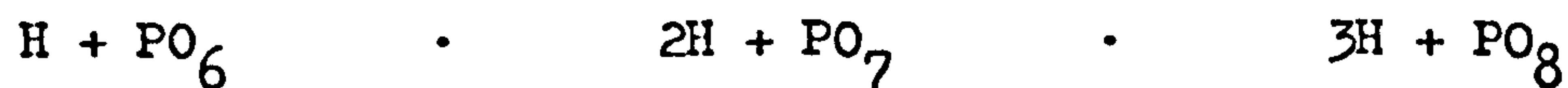
Graham chose the name 'sulphatoxide' for the new radical SO_4 . He referred to the 'binary theory of salts', rather than to the theory of hydrogen acids, because acids could be included as a special case of salts. He accepted that the binary theory had a number of advantages. Firstly, it included both chloride of sodium and sulphate of soda in the same class. Secondly, it accounted for basicity easily and thirdly, it explained more naturally the displacement of hydrogen from acids, by metals. He pointed out that the most serious objection to the binary theory was the creation of so many hypothetical radicals. In addition he wrote that "the peculiarities of the salts of phosphoric acid are supposed to be inimical to the new view. That acid forms three different and independent classes of salts, containing respectively one, two and three atoms of base to one of acid. On the binary theory, these three classes of salts must contain three different radicals, combined respectively with one, two and three

174. *ibid.* pp.165-166 (probably written in 1838).

175. Undated MS. note by Graham in the volume of Graham Autograph Letters and Notes. Wellcome Library.
This particular note appears to date from 1841, judging from a reference to an article in L'Institut dated June 1841, written at the head of these notes.

176. W. Gregory, Elements of Chemistry by the late E. Turner, edited by W. Gregory, 8th.edn. (London, 1847) 570-571; W. Gregory Outlines of Chemistry (London, 1847) See introduction p.v.

atoms of hydrogen or metal



Such radicals and such compounds with hydrogen startle us from their novelty, but it may be questioned whether they are really more singular than the anormal classes of phosphates, containing several atoms of base, for which they are substituted In conclusion, it may be stated that neither view of the constitution of the oxygen-acid salts, rests on demonstrative evidence - they are both hypotheses and are both capable of explaining all the phenomena of salts. But to whichever of them we give a preference, we can scarcely avoid using the language of the old theory in the present state of chemical science." 174

Later, in an unpublished note, Graham remarked that it did not occur to the partisans of either theory that both could be true. Taking the example of sulphuric acid he suggested that a number of attractions must be considered in any theory of the constitution of this acid, for example: sulphur for oxygen, hydrogen for oxygen, SO_3 for HO , S for O_4 , and this association SO_4 , for H . This seemed to be more "consonant with nature than a single dominant affinity. Hence it is the duty of chemists to discover all the attractions and not to develop one mode of association of atoms or one theory of its structure only, but to find of how many theories of constitution it fulfils the conditions. Still there are types of each kind of combination in which it [one particular attraction?] is fully-developed." 175

Therefore the binary theory of salts was a perfectly good alternative to the dualistic theory, but Graham still preferred to base his work on the well-established dualistic theory. In an extension to his unpublished note Graham viewed an acid as a molecular type and considered all the possible attractions, and he thereby incorporated all previous theories.

Other chemists were persuaded that the binary theory was preferable. They included Kane, Gregory,¹⁷⁶ and Daniell. Kane was clearly unhappy

177. R. Kane, Elements of Chemistry 2nd.edn. (Dublin,1849) 589.
178. J. F. Daniell, 'Abstract of Prof.Daniell's papers on the electrolysis of secondary compounds,' Phil.Mag. 3 Ser.17 (1840) 349-356. The full papers appeared in Phil.Trans. 129 (1839) 97-112 and 130 (1840) 209-224. Graham's student George Wilson also obtained evidence for the binary theory of salts and for the 'quasi-metallic character' of hydrogen. See G. Wilson: 'Experimental demonstration of the certain existence of haloid salts in solution'. B.A.Report (1839) 41-43, also Athenaeum (1839) p 619.
179. J. F. Daniell and W. A. Miller, 'Additional researches on the electrolysis of secondary compounds' read before R.S. February 25th 1844. Phil.Mag. 3 Ser.25 (1844) p.175.

with the old theory. He wrote that "the difference of properties of phosphoric acid, in its three states is totally inexplicable, on the idea of there being merely three degrees of hydration. Nitric acid forms three hydrates, but when neutralised by potash, it always gives the same saltpetre." ¹⁷⁷ In 1839, following Liebig's powerful advocacy of the binary theory of salts and acids, Daniell obtained some experimental evidence in support of the binary theory through his studies of the electrolysis of salt solutions. ¹⁷⁸ This research was extended further with the help of W. A. Miller. By the electrolysis of solutions of phosphates, Daniell and Miller established that the three hydrates of phosphoric acid were essentially different acids. They wrote the three acids as: $H + P_2O_6$ (protohydrate), $H_2 + P_2O_7$ (deuto-hydrate) and $H_3 + P_2O_8$ (trithydrate). The radicals of these acids could be disengaged from their respective salts by a voltaic current. All the acid radicals travelled to the positive electrode. There they were tested with silver nitrate or albumen. The tritoxophosphion, P_2O_8 , gave a yellow silver precipitate; the deutoxyphosphion, P_2O_7 , gave a white silver precipitate and the monoxyphosphion, P_2O_6 , precipitated albumen. Therefore, in 1844, they concluded that, "this establishes by independent testimony Professor Graham's theory of the phosphates and it is with pleasure that we also observe that his view of the basic character of water in certain saline compounds is confirmed by the electrolysis of the three tribasic phosphates; ($2NaO,HO,P_2O_5$; $3NaO,P_2O_5$ and NaO,NH_4O,HO,P_2O_5) from all of which the same acid was separated and in two cases water was one of the three equivalents of base. In our corresponding [binary theory] view, one of the three equivalents of the metals was represented by hydrogen." ¹⁷⁹

The role of water in salts had been a continuous preoccupation for Graham since his researches on the phosphoric acids and their salts. Between September 1833 and May 1834, he discovered that one atom of water was essential to the constitution of the sulphates of zinc, magnesium,

180. Graham, Notebook B, op.cit. (79).
Later, in 1846, J. Isidore Pierre, a research student of Dumas, tried to challenge Graham's work on the dehydration of zinc sulphate by claiming that all seven atoms of water were equally easy to remove. Thus he argued that both the concept of constitutional (or saline) water and the formation of double salts by substitution were erroneous. See Pierre, 'On double salts of the magnesian group'. Phil.Mag. 3 Ser.28 (1846) 235. Graham quickly replied to this attack, defending both his experiments and theory. He attributed Pierre's incorrect analysis to mechanically-trapped water and quoted independent testimony of his own analyses by George Fownes. Graham concluded correctly that the case was answered. See Graham, 'Reply to M. Pierre' Phil.Mag. 3 Ser.28 (April 1846) 289-291.
181. Graham, British Association Report (September 1834), op.cit. (105), see Researches.349.
Liebig accepted Graham's distinction between basic water, saline water or water of hydration as Liebig called it, and water of crystallisation. Liebig argued that saline water was not present as such in $MgSO_4 \cdot H_2O$. This compound was really $SO_4^{4-}H^2 + MgO$ in which the magnesium oxide was too difficult to reduce easily by the action of heat; but, on the other hand, H_2O could be replaced by another salt to give a double salt such as the sulphate of magnesia and potash $SO_4^{4-}Mg + SO_4^{4-}K$. He referred to the "beautiful experiments of Professor Graham" on the removal of water from magnesium sulphate crystals. Liebig, 'On the constitution of organic acids' Liebig Ann. 26 (1838) p 144 or Ann.de Ch. 2 Ser.68 pp 79-80 and Liebig's Giessen lectures Winter Session 1844 'Theory of acids' The Lancet (1844) pp 573-574.
182. Graham, 'On water as a constituent of salts', read to R.S.E. January 5th 1835, Edinburgh R.S. Trans. 13 (1836) 297-314, also Phil.Mag. 3 Ser.6 (1835) 327-334, 417-424 and Researches.352-365.

manganese, iron, nickel, copper and cobalt.¹⁸⁰ Graham referred to these sulphates collectively as the 'magnesian' sulphates. He found that hydrated zinc sulphate lost six atoms of water at 65°F, when it was placed over concentrated sulphuric acid in vacuo. However, the last atom of water was retained up to 410°F. Conversely, anhydrous zinc sulphate regained one atom of water when it was moistened, or slaked, and heat was evolved.

In the British Association report of 1834, Graham wrote the constitution of this salt as $\overset{\cdot}{\text{H}}\overset{\cdot\cdot}{\text{Zn}}\overset{\cdot\cdot}{\text{S}} + 6\overset{\cdot}{\text{H}}$ and commented that "this last atom of water appears to discharge a basic function in the constitution of the salt, and affords a clew [sic] to the disposition of this sulphate to form double sulphates. Sulphate of zinc combines with sulphate of potash and forms a well-known double salt, in which the basic water of the sulphate of zinc is replaced by sulphate of potash, without further change."¹⁸¹ He wrote the formula of this double salt as $(\overset{\cdot\cdot}{\text{K}}\overset{\cdot\cdot}{\text{S}})\overset{\cdot\cdot}{\text{Zn}}\overset{\cdot\cdot}{\text{S}} + 6\overset{\cdot}{\text{H}}$ and noted that the six atoms of water were retained with a somewhat greater force than in zinc sulphate itself; but even the double salt became anhydrous in vacuo at 212°F.

In January 1835 Graham read to the Royal Society of Edinburgh his first major paper on the role of water in salts.¹⁸² He distinguished three different types of water: basic water; saline water; and water of crystallisation. Basic water was absolutely essential to the constitution of a salt and it could be replaced by an alkaline base like soda, for example the basic water in $\overset{\cdot}{\text{Na}}\overset{2\cdot\cdot}{\overset{\cdot\cdot}{\text{H}}\overset{\cdot\cdot}{\text{P}}}$ could be replaced, to give $\overset{\cdot}{\text{Na}}\overset{3\cdot\cdot}{\overset{\cdot\cdot}{\text{P}}}$ or $\overset{\cdot}{\text{Ag}}\overset{3\cdot\cdot}{\overset{\cdot\cdot}{\text{P}}}$, by substitution of an alkaline base. This substitution differentiated basic water from the remaining water contained in salts. Saline water was also essential to the constitution of salts and it was recognised because it was replaced by a salt, but not by an alkaline base. Graham used the concept of saline water in his revised explanation of the formation of double salts. For example he now wrote hydrated zinc sulphate as $\overset{\cdot\cdot}{\text{Zn}}\overset{\cdot\cdot}{\overset{\cdot\cdot}{\text{S}}\overset{\cdot\cdot}{\text{H}}} + \overset{\cdot}{\text{H}}^6$. It contained one atom of saline water which could

183. Faraday, 'On electrochemical decomposition', 7th Series (1834), paragraphs 698-703, pp 205-206 of Faraday, Experiment Researches in Electricity (London, 1839) Vol.1.
Graham argued later that the double chlorides e.g. $KCl + CuCl_2 \cdot 2H_2O$ were not to be regarded as simple salts, where one of the chlorides behaved as an acid and the other as a base; they were true double salts. See Graham, Elements of Chemistry, (London, 1841) p 173. Bonsdorff had previously advocated the view that double chlorides were combinations of acids and bases. See Ann.der.Phys. 17 (1829) 115,247; 19 (1830) 336, but Berzelius like Graham regarded them as double salts. Jahresbericht. 7 (1828) 137.

184. Graham, op.cit. (182) Researches. 356.

be replaced by sulphate of potash to form the double salt $\dot{\text{Zn}}\ddot{\text{S}}(\ddot{\text{K}}\ddot{\text{S}}) + \dot{\text{H}}^6$. Finally, water of crystallisation was that water which was only held by a weak affinity. It was easy to remove this water at low temperatures and it was usually removed by heating to 212°C . Water of crystallisation could not be replaced by salts or bases.

Graham had introduced the concept of saline water to enable him to give an unambiguous definition of double salts. This extension of the role of water allowed him to clarify the distinction between polybasic salts like phosphates and true double salts. All true double salts were separable into two simple salts. This was not the case with polybasic salts like phosphate of soda and ammonia. Graham was not satisfied with the Berzelian dualistic view of a double salt in which one salt was electropositive and the other electronegative. Indeed, Faraday had been unable to separate double salts by electrochemical decomposition.¹⁸³

According to Graham, double salts were derived from neutral salts by the substitution of an atom of saline water by an atom of salt. Graham extended the class of double salts to include acid salts, like bisulphate of potash, or $\dot{\text{H}}\ddot{\text{S}}(\ddot{\text{K}}\ddot{\text{S}})$. The latter salt was supposedly derived from sulphuric acid of specific gravity 1.78, that is the monohydrate $\dot{\text{H}}\ddot{\text{S}}\dot{\text{H}}$. Graham explained that the first atom of water in this acid was basic, whereas the atom of water written at the end of the formula was saline water. The basic water was so strongly bound in this acid that it could only be removed by an atom of alkaline base.

Concentrated sulphuric acid $\dot{\text{H}}\ddot{\text{S}}$ contained one atom of basic water and Graham explained that concentrated sulphuric acid "in chemical character is an incomplete body. When it dissolves in any menstruum, we may be sure that it has first acquired its second or saline atom of water, or something in its place. Hence a set of reactions of sulphuric acid, which are peculiar to its concentrated condition, upon alcohol and many organic bodies."¹⁸⁴

A particularly striking example of the role of saline water in salts

185. E. Turner, Elements of Chemistry, 5th.edn., (London, 1834) 1037-1039 and in the 6th.edn. (London, 1842) see the inorganic section revised by Wilton Turner pp.631-632.
186. R. Kane, Elements of Chemistry, 1st.edn. (Dublin, 1841) 684-690.
187. Berzelius, Jahresbericht. 16 (1837) 122-123.
188. Graham, 'Researches in reference to the constitution of certain compounds as far as respects their constituent water.' British Association meeting, Dublin, August 11th 1835, Phil.Mag. 3 Ser.7 (1835) p 400.
189. James Young (Graham's laboratory assistant) Diary, August 1835, MSS. Fo. 48. Andersonian Library, University of Strathclyde.
"Mr. Graham - sulphate of water, oxalate and nitrate - the foundation of his view is that all the salts of these acids contain the same water as the acid. Graham got off well. Dalton tried to do Graham about sulphate of water and posed him pretty well."
190. Graham, 'Inquiries respecting the constitution of salts. Of oxalates, nitrates, phosphates, sulphates and chlorides,' Phil. Trans. 127 (1837) 47-74, received June 23rd 1836 and read for Graham by Richard Phillips on November 23rd 1836. See also Researches. 367-397.

was seen in gypsum according to Graham. At room temperature, gypsum crystals contained one atom of saline water and one atom of water of crystallisation i.e. $\overset{\cdot}{\text{Ca}}\overset{\cdot\cdot}{\text{S}}\overset{\cdot\cdot}{\text{H}} + \overset{\cdot}{\text{H}}$. The water of crystallisation was lost when gypsum was placed in vacuo over sulphuric acid at 212°F . The atom of saline water in $\overset{\cdot}{\text{Ca}}\overset{\cdot\cdot}{\text{S}}\overset{\cdot\cdot}{\text{H}}$ was then removed by heating to 270°F . The saline water could also be replaced by sulphate of soda to give a double salt $\overset{\cdot}{\text{Ca}}\overset{\cdot\cdot}{\text{S}}(\overset{\cdot}{\text{Na}}\overset{\cdot\cdot}{\text{S}})$ which existed naturally as the mineral called Glauberite. Between 270°F and 300°F Graham thought that there was a 'hiatus' in the dehydrated calcium sulphate because it was still capable of combining with added water. He referred to calcium sulphate at this stage as a *débris* composed of nothing but sulphuric acid and lime. He wrote its formula to show this hiatus $\overset{\cdot}{\text{Ca}}\overset{\cdot\cdot}{\text{S}}-$. Above 300°F true anhydrous calcium sulphate $\overset{\cdot}{\text{Ca}}\overset{\cdot\cdot}{\text{S}}$ was formed which had no inclination to combine with water.

These views on the role of water in salts were well-received in England and they were described by Turner¹⁸⁵ and Kane¹⁸⁶ in their textbooks. Berzelius found that Graham's researches on the role of water in salts were 'interesting and worthy of further development' but he could not see where Graham's theory was leading him.¹⁸⁷

At the meeting of the British Association in August 1835, Graham gave an account of his views on the water in: acid hydrates; oxalic acid; and its salts.¹⁸⁸ Interestingly, he was challenged at this meeting by Dalton for regarding sulphuric acid as a hydrate.¹⁸⁹ In recognition of his work, however, Graham was requested by the British Association to report back on the present state of knowledge of salts and their constitution.

In June 1836, Graham completed a paper on the constitution of salts which was read before the Royal Society of London.¹⁹⁰ The discovery of the polybasic nature of the phosphoric acids and their salts necessitated a complete reappraisal of the classification of salts. It had become more difficult to define precisely the terms: neutral; acidic; basic; and double salts. In this paper Graham attempted to classify nearly all

191. E. Turner, 'On the volatility of oxalic acid'. Phil.Mag. 2 Ser.9
(1831) 161-163.

the known salts as neutral salts. He suggested that neutral salts were those in which the number of atoms of acid was equal to the number of atoms of oxygen found in one atom of base, e.g. NaO, SO_3 ; $\text{Hg}_2\text{O}, \text{SO}_3$; $\text{SnO}_2, 2\text{SO}_3$; $\text{Fe}_2\text{O}_3, 3\text{SO}_3$. The only exceptions to this class of 'normal salts' were certain phosphates and arseniates and possibly also the phosphites. He now suggested that the normal phosphates were the metaphosphates which contained: one atom of protoxide base joined to one atom of acid, for example NaO, PO_5 , which he called monobasic phosphates. The other classes of phosphates were true sub-salts because they contained an excess of base. Graham introduced a new terminology for these salts calling them bibasic and tribasic phosphates respectively, for example $2\text{NaO}, \text{PO}_5$ and $3\text{NaO}, \text{PO}_5$. This new approach to classification involved an important change of view concerning the phosphates. The 'neutral' phosphate was now the metaphosphate of soda, and common phosphate of soda although it was almost neutral to indicators was formally classified as a basic or sub-salt.

In essence Graham was returning to the Berzelian concept of a neutral salt but he extended the concept to include acidic, basic, and double salts. As a guiding principle in the constitution of salts Graham chose the close analogy between the hydrated acid and the magnesian salt of the acid. A magnesian salt was one which contained magnesia MgO or an isomorphous metallic oxide, for example ZnO , CuO , PbO , NiO , FeO etc. There was a close resemblance between water and these magnesian oxides. Graham developed this analogy in his persuasive arguments on the constitution of salts. His conclusions were often fruitful although they could occasionally be misleading as we shall see.

Graham commenced his paper on the constitution of salts with an examination of the oxalates. Edward Turner had shown in 1831 that oxalic acid crystals were $\text{C}_2\text{O}_3 + 3\text{HO}$ and that two equivalents of water were lost when the acid was sublimed at temperatures as low as 212°F .¹⁹¹ Graham found that both hydrated oxalic acid and the magnesian oxalates contained

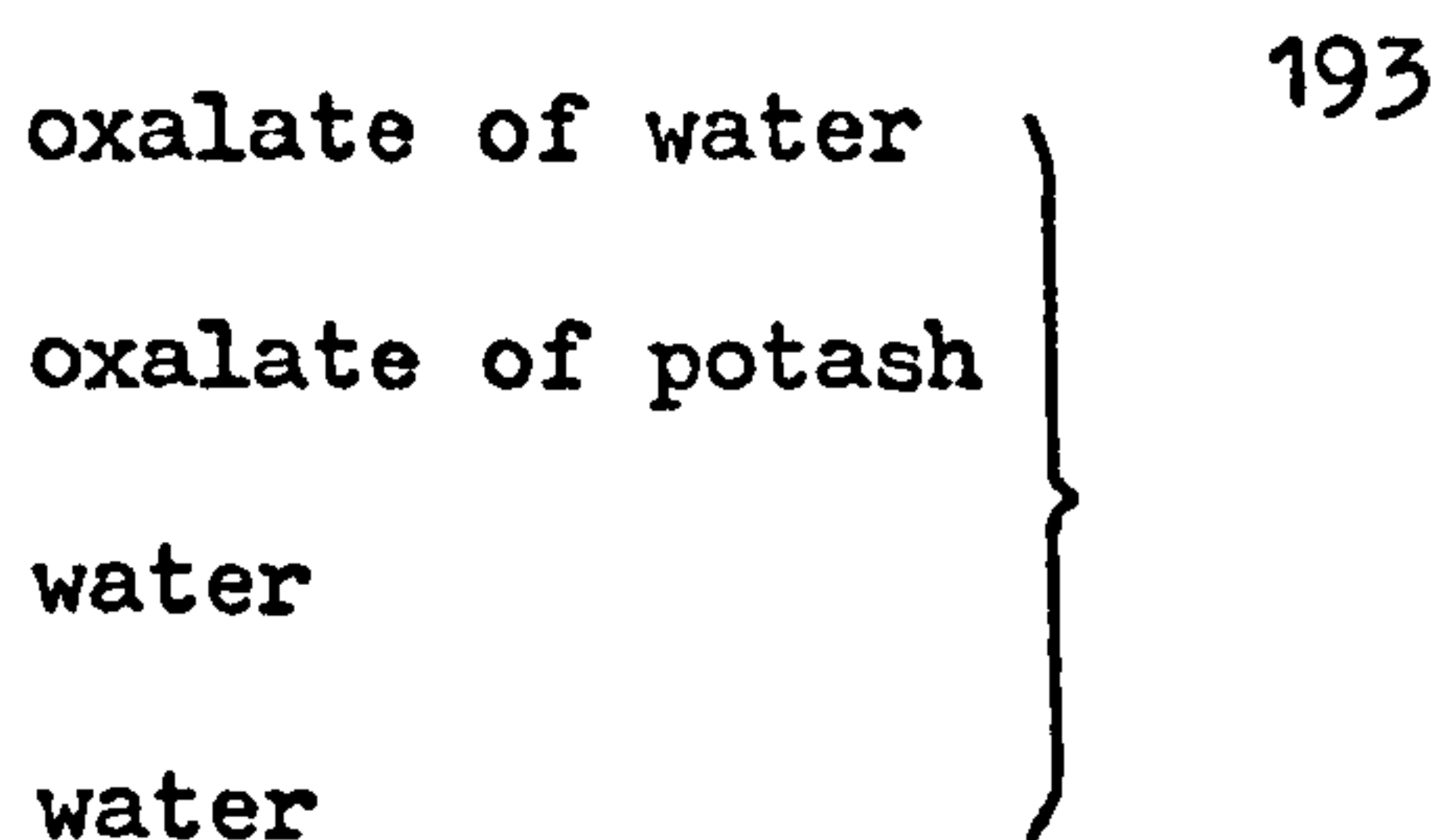
192. Graham, op.cit. (190) Researches.368.

193. Graham, MS. Notebook C (September 2nd 1834 - July 1835) pp 72-73.
Andersonian Library, Strathclyde University.

194. *ibid.* pp 70-71.

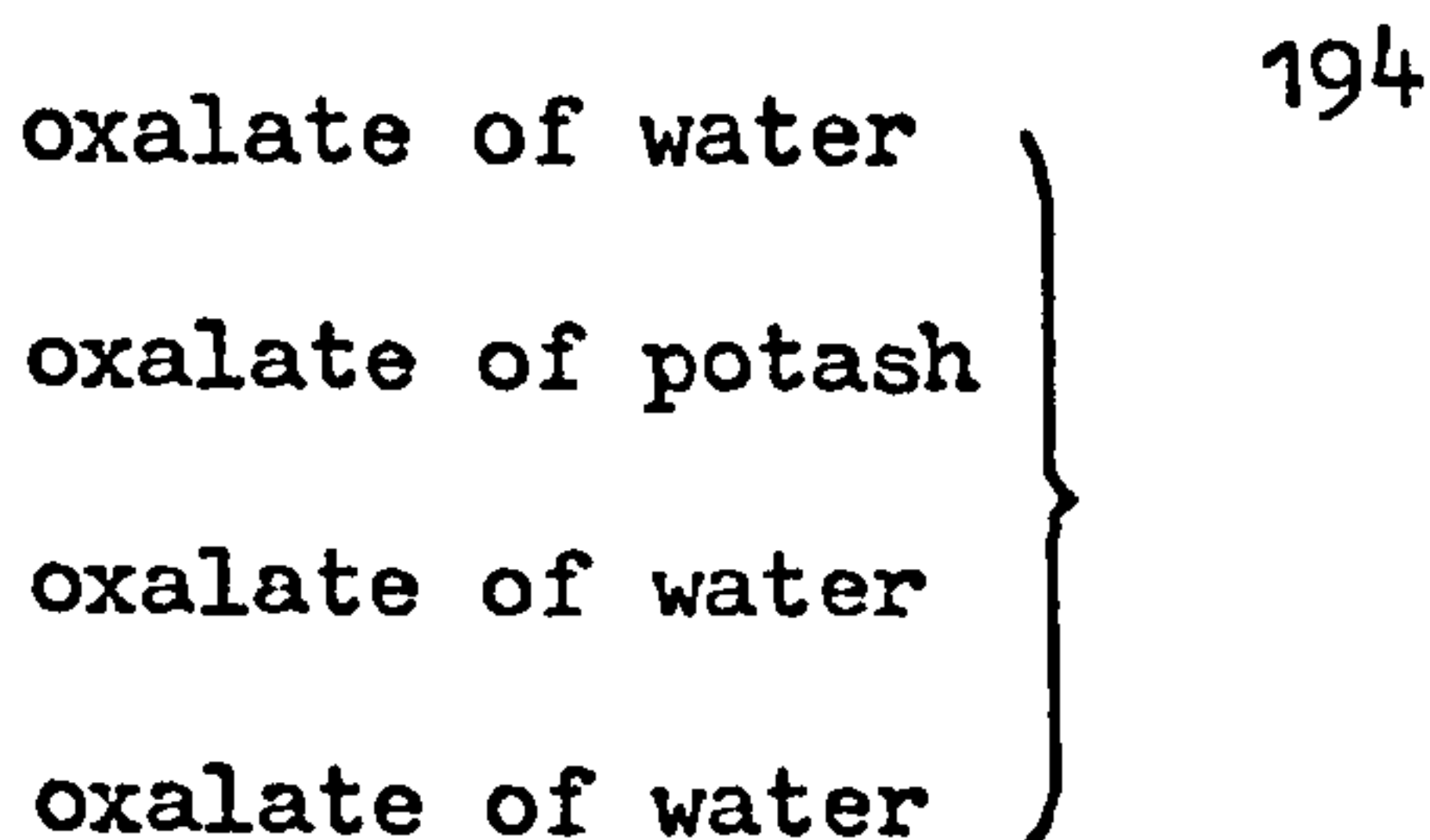
two atoms of constitutional water.¹⁹² He used this new expression 'constitutional water' in place of saline water presumably because he had now discovered that this kind of water could be replaced by acids, and sometimes even by metallic oxides, as well as by salts. Oxalic acid crystals were given the formula $\dot{H}\ddot{C}\ddot{C}\dot{H}^2$, the atom of water written before C_2O_3 was basic water and the two atoms of water at the end were constitutional water. The corresponding magnesian oxalate, $\dot{M}g\ddot{C}\ddot{C}\dot{H}^2$, also contained two atoms of constitutional water, but the neutral oxalate of potash $\dot{K}\ddot{C}\ddot{C}\dot{H}$ only contained a single atom of constitutional water.

With these preliminary formulae established, Graham was able to develop a correct view of the more complex oxalates. This marked an important advance in the formulation of organic acids and their salts. He showed that the acid oxalate of potash, or binoxalate of potash as it was then known, had been incorrectly analysed; it contained three atoms of water and not two as had been previously thought. He derived its formula from the neutral oxalate of potash by substituting one atom of hydrated oxalic acid for the constitutional atom of water in the former compound. This gave



or $\dot{K}\ddot{C}\ddot{C} + \dot{H}\ddot{C}\ddot{C}\dot{H}^2$ as he wrote it in his paper.

Likewise the binoxalate of potash could be substituted further by hydrated oxalic acid to give the quadroxalate of potash, which was



or $\dot{K}\ddot{C}\ddot{C} + \dot{H}\ddot{C}\ddot{C} + 2(\dot{H}\ddot{C}\ddot{C}\dot{H}^2)$.

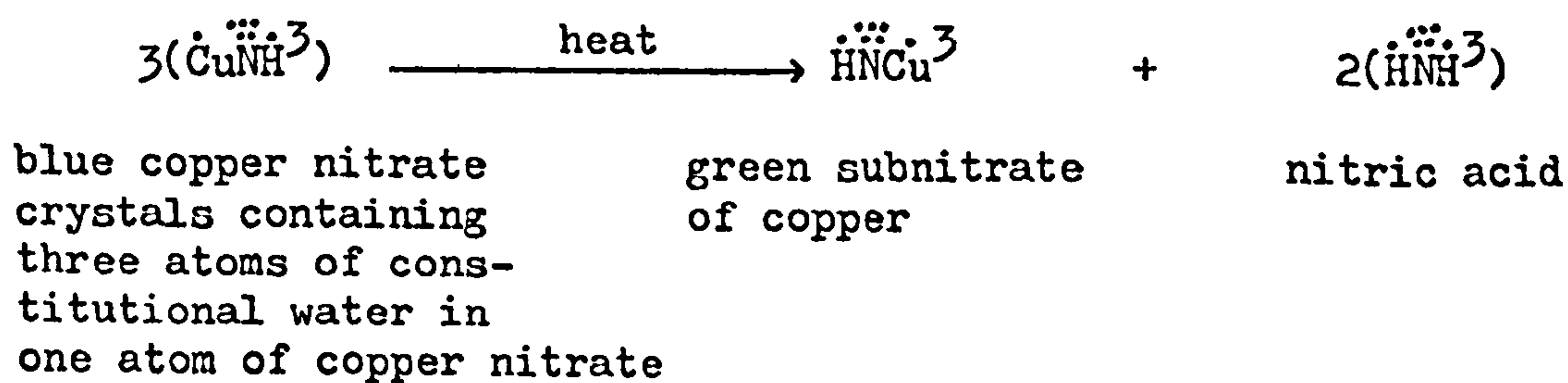
Graham also correctly formulated a number of double oxalates. These included the beautiful grass-green potassium ferrioxalate. He wrote the

195. L. Gmelin, Handbook of Chemistry, translated by Henry Watts, 9 (London, 1852) 158. Gmelin suggested that Wenzel had noticed this salt before Graham: C. F. Wenzel, Lehre von der Verwandtschaft der Körper (1777) p 314. The composition of these double oxalates was confirmed independently by A. Bussy in 1838. See J.de Pharm. 24 (1838) 609-620.
196. H. Rose, 'Concerning the behaviour of anhydrous sulphuric acid joined to metallic chlorides and salts' Pogg. Ann. 38 (1836) 117-123. Graham also referred to the analogous salts formed between potassium chloride and anhydrous chromic acid discovered by Eugène Peligot, e.g. $\text{KCl} + 2\text{CrO}_3$, Ann.de Ch. 2 Ser.52 (1833) 267-275.

formula of this salt as $\overset{\cdot\cdot}{\text{Fe}}\overset{\cdot\cdot}{\text{Fe}}\overset{\cdot\cdot}{\text{C}}\overset{\cdot\cdot}{\text{C}}^3 + 3\overset{\cdot\cdot}{\text{K}}\overset{\cdot\cdot}{\text{C}}\overset{\cdot\cdot}{\text{C}} + \overset{\cdot\cdot}{\text{H}}^6$. With this example Graham thought he had discovered an entirely new salt, but Gmelin mentions that Wenzel had referred to it previously.¹⁹⁵

Acid salts of monobasic acids were not regarded by Graham as exceptions to his rule that most salts were constitutionally neutral. He explained that these salts were simply double salts formed by the substitution of one atom of constitutional water by one atom of acid. Even anhydrous acid salts, like bichromate of potash, were only apparent exceptions to the rule of constitutional neutrality. He argued that the red bichromate of potash should be considered as a binary combination of chromic acid and neutral chromate of potash $(\overset{\cdot\cdot}{\text{K}}\overset{\cdot\cdot}{\text{Cr}})\overset{\cdot\cdot}{\text{Cr}}$ rather than a true acid salt $\overset{\cdot\cdot}{\text{K}}\overset{\cdot\cdot}{\text{Cr}}^2$ containing an excess of acid. To justify this view Graham referred to the salts which Henry Rose had prepared by passing sulphur trioxide over potassium chloride and potassium sulphate.¹⁹⁶ Graham supposed that these salts $\text{KCl}\cdot\text{SO}_3$ and $(\overset{\cdot\cdot}{\text{K}}\overset{\cdot\cdot}{\text{S}})\overset{\cdot\cdot}{\text{S}}$ were examples of a new order of salts in which an anhydrous acid was combined with a neutral anhydrous salt.

Sub-salts or basic salts of monobasic acids were likewise to be regarded as constitutionally neutral. Graham quoted the example of the subnitrate of copper. He suggested that this salt was formed by the substitution of copper oxide for constitutional water. Here the substituted copper oxide was not basic in the salt, but neutral. He argued that when copper nitrate crystals decomposed, on heating to 150°F , the subnitrate was formed thus:-



Because this green subsalt could be heated to 327°F without any decomposition, he decided that it must contain one atom of basic water, in addition to the three atoms of copper oxide which had replaced the constitutional

197. Berzelius, Jahresbericht. 'Salts in general' 20 (1841) 102-109.

198. Graham's views on the neutrality of acid salts and sub-salts were also criticised by J. Denham Smith in 1843. He maintained that in the sub-sulphates of copper the copper oxide could not be neutral but must be basic. (Joseph Denham Smith (1817-1888) was a pupil of Richard Phillips and he became a professional analyst of minerals, and drugs). J. Denham Smith 'On the constitution of subsalts of copper,' read to the Chemical Society, on April 4th 1843. Phil. Mag. 3 Ser. 23 (1843) 496-505.

water. In support of this view he referred to the reaction between concentrated nitric acid $\overset{\cdot\cdot\cdot}{\text{H}}\overset{\cdot\cdot\cdot}{\text{N}}$ and copper oxide. In this reaction, concentrated nitric acid gave only the green subsalt and not the blue salt, because there was no constitutional water in the concentrated acid. A similar subnitrate was also suggested for bismuth; by analogy, it had the formula $\overset{\cdot\cdot\cdot}{\text{H}}\overset{\cdot\cdot\cdot}{\text{N}}\text{Bi}^3$.

Both Graham's theory of the constitutional neutrality of most salts and his classification of salts as monobasic, bibasic, and tribasic, met with a mixed reception. Berzelius reviewed Graham's work on salts in 1841.¹⁹⁷ He accepted that there was some sense in the distinction between constitutional water and water of crystallisation. He repeated his criticisms of Graham's views on phosphates and the phosphoric acids and the extension of these views to explain the constitution of oxalic acid and its salts. He pointed out that, although it was possible to consider oxalic acid and the magnesian oxalates as compounds containing one atom of base, or basic water, and two atoms of constitutional water, it was only a partial explanation. He asked, how was it to be reconciled with the fact that the oxalates of sodium, potassium, and barium each contained one atom of base and only one atom of water? Likewise, a similar problem arose with the nitrates. The nitrates of sodium and potassium both possessed one atom of base and no water and so they could not be assimilated with the magnesian nitrates which took up three extra atoms of water or metallic oxide. Nevertheless, Berzelius agreed that Graham had completed an important piece of research on the water-content of salts, but he was still not prepared to admit that water could assume the role of a base in salts. Similarly, he was disturbed by Graham's view of sub-salts in which water neutralised the acid and not the attached atoms of a metallic oxide.¹⁹⁸

In contrast, Graham's explanation of sub-salts was praised by Kane in 1838 and he mentioned that he had found a yellow subnitrate of mercury which was "a striking example" of the replacement of constitutional water

199. R. Kane, 'Researches on the nature and constitution of the compounds of ammonia' read to the Royal Irish Academy on April 9th, May 14th and 28th, 1838. Trans.R.I.Acad. 19 (1843) 1-91, see pp 14, 65, 83.

200. C. Gerhardt, 'Facts towards a history of nitrates and nitrites'. Ann.de Ch. 18 (1846) 178-188.

Also see the letters of Gerhardt to Laurent in Correspondance de Charles Gerhardt by Marc Tiffenau Vol.1 (Paris, 1918):-

Gerhardt to Laurent 21st October 1845.

"... the facts of Graham on the nitrates cannot be exact. I have already proof of it for the nitrate of copper. Graham represents it as $N^{2O^5}.CuO.3H^2O + 3aq.$ The three equivalents of water are of crystallisation, the $3H^2O$ are not lost without destroying the salt - it is true, but according to me it is $N^{2O^5}.CuO.2H^2O + 4aq.$

Graham had not dried it well enough."

Gerhardt to Laurent 2nd May 1846.

"... I believe that all sub-salts have the constitution, the neutral salt + n times the hydrate and n reaches a maximum for certain salts e.g. for nitrates it is three. Graham is wrong with the sub-nitrate of copper, it is $N.CuO^2 + 3(CuH)O.$ I have not decided the amount of hydrogen. His formula supposes 4% water. I obtain from it 12%."

201. Gerhardt, 'Researches on salts', J.de Pharm. 3 Ser. 12 (July, 1847) 57-67.

by a metallic oxide giving $\text{HO}\cdot\text{NO}_5 + 3\text{HgO}$. 199

However, the theory of sub-salts suffered a setback in 1846 as a result of the researches of Gerhardt.²⁰⁰ He showed that the correct formula for the subnitrate of copper was $\text{N}^2\text{O}^5, 4\text{Cu}^2\text{O}, 3\text{H}^2\text{O}$ and not $\text{H}^2\text{O}, \text{N}^2\text{O}^5, 3\text{Cu}^2\text{O}$ as Graham had supposed. Thus Graham's theory of sub-salts was not supported by experiment. Gerhardt did recognise, however, that there was a difficulty, arising from the discovery of polybasic acids, this was how to define sub-salts precisely. He accepted the distinction drawn by Graham between constitutional water and water of crystallisation and so he represented basic salts in a similar manner to acid salts.²⁰¹ Taking his examples of acid salts from Graham's own researches on oxalates he wrote:-

neutral potassium oxalate	binoxalate of potash	quadroxalate of potash
$\text{C}^2\text{O}^3, \text{K}^2\text{O}$	$\left\{ \begin{array}{l} \text{C}^2\text{O}^3, \text{K}^2\text{O} \\ \text{C}^2\text{O}^3, \text{H}^2\text{O} \end{array} \right.$	$\left\{ \begin{array}{l} \text{C}^2\text{O}^3, \text{K}^2\text{O} \\ \text{C}^2\text{O}^3, \text{H}^2\text{O} \\ \text{C}^2\text{O}^3, \text{H}^2\text{O} \\ \text{C}^2\text{O}^3, \text{H}^2\text{O} \end{array} \right.$

Gerhardt assumed that although sub-salts contained the same constitutional water this water took the place of the acid rather than the base, for example

neutral lead nitrate	sub-nitrate of lead	subnitrate of quadrilead
$\text{N}^2\text{O}^5, \text{Pb}^2\text{O}$	$\left\{ \begin{array}{l} \text{N}^2\text{O}^5, \text{Pb}^2\text{O} \\ \text{H}^2\text{O}, \text{Pb}^2\text{O} \end{array} \right.$	$\left\{ \begin{array}{l} \text{N}^2\text{O}^5, \text{Pb}^2\text{O} \\ \text{H}^2\text{O}, \text{Pb}^2\text{O} \\ \text{H}^2\text{O}, \text{Pb}^2\text{O} \\ \text{H}^2\text{O}, \text{Pb}^2\text{O} \end{array} \right.$

The latter formula corresponded to the newly-corrected formula for the subnitrate of copper ($\text{N}^2\text{O}^5, 4\text{Cu}^2\text{O}, 3\text{H}^2\text{O}$).

Graham accepted Gerhardt's new formula for the sub-nitrate of copper and accordingly modified his theory of sub-salts. He now formulated the sub-salt as $\text{CuO}, \text{NO}_5 + 3(\text{CuO}, \text{HO})$; this formulation allowed him to retain

202. Graham, Elements of Chemistry, 2nd.edn. Vol.1 part 2 (London, 1848) p 195.
As a result of Gerhardt's work Graham had doubts about the corresponding subnitrate of bismuth and so he suggested to J.H.Gladstone, his research student, that he should follow this up. Gladstone confirmed Graham's analysis of the subnitrate ($\text{HO}, \text{NO}_5 + 3\text{BiO}$) but he found that the neutral nitrate did not contain 3HO as Graham had thought but between 3 and 4HO . Therefore Gladstone formulated the neutral nitrate $2(\text{BiO}, \text{NO}_5) + 7\text{HO}$. Memoirs and Proceedings of the Chemical Society 3 (1845-8) 480-485 'On the nitrates of bismuth and copper' read June 21st 1847.
203. Graham, 'Communications on the subject of inorganic salts and in particular on the function which water discharges as an element of their composition,' B.A.meeting at Liverpool, September 13th 1837. Phil.Mag. 3 Ser.11 (October, 1837) 396-398; the same report is found in The Athenaeum (September 23rd 1837) p 695.
204. 'Lettre de M. Liebig à M. Le Président', Comptes Rendus 6 (1838) p 825.
205. The letter, incorrectly-dated, is quoted in Berzelius und Liebig Ihre Briefe von 1831-1845 by Justus Carrière (Munich & Leipzig, 1893) and also in 2nd.edn. (1898), pp 121-123. This letter is incorrectly dated Giessen 5th January 1837. The correct date, which I have confirmed by examining a photocopy of the original letter obtained from the Royal Swedish Academy of Sciences, is January 5th 1838. This letter is one of a sequence of letters which Liebig wrote to Berzelius between November 1837 and April 1838. Liebig, himself, stated that he began a work on the constitution of organic acids in November 1837. (op.cit. 204). This was after he had returned to Giessen from England, via Paris. He had met Dumas in Paris and discussed with him the composition of silver citrate. In an extract from a letter which Liebig wrote to Wöhler on March 2nd 1838, Liebig says that he had been analysing organic acids for 18 months (i.e. since September/October 1836 at the time of his first meeting with Graham) and that it took 6 months to complete the writing of his paper, that is from November 1837 to April 1838. See Berzelius and Liebig Letters (as above) p 147.
References to this letter incorrectly-dated as January 5th 1837 are found in:- J. R. Partington, A History of Chemistry 4 (London, 1964) p 278 and F. L. Holmes article on Liebig, D.S.B. 8 (1973) p 339.
206. Graham, op.cit. (203). See also the report of Graham's talk in the Liverpool Mercury on September 15th 1837.

the three atoms of constitutional water in copper nitrate which were now replaced by three atoms of hydrated copper oxide rather than by three atoms of anhydrous copper oxide.²⁰² However, Graham was forced to abandon his view that there was an atom of basic water in the subnitrate of copper.

In September 1837, Graham presented his views on the constitution of salts to a meeting of the British Association in Liverpool, and he also described his new classification of phosphates as monobasic, bibasic, or tribasic salts.²⁰³ Liebig attended this meeting and presumably as a result of his discussions with Graham he used his same classification for his work on the constitution of organic acids. Indeed Liebig said his work on the constitution of these acids was begun in November 1837.²⁰⁴ Most historians of Chemistry have assumed that Liebig began to develop his theory of the constitution of organic acids in January 1837. This view is incorrect; it is based on a wrongly-dated letter from Liebig to Berzelius.²⁰⁵ The importance of this revised time scale is to show that Liebig was influenced not only by Graham's researches on phosphates but also by Graham's researches on the constitution of salts which were published early in 1837.

Following Graham's talk on the constitution of salts at Liverpool, a discussion developed, which revealed the differing opinions of his contemporaries.²⁰⁶ Richard Phillips, Golding Bird and Robert Kane appeared to think that Graham had unnecessarily altered the chemical nomenclature. Phillips suggested that the difference between basic and constitutional water was simply explained by the well-known law that the first proportion of water was held by a stronger affinity than the second or further proportions. Golding Bird could not accept that water behaved as a base in some compounds and he asked Graham what view he would take of water in oil of vitriol and in caustic potash. Although Graham's reply was not recorded it may be inferred that he would have regarded water in oil of vitriol as basic, because it was only replaced by bases, and he

207. Graham, 'On water as a constituent of salts', (1835) Researches.
pp 352-3.

208. E. M. Peligot, 'On sugars', Ann.de Ch. 2 Ser. 67 (1838) 113-136,
see pp 133-134.

had previously stated that water in caustic potash was strongly united and discharged an acid function.²⁰⁷ Kane was quoted as objecting to some of Graham's statements. These objections were probably directed at Graham's concluding remarks on the role of ammonia in salts, which will be considered presently. Faraday and J.F.W. Johnston were inclined to support Graham's views on the constitution of salts. Faraday expressed satisfaction that a variety of opinions should be proposed and maintained by powerful arguments upon this interesting subject. He believed that the truth would surely emerge from this collision of opinion, but he cautioned the chemists present against considering electrical relations as affording in every instance conclusive proofs of what is a base and what is an acid.

As we have seen the role of water in compounds did not always prove easy to define. In 1838, Peligot, who was a research student of Dumas, wrote a paper on sugars in which he described the preparation of a number of saccharates. These were compounds of cane sugar with lead oxide, lime, barytes, or common salt. Peligot assumed that cane sugar behaved as an acid towards these bases and suggested that the compound of sugar and sodium chloride was a double salt, in which one atom of common salt had replaced one atom of water present in the cane sugar. He explained that: "this fact finds its analogues in the beautiful researches of M. Graham, on the basic role of water in saline combinations."²⁰⁸ Graham was unhappy with this interpretation as he pointed out in a letter to Liebig in 1838. Graham wrote: "But there is another distinction to be made in saline combinations, [apart from basicity], which is at present overlooked and confusion thereby occasioned. I allude to combinations of sugar and several other neutral organic oxides, which last are not in the relation of base to the organic compound; to which my attention has been particularly recalled by Peligot's late excellent paper on sugars. It is not at all to be supposed that sugar is an acid and that lime, oxide of lead etc. are basic to it.

209. MS. letter from Graham to Liebig, dated 10th August 1838, Liebigiana 58, Bayerische Staatsbibliothek, Munich.
 Graham must have realised that Liebig knew of Peligot's research and accepted its interpretation. Hence Graham gave a careful explanation of his point of view to Liebig. Dumas had written to Liebig with regard to Peligot's work: "The question of sugar preoccupies me much ... Peligot has been very careful with all the analyses. He has repeated them satisfactorily. But before he announces anything it is necessary that you should be convinced. It would be too serious for him. I am, therefore going to make an analysis of some of his products with great care."
 MS. letter from Dumas to Liebig dated November 29th 1837 (Bayerische Staatsbibliothek, Munich).

210. E. Turner, Elements of Chemistry 7th.edn. edited by Liebig and Gregory (London, 1842) p 915. "Cane sugar forms with the alkalies, with oxide of lead and with common salt, what appear to be saline combinations."
 For Berzelius's view, see letter from Berzelius to Mulder, September 4th 1838, in J. J. Berzelius Correspondence by H. G. Söderbaum 2 (1915) pp 117-126, see pp 122-123.

211. Graham, 'Note on the constitution of salts,' August 22nd 1838, B.A. Meeting (September, 1838) at Newcastle Phil.Mag. 13 (1838) 219-221 and The Athenaeum (1838) pp 629-630.

212. Graham, ibid. The Athenaeum September 1st 1838:- p 630.
 "Constitution of salts of:-
 (M = atom of metal)

Cyanuric acid	$Cy_3O_3 + 3MO$	$\left\{ \begin{array}{l} \text{Acid salt } 2HO + KO \\ \text{Neutral } HO + 2KO \end{array} \right.$
Fulminic acid	$Cy_2O_2 + 2MO$	Salts $2KO$ and $KO + Ag$ and $CuO + KO$
Cyanic acid	$CyO + MO$	
Meconic acid	$C_{14}H_{11}O_{11} + 3MO$	Salts $3Ag$ and H + $2Ag$ and $2HO + KO$ and $HO + 2KO$
Metameconic acid	$C_{12}H_2O_8 + 2MO$	Salts $2Ag$ and $HO + KO$ and $2KO$ and $HO + Ag$
Pyromeconic acid	$C_{10}H_3O_5 + MO$	
Citric acid	$C_{12}H_5O_{11} + 3MO$	Salts $3AgO$; $3NaO$ dried at $200^\circ C$; $3PbO$; $2PbO + HO$
Tartaric acid	$C_8H_4O_{10} + 2MO$	Salts $2KO$, $HO + KO$, $KO + NaO$
Racemic acid	same	same
Tannic acid	$C_{18}H_5O_9 + 3MO$	Salts $3PbO$, $2HO + PbO$, $HO + 2PbO$
Gallic acid	$C_7HO_3 + 2MO$	Salts $2PbO$, $HO + PbO$
Mucic acid	$C_{12}H_8O_{14} + 2MO$	Salts $2KO$, $HO + KO$, $2Ag$ "

No, sugar if it belongs to any recognised class of compounds must itself be a salt; and lime, oxide of lead etc. are combined not in the salt, but with it, like the superadded water of crystallisation of so many bodies. Hence it is that part of this water or metallic oxide is replaceable by a salt (in the compound of sugar with chloride of sodium) which never happens with a true base. The circumstance that the water in sugar cannot be removed by heat without destroying it, is no proof that water is basic, for we know many nitrates, hyposulphites etc., the constitutional or superadded water of which cannot be removed without destroying them. The character by which lime and oxide of lead are proved not to be basic in the sugar compounds, is, that analogous compounds do not exist containing the strong alkaline bases potash and soda. It is not a saccharate of lime, because there is no saccharate of potash. No acid is known which forms a salt with lime or lead, that does not also form a salt with potash or soda. While lime, oxide of lead, oxide of copper and other oxides belonging to, or related with the magnesian family are the very bodies which attach themselves to salts, or are superadded in the capacity (which remains still ill-defined) of water of crystallisation or constitutional water." ²⁰⁹

Liebig accepted this closely-reasoned argument, but Berzelius regarded sugar as an acid in these compounds.²¹⁰ Graham gave an essentially-similar account of the role of water in sugars at the Newcastle meeting of the British Association in August 1838.²¹¹ He also discussed the extension of his views on monobasic, bibasic, and tribasic salts, of which phosphates were the types, by Liebig and Dumas in their researches on vegetable acids. He ended his address with a table which illustrated the newly-discovered constitutions of the organic acids and their salts. This table is only reported in The Athenaeum account.²¹² It is interesting to see that Graham used the older dualistic formulae instead of Liebig's hydrogen acid formulae in his table. William Gregory observed at the end of the lecture that, although Liebig had given a full

213. Graham, 'Communications on the subject of inorganic salts and in particular on the function which water discharges as an element of their composition', B.A. meeting, September 13th 1837, at Liverpool. Phil. Mag. 3 Ser. 11 (October 1837) 396-398. In support of the concept of basic adjuncts, Graham noted that microcosmic salt $\text{NaNH}_4\text{HP} + 8\text{H}$ lost both its water of crystallisation and ammonia on heating, but not the basic water, leaving the residue NaNH_2P . Researches, 'On the constitution of salts' (1837) p 387.

explanation of the apparent isomerism of cyanuric, fulminic and cyanic acids presented in this table, the researches of Mr. Graham had led the way to the explanation.

One of the difficulties of considering most salts as constitutionally neutral was highlighted by the salts of the oxyacids with ammonia. According to Berzelius these salts contained the oxide of the hypothetical radical ammonium. Graham was faced with the difficulty that sulphate of ammonia contained one atom of acid SO_3 and two atoms of base: water and ammonia. To overcome this difficulty he modified the ammonium theory by arguing that only water was the true base of this salt and so it could be classed as a truly neutral salt. He developed this view in his 1837 lecture to the British Association, from which it was reported that: "Mr. Graham considers water as the true base of these salts [i.e. ammonium salts of oxyacids] and that ammonia is not a base itself, but it belongs to class of bodies which might be called 'basic adjuncts', which admit of being attached to oxide of hydrogen, or to metal oxides, the only true bases." ²¹³ Therefore, sulphate of ammonia was really sulphate of water with ammonia as a basic adjunct: $\text{NH}_3\text{HO}, \text{SO}_3$ rather than $\text{NH}_4\text{O}, \text{SO}_3$. To extend this idea further, Graham suggested that the sulphovinates were analogous because they contained sulphate of water with olefiant gas as the basic adjunct e.g. $\text{C}_4\text{H}_4\text{HO}, \text{SO}_3$.

The theory of basic adjuncts was one part of Graham's metal-ammonium theory. This was an early forerunner of the co-ordination theory. The metal-ammonium theory was first mentioned in this 1837 lecture and Graham also described it in his textbook as follows: "The whole or a portion of the ammonia absorbed by certain anhydrous salts is retained with great force, and cannot be separated from them by heat. Anhydrous chloride of copper, for instance, absorbs a single equivalent of ammonia with the greatest avidity, and forms a green fusible matter, which the close analogy between copper and hydrogen would lead us to view as analogous in constitution to the compound formed by chloride of hydrogen and ammonia,

214. Graham, Elements of Chemistry (1842) 415-416.
215. Graham, Notebook C, op.cit. (121) pp 86-87.
216. Anatole Riffault, 'Note on the composition of phosphate of ammonia and magnesia', Ann.de Ch. 2 Ser. 19 (1821) 90-97.
217. Berzelius, Traité de Chimie (translated by Esslinger) 4 (Paris, 1831) 96-99.
218. Graham, op.cit. (190), See Researches. 390-391. Graham realised that accurate analyses of this salt had been given previously by F. Wach (1830), Schweigger's, J. 59 (1830) 297-312 and by F.J.Otto, Schweigger's, J. 66 (1832) 288-297, see:- Graham, Notebook C (May, 1835) p 178, but he did not acknowledge these analyses in his paper.

or chloride of ammonium. It will, therefore, be represented as composed of chlorine united with ammonium, containing an atom of copper in place of the fourth atom of hydrogen, or as $\text{NH}_3\text{Cu,Cl}$, which may be called chloride of cuprammonium. The sulphate of copper, in like manner, retains half an equivalent of ammonia with great force, and forms a compound which may be represented as sulphate of copper combined with sulphate of cuprammonium: $\text{CuO,SO}_3 + (\text{NH}_3\text{CuO} + \text{SO}_3)$, which is analogous to the double sulphate of copper and ammonium $\text{CuO,SO}_3 + (\text{NH}_4\text{O} + \text{SO}_3)$." ²¹⁴

The origin of this theory, which proved to be useful to subsequent researchers, can be traced through Graham's laboratory notebooks. The first reference to the theory is found on 12th December 1834 when Graham was attempting to resolve the constitution of magnesium ammonium phosphate. He wrote: "Ammonium - for the 4th H atom perhaps copper, magnesium may be substituted 'cupri-ammonium' NH^3Cu or perhaps $\text{NH}^3\text{Cu}^{\frac{1}{2}}$ i.e. $\text{N}^2\text{H}^6\text{Cu}$. By the first view, sulphate of cupri-ammonium is $\ddot{\text{S}}\text{O}(\text{NH}^3\text{Cu})$, analogous to sulphate of ammonium. The existence of 'magnesi-ammonium' is more likely NH^3Mg . Then the basic phosphate of magnesia and ammonia $\left[\ddot{\text{P}}\text{Mg}^2(\text{NH}^3)^2 \right]$ may be a phosphate of magnesi-ammonium $\ddot{\text{P}}(\text{NH}^3\text{Mg})^2$. It should perhaps have an essential atom of water besides, like phosphate of magnesia." ²¹⁵

Ironically, this first use of the metal-ammonium theory proved to be incorrect. The formula used by Graham was derived from a faulty analysis performed by Riffault in 1821. ²¹⁶ Berzelius had suggested, from this same analysis, that the basic phosphate of magnesia and ammonia was a double salt which contained ten atoms of water of crystallisation. ²¹⁷ During 1835, Graham analysed the salt and found that it contained one atom of phosphoric acid, two atoms of magnesia and only one, not two, atoms of ammonia. He correctly recognised that this was not a double salt but rather it was a neutral tribasic salt of phosphoric acid which he formulated as $2\text{MgO, NH}_4\text{O, PO}_5 + 2\text{HO} + 10\text{HO}$. ²¹⁸ Therefore Graham abandoned the concept of magnesi-ammonium, because analysis did not support it, but he did not forego the metal-ammonium theory.

Graham investigated the reactions of ammonia with a number of

219. Graham, Notebooks B & C (op.cit. 121) See entries: Notebook B p 300 July 20th 1835 - absorption of ammonia by zinc sulphate; Notebook C pp 121-124 Copper sulphate + ammonia, pp 236-240 copper chloride + ammonia, and nickel sulphate + ammonia. Reference is made to extensions of these studies in the missing notebooks D & E. The results of these researches were not published separately in a paper as promised but they are included in Graham's textbook. On May 15th 1837 Graham wrote to Faraday: "Since my return [to Glasgow] I have got fairly again into my experiments on ammonia and the salts, a subject on which I hope to be able to present a paper to the Royal Society before the vacation." Faraday correspondence, Institution of Electrical Engineers, London.
220. Henry Rose, 'Combinations of ammonia with anhydrous salts', Ann.de Ch. 62 (1836) 308-326.
221. Graham, Elements of Chemistry, (London, 1842) p 228, published as part 3 in September 1839.
222. C. Gerhardt, 'On the constitution of organic salts of complex acids, and their relations with ammoniacal salts', Ann.de Ch. 2 Ser. 72 (1839) 184-214, see pp 207-210.
223. W. Turner, Elements of Chemistry by E. Turner 6th.edn. (London, 1842) p 653. Wilton Turner edited the inorganic section of his late brother's textbook. It may possibly be significant that Wilton Turner was an unsuccessful rival to Graham for the Chair of Chemistry at University College in 1837.
224. R. Kane, 'Experiments on the action of ammonia on chlorides and oxides of mercury', Phil.Mag. 3 Ser. 8 (1836) 495-500.

anhydrous metal salts during 1835.²¹⁹ These reactions had also been studied by Henry Rose who found that, when mercury chloride was heated in ammonia, a liquid was formed with the formula $2\text{HgCl} + \text{NH}_3$.²²⁰ Graham interpreted this formula on the metal-ammonium theory by suggesting that the constitution was $\text{HgCl} + \text{NH}_3\text{HgCl}$ analogous to the well-known double salt sal alembroth $\text{HgCl} + \text{NH}_4\text{Cl}$.²²¹

Gerhardt adopted a similar view to Graham on ammonium salts, although he did not accept such 'hypothetical bodies' as ammonium or amide. Gerhardt said that an acid was saturated by oxide of hydrogen and not by ammonia. He regarded the ammonia as a 'copula'; essentially this was the same as a basic adjunct. This copula was not removed by acids and did not alter the saturation capacity of the base, water. He chose the same examples as Graham to show the presence of the ammonia copula: $\text{SO}_3, \text{CuO} + \text{SO}_3, \text{CuO} \cdot \text{Az}^2\text{H}^6$ and $\text{SO}_3, \text{CuO} + \text{SO}_3, \text{H}^2\text{O} \cdot \text{Az}^2\text{H}^6$ and he noted that Graham called $\text{CuO} \cdot \text{Az}^2\text{H}^6$ cuprammonium.²²² He accepted that the ammonia copula would indeed modify the properties of the bases, copper oxide, and water, with which it was coupled.

On the contrary, Wilton Turner was critical of Graham's conception of basic adjuncts. He argued that they were inconsistent with the theory of isomorphism, but he did not make it clear why this was so. He added that basic adjuncts were hypothetical and that they were introduced as a result of an effort by Graham to support the hypothesis that all salts were neutral in composition.²²³ Undoubtedly there is a measure of truth in this last comment.

A rival theory to the metal-ammonium theory was advocated at this time by Robert Kane. Kane explained the constitution of ammonium salts in terms of amidogen NH_2 or Ad for short. He had analysed the white precipitate, formed by adding ammonia to mercury chloride solution, and in 1836 he had proposed the formula $\text{HgCl} + \text{HgNH}_2$ for this precipitate.²²⁴ On the amidogen theory NH_2 was analogous to oxygen so that the base ammonia $\text{H} \cdot \text{NH}_2$ was analogous to water HO . Thus, Kane wrote $\text{H} \cdot \text{NH}_2, \text{HO} + \text{SO}_3$

225. Graham, Elements of Chemistry (London, 1842) p 417.
 Graham added generously: "At the same time, this hypothesis has enabled Dr. Kane to develop many new and interesting relations among the ammoniacal compounds, and may, perhaps present a closer and more distinct view of the intimate constitution of these bodies, than the ammonium theory exhibits. At present, however, our theories of the constitution of compounds are too uncertain to be regarded otherwise than as artificial aids to facilitate our conception of the manner in which the formation of these bodies occurs, and of the transformations which they undergo; and a theory of constitution is, therefore, adopted more for its convenience than its truth. This state of things leads to the retention of the ammonium theory, which has introduced a degree of simplicity into our views of that particular class of ammoniacal compounds to which it is applicable, that could not easily be exceeded. But its adoption must not be allowed to preclude the consideration of other theories, such as that of Dr. Kane, which facilitate investigations in the meantime, and may prove to be truer to nature in the end." *ibid.*
226. H. Rose, 'On anhydrous sulphate of ammonia', Ann.de Ch. 2 Ser.75 (1840) 388-404 and also in Taylor's Scientific Memoirs 2 (London, 1841) 551-564. According to Divers and Haga (J.Chem.Soc. 61 (1892) 943) NH_3, SO_3 is really ammonium amine disulphonate $\text{NH}(\text{SO}_3\text{NH}_4)_2$ - This reference is taken from J. R. Partington - History of Chemistry Vol.4 (London, 1964) 188.

for ammonium sulphate, and $\text{H.NH}_2, \text{CuO} + \text{SO}_3$ for cuprammonium sulphate. Kane regarded $\text{H.NH}_2, \text{HO}$ as equivalent to one atom of base, of the potash class e.g. KO. Graham remarked that to suggest that two atoms of magnesian base ($\text{H.NH}_2, \text{HO}$) were equivalent to one atom of potash base (KO) was too doubtful to form a safe basis for any theory.²²⁵

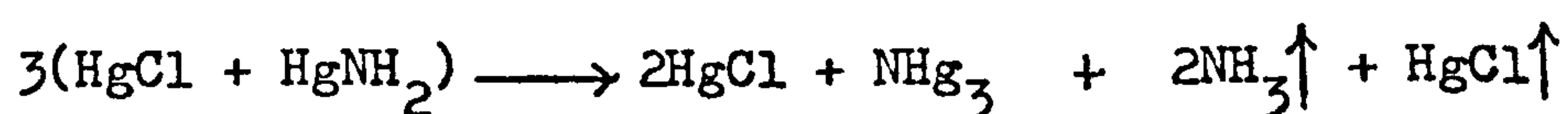
In 1840, Henry Rose compared the ammonium and amidogen theories with reference to a new salt which he had made. This was anhydrous sulphate of ammonia which he formulated as $\text{SO}_3 \cdot \text{Az}^2 \text{H}^6$. This salt was neutral, and it gave hardly any precipitate with barium chloride solution. Rose observed that Kane would consider NH_3, SO_3 as $\text{H.NH}_2, \text{SO}_3$ which would be analogous to the hydrate of sulphuric acid HO, SO_3 . Apart from the practical difficulties of explaining the observed properties of the salt from this view-point, he was doubtful in general terms about the credibility of the amidogen hypothesis. The evidence of the isomorphism of potassium and ammonium was opposed to Kane's view that two bases ($\text{H.NH}_2, \text{HO}$) saturated an oxyacid such as SO_3 . Rose felt that the ammonium theory was better for explaining the constitution of most ammonium salts although he recognised that his new salt could not be explained on the ammonium theory. He noticed that Graham supported the ammonium theory and that Kane's theory was not generally admitted.²²⁶

Kane was quick to reply to the criticisms made by both Graham and Rose. He therefore advised Graham to extend his metal-ammonium theory. He suggested that, instead of replacing just one atom of hydrogen in ammonium NH_4 by one atom of magnesian metal to give NH_3Zn , NH_3Cu or NH_3Hg , or even to give two atoms in white precipitate $\text{Hg}_2\text{H}_2\text{N}$, why not consider further substitution to give $\text{Cl.Hg}_3\text{HN}$? He regarded his real triumph over Graham's view came when the constitution of the product of the reaction between calomel and ammonia ($\text{Hg}_2\text{Cl} + \text{Hg}_2\text{NH}_2$) was contemplated. He said that this would require an extension of the ammonium theory to produce a new radical derived from NH_6 , that is $\text{Cl} + \text{NH}_2\text{Hg}_4$. But he was certain that the existence of NH_6 was "too violent a supposition" and this

227. E. Mitscherlich, 'On the relations which exist between crystalline form and chemical composition,' Ann.de Ch. 2 Ser.73 (1840) 384-398, see p 390.
228. R. Kane, 'On the theoretical constitution of compounds of ammonia,' Phil.Mag. 3 Ser.17 (1840) 120-126.
Ironically, Kane commented in 1849 that his suggested extension of Graham's metal-ammonium theory to new compound radicals derived from NH_6 etc., which was designed to show the inadmissibility of the theory, had been taken up and extended incorrectly by Millon in his theory of basic salts of compound radicals. Kane, Elements of Chemistry 2nd.edn. (Dublin, 1849) 593-594.
229. One of Graham's University College students wrote in 1847 that the amidogen theory had not received support since the discovery of NHg_3 by Mitscherlich; - no doubt this was a faithful expression of Graham's opinion. Exam notebooks of Graham's students Wellcome MSS. nos.2581,2582 in 2 box files.
230. A. W. Hofmann, 'Researches into the molecular constitution of the organic bases', Phil.Trans. 141 (1851) ii 357-398, see pp 397-398.
231. A. Laurent, Chemical Method (1854), translated by W. Odling, 220-221.
232. For the development of the ammonium theory see the useful accounts by George B. Kauffmann:-
G. B. Kauffmann, 'Early theories of metal-ammines - a brief historical review from Graham to Claus, (1837-1856)'. J.Chem.Ed. 51 (1974) 522-524 and G. B. Kauffmann, Classics in Co-ordination Chemistry (1798-1899), Classics of Science Vol.7 (New York, Dover, 1976) pp 39-45.
233. F. Claudet, Phil.Mag. 4 Ser.2 (1851) 253, dated October 1851.

example was "fatal to Graham's view". After adding further contrary examples, he concluded that the ammonium theory was no longer sound because it could not explain an extended series of compounds.

Similarly, Kane dismissed Rose's criticism and suggested that Rose's new compounds, the anhydrous carbonates and sulphates of ammonia, actually favoured the amidogen theory. One further difficulty for Kane, was to explain the recent research of E. Mitscherlich, who had suggested that white precipitate was more complicated than Kane had supposed. Mitscherlich had obtained a red compound by gently heating white precipitate. This new compound had the formula $2\text{HgCl} + \text{NHg}_3$ and according to Mitscherlich it required the tripling of the formula of white precipitate to explain its formation²²⁷ viz:



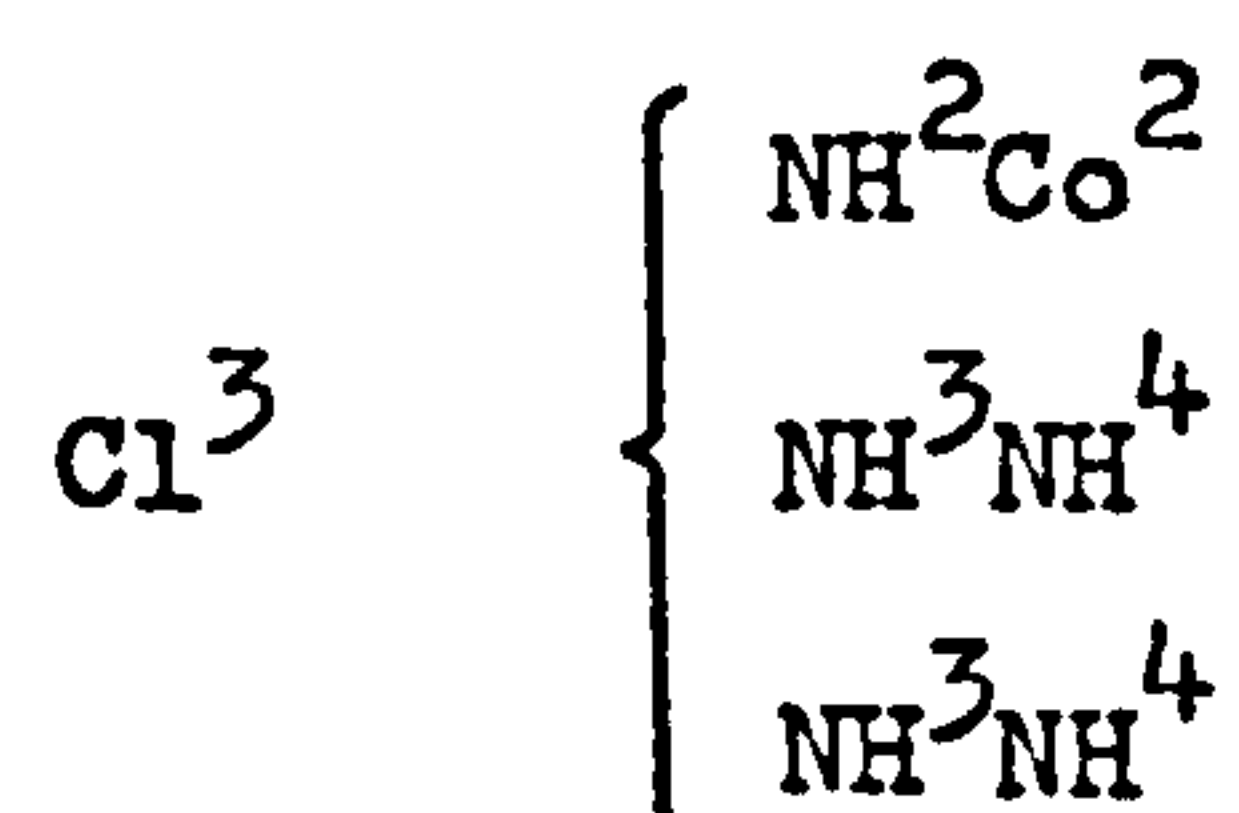
Kane merely dismissed this idea as an "irrational thought" saying that it would be "just as easy to call hydrated phosphorous acid $4\text{PO}_3 + 3\text{HO}$ " because it gave PH_3 and 3PO_5 on decomposition.²²⁸

With support both from Daniell's electrochemical researches and from Mitscherlich's discovery of NHg_3 , the ammonium theory gradually supplanted Kane's amidogen theory during the 1840's.²²⁹ This preference was reinforced by Hofmann's use of the ammonium theory in his researches into the constitution of organic bases.²³⁰ And in 1854 Laurent acknowledged that Graham had been the first to consider the ammoniacal salts of copper as salts of ammonium in which one hydrogen atom was replaced by one atom of copper.²³¹ The metal-ammonium theory actually survived in a modified form until Werner's time and was extended and refined by Reiset, Gerhardt, Wurtz, Hofmann and Weltzien etc.²³²

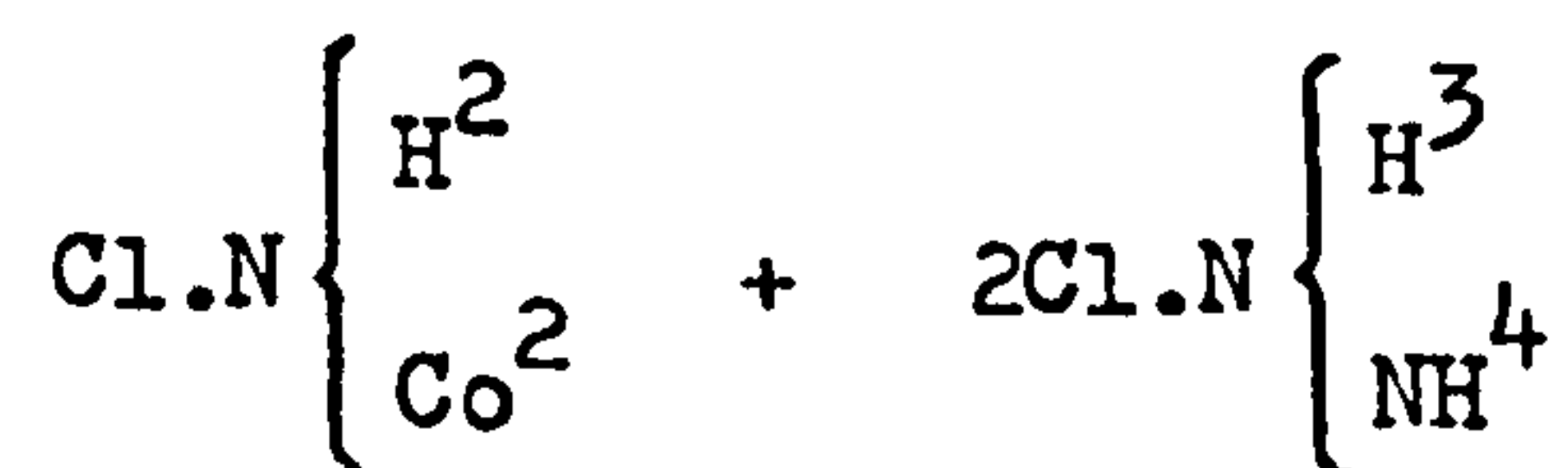
One interesting extension of the metal-ammonium theory was reported in 1851 by a student, Frederic Claudet, who was researching under Graham's direction at University College, London. Claudet synthesised the compound which we now call chloropenta-ammine cobalt (III) chloride, $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$.²³³ He prepared this compound by adding excess ammonia,

234. Hofmann made use of "the interesting observation made by Professor Graham, namely, that ammonia whenever it joins to a compound containing hydrogen, may be regarded as ammonium replacing one equivalent of hydrogen" *op.cit.* (230) p 398. Laurent contested strongly the priority of Graham's 'interesting observation ' *op.cit.* (231).
235. E. Frémy, 'Recherches sur le cobalt,' Ann.de Ch. 3 Ser.35 (1852) 257-311 and F. A. Genth and O. Gibbs, Researches on Ammonia-Cobalt Bases, (1856) or Amer.J.Sci. 2 Ser.23 234,319; 2 Ser.24 (1857) 86. These references were taken from the useful article by G. B. Kauffmann 'Frederick August Genth and the discovery of cobalt-ammines,' J.Chem.Ed. 52 (1975) 155-156, and also from J.Chem.Ed. 51 (1974) 522-524 (*op.cit* 232). Genth published his research first, in January 1851, in an obscure journal written in German and published in Philadelphia! Kauffmann supplies this reference: Genth, F.A., Keller-Tiedemann's Nord Amerikanischer Monatsbericht für Natur- und Heilkunde 2.8 (1851). See also Chem.Gaz. (1851) 266. See also G. B. Kauffmann, 'Early experimental studies of cobalt-ammines,' Isis 68 (1977) 392-403.
236. M. Dugniolle, 'Memoir on the different functions that water can fulfil in compounds of a simple radical and on their constitution,' Bruxelles Ann.Univ.Belgium 3 (1844) 91-232. This paper is wrongly attributed to Thomas Graham in the Royal Society Catalogue of papers where it is included as Paper No.40. Under the name Dugniolle the same paper is also recorded. On reading this paper, it is clear that it is not written by Graham. Presumably this journal did not have a wide circulation and Dugniolle's paper seems to have been little known. The catalogue of books in the Bibliotheque de l'Académie Royale, Bruxelles (1890) shows that Dugniolle's memoir was also published in book form in 1845 (8vo) - item 5542 (page 1235 of catalogue) but the book is not to be found in the B.M. catalogue. Maximilien Dugniolle's memoir was the prize-winning essay received for the natural science question set by the Faculty of Sciences of the Universities of Belgium for 1843-1844. The Faculty of Sciences included the following Professors of Chemistry: J.S.Stas of the Military School, L.G. de Koninck of Liège, C.J.Koene of Bruxelles, Mareska of Gand and Pagani of Louvain. The question they set was:- "It is generally known that water plays, in compounds containing simple radicals, the role of base, of acid, of salt, or of water of crystallisation. We ask: 1. for an exposition of the available methods for establishing the different functions of water 2. for an enumeration of the classes of compounds in which water plays two different roles and 3. how water can be envisaged in compounds where it is a major constituent? Dugniolle, of Ixelles near Bruxelles, was a candidate in the physical and mathematical sciences and a student of Liege University. Like Stas, he was taught chemistry at Liège by de Koninck (1809-1887).

to cobalt chloride solution containing ammonium chloride. Oxygen was absorbed from the air and after four days the solution was boiled strongly, and acidified, to give a crimson powder. Recrystallisation gave small octahedral, ruby-red crystals. The cobalt in these crystals was peroxidised and their analysis gave $3\text{Cl}, 2\text{Co}, 5\text{N}, 16\text{H}$ which was almost correct. Claudet formulated the compound in several ways. According to Berzelius's theory it was $3(\text{NH}^4\text{Cl}) + 2(\text{NH}^2\text{Co})$, that is, three equivalents of ammonium chloride and two equivalents of substituted ammonia. However, the salt was neutral to litmus so Claudet examined an alternative view grouping the atoms according to Graham's metal-ammonium theory:



where NH^2Co^2 represented ammonium, in which two equivalents of hydrogen were replaced by two equivalents of cobalt; the NH^3NH^4 group represented an ammonium radical in which one equivalent of hydrogen was replaced by another ammonium, in the same way that ethyl or methyl replace the hydrogen from ammonia in Wurtz and Hofmann's bases.²³⁴ Finally, he suggested that a further possible constitution might be, that the compound was a double salt comprising one equivalent of chloride of cobalt-ammonium and two equivalents of chloride of ammonium, in which the fourth hydrogen was replaced by NH^4 giving:



This work was contemporary with similar research published by F. A. Genth and E. Frémy.²³⁵ Therefore we must conclude that Graham played a part in the early study of co-ordination chemistry.

Graham's careful study of the role of water in salts, acids and bases had led to important consequences during the 1830's. It was reviewed in 1844 by a Belgian scientist, Maximilien Dugniolle.²³⁶ He rightly recognised that Graham's major achievement, in his investigations of phosphates,

237. Berzelius and Thenard simply regarded water as part of the composition of hydrated crystals. In 1844, however, Baudrimont did distinguish between water of crystallisation and water of constitution. The former was lost by 100°C and the latter was only lost above 100°C . Baudrimont, Traité de Chimie 1 (Paris, 1844) p 473.

238. C. J. Koene, 'Sur les fonctions de l'eau,' Bulletin de l'Académie Royale des Sciences, Bruxelles Vol.13 part 2 (1846) pp 272-290. Corneille Jean Koene (b.1809) gained his D.Phil. in 1840 and became Professor of Chemistry at Brussels University in that year.

was to emphasise the role of water in these compounds. The water in phosphates was basic water and not simply water of crystallisation. Five different roles were assigned to water by Dugniolle. In salts, water could be basic, acidic, saline, constitutional, or just water of crystallisation. In this assignment he was following the earlier work of Graham very closely. Dugniolle attempted to define, and distinguish between, saline water and constitutional water, with more precision than Graham. He pointed out that before Graham's studies, Berzelius and Thenard had not recognised the properties of saline or constitutional water.²³⁷ They had dismissed it as water of crystallisation or combination. Now Dugniolle explained that water of crystallisation was that water, combined by a weak affinity, which was usually driven off by heating to 100°C in air or in a vacuum. This water could not be replaced by an acid, base, or salt. Saline water played the role of a salt in compounds. Saline water could be replaced by an equivalent of neutral salt and it was not lost on heating until the temperature was raised above 100°C. Finally, constitutional water was retained by a powerful affinity. It could be lost on heating, usually above 100°C, but often with a profound alteration of the compound in which it was contained. Constitutional water could not be replaced by acids, bases, or salts.

The definition of constitutional water proposed by Dugniolle differed from that suggested by Graham, which allowed the substitution of constitutional water by metallic oxides, hydrated metallic oxides, hydrated acids, or salts. Dugniolle's classification of the roles of water was rather inflexible. It was essentially a survey of the previous work on this subject, which gave little further insight into the nature of this complicated problem. Belgian chemists continued to retain an interest in the role of water in compounds. C. J. Koene discussed the functions of water in 1846.²³⁸ He rejected the concept of constitutional water altogether, and only retained three major categories of water: basic water (including saline water); acidic water; and copulated water (which

239. E. Millon, 'Recherches sur la constitution chimique des acides et des bases,' Ann.de Ch. 3 Ser.13 (1845) 129-144. Millon, like Berzelius and Dugniolle, was critical of Graham's interpretation of the role of water in oxalates. See also E. Millon, 'Mémoire sur l'acide iodique libre et combiné,' Ann.de Ch. 3 Ser.9 (1843) 400-431.

included water of crystallisation and Graham's constitutional water). Likewise, Millon considered the role of water in compounds in a series of papers published between 1843 and 1845.²³⁹

Comparing Graham's work with later studies, it is evident that he had laid down the essential foundations for a proper understanding of the nature of acids and salts. The recognition of basic water in acids had enabled him to understand the polybasic character of the phosphoric acids. This work, as I have tried to indicate, was of far-reaching significance in both organic and inorganic chemistry. Graham's study of the role of water in salts and the introduction of the principle of the constitutional neutrality of most salts allowed him to make many useful deductions concerning the whole field of salts. His discussions concerning saline and constitutional water were useful, because they allowed him to draw important parallels and analogies between different classes of salts. However, it must be admitted that 'saline' and 'constitutional' water were rather imprecise terms. In Graham's own researches the study of the role of water in compounds quickly opened up new fields of research for him: in thermochemistry; electrochemistry; and on chemical combination in general. This led him finally to develop a molecular theory of compounds which applied to both organic and inorganic chemistry. These studies will be examined in the next chapter.

Chapter 5

POLYMERISM AND VOLTAIC CIRCLES

1. Graham, Wellcome letters and correspondence. Note dated October 16th 1865. The reference to Brodie is probably taken from the paper by B. C. Brodie 'On the peroxides of the radicals of the organic acids.' Phil.Trans. 153 (1863) 407-423, see pp 421-422 where Brodie points out an analogy between the properties of organic peroxides and chlorine in hydrochloric acid.

"The chemical 'elements' [are] themselves compounds of a lower order of elements which show themselves (shine through) in the properties of the current elements. Thus chlorine has the properties of a peroxide - see Brodie." ¹

As this quotation shows Graham believed that the chemical elements were complex. Underlying this belief Graham had an unstated but more fundamental belief in the unity of all matter. He was reluctant to commit himself openly to this view until 1863. In part, his reluctance might be traced back to the unfortunate experience of his teacher, Thomas Thomson, who had failed to demonstrate the truth of Prout's hypothesis that the weights of all atoms were integral multiples of hydrogen. Also Graham became increasingly aware that an admission of a unitary theory of matter with a consequent belief in the complexity of the elements could easily be misinterpreted. In 1837, J. F. W. Johnston had suggested that it might be possible to transmute elements and this was soon followed by Samuel Brown's attempt to produce such a transformation. Although Graham speculated about the complexity of the elements he was very reluctant to declare his belief in the unity of matter and he was strongly opposed to false experimental claims concerning transmutation of the elements.

In this chapter I shall show that between 1837 and 1844 Graham's adherence to a material theory of heat was important in his discussions of the problems raised by the phenomena of isomerism, polymerism and dimorphism. In 1839, Graham rejected the existence of fluid electricity, as such, and referred instead to polarity and chemical affinity in order to explain voltaic phenomena. The fundamental concept of chemical affinity was also used to account for both the attractions inside binary salt molecules and the existence of polymeric groupings of these molecules in elements and compounds. This led Graham to propose a molecular theory which included the attractions between like and unlike atoms. This

theory made it possible to extend the analogy between inorganic and organic compounds.

To begin with, let us look at Graham's evident interest in the advances being made in the molecular theory of organic chemistry. He regarded the radical and substitution theories as being particularly significant developments. These new theories encouraged Graham to think about chemical affinity and the force of attraction between all atoms. He continued to be interested in the problem of isomerism and he used both polymerism and differences in heat content to account for certain examples of apparent isomerism. From 1841 to 1843 Graham was engaged in practical studies of thermochemistry. These were mainly concerned with testing his views on the constitution of salts. Just before this time, Graham had developed a new theory of voltaic circles based on the transmission of chemical affinity through polymeric chains of binary molecules which could be found in liquids and even in metals. This work led Graham to propose a theory of molecular grouping or salimolecules which seemed to have applications in many areas of chemistry. Graham's heat studies also appeared to reveal the existence of molecular grouping and polymerism and his study of voltaic circles showed the importance of the concepts of chemical affinity and polarity. Using these ideas Graham worked out a molecular theory of organic chemistry. The study of the complex nature of the elements and their compounds seemed to lead Graham to a view of matter composed of the same primary atoms but he was reluctant during this period to express this belief openly. Certainly it would seem that his writings: on salimolecules; on Prout's hypothesis, and on the natural classification of the elements, suggest an underlying conviction that all matter possessed an ultimate simplicity. However the erroneous attempts of Samuel Brown to achieve transmutation and the adverse criticism which Graham's molecular theory of organic compounds received from Berzelius must have persuaded Graham to be increasingly cautious about speculative theories of matter.

2. Graham, Presidential address to Section B, Chemistry and Mineralogy section of the British Association for the Advancement of Science, held at Birmingham on August 26th 1839. See The Athenaeum (1839) p 644.

3. Graham, *ibid.*

Like most chemists of the late 1830's Graham was extremely interested in the advances being made in Organic Chemistry. In 1839, Graham was President of the Chemical Section of the British Association for the Advancement of Science. In this capacity, he reviewed chemical progress by saying that "the organic department was the most productive, and at the present moment engrossed almost exclusively the attention of chemists and was likely from the important results it afforded to continue to do so." ² He drew attention to two 'grand features of recent progress': the law of substitutions of Dumas and the binary theory of the constitution of bodies so powerfully advocated by Liebig. Graham stated that the application of substitution had been beautifully demonstrated by Regnault. For he had shown that olefiant gas (C_4H_4) could be substituted progressively by chlorine to yield ultimately the protochloride of carbon which had been originally discovered by Faraday. According to Regnault, the formula of this compound was C_4Cl_4 . A particularly interesting aspect of this substitution was that it showed that the four atoms of carbon in olefiant gas could be traced back to the four carbon atoms in alcohol from which it had been derived. All these compounds therefore belonged to the alcohol series.

Graham then pointed out that Liebig's important contribution to organic chemistry was the theoretical resolution of bodies into two proximate parts, one of which was generally a simple substance and the other a compound radical. He concluded this survey by saying that "there could be no doubt that compound radicals would be the basis of the classification of organic compounds; and that thus the simplicity of arrangement would be introduced into organic compounds as already existed in the metallic combinations of inorganic compounds." ³ Graham's interest in organic chemistry will be shown again later by considering his attempt to develop a molecular theory of organic chemistry. This theory was developed from earlier studies of voltaic circles and the nature of chemical affinity.

4. Berzelius, 'The distinction of isomerism from analogous conditions,'
Jahresbericht. 1832 (1833) pp 65-69 or Pogg. Ann. 26 (1832) 320-322.
5. Graham, Elements of Chemistry, 1st.edn. part 2 (London, 1838) 155-156.

Graham's interest in isomerism has been discussed in the previous chapter. He had shown that isomerism could be explained without recourse to differences in the arrangements of atoms. With isomerism it was necessary to take into account both the water content and heat content of compounds and also the possible existence of polymerism.

In 1832 Berzelius had clarified the distinction between isomerism and 'polymerism.' Isomeric substances were those which were "composed of the same absolute and relative number of the same elements, and which have the same atomic weight, as for instance the two oxides of tin, the two phosphoric acids, etc. But such cases must not be confounded with others in which the relative number of atoms is the same, but not the absolute number. Thus the relative number of carbon and hydrogen atoms in olefiant gas and 'weinöl' is identically the same (i.e. the number of atoms of hydrogen is twice that of carbon), but one atom of the gaseous substance contains only one atom of carbon and two of hydrogen, = CH_2 , whilst one atom of the oil contains four atoms of carbon and eight atoms of hydrogen, = C_4H_8 . For the designation of this type of similarity in composition, combined with dissimilarity in properties, I would suggest the term 'polymeric'." ⁴

In 1838 Graham listed four of the best characterised polymeric hydrocarbons: ⁵

methylene	C_2H_2
olefiant gas	C_4H_4
gas from oil	C_8H_8
cetene	$\text{C}_{32}\text{H}_{32}$

To these he added other examples of polymerism which included:

$\left\{ \begin{array}{l} \text{Oil of lemons } \text{C}_{10}\text{H}_8 \\ \text{Oil of turpentine } \text{C}_{20}\text{H}_{16} \end{array} \right.$	$\left\{ \begin{array}{l} \text{naphthaline } \text{C}_{20}\text{H}_8 \\ \text{paranaphthaline } \text{C}_{30}\text{H}_{12} \end{array} \right.$	$\left\{ \begin{array}{l} \text{alcohol } \text{C}_4\text{H}_4 + 2\text{HO} \\ \text{ether of} \\ \text{wood spirit } \text{C}_2\text{H}_2 + \text{HO} \end{array} \right.$

6. Berzelius: 'Composition de l'acide tartrique et l'acide racémique; poids atomique de l'oxide de plomb, et remarques générales sur les corps qui ont la même composition, et possèdent des propriétés différentes.' Ann.de Ch. 2 Ser.46 (1831) 128-147, see pp 139-140. Ignition was noticed with phosphate of magnesia and ammonia, antimonates, zircon, oxide of chromium, oxide of iron, carbide of iron etc. p 139.

7. E. Mitscherlich: Éléments de Chimie trans. by B.Valérius, (Bruxelles, 1836) Vol.2 (1836) p 101.

As he recognised, polymeric bodies comprised the most numerous class of isomeric bodies and therefore it is not surprising that Graham should look for further examples of polymerism. As we shall see, polymerism became an important part of his vision of molecular structure.

Differences in heat content between isomers had been noticed by Berzelius. The phenomenon of ignition was observed during the change of one isomer into another by the action of heat. Indeed this 'glowing' appeared to be a visible sign of an isomeric transition. In contrast, Berzelius believed that dimorphism was only caused by a mechanical difference between the two forms whereas isomerism involved chemical differences.⁶ Mitscherlich also drew attention to the changes which isomeric substances underwent on heating. He observed that antimoniate of deutoxide of copper, prepared by precipitation, could be decomposed by weak acids. But, he wrote, "when one heats it in a closed vessel a point is reached when it begins to redden and this spreads throughout the mass like a burning substance. After this ignition, which does not change the weight of the salt, the affinity of the antimoniate of deutoxide of copper becomes so increased that the strongest acids cannot destroy the compound. One sees similar vivid combustions on heating phosphate of magnesia, while this salt is being transformed into paraphosphate. The development of caloric and light appear to be the result of a more intimate combination of the constituents."⁷

In February 1833, Graham examined the problem of the action of heat on biphosphate of soda. He recorded the note: "shall we conclude that the anhydrous biphosphate is insoluble $\overset{\cdot\cdot}{\text{P}}\text{Na}$? or, that this is a case of 'idio-synthesis' of the salt (not of the acid) and that its formula is $\overset{\cdot\cdot}{\text{P}}\text{Na} + \overset{\cdot\cdot}{\text{P}}\text{Na}$ or some such?

Query: does the circumstance of the above biphosphate containing two atoms of basic water dispose it, in the act of losing them, to enter into a metidionic compound? When the bibasic phosphate of magnesia and ammonia is heated it is said to become luminous and become completely

8. Graham: MS. Notebook B (July 1832-August 1834, 450 pp) pp 132-133.
The Andersonian Library, University of Strathclyde.
9. Graham, *ibid.* pp 146-148. (April 1833) Graham took examples from Berzelius, *Traité de Chimie* (translated by M. Esslinger) Vol. 4 (Paris, 1831) pp 136, 142, 147-148, 234 and 240. Chrysoberyl, native clays or silicates of alumina, silicate of yttria were given as examples. Then Graham added his own comment: "Are there 2 metaphosphoric acids? a true and a pyrometa? Will metaphosphate of soda dissolved in an excess of the acid crystallise on concentration? Ditto of barytes. Does the compound of phosphoric acid and soda in the proportion of biphosphate but which has not been crystallised possess powers of combination which the crystallised salt does not possess?" Finally, he quoted further examples from Berzelius: zircon, sulphate of thoria, "it appears that the arseniate of iron exhibits the deflagration. It appears that supersalts such as bitartrate of potash act occasionally with more energy than the acid itself. Action of that salt on iron? On oxide of antimony? The double salt called ferrocyanic acid is much more powerful than hydrocyanic acid [later he concluded that ferrocyanic acid contained a compound radical called prussine] Heat fusible (per se) similiform oxides together - aggregated or fusible compound? oxide of zinc and oxide of nickel. Does the light appear?"

insoluble in acids. I believe this is not the case with crystallised phosphate of magnesia itself. Over-dried Paris plaster? and Anhydrite are probably cases of saline idiosynthesis. There is a native compound of sulphate of soda and sulphate of lime $[\dot{\text{N}}\ddot{\text{a}}\ddot{\text{S}} + \dot{\text{C}}\ddot{\text{a}}\ddot{\text{S}}]$ which proves the disposition of salts to unite. It is also anhydrous and insoluble. Is there such a thing as a soluble anhydrous biphosphate (not meta) of soda or potash? I suspect there is from the proportion which dissolves of a specimen of biphosphate of soda slowly dried on a bath till it contained only $1\frac{1}{2}$ or 2% of water." ⁸

It is possible to infer from this passage that Graham believed that, when a salt lost water and became anhydrous, polymerisation followed or as he expressed it 'saline idiosynthesis'. This polymerism could be accompanied by ignition in which case the properties of a compound were altered. This process produced a compound polymer of the same salt possessing new properties such as a different degree of solubility in acids. These altered compounds, he referred to as 'metidionic compounds.' Graham drew up a list of compounds 'illustrative of metidionic bodies' which he had found from Berzelius's text-book. This led him to suggest further speculations of a similar kind. ⁹

In 1838, when Graham wrote about dimorphism in his text-book, he stressed the importance of the role of heat as a real constituent of these compounds. A number of metallic peroxides, such as alumina, oxide of chromium, and peroxide of tin were no longer soluble after heating to redness. The same was true for a number of salts such as the phosphates, antimonates and silicates. He argued that before heating, these compounds contained combined water and were easily soluble in acids. On heating, the combined water was lost. Generally there was also a fall in the solubility although this usually occurred at even higher temperatures. Therefore the presence of combined water was not the only cause of the solubility of these compounds. He then referred to Berzelius's observation that ignition accompanied the transition of

10. Graham: Elements of Chemistry Part 2 (London, 1838) 154.

11. R. Phillips, 'Observations on isomorphism' Phil.Mag. 3 Ser 12 (1838) pp 407-412. Both Clark and Johnston had recommended alterations in atomic weights. Johnston wanted to halve the atomic weights of silver, mercury, gold, potassium and sodium, as a result of Dulong and Petit's work on specific heats; whereas Clark wanted to double the atomic weights of sodium and silver. Because there were too many exceptions to Dulong and Petit's law, Phillips could not see the necessity for altering these atomic weights. In May 1838, he suggested an alternative proposal that heat might be combined with bodies in definite proportions. He wrote "it may in some cases like other elements combine in double proportions, instead therefore of halving the equivalents of these metals let us suppose that they are combined with two equivalents of heat and the revolution of atoms with which we are threatened will be rescued from this source of discrepancy." p 412.

a compound from the soluble to the insoluble state.

Graham explained that: "this change in bodies which affects so deeply their chemical properties is that the bodies do not contain a quantity of heat, after the change, which they must have possessed before its occurrence in a combined or latent form. No ponderable constituent is lost, but there is this loss of heat. A change of arrangement of the particles, it is true might occur at the same time in some of these bodies, such as is observed when sulphite of soda is converted by heat into a mixture of sulphate of soda and sulphuret of sodium, without change of weight; but it would be difficult to apply an explanation of this nature to oxides, such as alumina and peroxide of tin, which contain only two constituents. The loss of heat observed will afford all the explanation necessary if heat be admitted as a constituent of bodies equally essential as their ponderable elements. As the oxide of chromium possesses more combined heat when in the soluble than in the insoluble state, the first may justly be viewed as the higher 'caloruret', and the body in question may have different proportions of this as of any other constituent." ¹⁰

The possibility that heat might combine with bodies in definite proportions had ^{also} been put forward — in 1838, by Richard Phillips as a reason for not altering atomic weights of certain elements.¹¹ When Graham recognised that combined heat was a true constituent of bodies he was able to solve the problem of the isomerism of soluble and insoluble alumina etc. The two forms really differed in composition by a definite amount of combined heat. Thus they were no longer truly isomers and therefore another example of isomerism had been explained without recourse to differences in atomic arrangement.

The heat which combined in definite proportions was not to be confused, Graham insisted, with specific heat or sensible heat. With regret he accepted that "our knowledge respecting heat as a constituent of bodies is extremely limited the influence which its addition or

12. Graham, op.cit. (10) pp 154-155.

13. Graham; Wellcome MS Notebook III (1837-8) No.2554 (Old no.3179).

14. G.H.Hess, 'Recherches thermochimiques,' Ann.de Ch. 3 Ser.4 (February 1842) pp 225-229 from Pogg. Ann. 52 (1841) pp 97-118.

Hess sent each of his new scientific works to Berzelius. On December 28th 1840 he wrote to Berzelius: "...I send you the second sheets of my thermochemical investigations, I am continuing these investigations which are more interesting than any other questions because this field which is completely new for science, yields rich fruit. In the continuation, on which I am working, you will see among other things proof of the error of assuming that an acid can be a hydrogen acid; that, for example, we must write $\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{H}}} + \overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{S}}}$ and it is incorrect to write $\text{H}^2 + \overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{S}}}$. It is time to settle this question because such an effort as that of Graham is directed to the idea that it will be shown convincingly that everything which has been assumed to be fully possible is only a simple play of formulas ... I have no doubt of the cause of the main effect: the heat produced is the measure of affinity. This gives a different character to all Chemistry. Perhaps it will be my good fortune to discover the general law of affinity, but in any case, I am sure that I have prepared the way for this discovery." This letter is taken from Y.I.Solov'ev, 'New materials for the scientific biography of J.J.Berzelius.' Chymia 7 (1961) pp 116-117.

subtraction may have on the chemical properties of a body is at present entirely a matter of conjecture." ¹²

Presumably, in order to test his theory that dimorphous substances possessed different quantities of combined heat Graham made a few experiments on the subject in June 1838. His notebooks show that he examined the rise in temperature when the two forms of calcium carbonate ($\text{CaO} \cdot \text{CO}_2$), arragonite and calcareous spar, were dissolved in dilute nitric acid. ¹³ The results were virtually identical: for arragonite, the temperature rise in three experiments was 17°F in each case, whereas for calcareous spar, the rises were $16\frac{1}{2}^\circ$, $16\frac{3}{4}^\circ$, and 18°F or an average of 17.08F . Likewise, he compared the solubility of the two forms of sulphur and its effect on the temperature. With both monoclinic sulphur dissolved in turpentine and rhombic sulphur in carbon disulphide the temperature fell about 1°F . He must have been disappointed by the failure of these experiments to show any significant differences in the heat released and these experiments remained unpublished.

The immediate impetus for Graham's thermochemical studies was the criticism of his theory of salts made by G. H. Hess who was a student of Berzelius. The point at issue was the constitution of sulphates. ¹⁴ Hess rejected the views of both Berzelius and Graham. Berzelius regarded the bisulphate of potash as a double salt $\overset{\cdot\cdot}{\text{K}}\overset{\cdot\cdot}{\text{S}} + \overset{\cdot\cdot}{\text{H}}\overset{\cdot\cdot}{\text{S}}$ and Graham thought that the bisulphate was a derivative of bihydrated sulphuric acid in which the atom of saline water was replaced by an atom of sulphate of potash:



Hess said that Graham was a 'useful thinker' and he accepted that it was possible in theory that the involatile sulphate of potash might replace the volatile water. But, he argued that, if Graham was correct in his view of the constitution of this salt, then, it must be formed by an equivalent substitution process with no release of heat. Now, Hess found that heat was released in the formation of this salt and therefore

15. T. Andrews, 'On the heat developed during the combination of acids and bases', Trans.R.I.Acad. 19 (1841) part II, pp 228-248 - read January 11th 1841 and published in 1843. An abstract of these researches appeared in Phil.Mag. 3 Ser 19 (July-December 1841) pp183-184. See T. Andrews: Scientific Papers.(Edinburgh, 1889), edited by Tait and Crum Brown, pp 70-89.

16. Graham, 'On the constitution of sulphates as illustrated by late thermochemical researches.' read January 18th 1842 Chem.Soc.Memoirs 1 (1841-1843) 82-84 or Researches.400-402.

Graham's suggested constitution must be incorrect and for similar reasons Berzelius's constitution was also invalidated. As an alternative, Hess proposed a new constitution for this salt. He said that there were two acid sulphates of potash, one of which was anhydrous, K_2S^2 , and the other, which Graham and Berzelius had prepared, was simply a hydrated salt, $\text{K}_2\text{S}^2 + \text{H}_2\text{O}$. The release of heat came from hydration of the anhydrous acid salt; further addition of water did not release any more heat. However the problem was complicated because Thomas Andrews had also studied the heat released in the formation of acid salts. He had prepared them by the addition of a neutral salt to an acid. His result was quite opposite to those of Hess.

Andrews had shown that when sulphate of potash was added to dilute sulphuric acid the temperature rose by only 0.1°F , which was negligible. ¹⁵ Who was correct, Andrew or Hess?

In December 1841, Graham decided to attempt to resolve this question and in January 1842 he gave a preliminary account of his experiments to the Chemical Society. ¹⁶ He found that Andrews was correct. There was no release of heat when a double salt was made directly by mixing together two simple salts, for example he mixed sulphate of ammonia with sulphate of magnesia. The crucial experiment was the preparation of bisulphate of potash by adding sulphate of potash to dilute sulphuric acid. This experiment posed difficulties. As Hess had found out, part of the heat released was caused by the dilution of the unreacted monohydrate of sulphuric acid by the water from the sulphate of potash solution. Accordingly, Graham tried the direct experiment of mixing a saturated solution of the more soluble salt, sulphate of ammonia, with diluted sulphuric acid (s.g. $1.256 \text{HO}\cdot\text{SO}_3 + 10\text{HO}$). Even allowing for the dilution of the former salt, there was a fall in temperature of 3.88°F . This was easily explained because ten atoms of water were released in the formation of the acid sulphate of ammonia. Heat was absorbed to release this water and so the temperature fell. Thus Graham concluded

17. Graham, *ibid.* Researches 402.

18. Andrews found that no heat was released in the formation of double salts, for example when potassium tartrate solution was mixed with sodium tartrate solution. Subsals, on the other hand, evolved heat in their formation, and this could be explained, said Andrews:

"by referring to the observations of Graham, we can understand the evolution of heat during the conversion of neutral phosphates and arseniates into basic salts. In reality one equivalent of water is here again replaced by one equivalent of alkali just as occurs in the direct combination of acids and alkalis."

Further confirmation of Graham's view of the constitution of the phosphates came from the fact that heat was released when caustic soda was added to $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$ converting it to $\text{Na}_2\text{P}_2\text{O}_7$, whereas no heat was released when caustic soda was added to sodium pyrophosphate $\text{Na}_2\text{P}_2\text{O}_7$ because no basic pyrophosphate was formed. See *op.cit.* (15).

19. Graham, 'Experiments on the heat disengaged in combinations.' These researches were read in two parts to the Chemical Society. Part 1 was read on November 1st 1842 and part 2 was read on January 1st 1844. Graham appears to have rushed the second part. He gave few conclusions, instead, he relied simply on statements of experimental results with little interpretation. An explanation for this hurried account might be that Graham found that he was simply confirming results previously obtained by Andrews and furthermore the latter had just read another paper on the same subject before the Royal Society on December 14th and 21st 1843. (Andrews: 'Thermal changes accompanying basic substitutions.' Phil.Trans. 134 part I (1844) 21-37). Graham's two-part paper is found in Chem.Soc.Mem. 1 (1841-43) 106-126 and Chem.Soc.Mem. 2 (1843-45) 51-70 or Researches: 402-441.

20. Andrews, 'Report on the heat of combination for the British Association in 1849' Phil.Mag. 3 Ser 36 (1850) 511-529 or Scientific Papers of T. Andrews (Edinburgh, 1889) 196-220.

21. Graham, MS. Notebook B, *op.cit.* (8), pp. 339, 340, 373 (May 16th 1834).

that his experiments were "sufficient to demonstrate that no heat is evolved in the formation of double sulphates [this group of salts included bisulphate of potash] Sulphate of potash and water are therefore equivalent in the constitution of such salts, or 'equicalorous', if a term may be coined to express this relation." ¹⁷ Therefore Andrews was correct and Graham had experimentally vindicated his views on the constitution of double and acid salts; indeed Andrew's results, in general, provided an important experimental confirmation of Graham's views on the constitution of salts. ¹⁸

Between 1842 and 1843 Graham extended his thermochemical researches with the aim of verifying his views on the constitution of salts. Therefore he did not attempt to obtain precise measurements of the heat evolved in chemical reactions. ¹⁹ As Andrews pointed out in 1849, Graham did not give sufficient data for an accurate calculation of the heat set free in thermochemical changes. ²⁰ Also he failed to make corrections for the heating or cooling influence of the surrounding air and he did not determine the specific heats of those solutions formed in his experiments. Graham had claimed that he used sufficiently large quantities of water to be able to disregard any changes in specific heat; but this claim is not adequate for precise work. It is worth noting that, to avoid loss of heat to the surroundings, Graham had taken care to make preliminary experiments for estimating the rise in temperature. He then cooled his chemicals before mixture so that the temperature would rise on mixing to that of the surrounding air. His results were simply stated as temperature changes instead of heat changes. That Graham's work was reasonably accurate can be seen by a comparison of his results with those of Andrews and Thomsen.

Graham's interest in heat studies and their relation to the constitution of salts can be traced back in his notebooks to at least 1834. ²¹ For example in May 1834 he measured the rise in temperature when anhydrous copper sulphate was placed in a muslin bag over boiling water. The

22. Graham, MS.Notebook C (September 2nd 1834 - July 1835) Andersonian Library, Strathclyde University. p 110 - entry dated January 31st 1835.

23. Hess, 'Thermochemical researches,' Ann.de Ch. 2 Ser 74 (1840) 325-330 and Ann.de Ch. 2 Ser 75 (1840) 80-103. Graham op.cit.(19).

I have drawn up the following table of comparative results which shows that Hess was wrong to believe that there was a whole number relationship between the heat evolved in successive stages of hydration of sulphuric acid.

<u>Hydrate formed</u>	<u>Ratio of heat evolved in successive stages of hydration</u>					<u>(x = a large number)</u>
	HO,SO_3	$\text{HO,SO}_3 \cdot \text{HO}$	$\text{HO,SO}_3 \cdot 2\text{HO}$	$\text{HO,SO}_3 \cdot 5\text{HO}$	$\text{HO,SO}_3 \cdot x\text{HO}$	
Hess (1839)	8	2	1	1	1	
Graham (1842)	-	2	0.72	1.35	1.18	
T.Thomson (1836)	-	2	0.76	1.12	-	
Abria (1844)	6.02	2	0.95	1.14	-	
Favre & Silbermann (1849)	-	2	0.93	1.11	-	
J.Thomsen (1885)	-	2	0.95	1.16	1.18	

The other results were taken from T.Thomson, 'Combinations of sulphuric acid and water,' B.A.Report (1836) 56-61; Abria, 'Note sur la chaleur dégagée dans l'hydratation de l'acide sulphurique,' Ann.deCh. 3 Ser 12 (1844) 167-176. Abria took up his researches as a result of the disagreement in the results between Hess and Graham, but his results did not agree exactly with either of the aforementioned. Favre and Silbermann - See Andrews B.A.Report op.cit. (20); Thomsen's results are usually considered to be reasonably accurate. They were taken from M.M.P.Muir: Elements of Thermal Chemistry (London, 1885) 155-157.

temperature rose to 276°F , whereas in a corresponding experiment with copper sulphate monohydrate the temperature only rose to 226°F . In January 1835 Graham recorded a list of work to be performed which included: "Latent heat - compare the latent heat of sulphate of magnesia, zinc and of bodies of the same formula. Of the double sulphates of magnesia, copper and zinc with sulphate of potash among themselves. Of the single and double salts of potassium and ammonium. Of the phosphates and arseniates of soda. The same with subphosphate or subarseniate." ²² These suggestions do not appear to have been taken up immediately. However, in 1842 he examined the heat released when the isomorphous oxides MgO , CuO and ZnO were dissolved in very dilute sulphuric acid. To his surprise the results were not identical as he had expected from the reported isomorphism of these oxides. To understand the nature of these differences Graham examined firstly the heat released on hydration of the sulphates and secondly the heat absorbed by their solution in water. He found that the heat released by the gain of one atom of water was very similar for CuO,SO_3 ; MnO,SO_3 and HO,SO_3 but it differed slightly from that released by MgO,SO_3 and ZnO,SO_3 . He concluded, however, that there was sufficient agreement to suppose that the magnesian oxides had related thermal properties.

The progressive hydration of sulphuric acid had already been studied by Hess. He believed that there was a simple whole-number relation between the quantities of heat evolved during the successive stages of hydration of sulphuric acid. Graham and others demonstrated that this was not the case. ²³

This first part of Graham's thermochemical researches was presented to the Chemical Society on November 1st 1842 and the second part concerning the neutralisation of acids by alkalies was also read to the Chemical Society on January 1st 1844. In the latter part, Graham stated his results almost without comment, presumably because they were essentially a confirmation of the experiments made on the same subject by

24. Andrews, 'On the heat developed in chemical reactions', Extract of a scientific memoir sent to the French Academy Prize Essay contest of 1849. See Comptes Rendus 28 (1849) 666 on the Essay contest and for the actual paper:- T. Andrews, Scientific Papers. (Edinburgh, 1889) pp 495-504, see p 501:-

"Acid neutralised with an equivalent of caustic potash

Acid	<u>Rise in temperature for each acid given</u>								
	<u>Sulphuric</u>	<u>Nitric</u>		<u>Phos-</u>	<u>Hydrochloric</u>		<u>Arsenic</u>	<u>Oxalic</u>	<u>Acetic</u>
		at 62°	at 40°	phoric	at 60°	at 40°			
Graham's results (1844)	7.28°	6.72°	6.64°	6.40°	6.40°	6.44°	6.53°	6.71°	6.62°
Andrews' results (1841)	7.17°	6.63°		6.48°	6.43°		6.48°	6.49°	6.21° "

25. Berzelius: Rapport Annuel sur les Progrès de la Chimie (French translation by Plantamour) 4 (1844) 9-13 and 5 (1845) 3-8. Berzelius compared Graham's work on heat of solution with that of A.Chodnew ('Thermochemical researches' J.für practische Chemie 28 (1843) 116-124). He noted that their results did not agree in detail but they were in the same direction.

Andrews in 1841. Indeed, both Hess and Andrews had made detailed investigations of the heats of neutralisation before Graham. They had found that a constant amount of heat was evolved in the neutralisation of equivalent quantities of diluted acid and alkali. Hess showed that a given acid released a constant amount of heat with different bases whereas Andrews showed that a given base released a constant amount of heat with different acids. Curiously, both men failed to combine their results and therefore they developed a rather one-sided view of the thermochemistry of neutralisation. Andrews noticed that less heat was evolved in neutralisation when he used weak bases like mercuric oxide or weak acids such as prussic and tartaric acids. In 1849, Andrews compared his results for neutralisation with those determined by Graham, reducing them both to the same standard.²⁴ He confirmed that their results were in close agreement; this demonstrates the reasonable accuracy of Graham's work.

Graham's thermochemical researches provided a useful experimental confirmation of his theoretical views on the constitution of salts. But they proved to be less influential results than those of Hess, Andrews and later workers. The reasons for this are several. Graham failed to give an adequate interpretation of his results and he failed to express them in thermal units which made comparisons difficult. Furthermore, he did not make detailed corrections either for loss or gain of heat on the mixing of solutions, or for changes in the specific heat of solutions. Nevertheless Andrews referred to "Graham's valuable paper on heat of combination" and Berzelius reviewed this "highly important work" in his yearbook.²⁵

The material theory of heat and the binary constitution of salts will be seen to be important in Graham's writings on voltaic circles and electrolysis, which will now be considered.

Graham's interest in electrolysis during the 1830's is understandable following the important discoveries which had been made, notably by Davy

26. Graham, MS. Notebook B, op.cit. (8), September 1832, p 55.

26a. Graham, ibid.

27. Graham, ibid. p 59.

and Faraday. In 1832 Graham examined the electrolysis of solutions of aluminium chloride and ferric chloride. With aluminium chloride solution, hydrogen and gelatinous alumina were produced at the negative wire, whilst, at the positive wire there was "remarkably little gas dis-engaged, not $\frac{1}{10}$ th of what was disengaged on the other side - very singular. A cloud of alumina also appeared not in immediate contact with the wire and fell down to the bottom of the glass - not gelatinous but more like idiogenic alumina." ²⁶ By 'idiogenic' alumina Graham meant a polymer of anhydrous alumina molecules as opposed to the hydrated gelatinous alumina. For a comparison he then tried the electrolysis of a solution of alum. This gave hydrogen and oxygen in the usual proportions of two to one by volume.

The use of chlorides in electrolysis experiments appeared to give anomalous results. This was borne out when he electrolysed ferric chloride solution. At the negative wire the peroxide of iron was partially "deoxidised to give some oxide of a green colour." ^{26a} The liquid smelled of chlorine and on testing near the positive wire he found that cudbear was reddened and then bleached. To examine the electrolysis of chlorides more carefully, he turned to the electrolysis of water acidulated with a few drops of commercial muriatic acid. Using a glass and tubes with platinum wires connected to a 12 - plate battery of Wollaston's construction, he found that after half an hour, he obtained a tube full of hydrogen at the negative wire and a tube about one third full of oxygen at the positive wire. The liquid in the oxygen tube again smelled strongly of chlorine and bleached powerfully. To explain this, Graham wrote: "suppose water to consist of two atoms or volumes of hydrogen and one atom of oxygen. Muriatic acid - of one atom of hydrogen and one atom of chlorine. One atom of oxygen and one atom of chlorine go to the positive pole but the chlorine is absorbed by the water - and three volumes or atoms of hydrogen to to the negative pole. Hence only one volume of oxygen against three volumes of hydrogen. Corollary - hence the propriety of halving the atom of chlorine as done by Berzelius." ²⁷

28. Graham, 'Communication on the subject of inorganic salts and in particular on the function water discharges as an element of their composition.' B.A. meeting at Liverpool September 13th 1837 Phil. Mag. 3 Ser 11 (1837) 396-398. "The hydrated acids are unquestionably salts having water as a base and they correspond in a remarkable manner with the salts having for base, MgO, ZnO, CuO or any other oxide isomorphous with magnesia. Hence water as a base belongs to the magnesian class of oxides." p 396.
29. Graham, Elements of Chemistry Part 2 (London, 1838) p 94 and Berzelius Traité de Chimie translated by M.Esslinger Vol.5 (Paris, 1831) 'Table synoptique des poids atomiques des corps simples' p 1 (appendix)
30. Graham, MS. Notebook C, op.cit. (22), June 11th 1835 pp 210-224, 235-236. With dilute nitric acid the temperature rose at both positive and negative wires in 9 minutes from 72° to 94°; the evolution of hydrogen at the negative pole soon diminished. After 1 hour 10 minutes the electrolysis was stopped. The positive pole gained 0.47 gr. and the negative pole lost 0.74 gr. "The secondary absorption of hydrogen at the negative pole would have the effect of raising the temperature there (hence an inequality of temperature^{is} observed)", p 219. From a further experiment he wrote that "in seven minutes temperature of positive branch 100°, of negative 93° but the Pt wire did not descend as far into the positive as into the negative by $\frac{1}{2}$ ". Hence the centre of decomposition must be nearest the positive. This must be attended to." p 220.

This explanation written in 1832 is interesting. Graham seems to have equated volumes of gases with atoms as Berzelius had done. But Graham wrote water as HO in his paper on phosphates in 1833; that is he accepted that two volumes of hydrogen were equivalent to one atom and not two atoms. He later justified this choice by pointing out that there was a strong analogy between water HO and the magnesian oxides MgO, CuO, ZnO etc.²⁸ Graham must have changed his opinion on the relation between atoms and volumes because in 1838 he wrote that 2 volumes of chlorine contained one atom of Cl = 442.65 (on the scale O = 100), whereas Berzelius wrote that one volume of chlorine contained one atom of Cl = 221.326.²⁹ It would appear that Graham had not entirely abandoned the possibility that an atom of chlorine might be divisible in theory for, as we shall see, he suggested later that it might well be composed of two metallic atoms so strongly combined that division appeared to be impossible.

From a notebook entry of June 1835 it is evident that Graham was again investigating the electrolysis of diluted acids. He placed these acids in positive and negative compartments of a glass 'W' tube separated by asbestos.³⁰ His interest in the connection between heat and electricity can be seen in his observation that there was a rise in temperature at both electrodes. The rise in temperature was greatest at the positive wire. With both dilute sulphuric acid and dilute nitric acid as electrolytes he observed a relative increase in the amount of acid around the positive wire compared to the negative wire. He might well have interpreted this as evidence for the movement of the acids SO_3 and NO_5 from the negative to the positive wire. With hydrochloric acid Graham observed some important differences: the negative pole became hotter than the positive pole and there was a greater loss of mass at the negative pole [due to loss of the heavy gas chlorine?]. No comments were offered on these results in his notebooks, although it is possible that he may have continued his experiments because he referred here to notebook D which is at present unfortunately missing.

31. James Young, MS. Notebook 1834/40. Andersonian Library, University of Strathclyde. "Galvanism - February 8th 1836 Made a battery of 12 double zinc plates ... a large one was made on this plan for Mr. Graham and shown to Glasgow Phil.Soc. on the 10th, in the soirée on the 15th. On the 1st March I sent away to London ... a battery of the small size above-mentioned to Dr. Faraday with a letter (March 1836). Dear Sir, Confident that anything connected with electricity cannot come amiss to you however humble the source from which it proceeds. I take the liberty of furthering to you by a friend going to London a small galvanic battery which I have constructed ... P.S. Our Professor [Graham] intended writing you ere this time connected with this subject but very unfortunately he is at present confined to bed by an attack of inflammation of the eyes. April 22nd reply received" - began designs - compared his battery with Faraday's. See J. Young 'An account of a new voltaic battery being a modification of the construction recommended by Mr. Faraday' Glasgow January 4th 1837 Phil.Mag. 3 Ser.10 (1837) 241-244.
32. Thilorier first described his apparatus in 1835. ('On liquid carbonic acid' Ann.de Ch. 2 Ser.60 (1835) 427). Graham enlisted Liebig's help to obtain Thilorier's apparatus. On October 17th 1837 he wrote to Liebig: "But if you should see Thilorier [in Paris], you would oblige me, by letting me know his terms for the carbonic acid apparatus, and how soon he would undertake to furnish it. I shall write to him after I hear from you." Graham-Liebig letters, Bayerische Staatsbibliothek, Munich. Graham demonstrated the apparatus for the President of the Royal Society, the Duke of Sussex on March 24th 1838 and again at a University College Soirée on April 25th 1838. See Wellcome MS. Notes on Thilorier's apparatus (1838) 1611, (MS2576) Wellcome Library and a report of the Soirée in The Lancet (1838) 234-235.
33. Faraday, 'On the solid, liquid and gaseous states of carbonic acid illustrated by Thilorier's apparatus.' In this R.I. Lecture given on May 18th 1838 Faraday commented "not impossible that hydrogen is a metal" H.Bence Jones, Life and Letters of Faraday 2 (London, 1870) 87. James Young wrote to J.H.Gladstone that Faraday on hearing that Graham had obtained Thilorier's apparatus from Paris ... "came to Graham's laboratory, and, as one might expect, showed great interest in this apparatus, and asked Graham for the loan of it for a Friday evening lecture at the Royal Institution which of course Graham readily granted, ... Faraday had a theory at that time that all metals would become magnetic if their temperature was low enough; and he tried that evening some experiments with cobalt and manganese, which he cooled in a mixture of carbonic acid and ether, but the results were negative." J.H.Gladstone, The Life of Faraday (London, 1872) pp 129-130. Faraday subsequently used Thilorier's apparatus in his researches on the liquefaction of gases in 1845.
34. A.E.Jeffreys, Michael Faraday, A List of his Lectures and Published Writings (London, 1960) 282. 'Eight lectures on electricity' 1838 (1) April 28th, (2) May 5th, (3) May 12th, (4) May 19th, (5) May 26th, (6) June 3rd, (7) June 9th, (8) June 16th. MS. Notes at R.I. Graham: Wellcome MS. notes on Faraday's lectures on electricity, May 5 - June 9th (1838). 511. MS. No.2577 (Old No.3389). Graham appears to have attended lectures 2,3,5,6,7.

That Graham continued to be interested in electrolysis can be inferred from the fact that his laboratory assistant James Young constructed a new battery for him in February 1836. Young had followed suggestions made by Faraday for modifying Hare's battery. A copy of the new battery was dispatched to Faraday in March 1836 and Graham demonstrated this new battery to the Glasgow Philosophical Society,³¹ in February 1836.

The following year marked an important change for Graham. He began writing his textbook Elements of Chemistry and he was appointed to the Professorship of Chemistry at University College, London. This move allowed Graham to meet Faraday and this must have further stimulated Graham's interest in electricity. In addition, Graham needed to write about electricity in his new textbook and also to discuss the subject in his lectures.

In February 1838 Graham acquired Thilorier's apparatus from Paris for the purpose of liquefying and solidifying carbonic acid.³² He was the first to demonstrate this apparatus in England and Faraday soon asked to borrow the apparatus. He wanted to use it for a Friday evening lecture at the Royal Institution and also for testing his theory that metals like cobalt and manganese might become magnetic at low temperatures.³³ At the same time Graham attended a series of eight lectures on electricity given by Faraday. The notes which Graham wrote down at these lectures show that he was interested both in the experimental demonstrations and in Faraday's views on the nature of matter and electricity.

Thus Graham wrote that Faraday "spoke of electricity as a power obtained or developed or called into existence in different ways. Spoke of matter generally without condescending upon particular kinds of matter he never used the gold leaf electrometer for discrimination of the two electricities. Never spoke of the two [electricities] or of electricity as a substance [but as] a power of matter spoke of positive and negative electricity each repelling itself and attracting the other. Thus the 'key to the phenomena but not the principle'."³⁴ Bence Jones recorded that Faraday ended these lectures with an exposition

35. H.Bence Jones: Life and Letters of Faraday 2 (London, 1870) 87.
36. Faraday, 'On the electricity of the voltaic pile; its source, quantity, intensity, and general characters,' [read June 5th 1834]
See:- Experimental Researches in Electricity 1 (London, 1839)
paragraphs [918] and [919] or pp 272-273.
37. Graham, 'Galvanism and organic action,' Unpublished MS. Essays of the Glasgow Medical Society Volume 19 (1831-2). This 8-page essay was written out by Graham. It is kept in the Library of the Faculty of Physicians and Surgeons, Glasgow.

of the conservation of force. His lecture notes finished with: "general experimental relation of the powers; ignite wire; give spark; decompose; made magnet by one current, and hence the universality of the common cause, whatever it may be, the force is nowhere destroyed; all effects are convertible." ³⁵

Faraday did not accept either of the fluid theories of electricity and, as he stated in 1837, he was not an atomic chemist. Faraday wrote in 1834 that "all the facts show us that power commonly called chemical affinity, can be communicated to a distance through the metals and certain forms of carbon; that the electric current is only another form of the forces of chemical affinity; the forces termed chemical affinity and electricity are one and the same Thus, when zinc, platina, and dilute sulphuric acid are used, it is the union of zinc with the oxygen of water which determines the current" ³⁶

Graham recognised that Faraday had definitely rejected the notion of two electricities in his 1838 lectures. This confirmed earlier accounts which Faraday had given of electricity. When Graham wrote about galvanism or voltaic circles in 1839 he had clearly accepted Faraday's views which were first stated in 1834. No longer did Graham explain galvanism in terms of two electricities as he had done in 1832. ³⁷ Now he regarded chemical affinity as the fundamental concept in any explanation of voltaic circles and he entirely rejected the idea of either electricity or electric fluids. He explained the action of chemical affinity at a distance by assuming that induction occurred via the progressive action of chemical affinity. This inductive action polarised molecules in both metallic conductors and electrolytes. In order to explain the transmission of chemical affinity over distances he had to assume polymeric chains of molecules in voltaic circles. Faraday had also made use of the action of induction in polarising molecules thereby allowing chemical affinity to exert its effects in electrolysis.

When Graham decided to abandon the idea of electricity altogether he

38. Graham, Elements of Chemistry, 2nd.edn. Vol.1 (London, 1848) p 273. In 1839 Graham wrote about the production of electricity from friction: "When a silk handkerchief or a piece of resin is rubbed upon glass, both are found after separation, in a polar condition, and continue in it. The rubbing surface of the glass becomes and remains zincous, and that of resin or silk is chlorous; and a molecular polarisation is at the same time established through the whole mass of both glass and resin, reaching to their opposite surfaces, which exhibit the other polarity. The powers thus appearing on the two rubbing surfaces, being manifestly different, were distinguished by the names of the bodies on which they are developed; that upon the glass as vitreous electricity (basylous affinity) and that upon the resin as resinous electricity (halogenous affinity)" Graham, Elements of Chemistry, part 3 (London, 1839) p 234.
39. Faraday wrote "particles of the dielectric (now an electrolyte) are in the first instance brought, by ordinary inductive action into a polarised state, and raised to a certain degree of tension or intensity before discharge commences, the inductive state, is in fact a necessary preliminary to discharge,"
From 'On induction (continued)' (read February 8th 1838) See:- Faraday, Electrical Researches in Electricity 1 (London, 1839) Paragraph [1345] or p 428.

also rejected the terms positive and negative, replacing them by zincous and chlorous affinities, resembling the affinities of zinc and chlorine in compounds. The only clue which Graham gave concerning the nature of these different affinities was, in 1848, when he said that they might possibly depend on unequal amounts of combined heat. This curious suggestion is reminiscent of his earliest attempts to explain the electricity produced during friction as superficial heat.³⁸ However, this superficial heat was not heat combined with matter but merely heat which was attracted weakly to all matter.

Davy had argued that chemical affinity and electrical effects had a common origin and subsequently Faraday believed he had demonstrated that chemical affinity and electricity were identical. Indeed, this was a view which Oersted had suggested was theoretically necessary. Faraday also supposed that particles of matter could be polarised by an exaltation of their chemical affinity; this inductive action had to precede the discharge of particles in a voltaic circle.³⁹ A typical example of a voltaic circle consisted of plates of zinc and copper joined by a connecting wire, with the plates dipping into hydrochloric acid.

In 1839, Graham discussed the voltaic circle in his textbook. He wrote that: "to explain the phenomena of the voltaic circle, the existence of a substantial principle, the electric fluid, has been assumed of such a nature that it is readily communicated to matter, and capable of peculiar attractive and repulsive forces which occasion the decompositions observed. A vehicle was thus created for the chemical affinity which is found to circulate. But it is generally allowed that this form of the electrical hypothesis has not received support from observations of a recent date, particularly the great discoveries of Mr. Faraday, which have completely altered the aspect of this department of Science, and suggest a very different interpretation of the phenomena. All electrical phenomena whatever are found to involve the presence of matter so the phenomena may really be exhibitions of the inherent properties of matter.

40. Graham, Elements of Chemistry, part 3 (London, 1839) 200.
41. Graham, Elements of Chemistry, 2nd.edn. Vol.1 (London, 1848) 273.
42. Graham, op.cit. (40) p 201.
43. Graham, 'On the voltaic circle,' Literary Gazette (1839) p 564.
See also Graham, 'On the theory of the voltaic circles,' British Association Report, part ii 29-31, or Researches.398-399, from The Athenaeum report of the lecture given on Tuesday, August 27th 1839 p 660 and also Graham, Elements of Chemistry, part 3 (London, 1839) 197-241.

The idea of the circulation of electricity through the voltaic circle appears to be abandoned. Electrical induction, by which certain forces are propagated to a distance, is found to be always an action of contiguous particles upon each other, in which it is unnecessary to suppose that anything passes from particle to particle, or is taken from one particle and added to another. The change which a particle undergoes, takes place within itself, and is looked upon as a temporary development of different powers in different points of the same particle. The doctrine of polarity has thus come to be introduced into the discussion of electrical phenomena." ⁴⁰

Although Graham does not refer to heat in this extract he did suggest in 1848 that polarity in binary molecules might have its origin in the "inequality in their proportions of combined heat." ⁴¹ Graham argued that the chemical phenomena of the voltaic circle could therefore be considered as "an exhibition ^{of} ordinary chemical affinity, acting in particular circumstances, without any electrical hypothesis." ⁴² Thus Graham entirely excluded the existence of the electric fluid. He was opposed to any explanation which involved electricity and in this sense he was more extreme in his views than Faraday; this is particularly true with regard to the explanation which Graham gave of the role of metals in the voltaic circle, as we shall see presently.

Graham first presented his views on the voltaic circle to a meeting of the British Association for the Advancement of Science at Birmingham in August 1839. He was reported to be in favour of referring the phenomena of the voltaic circle "directly to chemical affinities, and to omit entirely the idea of electricities being possessed by molecules." ⁴³ He advocated a change in the language used to rid voltaic phenomena of electrical terms. He suggested that the terms positive and negative should be replaced by 'zincous' and 'chlorous' respectively and that anode and cathode should be called 'zincoïd' and 'chloroid' respectively. The term zincoïd was meant to be like-zinc which was at the head of its

class. Likewise, chloroid was chosen because, of all salified bodies, chlorine was the head element. Having dealt with nomenclature Graham turned to the theory of the voltaic circle. He assumed that both zinc and hydrochloric acid contained binary molecules which could be polarised. Polarity was not an ordinary condition of these molecules but it was developed when two chemically different substances were brought into contact. A polarised molecule had two ends; one end having a zincous affinity or attraction and the other a chlorous affinity or pole. The electrolyte was renamed a 'zincolyte', and its molecules had to possess positive or negative parts or as Graham preferred to call them, 'basyles' and 'salt-radicals' respectively. The character of the body could be determined by its surroundings; thus mercury and the more negative metals although clearly basyles appeared at times to assume a salt radical character in relation to highly positive metals.

The transfer of chemical affinity in a voltaic circle occurred by a process of induction. The terminal zincous atom of a plate of zinc engaged part of the affinity of a chlorine atom in an adjacent hydrochloric acid molecule. When the circuit was completed, the affinity of the zinc atom for the chlorine atom overcame the affinity of chlorine for the hydrogen atom to which it was united. The chlorine atom then joined to the zinc and the hydrogen atom became separated. This process was continued through a chain of HCl molecules in a Grotthuss-like mechanism, as Faraday and others had suggested, until an atom of hydrogen was released at the other pole. This chain of decompositions and recompositions was repeated many times and constituted the 'current'. Graham added that these notions of induction and polarity were suggested to him by a consideration of magnetism.

The response to Graham's theory of the voltaic circle was guarded. Kane accepted the occurrence of polar excitation accompanied by the passage of current but he could not accept the pre-existence of a binary condition in all conducting bodies and furthermore he refused to accept

44. R. Kane, Elements of Chemistry (Dublin, 1841) 325.
45. C. Daubeny, An Introduction to the Atomic Theory 2nd.edn. (London, 1850) "Graham in his Elements has attempted by following up views which Faraday put forth with respect to the theory of the voltaic pile to bring under the same general law the phenomena of chemical and inductive affinity. He has abandoned the idea of electricity being concerned ... Nevertheless as it cannot be denied, that an attraction however produced does take place between the masses of two bodies, at the very time when a chemical affinity is exerted between their particles; and as it has been assumed that the former species of attraction is due to a particular fluid called electricity, it may render our views more intelligible if we adopt the ordinary hypothesis which regards electricity as the agent concerned in both series of effects." pp 207-208.
46. Graham, 'On the voltaic circle', Literary Gazette (1839) p 564.
47. R. Hare, 'A new theory of galvanism' Ann.Phil. 14 (1819) 176.
48. R. Hare, 'Dr. R. Hare's objections to the theories of Franklin, Dufay and Ampère' Phil.Mag. 3 Ser 32 (1848) p 470.

the abandonment of the electric current.⁴⁴ Likewise, Daubeny was reluctant to reject the electric current.⁴⁵ Immediately after Graham's talk to the British Association, Grove said that he objected to the new terminology which had been introduced. He regarded the terms zincous and chlorous as being too specific because they were not the extremes of their class. He added: "for instance in chloric acid, oxygen must according to Professor Graham's views be chlorous to chlorine and at the other extreme potassium and the earthy radicals were more zincous than zinc."⁴⁶ Even if extreme terms were chosen, he continued, then it would necessitate further change if substances of a greater extent of difference were discovered in the future. Therefore he preferred to retain the terms positive and negative which were "essentially generic" and applicable to any change which could be foreseen. This was valid criticism.

Robert Hare, who had previously suggested that the principle drawn from the voltaic pile was a compound of caloric and electricity,⁴⁷ commented on Graham's statement that all electrical phenomena whatever involved the presence of matter. He wrote: "unless the distinguished author, Graham, wished to restrict the word matter to ponderable matter, there is no novelty in the idea since the hypotheses of Franklin and Dufay assume the existence of one or more imponderable material fluids. But if the meaning of the word matter, is only to comprise that which is ponderable the allegation is inconsistent with the authority cited [Faraday]. According to the researches of Faraday there is an enormous electrical power in metals and according to his speculations such powers must be considered as imponderable material principles, pervading the space in which they prevail, independently of any ponderable atoms acting as a basis for material properties, the existence of such atoms being represented as questionable."⁴⁸ These comments were made by Hare in 1848 and they remained unanswered by Graham.

Pearce Williams has argued that Faraday regarded the exaltation of chemical affinity during induction from the view-point of Boscovichian

49. L. Pearce Williams: Michael Faraday ——— (London, 1965) p 245.
50. James Napier (1810-1884), was a dyer and antiquary, who attended Graham's lectures along with James Young and David Livingstone. J. Napier, A Manual of Electrometallurgy, 2nd. edn. (London, 1852) 140-141.
51. Alfred Smee (1818-1877) Surgeon. [See: Memoir of Alfred Smee, F.R.S. by his daughter (London, 1878) p 60 "The distinguished chemist and investigator Professor Graham had similar tastes to my father. How amusing it was to spectators to hear them intermingling their conversations on abstruse chemical and philosophical theories with their theories on the art of fishing!"] See Alfred Smee, Elements of Electro-metallurgy 2nd.edn. 1842 (London, 1843) pp 306-327.
52. On June 23rd 1838, Graham wrote to Schönbein thanking him for the papers which he had sent to him during the Winter, and on May 28th 1839, Graham expressed his own opinion in a letter to Schönbein that "your researches on the galvanisation of metals would, I have no doubt, greatly interest the [British] Association in theory and practice" and so in August 1840 [?] Schönbein sent a memoir for Graham to present to the British Association meeting at Glasgow. Unpublished letters from Graham to Schönbein, Universitäts Bibliothek, Basel.

atomism and that a Daltonian atomist could not have conceived of the addition or subtraction of such forces.⁴⁹ Graham might possibly have been thinking along similar lines but there does not appear to be any firm evidence for this view.

Voltaic circles were also discussed in contemporary works of electrometallurgy. James Napier, a former student of Graham's, included an account of Graham's theory of the voltaic circle in his textbook. Napier subsequently modified Graham's theory to take into account the later researches of Daniell and Miller.⁵⁰ The latter had shown that only the negative element was transferred in electrolysis and not the positive element. Another view of the voltaic circle in electrometallurgy was given by Graham's friend, Alfred Smee. Like most of his contemporaries, Smee supported the view that electricity had a real existence. Interestingly, he concluded his textbook with the comment that the hypothesis of the unity of matter was rendered probable from the considerations of the actions in the galvanic battery.⁵¹ He argued that the known chemical elements could be explained easily by different arrangements of a single element. He quoted Proutian examples such as $8H = \text{oxygen}$ and $108H = \text{Ag}$ etc. He referred to a probable experimental confirmation of this view, presumably alluding to the work of Samuel Brown, but he pointed out that his support for the idea of unity of matter was not derived from these experiments.

Whilst Graham was discussing voltaic circles he was also in correspondence with Schönbein and it is possible to see certain similarities in their work.⁵² For example Schönbein believed that iron particles possessed two poles one of which attracts and the other repels. When iron was treated with concentrated nitric acid, Schönbein wrote that, the poles of the iron molecules facing outwards repelled oxygen and therefore caused passivity. In 1838, Schönbein put forward his 'tendency theory' of voltaic electricity, in which he argued that any tendency for two different chemicals to unite was a chemical action, whether it was successful or

53. On Schönbein, see the article in D.S.B. by H.A.M. Snelders, and C.F. Schönbein: 'Letter to Faraday' December 31st 1837 Phil. Mag. 3 Ser 12 (1838) 225-228; Schönbein: 'Conjectures on the cause of the peculiar condition of iron' May 24th 1838. Phil. Mag. 3 Ser 13 (1838) 256-261 and 'Notice on some peculiar voltaic arrangements' Phil. Mag. 3 Ser 15 (1839) 136-145.

54. Graham, op.cit. (41)

55. Graham, 'Chemical observations on the application of spongy platinum to eudiometry.' Quart. Journ. of Science 2 (1829) 354-359 or Researches. 41-43.

56. Graham, Elements of Chemistry 1st. edn. part 2 (London, 1838) 185, or 2nd. edn. Vol. 1 part 2 (London, 1848) 223.

not and that such a tendency would effectively put electricity in circulation. He added that he was convinced that chemical affinity and electricity were different forms of the same thing.⁵³ There is certainly some resemblance between the tendency theory and Graham's concept of inductive affinity. Like Schönbein, Graham accepted that molecules of iron possessed two poles. For example Graham wrote in 1848 that: "the molecular condition of conductors such as carbon and the metals, in a voltaic circle appears to be that of a polymeric combination. Their atoms must be feebly basylous and chlorous to each other; the distinction depending possibly upon inequality in their combined heat many of these binary molecules are associated together like the many similar atoms of carbon or of hydrogen which we find associated in the polymeric hydrocarbons. The whole must be held together by their chemical affinities, and the aggregation of the mass be the final resultant of the same attractions."⁵⁴

The behaviour of metals like platinum in voltaic circles remained a continuing interest for Graham. In 1829, he mentioned that Henry had found that the oxidation of hydrogen by oxygen, in the presence of platinum, was suspended by the addition of a minute quantity of carbon monoxide. This continued until all the latter chemical had been removed by a slow oxidation process.⁵⁵ Graham suggested later that the interference by carbon monoxide seemed "to point to a chemical, perhaps to an electrical explanation of the action of platinum, rather than to the adhesive attraction of the metal."⁵⁶ The gas battery was yet another interesting example of a voltaic circle discussed by Graham. If a cell was divided into two halves each containing a platinum plate and hydrochloric acid, then a voltaic circle was made, by bubbling hydrogen into one chamber and oxygen into the other. Schönbein had shown that polarisation occurred when the plates were joined and the gases disappeared, because hydrogen was removed by oxidation. Graham suggested that the polar molecule, platinum with hydrogen, was the positive pole and that platinum

57. Graham, Elements of Chemistry 2nd.edn. Vol.1 part 2 (London, 1848)
267-269.

58. Graham, 'On the occlusion of hydrogen gas by metals' Proc.R.S. (June
11th 1868) 16 (1868) 422, or Researches.283-290, see p 286.

with oxygen, was the negative pole. He represented this diagrammatically as follows:-

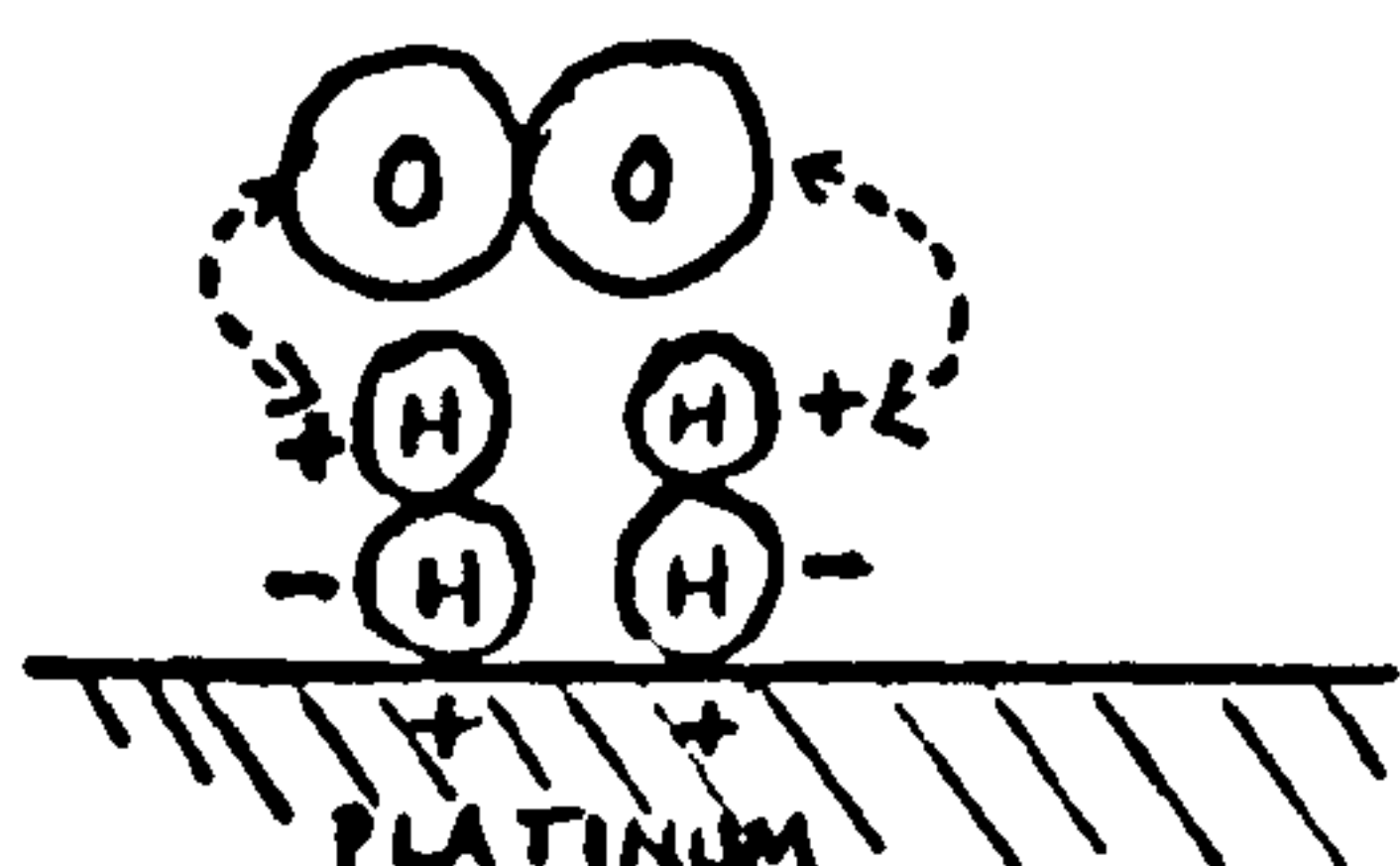
$$\begin{array}{ccccccc} \text{Pt} & \text{H} & . & . & . & . & . & . & . & . & \text{O} & \text{Pt} \\ & - & + & & & & & & & & - & + \end{array}$$

acid

He believed that platinum was well-suited to form such combinations because it had an intermediate character between basyle and salt-radical. The polar action was intensified because at the positive pole, hydrogen joined to chlorine of HCl, and at the negative pole, oxygen joined to the hydrogen of HCl. Likewise he argued that the catalytic inflammation of hydrogen and oxygen by platinum occurred by the formation of a voltaic circle in which there was a platinide of hydrogen and an oxide of platinum. The polar H and O, either came into direct contact to form water, or they were separated by a previously-formed water molecule.⁵⁷

Even in 1868, Graham gave a similar explanation for the igniting power of platinum on a jet of hydrogen in air. The occluded hydrogen was polarised and therefore its attraction for oxygen was enhanced. Still, he talked of platinum being capable of polarising molecules, and increasing their chemical affinities so that chemical reactions could take place. He wrote that: "the gaseous molecules of hydrogen being assumed to be an association of two atoms, a hydride of hydrogen, it would follow that it is the attraction of the platinum for the negative or 'chlorylous' atom of the hydrogen molecule which attaches the latter to the metal. The tendency, imperfectly satisfied, is to the formation of a hydride of platinum. The hydrogen molecule is accordingly polarised, orienté, with its positive or 'basyulous' side turned outwards, and having its affinity for oxygen greatly enlivened. It is true that the two atoms of a molecule of hydrogen are considered to be inseparable; but this may not be inconsistent suppose that a pair of contiguous hydrogen molecules act together

My diagram of this action

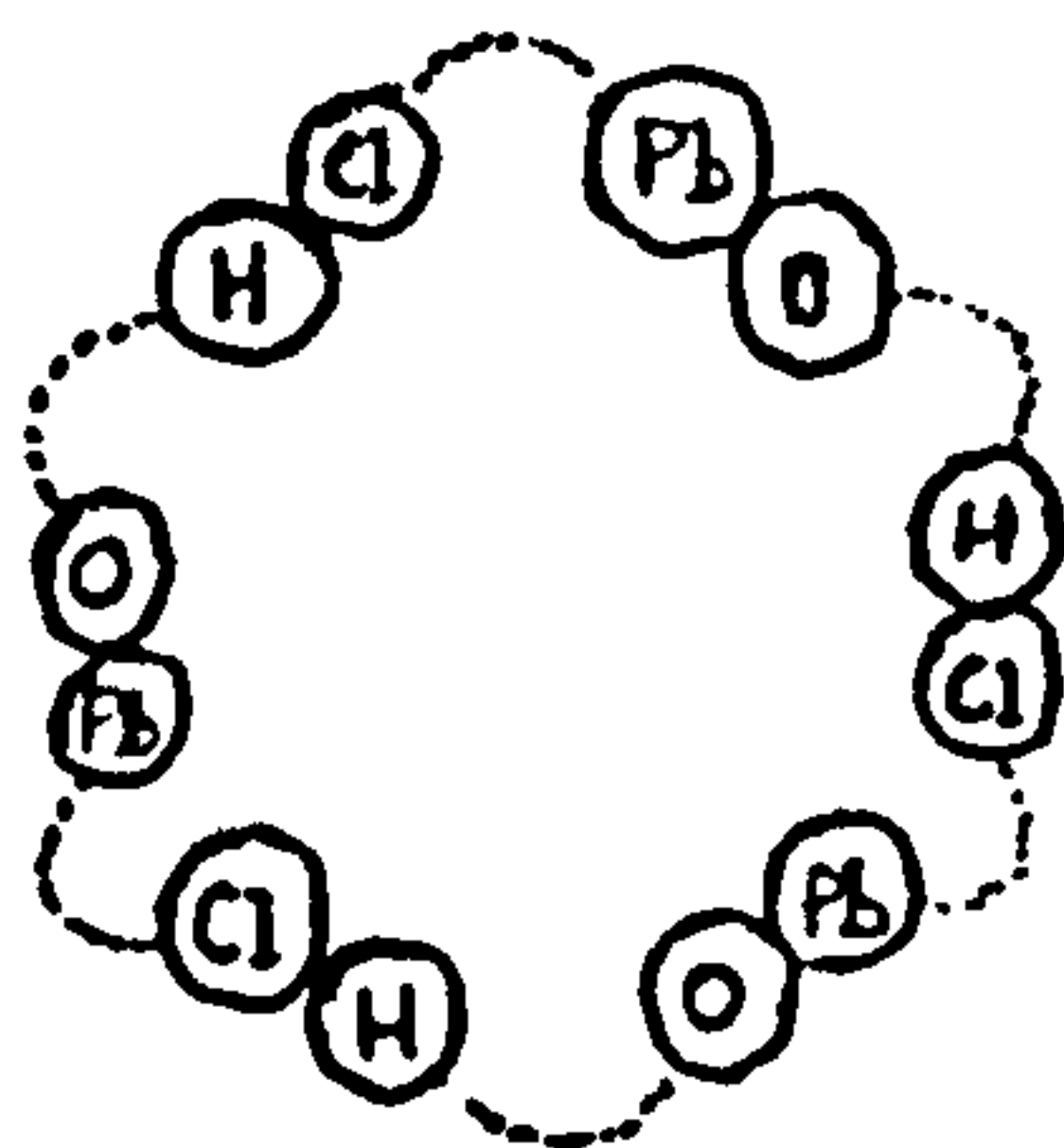


upon a single molecule of external oxygen. They would form water, and still leave a pair of atoms, or a single molecule of hydrogen, attached to platinum." ⁵⁸

59. Graham, Elements of Chemistry 2nd.edn. Vol.1 part 2 (London, 1848)
238-239.

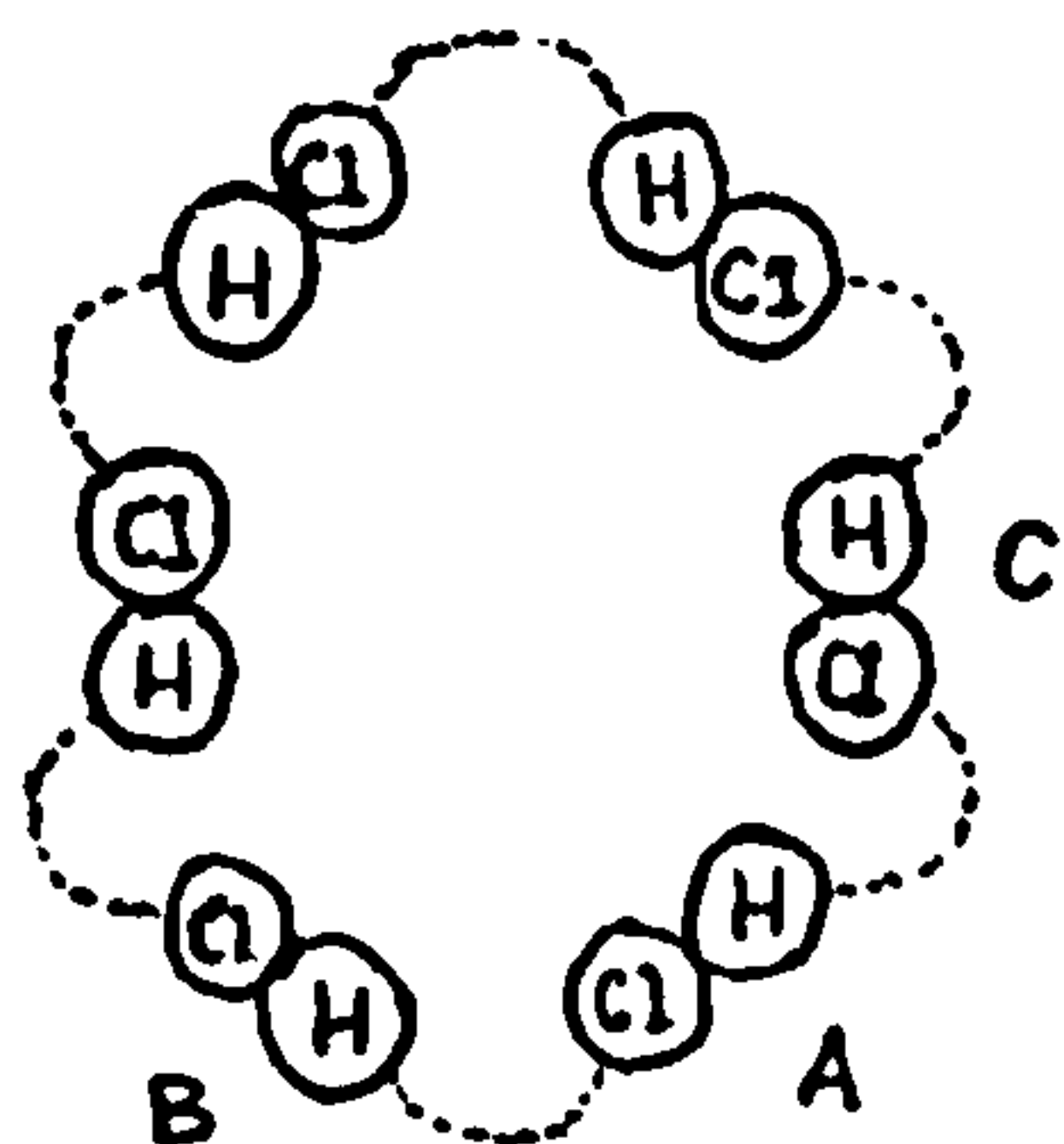
60. Graham, Elements of Chemistry part 4 (London, 1840) 545.

The simplest form of a voltaic circle was found in double decomposition reactions. Graham gave the example of the reaction between litharge PbO and hydrochloric acid HCl. Their mutual contact would arrange the molecules as $\begin{cases} \text{PbCl} \\ \text{O H} \end{cases}$, and would promote the combination by attraction of unlike poles. But there would also be repulsion between like poles, for example between lead and hydrogen. The best way of reducing this repulsion was for the reaction to occur in a polar circle:-



The reaction was a double decomposition:
 $\text{PbO} + \text{HCl} = \text{PbCl} + \text{HO}$

These polar circles also explained the rapidity of double decomposition reactions.⁵⁹ It was possible to envisage circles of like molecules in which double decomposition occurred with very little consumption of force for example with hydrochloric acid. By analogy Graham argued that:



"We pass at once from this to the voltaic circle by supposing that part of these molecules are acid (A), part zinc (B) and part copper (C) but all having the same binary or saline organisation This which I previously described as the inductive action of

affinity from its analogy to magnetic induction, I now think may be with more propriety be distinguished as the rotal action of affinity, and founded on as a fundamental law of affinity."⁶⁰ When the affinity of the chlorine in molecule A was engaged by the hydrogen of molecule B, then the hydrogen of molecule A was proportionately relieved so that it could engage the chlorine of molecule C and so on.

The influence of the concept of polar circles can be seen in the

61. A.W. Williamson, 'Theory of Aetherification' Phil. Mag. 3 Ser 37 (1850) 350-356. "... in an aggregate of molecules of any compound, there is an exchange constantly going on between the elements which are contained in it. For instance, a drop of hydrochloric acid being supposed to be made up of a great number of molecules of the composition ClH, ... each atom of hydrogen ... is constantly changing places with other atoms of hydrogen, or, what is the same thing, changing chlorine ... suppose we mix with the hydrochloric acid some sulphate of copper, the basilar elements hydrogen and copper do not limit their change of place to the circle of atoms with which they were at first combined, the hydrogen does not merely move from one atom of chlorine to another, but in its turn also replaces an atom of copper, forming chloride of copper and sulphuric acid ... In using atomic theory, chemists have added to it of late years an unsafe, and, as I think, an unwarrantable hypothesis, namely that atoms are in a state of rest. Now this hypothesis I discard, and reason upon the broader basis of atomic motion."
62. See, for example, Brodie, 'On the condition of certain elements at the moment of chemical change' Phil. Trans. 140 (1850) 759-804, see pp 802-804.
63. Graham admitted later in his lectures that "the assumption that metals contain two atoms like compounds is the weak point of the theory for we have no direct proof that such is the constitution of metals." Manuscript of lectures given by Thomas Graham in the session 1848-9 written by William J. Russell Vol. 1 115-116. National Library of Scotland MS. 8920.
64. Graham: Elements of Chemistry 1st. edn. part 3 (London, 1839) 226.

theories of Graham's colleague, Williamson, who discussed the exchange of elements between molecules in his theory of atomic motion.⁶¹ Likewise, Brodie used polar molecules in his explanations of double decomposition reactions.⁶²

The most novel part of Graham's theory of the voltaic circles will now be considered. This was his explanation of the 'salimolecular' structure of metals. This theory was further extended to a molecular theory of organic chemistry and it was used to illuminate many obscure problems in Chemistry. Initially Graham assumed that metals contained binary salt-like molecules which he called 'salimolecules'. The metallic salimolecule was polar, containing zincous or positive and chlorous or negative ends.⁶³ By analogy with salts, he assumed that these salimolecules might also contain analogues of constitutional water and water of crystallisation.⁶⁴ As we have seen Graham appears to have regarded heat as the essential basis of electricity and therefore he commented, in 1848, that polarity or the development of zincous and chlorous affinities in a molecule might be due to an inequality of combined heat.

To give a clearer conception of salimolecules Graham referred to the relations and analogies which could be deduced from the principle of isomorphism. A careful study of the compounds of manganese appeared to establish isomorphous links between manganese and many other elements. It is possible that these connections might have been considered by Graham as evidence for his unstated belief in an underlying unity of matter. He drew attention to the following isomorphous connections: the oxide MnO was isomorphous with ZnO and HO; and the sulphates and manganates were similarly isomorphous. Thus manganese was isomorphous with zinc, hydrogen and sulphur. This isomorphism could be extended to include oxygen, from the analogy between the constitution of sodium sulpho-sulphate ($\text{NaS} + \text{SO}_2\text{S}$) and sodium sulphate ($\text{NaO} + \text{SO}_2, \text{O}$) which had been established by Persoz. But the most interesting isomorphous relationship which existed was that between chlorine and manganese. From the

65. Graham, Elements of Chemistry 1st.edn. part 5 (London, 1841) 540
He added to this extract the comment: "this molecular theory modifies, in some degree, while it simplifies, and renders greatly more precise, the view of voltaic action maintained in this work." 540-1.
66. H. Davy, Elements of Chemical Philosophy, (London, 1812) 483-484.
67. H. Davy, 'On a combination of oxymuriatic gas and oxygen gas'
From Phil.Trans. 101 (1811) See The Collected Works 5 (1840) 356.

isomorphism of permanganic acid Mn_2O_7 and perchloric acid ClO_7 , and from that of the oxides Mn_2O_4 and ClO_4 , it was evident that two equivalents of manganese were isomorphous with one equivalent of chlorine, that is $2Mn \equiv Cl$. Furthermore, Graham pointed out the significant absence of analogous compounds of chlorine to the manganese compounds MnO and MnO_3 , containing a single equivalent of manganese. He explained that this was caused by the indivisibility of the single equivalent of chlorine.

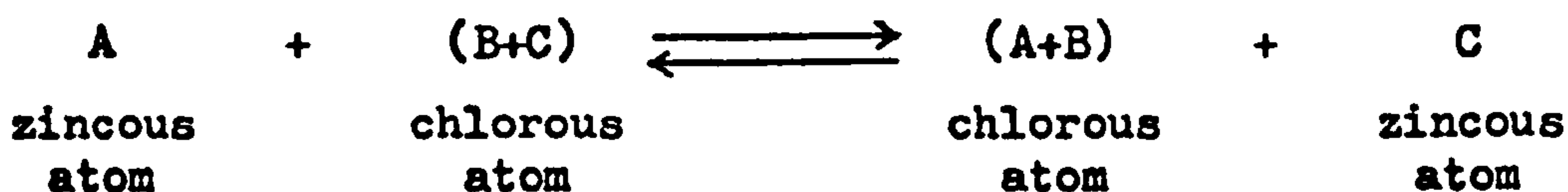
The analogies shown by manganese to other elements led Graham to a quite remarkable speculation in 1839. Thus he commented: "that $2Mn$, $2Zn$, $2S$, $2O$, $2H$, etc., have the same value and character in combination as Cl , is certainly a very remarkable circumstance. It suggests the idea, that it is by the intimate association or conjunction of two basyle atoms, that one salt radical atom is produced; and consequently that the basyle or salt radical character of an elementary body is not absolute but relative to the grouping of its atoms. In discussing the molecular condition of the metallic portions of the voltaic circle, it was assumed that the ultimate atoms of a metallic mass are under the influence of chemical affinities, being in a state of chemical combination with one another, and not isolated and independent of each other like loose grains of sand. The binary or saline structure of the metallic molecule there assumed, may be more precisely described by assigning to it three atoms of metal, two of which conjoined form the salt radical or chlorous atom, and one the basyle or zincous atom." ⁶⁵

The complexity of the chemical elements was a view which had been developed by Prout and it was stressed especially by Davy. The latter chemist had suggested that the metals were compounds of hydrogen and an unknown base. ⁶⁶ With regard to chlorine, Davy claimed that it was certainly possible to defend the hypothesis that chlorine gas "consists of oxygen united to an unknown basis; but it would be possible likewise to defend the speculation that it contains hydrogen." ⁶⁷ It is therefore not surprising that Graham should also speculate on the nature of elements

68. Wellcome MSS. Unbound manuscripts No.2580 (old no.3390) in a box file; (1) Folder on molecular theory etc. (1840) 181L, see page 1 marked Theory of the Voltaic Circle November 1839.

and suggest in particular that chlorine might be a compound of two metallic atoms.

By accepting that the salimolecule of manganese was made up of three atoms of manganese, one atom of which was a zincous atom and the other two being intimately associated as a chlorous or salt radical atom, Graham was able to explain the reversal of polarities in a voltaic circle. Assuming that there was nothing absolute about either the basyle or salt radical character, he argued that the metallic salimolecule could decompose thus:



This idea produced a whole train of speculative thought for Graham which is revealed in his manuscript notes on the molecular theory dated November 1839. He wrote of: "the double atom of metal being equivalent to the atom of chlorine; two atoms [of] manganese [are] isomorphous with one of chlorine. Hence if we could split the atom of chlorine into two, we might have two metallic atoms. The aggregation of the metal comes thus to depend upon the same force as chemical affinity. Of the induction - the true representation seems to be that the attractive force in Zn for Cl and in Cl for Zn is a constant quantity, say 1,000. But when Cl is exposed to Zn' in its neighbourhood, it may come that a portion of the force of the chlorine is engrossed by Zn', say 100 parts; then Cl has an attractive force of only 900 for Zn [the zinc atom to which it is attached], its whole attractive power being constant, but divided between Zn and Zn'. Indeed Cl may affect several zincous atoms around it, but those most distant less than those near it. But [the zinc atom] Zn' most affected approaches or arranges itself in reference to Cl, so as to be more affected, and acquires a greater and greater share of the attractive force of Cl, till it may have more than the moiety [half], and finally prevailing, the whole. It is only the ultimate result that we in general witness or attend to in the voltaic circle." 68

69. Graham, Elements of Chemistry 1st.edn. Part 4 (London, 1840) p 541.

70. Graham, *ibid.* pp 542-543.

Graham was thinking in terms of a quantitative basis for the attractive force of chemical affinity. The absolute chemical affinity was a constant quantity, but it could be shared by adjacent atoms. Under the influence of induction, chains of polar salimolecules were established in both metals and electrolytes. These chains were themselves mutually repulsive like the magnetic lines seen with steel filings. Also, the conducting wire was heated in proportion to the number of polar chains established.

Graham provided many examples to illustrate the existence of triple salimolecules in metals. The black oxide of iron Fe_3O_4 contained two metallic oxides $\text{FeO} + \text{Fe}_2\text{O}_3$. He explained that the black oxide was formed by the oxidation of the metal without any disturbance of its salimolecule, $\text{Fe} + \text{Fe}_2$. Indeed, he wondered whether there was some connection between the salimolecules, found in both the black oxide and metallic iron, and their known magnetic properties.⁶⁹

Davy had noticed that zinc became positive when it was in contact with copper and Graham explained that the chlorous atom of copper tended to join with the zincous atom of zinc. Thus alloys such as ZnCu_2 , ZnCd_2 and ZnHg_2 provided further evidence for the existence of salimolecules. If adjacent salimolecules of bismuth and antimony were heated together, molecular changes occurred and thermoelectricity was released. Indeed, Graham observed that his theory of salimolecules had more in common with the contact theory of galvanism, where electricity was produced by the contact between two different metals, than with the generally accepted electrochemical theory. He was, however, careful to point out that the fundamental assumptions, on which the contact theory was based, differed from his own chemical theory.⁷⁰

Salimolecules showed variations in their characters. Highly negative metals such as gold, platinum and mercury contained a strong salt radical joined to a weak basyle. They were comparable to hydrochloric acid and the hydrates of strong acids. Conversely, the highly positive

71. Graham, *ibid.*

72. Graham, *op.cit.* (68) See part of the notes on the molecular theory dated May 24th 1840 which have the title 'Salimolecular theory of metals: outlines of a molecular theory to explain the voltaic circle' page 2. Graham seemed to consider hydrogen to be a metallic vapour in these notes. This is seen from the exact quotation "In zinc, hydrogen etc. the least equivalent is the single atom. The molecules of these metals thus admit of the utmost division - least intense. But others do not admit of this actual divisibility - aluminium and chromium". This quotation comes from the MS. notes on the molecular theory page 1.

73. Graham, *op.cit.* (68), November 1839, page 3.

metals, zinc and potassium, contained a powerful basyle joined to a weak salt radical, like the hydrated alkalies. However, iron possessed a very stable salimolecule containing a strong basyle and a strong salt radical. This fact explained why iron was a difficult metal to amalgamate. So, it was not easy to substitute mercury for the salt radical of iron in such a well-balanced combination.⁷¹

In Graham's theory, the force of aggregation in metals was chemical affinity itself. This affinity varied in strength. With zinc and hydrogen, the binary attraction between atoms was weakest. Therefore the least combining equivalent was the single atom. Iron could be separated into single atoms, but two atoms of iron were more strongly linked together than two atoms of zinc. This could be seen in the stable molecule Fe_2O_3 . The binary attraction of two atoms was more intense in aluminium and chromium because they always contained two atoms joined together in their compounds. Finally, with metals, the intensity of attraction of two atoms in molecules of manganese was greater still. This could be seen in the compounds Mn_2O_3 , Mn_2O_4 and Mn_2O_7 . Graham recorded these examples in May 1840 and he concluded by saying that "again in chlorine, iodine etc., we have this idio-combination of the highest intensity, Cl being equivalent to Mn_2 . So intense as completely to overpower and obliterate the special attractions of the two individual atoms composing Cl. I do not know an instance where the attraction of the single molecule shows itself - always that of the double molecule."⁷²

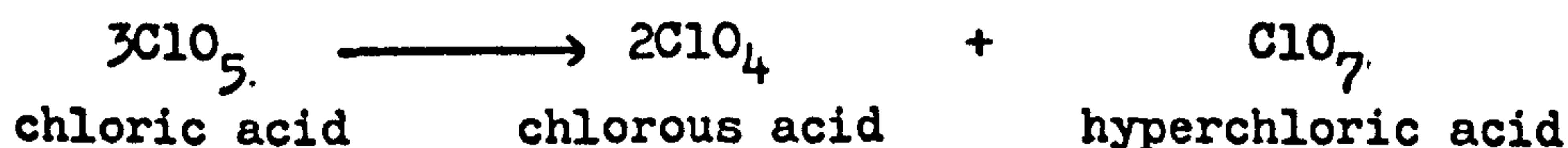
It is evident that Graham did not restrict salimolecules to metals; they were also present in compounds. He regarded the atom of chromic acid to be $\begin{cases} \text{CrO}_3 \\ \text{CrO}_3 \end{cases}$ or Cr_2O_6 ; the double atom of chromium Cr_2 was not separable into individual atoms. The triple salimolecule $\text{Cr} + 2\text{Cr}$ was also found as $\text{CrO}_3 + 2\text{CrO}_3$,⁷³ in the terchromate of potash $\text{KO}, \text{Cr}_3\text{O}_9$. By analogy with certain organic acids it was even possible, he thought, that the double molecule Cr_2O_6 might be both monobasic and bibasic. Liebig had shown that radicals could be polymerised to give acids of

74. Graham, Elements of Chemistry 1st.edn. part 3 (London, 1839) 328-330.

"These duplicated and triplicated sulphuric acids are supposed to form each a monobasic class of sulphates; but if moreover it be assumed that one of them, the duplicated sulphuric acid S_2O_6 , with the corresponding chromic acid Cr_2O_6 , is also capable of forming a bibasic class of salts, then some other salts of the same class will be brought more in accordance with the general views entertained respecting salts." p 329.

Also there is an undated note in the Wellcome MS. letters and correspondence "Although chromic acid has been represented by CrO_3 in its salts and compounds, there can be little doubt that it should be Cr_2O_6 , the single atom Cr, being found in combination. Hence yellow chromate of potash is $2KO, Cr_2O_6$. As this salt is isomorphous with sulphate of potash it follows that the formula of this latter salt when free and crystallised is truly $2KO, S_2O_6$ [it] contains 12 atoms in its molecule as does the bisulphate HO, KO, S_2O_6 . The double sulphate of magnesia and potash will be $MgO, KO, S_2O_6 + 6HO$ " This note was probably written before his textbook comments above. Graham abandoned these views on anhydrous bisulphate of potash when he was unable to repeat the preparation of this salt in November 1842. See Researches, p 417.

75. Graham, op.cit. (68), November 1839, p 6 "Triple chloric acid molecular combination. It would be well to bring broadly into view the distinction between atomic combination, or the combination of atoms of different kinds, and molecular combination or combination of atoms of the same kind. In iodic acid we have probably the association of three molecules if Mr. Penny's observation respecting [the] teriodate of soda be correct. The same thing in chloric acid, if such an inference may be drawn from the circumstances of its decomposition by oil of vitriol; three equivalents (least combining proportions) being simultaneously affected, and affording two of chlorous acid and one of hyperchloric acid. It may be in all cases of decomposition a safe canon to go by, that the new products have individually a less molecular weight than the original compound." See also Graham, Elements of Chemistry 1st.edn., part 4 (London, 1840) p 543:-



different basicities, for example cyanic acid $\text{HO} + \text{C}_2\text{NO}$ was monobasic; fulminic acid $2\text{HO} + \text{C}_4\text{N}_2\text{O}_2$ was bibasic; and cyanuric acid $3\text{HO} + \text{C}_6\text{N}_3\text{O}_3$ was tribasic. Thus bichromate of potash $\text{KO},\text{Cr}_2\text{O}_6$ was a monobasic salt and chromate of potash $2(\text{KO},\text{CrO}_3)$ or $2\text{KO}.\text{Cr}_2\text{O}_6$ was a bibasic salt and so was terchromate of potash $\text{KO},\text{CrO}_3 + 2\text{CrO}_3$ [?]. Using the isomorphism of sulphates and chromates, Graham suggested that there could be an analogy between bichromate of potash $\text{KO},\text{Cr}_2\text{O}_6$ and the newly-discovered anhydrous bisulphate of potash $\text{KO},\text{S}_2\text{O}_6$. He predicted that an undiscovered tersulphate of potash $\text{KO},\text{S}_3\text{O}_9$ might possibly exist, analogous to the known terchromate of potash.⁷⁴

The duplication and triplication of acids like SO_3 and CrO_3 allowed Graham to retain his important principle that most salts were constitutionally neutral. Duplicated sulphuric acid S_2O_6 could also form bibasic salts, for example bisulphate of potash: $\text{KO}.\text{HO},\text{S}_2\text{O}_6$; and gypsum $2\text{CaO},\text{S}_2\text{O}_6 + 4\text{HO}$. However, the double acid Cr_2O_6 was apparently more strongly-linked than S_2O_6 because there was no evidence for the existence of a corresponding double chromate analogous to $\text{MgO},\text{SO}_3 + \text{KO},\text{SO}_3$. Other examples of the polymerism of radicals were quoted by Graham, for example there was the series: iodate, biniodate and teriodate of soda. Likewise, the triplication of chloric acid could be inferred from its decomposition products;⁷⁵ and also the triplication of white precipitate $3(\text{HgNH}_2 + \text{HgCl})$ had been proposed by Mitscherlich to explain the formation of the molecule NHg_3 .

The theory of the polymeric grouping of atoms was not new. Dumas and Ampère had previously advocated molecular grouping. Graham wrote that: "Dumas is disposed to modify the atomic theory so far as to allow the divisibility of the atoms or ultimate masses in which a body enters into combination, and to suppose there are groups of more minute atoms, into which they may be divided by physical, but not by chemical forces. He distinguishes the atoms which correspond with equivalents as chemical atoms, and allowing them to represent truly and constantly the least

76. Graham, Elements of Chemistry, 1st.edn. part 2 (London, 1838) p 122.

77. Graham, op.cit. (68), November 1839, p 7.

78. Graham, op.cit. (70).

quantities in which bodies combine, still supposes that under the influence of heat and perhaps other physical agencies, these molecules may be subdivided into atoms of an inferior order, of which for example two, four or a thousand are included in a single chemical atom. But surely such a view is entirely subversive of the atomic theory." ⁷⁶ Graham was quite correct in his comment but it is only fair to add that his own development of the theory of salimolecules and polymerism was equally subversive of atomic theory.

Graham wrote that the primary point of his work was "to establish the duplication or triplication of the atom, whatever that may be due to." ⁷⁷

The triplication of sulphur was deduced from the fact that its molecule contained twelve atoms. Therefore, one form of sulphur crystals contained

$$\left\{ \begin{array}{l} S + 2S \\ S + 2S \\ S + 2S \\ S + 2S \end{array} \right. \text{ which was isomorphous with bisulphate of potash } \left\{ \begin{array}{l} S + O \\ K + O_2 \\ S + O_2 \\ H + O_2 \\ + O_2 \end{array} \right. ; \text{ or this}$$

could be written alternatively as $(SS, SS_3 + SS, SS_3)$ being isomorphous to $(KO, SO_3 + HO, SO_3)$. Another important example of triplication of atoms was seen in the phosphorus class of elements N, P, As and Sb. In each case one equivalent of the element contained a triple atom which was equivalent to three atoms of certain other bodies, for example $3H$, $3O$, $3Cu$ and $3Hg$. This triple atom did not appear to be separable. The evidence for its existence was partly drawn from thermochemistry and partly from a fact observed by Liebig and Dumas that one equivalent of antimony combined with at least three equivalents of oxygen. This was deduced from the fact that one equivalent of antimony replaced three equivalents of hydrogen from a strongly-dried sample of tartar emetic. ⁷⁸

These examples showed that polymerism was a feature of both elements and compounds. The polymeric nature of metals allowed Graham to explain the transmission of chemical affinity over sensible distances. Underlying all these examples of isomerism there is, however, the question of whether Graham believed in a unitary theory of matter at this time. His speculations on the complex nature of the elements seem to indicate that

79. Samuel Brown, Lectures on the Atomic Theory and Essays Scientific and Literary 1 (Edinburgh, 1858) lecture 4 (April, 1843) pp 78-79.

he was probably thinking along these lines.

Certainly Samuel Brown suspected this, in 1843, when he said that the hypothesis can be suggested that the "elements are compounds of equal and similar atoms, so that it is within the scope of natural possibility that they may all be derived from one generic atom it renders the atomic disposition of the solid element of the electrolysed circle easily understood - a desideratum [a felt want] which has been ably pointed out, and ingeniously evaded by Professor Graham. Copper or zinc or other solid conductor is represented as $\overset{\text{negative}}{x} + \overset{\text{positive}}{\chi}$, $x + \chi$, $x + \chi$, or $\overset{n}{y} + \overset{p}{\gamma}$, $y + \gamma$, $y + \gamma$; and so on. Chemico-polar induction has [taken] place, but there is of course no decomposition of the metals, as is the case with the electrolyte compound of unequal elements in the cells, water, hydrochloric acid, or salts. In fine, every reflecting chemist must observe the facility with which this hypothesis accounts for the relative physical characters and chemical properties of the different natural groups of elements, whether they be associated on the principle of isomorphism, or this of isomerism, and reduces all the multiformity of constitutions to consummate simplicity." 79

The attitude of Graham towards both Prout's hypothesis and the natural classification of the elements is another helpful indication of his probable views on a unitary theory of matter. Graham had seen the rejection of Thomas Thomson's efforts to justify Prout's hypothesis, that the atoms of all elements had atomic weights which were integral multiples of the atomic weight of hydrogen. In 1838, Graham wrote that: "several of Berzelius's numbers received a valuable confirmation from Dr. Turner, whose inquiries were especially directed to test an hypothesis respecting them, advocated by some of his contemporaries; namely that the equivalents of all the elements are multiples of the equivalent of hydrogen, and consequently if that equivalent be made equal to 1, all the others will be whole numbers. Dr. Turner's results are incompatible with such a relation among the equivalent numbers, the existence of which indeed is

80. Graham, Elements of Chemistry, 1st.edn. part 2 (London, 1838) p. 118. In 1839 Graham was asked to act as a referee for two papers concerning the determination of atomic weights for the Royal Society. The first paper by Frederick Penny concerned the determination of the equivalent numbers of Cl, N, Na, K and Ag. He was very impressed by Penny's skill and accuracy and noted that his results "like those of Dr. Turner published in the Phil. Trans. on the same subject confirm the general accuracy of the Berzelian equivalent numbers" See Referees Report of R.S. 180 (February 21st 1839) by Graham and for Penny's paper 'On the application of the conversion of chlorates and nitrates into chlorides, and of chlorides into nitrates, to the determination of several equivalent numbers': Phil. Trans. 129 (1839) 13-33. Graham also refereed a paper by Richard Phillips on the determination of the equivalents of certain elementary bodies, particularly chlorine. Graham wrote "the method adopted is to mix two precipitating salts in the proportions of their assumed equivalents and then to look for and determine the excess of one of the two left in solution is certainly not of general application in this inquiry, having already signally failed in the hands of Dr. Thomson. But the method appears to be unobjectionable in the particular case to which it is applied by Mr. Phillips namely the precipitation of sal ammoniac by the nitrate of silver. The results accorded very well with each other and give the equivalent of chlorine .. 35.688. This number is 0.23 or 0.26 greater than the number determined by Berzelius and Dr. Turner and also by Mr. Penny which do not differ more than 0.03 from each other. Mr. Phillips is disposed to conclude that the difference should be still greater and views his results as compatible with and indeed as favouring the theory that the equivalent of chlorine is a whole number 36 of which his own number falls short by 0.32." Unlike Penny, Phillips supported Thomson's atomic weight values which favoured Prout's hypothesis. Graham said that this paper should be published, despite the disagreements between the values of the atomic weight of chlorine given by Phillips and those of Berzelius and Turner, so that the method pursued could be discussed. See Graham's Referees Report 184 (February 21st 1839) and for the paper by R. Phillips, 'Researches on the chemical equivalents of certain bodies' Phil. Trans. 129 (1839) 35-38.
81. T.J. Pelouze, 'Note on the chemical equivalents considered as simple multiples of hydrogen,' Comptes Rendus 15 II (1842) 959-962 and 20 II (1845) 1047. If the equivalent of potassium chloride had been 74 or 75 instead of 74.583 then it would have been an integral multiple of hydrogen.
82. M.E. Maumené, 'Memoir on the chemical equivalents of chlorine, silver and potassium,' Ann. de Ch. 3 Ser. 18 (1846) 41-79.
83. C.F.G. Marignac, 'Réunion de la Soc. Helvétique des Sciences Naturelles - discussion of two memoirs by Marignac,' Schweizer Gesell. Verh. (1843) 62-66. See Marignac Complete Works 1 (Geneva, 1902) 95-97: "peut-être, faudrait-il admettre que le chlore et d'autres corps ont un équivalent qui serait un multiple de l'atome d'hydrogène avec l'équivalent $\frac{1}{2}$ " p 96. See also Marignac, 'Analyses diverses destinées a la vérification de quelques équivalents chimiques,' Bibl. Universelle 46 (1843) 350-377, see p 370 or Complete Works 1 p 92.
84. Graham, Elements of Chemistry, 2nd.edn. Vol. 1 part 1 (London, 1846) p 132.
- 84a. W.C. Henry, Memoirs of the Life and Scientific Researches of John Dalton, (London, 1854) p 114. Henry quotes Graham's opinion that the equivalents are multiples of 0.5 but then adds some comments from a letter which Graham had written to him probably in 1853. He reported that Graham

cont...

disproved by all accurate analyses." ⁸⁰ However, he conceded that Dumas was correct when he pointed out that certain pairs of equivalents were simply-related, for example Graham selected the following relations as being acceptable: $\text{Co} = \text{Ni}$, $\text{Os} = \frac{1}{2}\text{Au}$, $\text{Pt} = \text{Ir}$ and $\text{S} = \frac{1}{4}\text{Te}$.

The question of the validity of Prout's hypothesis was raised again in 1840, when Dumas redetermined the atomic weight of carbon. He demonstrated that the atomic weight of carbon was an integral multiple of hydrogen and subsequently he established an integral multiple relationship for both oxygen and nitrogen. On the other hand, Pelouze showed that the equivalent of potassium chloride (74.583) was not an exact multiple of hydrogen (1.0). ⁸¹ The debate was continued, however, when Maumené, a pupil of Dumas, suggested that the equivalents of chlorine, silver, and potassium were multiples of half the equivalent of hydrogen, ⁸² a view which had been advocated before by Marignac in 1843. ⁸³

The revived interest in Prout's hypothesis persuaded Graham to support the revised hypothesis that the weights of atoms were integral multiples of half an atom of hydrogen. Seemingly, he was actually favouring a unitary theory of matter when he wrote in 1846 that "the accurate determinations of the equivalents of chlorine, silver, and potassium by Mauminé [sic], lend positive support to the opinion that these and all other equivalents are multiples of half the equivalent of hydrogen. So do the recent determinations of carbon and hydrogen in reference to oxygen, and those of nitrogen, sodium, iron, and calcium. The number for lead also, upon the determination of which extraordinary pains have been bestowed by Berzelius at different times, namely 103.56, is favourable to the same view. Now these are the equivalents upon which, above all others, our knowledge is most precise and certain." ⁸⁴ However, Graham expressed caution concerning these opinions later in 1853. ^{84a}

By arguing from the isomorphism of compounds Graham was able to deduce information about the isomorphism of the elements which composed

84a. cont...

wrote: "it is a view, however, which must be recognised with extreme caution, very faulty numbers have been proposed at different times under its authority, as 36 for chlorine instead of 35.5; 24 for sodium instead of 23; 40 for potassium instead of 39. The apparent tendency of discovery is no doubt favourable, to the view, or at least to that modification of it, in which the half equivalent of hydrogen is made the unit." The wrong figures were those which had been quoted by Thomas Thomson in 1825.

85. Graham, Elements of Chemistry, 1st.edn. part 2 (London, 1838) p 149.

86. 'Letter from Berzelius to Wöhler on substitution theory,' Liebig Annalen 31 (July 15th 1839) 113-119 to which a note was added, on p 119, by Liebig. He pointed out there was one remarkable observation to be recognised "that the manganese in permanganic acid may be replaced by chlorine without altering the form of the compounds which it can produce with the bases. There can scarcely be a greater dissimilarity in chemical properties than that between manganese and chlorine ... chlorine and manganese can replace each other in certain compounds. I do not see why a similar behaviour should be impossible with other substances - with chlorine and hydrogen, for example, and this very view of these phenomena, in the form in which it has been advanced by Dumas appears to me to furnish the key to most of the phenomena of organic chemistry."

87. R.Kane, Elements of Chemistry, 2nd.edn. (Dublin, 1849). Kane said that bodies might replace each other in proportions quite different from those of their ordinary equivalents, and so they might pass by doubling or tripling of their atomic weights into a different natural group (p 312). With allotropes, he continued "we must admit in allotropes that the same elementary body may in forming different classes of compounds abandon that absolute simplicity and act in as totally different capacity as if those series arose from different elementary bases ... Thus, the Mn which forms a powerfully basic protoxide [MnO], may be a different body from the Mn which forms with oxygen a powerful acid, and that it might have a different atomic weight. I therefore believe that permanganic acid [Mn₂O₇] is not formed of two atoms of manganese, a strongly electropositive metal, ... but of an atom of manganese with the equivalent 56, which is a powerfully electronegative metal like gold or platinum ... the degrees of combination of metal may really have totally different radicals and be as perfectly independent and unconnected as are the compounds of quite different metals, the only tie embracing them [both] being, that by certain processes we are enabled to extract the same metal from both. But that each allotropic state of the metal which gives it its different atomic weight, and its different chemical properties, really constitutes it for the time a different metal, and thus a transmutation." (pp319-320).

88. Graham, Elements of Chemistry, 1st.edn. part 2 (London, 1838) pp 142-149.

them. From the isomorphous connections between the elements he constructed a natural classification of the elements in which groups of isomorphous elements were related in such a way that their properties shaded into one another. Surely this classification must have arisen from a belief in the ultimate unity and continuity of matter. As Graham expressed it: "the tendency of discovery is to bring all the elements into one class, either as isomorphous atom to atom, or with the relation to others which chlorine and sodium exhibit."⁸⁵ The latter elements were related to the former group by the isomorphous relation of, one atom of the latter group, to two of the former. For example one atom of chlorine was equivalent to two atoms of manganese and also one atom of sodium or silver was equivalent to two atoms of copper in the compounds AgS and Cu_2S .

Liebig later stressed the importance of the isomorphous replacement of manganese by chlorine showing that, although their properties were very dissimilar, they could replace each other. Therefore he claimed that Berzelius was wrong to challenge Dumas's views on the substitution of hydrogen by chlorine.⁸⁶ A quite different view of manganese was adopted by Kane. He argued that in the compounds MnO and Mn_2O_7 , two different kinds of manganese existed, which possessed different equivalents and different properties. He said that these two forms of manganese could almost be considered as entirely different metals.⁸⁷

A partial classification of the elements into isomorphous families had been drawn up previously, in 1828, by Dumas, but he had not attempted to include the metals in his scheme. Graham's classification was drawn up in 1838. He divided the elements into eleven isomorphous families or classes:⁸⁸

- Class 1 O, S, Se, Te, was connected with class 2 by the isomorphism of SO_3 and MnO_3 .
- Class 2 Mg, Ca, Mn, Fe, Co, Ni, Cd, Cu, H, Bi, Cr, Al, G, V, Zr, Y and Th.
- Class 3 Ba, Sr, Pb, was connected with class 2 by the isomorphism of one form of CaCO_3 with PbCO_3 and BaCO_3 .

89. R. Kane, op.cit. (87) pp 327-330. This is identical to the account given in the 1st.edition of Kane's, Elements of Chemistry, (Dublin, 1841) pp 386-390.

90. T. E. Thorpe, History of Chemistry, (London, 1910) Vol.2 p 24.

91. J. H. Gladstone, 'On the relations between the atomic weights of analogous elements,' Phil.Mag. 4 Ser.5 (1853) 313-320.

Class 4 K,Na,NH₄,Ag, was connected with class 2 by the isomorphism of Cu₂S⁴ and AgS.

Class 5 Cl,I,Br,F, was connected with class 2 by the isomorphism of Mn₂O₇ and ClO₇.

With class 5, Graham felt, that halving the atomic weight of chlorine was less improbable than Johnston's alternative suggestion, of halving the atomic weights of sodium and silver; nevertheless, chlorine did not appear to combine in less proportions than its present equivalent so Graham did not alter the atomic weight of chlorine.

Class 6 N,P,As,Sb, was connected with class 1 by the isomorphism of Fe₂S₄ and Fe₂AsS₂,

in which one atom of arsenic was equivalent to two atoms of sulphur. This isomorphism was noticed in his later table of 1846.

The other classes were: 7 Sn,Ti; 8 Ag,Au; 9 Pt,Pd,Os,Ir; 10 W,Mo and 11 C,B,Si.

This natural classification of the elements was adopted by a number of later writers. Kane regarded it as a better alternative than either the electrochemical classifications of Berzelius and Ampère, or the division of the elements into supporters or non-supporters of combustion which had been favoured by Thomas Thomson.⁸⁹

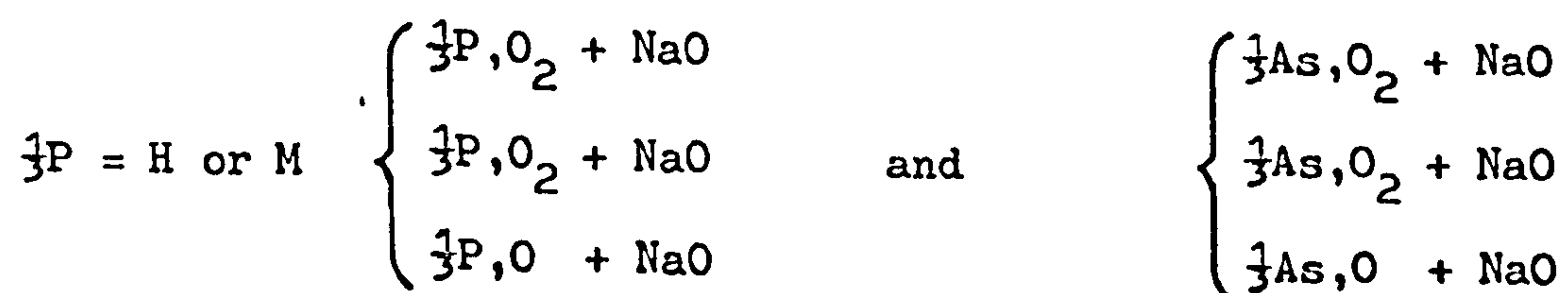
Graham's classification was modified later by considerations of valency and by corrections which became necessary with increasing knowledge about the elements. T. E. Thorpe wrote that it was in general use for a quarter of a century - "in fact until it was superseded by the gradual adoption of Mendeléeff's arrangement based on periodicity. There can, however, be little doubt that this attempt by Graham at a natural classification paved the way along which Newlands and eventually Mendeléeff were led to devise our present rational system of grouping the elements."⁹⁰ He might have added that J. H. Gladstone's attempt in 1853⁹¹ to arrange the elements in order of equivalents was presumably also drawn up with the encouragement of his former mentor Graham.

The possible existence of polymerism in metals had revealed new relationships as Graham had shown. Laurent also recognised this when he

92. Letter of A. Laurent to J. Berzelius (5th January 1844)
 H. G. Söderbaum, editor, Berzelius Bref. (Uppsala, 1920) Section VII
 (Miscellaneous) p 199. This reference is taken from J. H. Brooke,
 'Chlorine substitution and the future of organic chemistry,' Studies
in History and Philosophy of Science, 4 (1973) 60-61.
93. A. Laurent, 'On nitrogenous organic compounds' Comptes Rendus 20 (1845)
 850-855. In a footnote, on page 851, he said that the atoms of metals
 were divisible and that the atoms of these elements by joining in
 various proportions gave rise to different atoms or equivalents
 endowed with different properties. Thus the salts of peroxide of
 iron and of protoxide of iron only differed because of the grouping
 of the atoms in the metal, the two sulphates were SO^f and SO^F , and
 not $S^3O^{12}F^2$ and SO^4F , where f and F represent different numbers of
 iron mini-atoms e.g. 8 and 12.
94. A. Laurent, Chemical Method, translated by W. Odling (London, 1855)
 p 102.
95. Graham, op.cit. (68), May 24 1840 p 3 and lecture 144, 1840.

wrote to Berzelius in 1844 saying that the atom of manganese was really polymeric. If the atom of manganese Mn could be divided into 24 smaller atoms (mn^{24}) then manganous manganese might have the arrangement $4mn^6$, and manganic manganese might be $6mn^4$ and finally permanganic manganese might be mn^{24} . This subdivision of the atom of manganese allowed Laurent to explain the different electrical states of manganese in its compounds.⁹² In 1845 Laurent extended his views to explain the different iron compounds.⁹³ He returned to these views in his book, of 1854, Chemical Method, when he criticised Berzelius for saying that all the different modifications of phosphoric acid, PO_5 , must contain an indivisible atom of phosphorus. Laurent argued that it would be much more sensible to assume that the three modifications of phosphoric acid contained different numbers of smaller atoms inside a polymeric atom.⁹⁴

Graham had previously argued that the 'atom' of phosphorus was an indissoluble triple salimolecule. He used this belief in 1840 to explain the tribasic natures of phosphoric acid and arsenic acid. Presumably, this was his response to the criticisms made by Berzelius and Liebig that the number of atoms of basic water found in one atom of acid was an insufficient criterion of basicity. Graham assumed that the three component atoms in a triple salimolecule of phosphorus or arsenic acted separately. So the phosphorus molecule could be joined to three equivalents of other elements and this was the origin of its tribasicity. In his notes on molecular theory Graham wrote down the formulae of the phosphate and arseniate of soda, incorporating his triple salimolecules, as follows:-⁹⁵



He explained the alkaline character of these salts by saying that the last number ($\frac{1}{3}P, O + NaO$) was equivalent to the alkali $HO + NaO$. Indeed,

96. Graham, *ibid.*

97. Graham, Elements of Chemistry, 2nd.edn. Vol.1 part 2 (London, 1848) pp 208-209. For Liebig's opinion see 'Liebig's Giessen lectures on organic chemistry' The Lancet (July 20 1844) 517-519 and for W. Gregory, Outlines of Chemistry, (London, 1847) 117-118.

he suggested that phosphate of soda could be compared to two equivalents of a neutral salt, like a carbonate ($\text{CO}_2 + \text{NaO}$), joined to one equivalent of a hydrated alkaline oxide ($\text{HO} + \text{NaO}$). This formulation was also extended by Graham to include the pyrophosphate of soda which he wrote

down in his notes as:-

$$\begin{cases} \frac{1}{3}\text{P}_2\text{O}_5 + \text{NaO} \\ \frac{2}{3}\text{P}_2\text{O}_5 + \text{NaO}. \end{cases}$$

He compared this salt to a combination of carbonate of soda and an aluminate of soda, which was slightly alkaline because alumina did not entirely neutralise the soda.⁹⁶

Shortly afterwards Liebig and Gregory gave a similar explanation for the formula of phosphate of soda except that they divided the whole 'atom' PO_5 by three instead of the phosphorus atom itself. Their formula was

$$\begin{cases} \frac{1}{3}\text{PO}_5 + \text{NaO} \\ \frac{1}{3}\text{PO}_5 + \text{NaO} \\ \frac{1}{3}\text{PO}_5 + \text{NaO}. \end{cases}$$

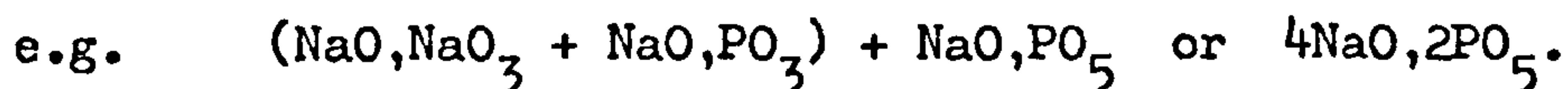
When Graham rewrote his textbook in 1848, he explained the tribasicity of phosphoric acid differently although it seems probable that he drew on his earlier speculations but he no longer referred to triple salimolecules.⁹⁷ He supposed that phosphoric acid was a compound of phosphorous acid PO_3 weakly joined to two extra oxygen atoms i.e. $\text{PO}_3 + 2\text{O}$. When phosphoric acid reacted with soda, the two weakly-held oxygen atoms joined with an atom of soda thus producing a new acid NaO_3 . Two further atoms of soda were then required to neutralise the two acids NaO_3 and PO_3 . Therefore, one atom of phosphoric acid was neutralised by three atoms of soda giving a salt which conformed to his principle of the constitutional neutrality of salts. A further analogy could be seen between the double salt, sulphate of both magnesia and potash, $\text{MgO}, \text{SO}_3 + \text{KO}, \text{SO}_3$ and phosphate of soda $\text{NaO}, \text{NaO}_3 + \text{NaO}, \text{PO}_3$.

Liebig had previously suggested that the metaphosphates were compounds of $\text{PO}_3 + 2\text{O}$, in which the two atoms of oxygen were very strongly bonded to phosphorous acid. This stronger binding occurred as a result of a loss

98. Dumas and Piria, 'Fifth memoir on types', (July 1842) Ann.de Ch.
3 Ser.5 (1842) 353-395.

99. Graham, 'On the division by three of the equivalents of the phosphorus family of elements'. This paper was read to the Chemical Society on December 20th 1842. Chem.Gazette 1 (1842-3) 158. The paper is not mentioned in the Royal Society Catalogue of Scientific Papers and it is not included in Researches.

of combined heat during the formation of metaphosphates. This gave a monobasic metaphosphate NaO,PO_5 . Finally, the pyrophosphate of soda was envisaged by Graham as a compound of common phosphate of soda and the metaphosphate of soda, as Berzelius had suggested:-



Hence, one equivalent of pyrophosphate of soda contained four equivalents of base and two equivalents of phosphoric acid; this explained the existence of a large number of double pyrophosphates. This revised view of the constitution of phosphates avoided a denial of the accepted opinion that an atom of phosphorus was indivisible. This view was therefore less contentious than Graham's earlier theory found in his notes.

Although, by 1848, Graham may have become less certain about the existence of elementary salimolecules he had not given up the possible underlying belief in the unity of matter. His explanation of the constitution of phosphates resembled, as he admitted, that given by Dumas of the conjugate organic acids,⁹⁸ which combined with two equivalents of base. Like the conjugate acids, the phosphates contained the elements of two different acids; the two acids were NaO_3 and PO_3 . Graham's reticence, in not advocating the existence of polymeric elementary molecules in 1848, might be connected with the controversy in which he had become involved during 1843. This was caused by Samuel Brown's claims that elements were isomeric and so they could be transmuted. This controversy is examined later in this chapter.

Certainly, in 1842, Graham believed that he had found experimental evidence for the existence of triple molecules in the phosphorus class. In December 1842, he read a paper to the Chemical Society, on the division by three of the equivalents of the phosphorus family of elements.⁹⁹ The evidence for this view came from Graham's thermochemical researches rather than from purely theoretical speculations. He observed an identical fall in temperature when equivalents of bichromate of potash ($\text{KO,Cr}_2\text{O}_6$) or nitrate of potash (KO,NO_5) were dissolved in water. This

100. Graham mentioned that the division of the equivalents of N,P,As,Sb had already been advocated by Laurent, Bineau and himself. Likewise, in 1840, Graham had also referred to this division in his textbook. See Graham, op.cit. (77). In 1836, Laurent wrote the formula for hydrobenzamide as $C^{28}H^{12}Az^{4/3}$. He noted that the quantity of nitrogen was fractional, without giving any interpretation.
- A. Laurent, 'Sur l'hydrobenzamide', Ann.de Ch. 2 Ser.62 (1836) 23-31. See pp 27-28. [Hydrobenzamide is now written as $(C_6H_5.CH)_3N_2$] Bineau pointed out that the atomic weight of nitrogen should be reduced by dividing it by three. Bineau, 'On some ammoniacal combinations,' Ann.de Ch. 2 Ser.67 (1838) 225-251. Laurent accepted Bineau's suggestion and used it in a table of formulae of benzoyl derivatives. A. Laurent, 'Recherches diverses de chimie organique,' Ann.de Ch. 2 Ser. 66 (1837) 136-212. See p 182. Nitrogen was equivalent both to 3 atoms of hydrogen in ammonia and to three atoms of oxygen.
101. Graham, 'Experiments on the heat disengaged in combinations' part 1, November 1st 1842, Researches.p 413.
102. Graham; ibid. Researches.414-415.

'thermal equivalency' was explained by the hypothesis that nitrogen was really a compound atom. He wrote: "it is possible that this coincidence [of an equal fall in temperature] is not accidental, but depends on a thermal equivalency of NO_5 , and Cr_2O_6 if the single equivalent of nitrogen be divided by three, or considered as three atoms instead of one, as has been inferred on other grounds,¹⁰⁰ then the acid constituents of both salts will contain the same number of atoms namely eight [i.e. Cr_2O_6 and N_3O_5], and the bichromate of potash which has hitherto been so anomalous among salts be assimilated to the nitrate of potash."¹⁰¹ In support of this view, Graham pointed out that there was similar thermal equivalency in the salts: terchromate of potash ($\text{KO},\text{Cr}_3\text{O}_9$); biphosphate of potash ($\text{KO}.2\text{HO},\text{PO}_5$); and binarsenate of potash ($\text{KO}.2\text{HO},\text{AsO}_5$). These three salts could be assimilated if they each contained fourteen atoms, which would be possible if one equivalent of phosphorus or arsenic contained three atoms.

Graham was clearly aware of the inadequacy of traditional formulae to express the polar relations of elements. This can be seen from his discussion of Wurtz's observation, that hypophosphites contained two atoms of water which, although they were not basic, formed a part of the acid. Graham suggested that a neutral hypophosphite should be represented by $\text{RO} + \text{PO},\text{H}_2\text{O}_2$ or rather $\text{RO} + \text{PO}_3\text{H}_2$. The corresponding biphosphate of potash could be written similarly, as $\text{RO} + \text{PO}_7\text{H}_2$ [i.e. $\text{RO} + \text{PO}_5.2\text{HO}$]. In the latter compound the two atoms of water were replaceable by a strong base but this was not the case with hypophosphites. This explanation demonstrated the gradual transition of the basic elements in a salt into its acid constituents.¹⁰² There might even be intermediate conditions where water was neither basic nor acidic but conventional formulae expressing only extreme conditions failed to allow Graham to delineate intermediate conditions.

In his laboratory notebooks for 1842-3, Graham wrote out polar formulae to express in a more subtle way the thermochemical and

103. Graham, Wellcome Notebook 7, 'Hydration and solution of salts' (1842) 44 pp. Wellcome Library. MS.2558 (old no.3183).

104. Graham, Wellcome Notebook 9, 'On sulphates etc.' (1843) 84 pp. Wellcome Library MS.2560 (old no.3185).

105. Graham, Wellcome Notebook 10, 'Notes on chemistry, diabetes, diet etc.' 36 pp. (August 1843-4) Wellcome Library MS.2561 (old.no. 3186).

The figures in brackets are given in 'Experiments on the heat disengaged in combinations' Part 2 (January 1st 1844) Researches.⁴⁴¹. Graham must have intended to continue his researches further, but by 1844 he appears to have abandoned his study of heat. In his last notebook on heats of solution (Notebook 10; August 1843) he added the note "In the enquiry 'heat of liquefaction' find latent heat of ice in apparatus used; the number for the equivalent of HO make the unit. Then hydrated sulphate, carbonate, phosphate, arseniate, subarseniate, iodate of soda, [also] hyposulphite, acetate and observe the fusibility by heat of the salts. Compare particularly the hydrated salts. Compare in this respect sulphates of Mg, Zn and Fe. Sulphates of Mn, Cu and Cd. Sulphates of Mg and Zn differ sensibly in cold of liquefaction. Why? Also how they affect boiling point." This programme of work remained incomplete.

constitutional relations which his researches had revealed.¹⁰³ Negative constituents were written over positive constituents, for example

"10 atoms: nitrate $\frac{O.NO_5}{K.N_2}$; bichromate $\frac{O.O_6}{K.Cr_2}$; hypophosphite $\frac{O.H_2O_3}{K.P_3}$
of of of
potash potash potash

.... the phosphorus series = $\frac{1}{P_3}$ while nitrogen = $\frac{N}{N_2}$

14 atoms: terchromate $\frac{O.O_9}{K.Cr_3}$; biphosphate $\frac{O.H_2O_7}{K.P_3}$ here the H₂ is made chlorous as in hypophosphite of potash."
of of
potash potash

104

Graham used similar polar formulae in his molecular theory of organic chemistry in the final part of his textbook written in 1841. However, he did not include polar formulae in the final 1844-part of his thermochemical researches, presumably, because these formulae had been rather unfavourably received.

Graham's notebooks on thermochemistry for 1843 show that he was searching for some relationship between the cold produced on solution and the number of atoms in a compound. Taking the equivalent of carbon to be 150 (O = 100), as Regnault had fixed it in 1840, Graham found that the cold produced by dissolving equivalents of oxalic acid and its salts in water revealed an almost whole number relationship e.g.

<u>Chemical</u>	<u>Formula</u>	<u>Number of atoms</u>	<u>Ratio of cold on solution</u>
Crystallised oxalic acid	HO,CO ₃ + 2HO	10	$2\frac{2}{9}$ (7)
Oxalate of potash	KO,CO ₃ + HO	8	2 (6)
Binoxalate of potash	KO,CO ₃ + HO,CO ₃ + 2HO	16	5 (15)
Quadroxalate of potash	KO,CO ₃ + HO,CO ₃ + 2(HO,CO ₃ +2HO)	32	8 (25)

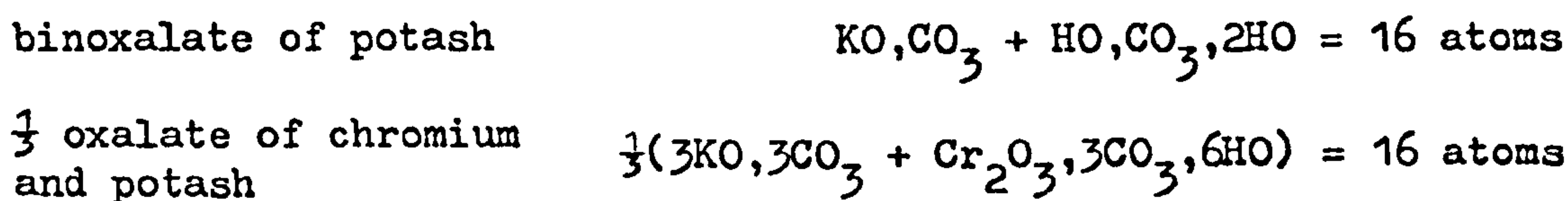
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106. Graham, *ibid.* Notebook 10.

There appeared to be various related classes of compounds, for example:

	<u>Chemical</u>	<u>Number of atoms</u>	<u>Relative cold</u>
Class 1	crystalline oxalic acid	10	20
Class 2	nitrate and bichromate of potash	10	40
Class 3	sulphate of potash	6	15
Class 4	chromate of potash	6	12

In classes 1 and 2 the number of atoms were equal but the cold developed was twice as much in class 2 as in class 1; in classes 1 and 4 the relative cold produced was double the number of atoms. However, the relationship was not always simple. He compared one equivalent of binoxalate of potash to one third of an equivalent of the oxalate of chromium and potash; both contained 16 "thermal atoms" and both gave the same cold on solution. Their formulae were:



This example showed that $\frac{2}{3}\text{Cr}$, $\frac{2}{3}\text{Al}$ or $\frac{2}{3}\text{Fe}$ were thermally equivalent to one atom of hydrogen and this was the proportion of metal joined to one atom of oxygen. Accordingly Graham reasoned that the 'material thermal atom' was not fixed because it was Fe in the protoxide of iron (FeO) and $\frac{2}{3}\text{Fe}$ in the peroxide of iron (Fe₂O₃).¹⁰⁶ Was this evidence for an inequality in the distribution of combined heat in a triple salimolecule and its connection with polarity?

It would appear that Graham was probably attempting to relate the cold on solution to atomic heats i.e. specific heat x atomic weight. In 1840, Regnault had defined atomic heats, and had doubled the atomic weight of carbon so that he obtained a 'thermal equivalent' for carbon, which agreed with Dulong and Petit's law. The latter chemists endeavoured to show that most elements had the same atomic heat for equivalent quantities. Graham seems to have been working towards a theory of thermal atoms which were related in a simple manner to atomic heats, but his ideas were only sketched in his notebooks and they were never developed.

107. Graham, Elements of Chemistry, 1st.edn. part 2 (London, 1838) 174.
108. R. Kane, Elements of Chemistry, 2nd.edn. (Dublin, 1849) 748-9.
109. MS. letter to Graham from Liebig, dated August 8th 1838. Liebig Museum, Giessen.
110. Graham, Elements of Chemistry, 1st.edn. part 4 (1840) 450-451.
111. Gay-Lussac, 'Nature of the acid in triple prussiates', Ann.de Ch. 2 Ser.22 (1823) 320-323.
Gay-Lussac had suggested that hydrogen was attached to FeCy_3 in hydrocyanoferric acid: $2\text{H} + \text{FeCy}_3$, whereas Berzelius had suggested that potassium ferrocyanide was a double salt $2\text{KCy}^2 + \text{FeCy}^2 + 6\text{Aq}$ (Cy = NC^2). Ann.de Ch. 2 Ser.15 (1820) 144-170.
112. E. Turner, Elements of Chemistry, edited by Liebig and Gregory, 7th. edn. (London, 1842) 742-3.

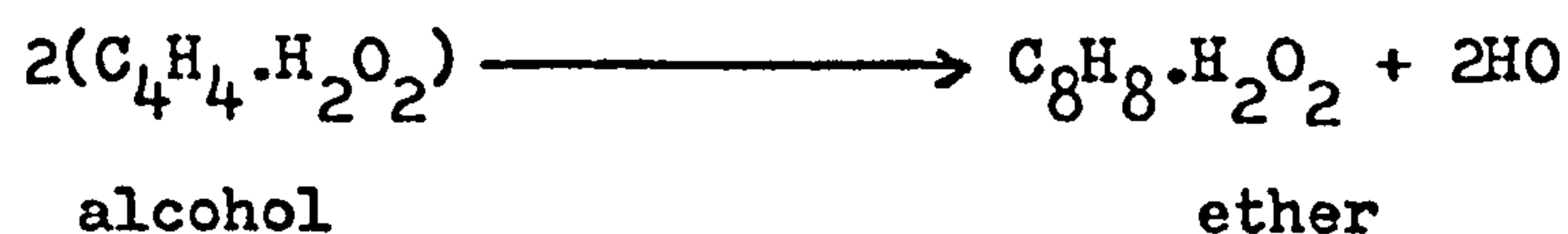
We have seen that Graham thought in terms of the polymerism of the atoms of elements and of acids. He also assumed that radicals could be polymeric, as Liebig had found, with certain organic acids. Let us now examine Graham's use of polymerism: firstly, in complex cyanides; secondly, in the production of ether; and finally, in water itself. In 1838, Graham suggested that ferrocyanides were salts of a new tribasic compound radical, which he called 'prussine', containing three atoms of cyanogen joined together. This new radical was yet a further example of a triple salimolecule Cy^3 . Prussine had the formula N_3C_6 or Pr; it was a tribasic radical which could combine with three atoms of hydrogen or with three atoms of metal. Therefore, potassium ferrocyanide was K_2Fe, N_3C_6 and potassium ferricyanide was a 'double prusside' with the formula: $- Fe_2, N_3C_6 + K_3, N_3C_6$ [Fe_2 was tribasic because it joined to 3 atoms of oxygen in Fe_2O_3 , which was equivalent to $3HO$, i.e. $Fe_2 \equiv 3H$].¹⁰⁷ Kane subscribed to the prussine theory and suggested that Graham should extend it to include ferricyanides by introducing a new pentabasic radical, Cy_6 or N_6C_{12} , another polymeric cyanogen.¹⁰⁸ Liebig wrote to Graham: "your notes on the ferrocyan have interested me greatly. I have shown Mr. Crum the manuscript of my Organic Chemistry, in which surprisingly enough the same theory is developed; such agreement gives me that more courage to carry on and to believe that we are on the way to the truth."¹⁰⁹ Liebig's theory, which Graham adopted by 1840,¹¹⁰ was essentially the same as that proposed by Graham, except that Liebig created two radicals: the bibasic radical, $FeCy_3$ ferrocyanogen, in ferrocyanides and the tribasic radical, Fe_2Cy_6 ferridcyanogen, in ferricyanides. Undoubtedly, 'ferrocyanogen' was taken from his teacher Gay-Lussac's 'cyanoferre'; which was one atom of iron joined to three atoms of cyanogen. Gay-Lussac had discovered this radical in the hydracid, ferrocyanic acid.¹¹¹ Liebig admitted that Graham's theory would have been preferable to all others if it had been capable of explaining why iron was not replaced by other metals.¹¹²

Whilst Alexander Williamson was studying the synthesis of ethers,

113. Graham: 'Observations on etherification', J.Chem.Soc. 3 (1851) 24-28 or Researches.646-650, see pp 649-650. This paper was read on February 4th 1850 to the Chemical Society.
114. Graham: Elements of Chemistry 2nd.edn. part 2 (London, 1848) 273-274.
115. Graham: 'On the absorption of gases by liquids'. Ann.Phil.ns12 (1826) 69-74.

Graham published his own study of etherification. Curiously, these two professors, working together at the same college, produced quite different interpretations of the synthesis of ether. Williamson's explanation is well known, but Graham's incorrect explanation is less well known.

Graham assumed that olefiant gas was C_4H_4 and that alcohol was hydrated oxide of ethyl $C_4H_5O.HO$ or alternatively $C_4H_4.H_2O_2$. He argued that etherification did not require the formation of the supposed intermediate, sulphovinic acid, instead it was a contact action as Berzelius and Mitscherlich had stated. Ether was formed by the polymerisation of the hydrocarbon C_4H_4 , olefiant gas, accompanied by a loss of water, as follows:-



Ether was here formulated as $C_8H_8.H_2O_2$ [i.e. $C_8H_{10}O_2$ or $2C_4H_5O$; this is double the usual formula given for ether or oxide of ethyl at this time.]

Likewise, he explained that when oil of turpentine was mixed with sulphuric acid, the "hydrocarbon does not combine with the acid, but is merely increased in atomic weight and gaseous density without any further derangement of composition, by a remarkable polymerizing action (as it may be termed) of the sulphuric acid. So of the hydrocarbon of alcohol; its density is doubled in ether, by the same polymerizing action." ¹¹³

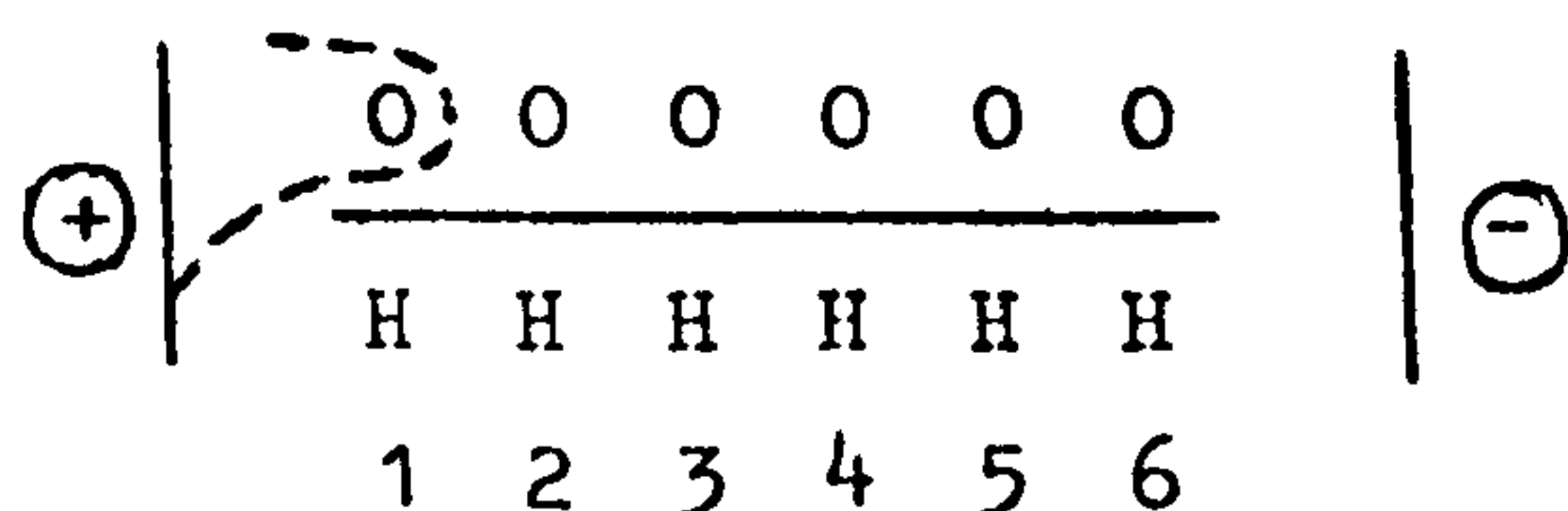
In the liquid state, polymeric chains of molecules could also be found, for example in water itself. Thus Graham wrote: "the cumulative nature of chemical combination is well illustrated in such compounds as the acid hydrates, for example in dilute sulphuric acid, where we find an atom of acid uniting with more and more atoms of water with a decreasing affinity but without any assignable limit to their number." ¹¹⁴

The concept of chemical union in the liquid state was the subject of Graham's first research paper of 1826 ¹¹⁵ and he retained an interest in this concept throughout his life. He was able to describe the process more precisely by making studies of the heat of solution. He found that

116. Graham, op.cit. (114).

heat was still evolved when the fiftieth equivalent of water was added to sulphuric acid, indicating a continued chemical union. Graham gave an interesting interpretation of the process: the addition of water gradually reduced the excess chlorous affinity found in sulphuric acid SO_3 . Using polar formulae, sulphuric acid $\frac{\text{O}_3}{\text{S}}$, contained three chlorous oxygen atoms to one basylous atom of sulphur. The addition of one or two atoms of water gave $\frac{\text{O}_3 \cdot \text{O}}{\text{S} \cdot \text{H}}$ and $\frac{\text{O}_3 \cdot \text{O} \cdot \text{O}}{\text{S} \cdot \text{H} \cdot \text{H}}$ so that the excess chlorous affinity was reduced from 3:1 or 3, to 4:2 or 2, then to 5:3 or 1.67, and so on.¹¹⁶

His explanation of osmotic phenomena also involved a consideration of polymeric water molecules. This subject was of great interest to Graham and we shall examine it in detail later. However, it is perhaps appropriate to consider here how he used the concept of polymeric water molecules in his explanation of voltaic endosmose. Both Reuss and Porrett had independently observed the phenomenon of voltaic endosmose or electrofiltration. In 1816 Porrett had examined what happened to water in a vessel containing a bladder partition when a platinum wire from the positive pole of a voltaic cell was placed in one half and a platinum wire from the negative pole was placed in the other half. A flow of water was observed moving from the positive to the negative wire. This was 'voltaic endosmose', a phenomenon which occurred with poor conductors like water. To explain this transport, Graham assumed that a polymeric water molecule was dissociated to produce a large basyle, containing hydrogen joined to a long chain of water molecules. This was formed by the loss of a single chlorous oxygen atom. The transfer of hydrogen to the negative pole along with the attached water molecules constituted the voltaic endosmose. For example if six water molecules were associated as H_6O_6 , then the polar molecule would assume the binary form $\text{H}_6\text{O}_5 + \text{O}$. Thus Graham drew the diagram below to represent this process

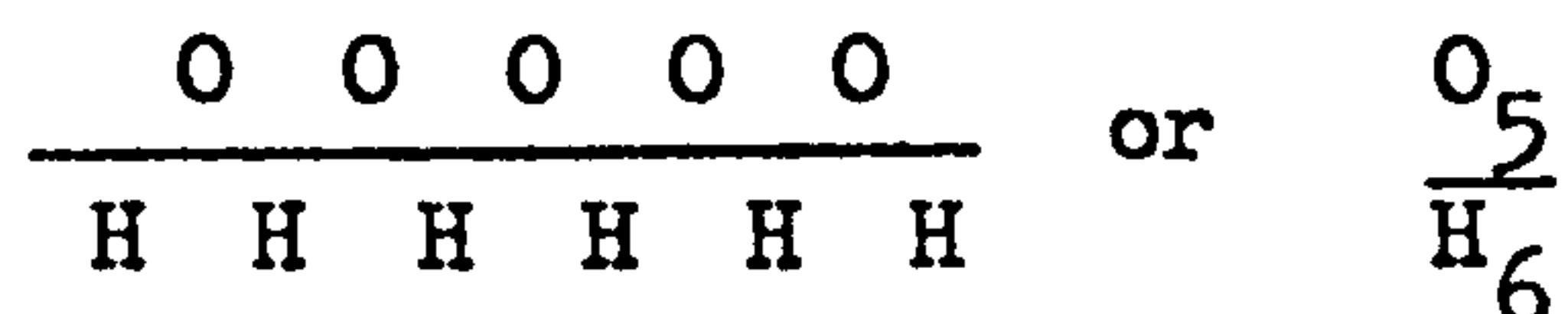


117. Graham, Elements of Chemistry 2nd.edn. Part 2 (London, 1848) 266-267.

118. MS. letter from Graham to Dumas, dated November 30th 1841. Graham dossier, Académie des Sciences, Paris.

119. 'Lettre de M. Graham à M. Dumas 'Sur quelques considérations qui dérivent de la loi des substitutions et sur un système de notation applicable aux formules des types', Ann.de Ch. 3 Ser.4 (February, 1842) 177-186 or Researches. 636-643. This letter is simply a translation of: Graham's Elements of Chemistry 1st.edn. (London, 1842) pages 728-736, with one footnote added by Dumas.

and he explained that: "the oxygen (1) was alone attracted to the positive pole, while the hydrogen (1) being so far relieved from the attraction of its own oxygen (1) comes under the influence of oxygen (2) and so on. As the oxygen (1) separates we thus have the temporary formation of a basylous atom:



But instead of involving six atoms of water as in this illustration the compound water molecule may embrace hundreds or thousands of atoms.

It will always be represented by $\text{H}_n \text{O}_{n-1} + \text{O}$ where $\text{H}_n \text{O}_{n-1}$ is the basylous atom which is transferred to the negative pole and O is the salt-radical atom which is transferred to the positive pole. It appears to be by polarisation of this sort that mass compensates for conducting power." ¹¹⁷

This explanation influenced Graham's earlier attempts to understand the nature of osmosis.

When Graham wrote the concluding section on Organic chemistry for his textbook in 1841 he extended his molecular theory to include organic compounds. This theory drew together the themes of chemical affinity, voltaic circles, isomorphism and polymeric molecules which have been discussed in this chapter. In November 1841, Graham sent the final part of his textbook on Organic chemistry to J. B. Dumas and he wrote:

"I beg to call your attention to some speculations which it contains founded principally on your law of substitutions. I refer particularly to the section on pp. 728-736 on a 'Molecular theory of organic compounds'. It contains also a method of notation which I think particularly applicable to the formulae of types in contradistinction to those of compound radicals." ¹¹⁸ Dumas duly published this section in the Annales de Chimie et de Physique of February 1842. ¹¹⁹

Graham began by urging the adoption of the view that it was important to consider the attractions of the same atoms for one another as well as for different atoms; a theme which he had developed previously with

120. Liebig, 'On the phenomena of fermentation and putrefaction, and on the causes which provoke them.' (being an extract taken from Liebig's Traité de chimie organique) Ann. de Ch. 2 Ser. 71 (1839) 147-195, see p 149.
121. Graham, Elements of Chemistry 1st.edn. (London, 1842) 723.
122. Graham, op.cit. (68).
123. Dumas, 'Memoir on the law of substitutions and the theory of types.' Comptes Rendus 10 (1840) 149-178.

metallic salimolecules. He referred to Liebig's view of organic chemistry at the outset. Liebig had written that: "in an organic molecule two or more elements or chemical equivalents are found in the state of compound radicals; these radicals affect a particular form and it is their form as well as their composition which gives rise to the chemical characters shown by organic compounds. In all organic molecules it is therefore necessary to consider two species of attraction: 1. The affinity of the compound radical, of carbon and nitrogen; of carbon and hydrogen; of nitrogen and hydrogen; for the oxygen, or for the other radicals simple or compound with which it is combined. 2. The extremely different affinity of each element in particular for other elements." ¹²⁰ Liebig's theory of compound radicals grouped organic compounds into different classes which contained common radicals, for example benzoyl, acetyl, or cyanide.

Dumas, from his study of the substitution of hydrogen by chlorine in organic compounds, argued that it would be simpler to classify compounds according to chemical types. Compounds of a given type possessed a constant number of atoms with a common constitution. The use of chemical types avoided argument about which radical was present in a compound, for example whether alcohol contained the radical, olefiant gas, ethyl, or acetyl. Graham preferred type theory because it was less speculative than the radical theory and also because it was possible to write a simple empirical formula which showed more clearly any changes resulting from substitution. ¹²¹ He referred to type theory in his notes as "a haven or shelter from the troubled sea of controversy." ¹²²

The law of substitutions advocated by Dumas posed no problems for Graham. He had always accepted isomorphous substitution which included, for example the substitution of two equivalents of manganese for one of chlorine. As Dumas acknowledged "the most eminent of English Chemists, Graham, adopts it [the law of substitutions] without reserve." ¹²³ For Graham there was none of the difficulty which Berzelius encountered

124. Graham, Elements of Chemistry 1st.edn. (London,1842) 721.

125. Graham, *ibid.* 728-729.

with the substitution of positive hydrogen by negative chlorine. This can be seen from the following clearly expressed statement made by Graham: "But it is to be remembered that no body is absolutely chlorous (electro-negative), or zincous (electro-positive), but only relatively so to certain other bodies. Hence although zincous to chlorine, hydrogen is chlorous to carbon, or hydrogen is the chlorous constituent of the organic compounds in question [acetic acid and olefiant gas etc.]. Even among inorganic compounds, we have instances of hydrogen discharging the same function, as in the class of phosphuretted hydrogen and arseniuretted hydrogen when 3 atoms of hydrogen are chlorous, and may be replaced by oxygen, chlorine etc. (In ammonia, on the contrary, nitrogen appears to be the negative, and hydrogen the positive constituent.) In this way that universal dualism in the constitution of a compound, or distribution of its elements into two opposed classes, conducing to binary combination, which has never ceased to be a recognised doctrine of chemical science, in some form or another, with reference to inorganic compounds, is extended also to organic compounds." ¹²⁴

Graham argued that any theory of combination must include the propagation of chemical action over a distance such as was found in voltaic circles. Even in a free metal there was a complex structure of binary molecules. Hence in combining two elements there was a replacement of a less stable molecular structure by a more stable one, a form of double decomposition or substitution. He suggested that evidence for this view came from "the universal susceptibility of compounds of all kinds to decomposition under electrical action of high intensity, [which] appears to argue a greater simplicity and sameness of constitution of chemical compounds than is generally recognised." ¹²⁵ In other words, elements and compounds could all be considered in the extreme case as constructions of binary molecules, from which he derived the important concept that combination was the natural condition of all matter. Combination was the source of the cohesion and aggregation of matter.

126. Graham, *ibid.* 729.

127. Graham, *ibid.* 730.

Decomposition required the application of a force, "such as the communication of heat to atoms which supplies them with the repulsive power..to overcome their combination." 126

For binary compounds, Graham divided the elements into negative and positive groups, by writing the negative elements over the positive elements in polar formulae. Thus water HO was written as $\frac{O}{H}$, carbonic acid $\frac{O_2}{C}$, hydrate of potash $\frac{O.O}{K.H}$ and ether $\frac{H_5O}{C_4}$. Many compounds could be subdivided into even simpler binary compounds. For example olefiant gas $\frac{H_4}{C_4}$ could be $\frac{H_2.H_2}{C_2.C_2}$ or even $\frac{H.H.H.H}{C.C.C.C}$. The assumptions which he used to construct polar formulae were: "1. That the basic or positive element or elements are in immediate combination with the chlorous..elements placed above them in the formulae. 2. That these binary compounds..are associated together so as to form the compound molecule, from an attraction of all the basic elements for each other, and of the chlorous elements for each other, of such a nature as retains together the 3 atoms of the same kind which form a single equivalent of nitrogen or phosphorus, the 3 atoms of cyanogen in cyanuric acid, the various multiples of C_2H_2 grouped together in the molecules of olefiant gas and hydrocarbons isomeric with it, or the multiples of C_5H_4 in the molecule of oil of turpentine and large class of essential oils. A complex organic molecule is thus represented as an association of two or more binary compounds, comparatively simple in constitution, often isolable substances and possessed of considerable stability." 127 The positive or basylous elements were carbon, or carbon and hydrogen. The negative or chlorous elements were ranked in decreasing order of chlorous affinity:-

chlorine
oxygen
sulphur
nitrogen
hydrogen

so that an element higher in the table could be substituted for an element beneath it. Graham here stressed the importance of substitution and

128. Graham, *ibid.* 732.

129. Graham, *op.cit.* (119) Researches.639.

In an annotated edition of his textbook (see note 130) Graham added a note opposite page 732: "Ignited potassium, however, combines intimately with cyanogen, owing to excess of chlorous attraction in N. Indeed N appears from this to be more chlorous than 2O; or cyanogen more so than carbonic oxide - $\frac{N}{C_2}$ than $\frac{O_2}{C_2}$:- carbonic oxide

combining with K, but with less energy than cyanogen does. On the other hand we have in sulphocyanogen an indication of the distinction of N to act along with another chlorous body sulphur. Sulphocyanogen $\frac{NS_2}{C_2}$.

This with basylous H forms a strong acid $\frac{NS_2}{C_2H}$. Salt $\frac{NS_2}{C_2K}$

Nitrate of potash $\frac{O.O.O_3}{K.NO}$? $NO_4 = \frac{O_3}{NO}$? Like $\frac{O_3}{H_3}$

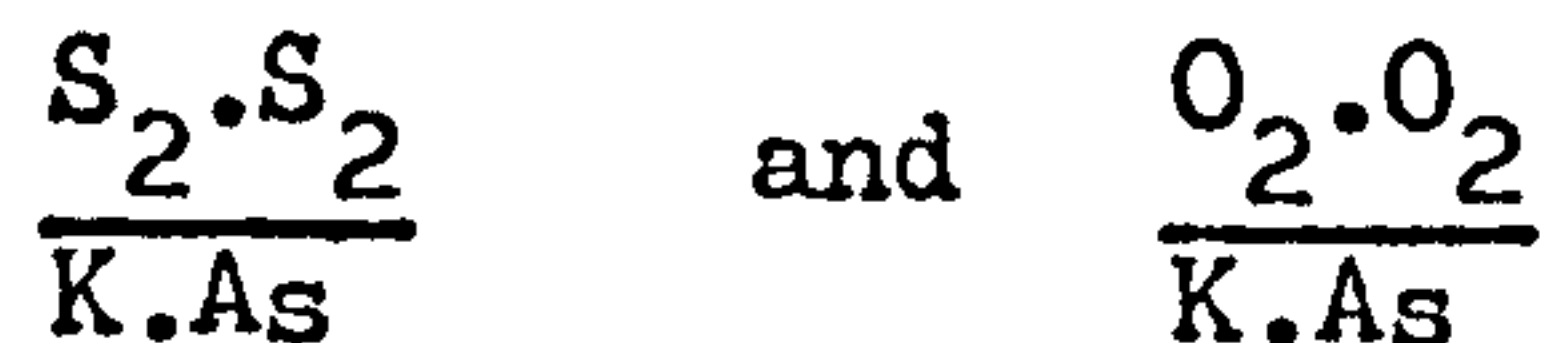
$NO_2 = \frac{O_2}{N} = \frac{O_2}{H_2}$? "

Another interesting example of the difficulties presented by polar formulae was given by Graham with an attempted resolution of them in a note which he added opposite p 733:-

"Why do sulphur acids combine with sulphur bases?



The combining attraction may be



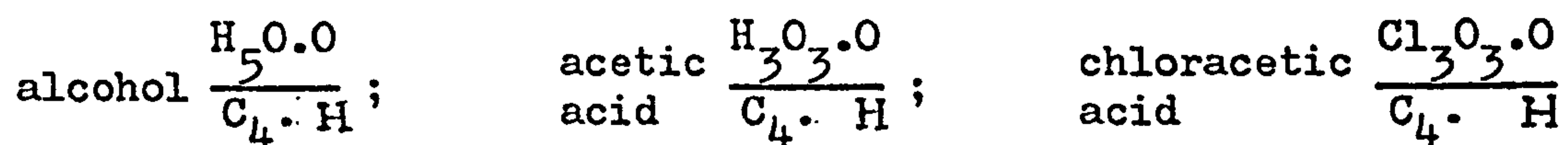
If a sulphur acid and oxygen base united, it would be $\frac{O.S_3}{K.As}$, with

the combining attraction - $\frac{OS.S_2}{K.As}$. But this $\frac{OS}{K}$ cannot be.

For what reason? O and S are disposed to antagonise than to act together."

polymerism, and above all of the neglected feature, that atoms of the same kind were attracted to one another and joined together by the same force of chemical affinity which united dissimilar atoms.

With compounds of the same type, the number of elementary atoms was always identical and also the total number of negative or positive atoms remained the same. For example the alcohol type contained twelve atoms of which seven were chlorous and five were zincous:

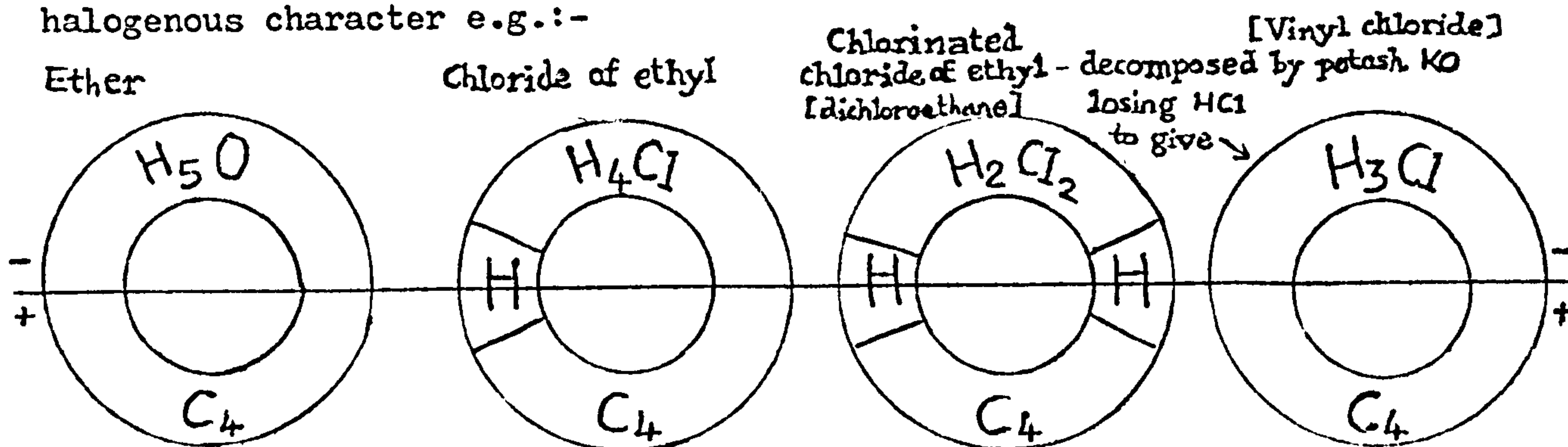


As Graham admitted, polar formulae were not without their difficulties. There were occasions when it was not easy to decide whether an element was zincous or chlorous. For example hydrocyanic acid could be written $\frac{\text{NH}}{\text{C}_2}$ or $\frac{\text{N}}{\text{C}_2\text{H}}$. Graham decided that the polar formula for hydrocyanic acid should be $\frac{\text{NH}}{\text{C}_2}$, because the chlorous hydrogen was replaced by chlorine to give cyanogen chloride $\frac{\text{NCl}}{\text{C}_2}$. Also, he pointed out that the feeble action of the strong bases, like potash, on hydrocyanic acid appeared to support the view that the hydrogen was not zincous.¹²⁸ Further evidence to show that hydrogen was really chlorous was that the chlorous metals, such as mercury, readily replaced the hydrogen giving, for example $\frac{\text{NH}}{\text{C}_2}\text{g}$. The latter salt was not decomposed by strong acids, as it would have been if its constitution had resembled that of cyanide of potassium $\frac{\text{N}}{\text{C}_2\text{K}}$.

The difficulty posed by this example was crucial; hydrogen did not seem to be convincingly chlorous or zincous. Dumas was clearly aware of this problem and so he added just one significant comment to this theory when he published it in 1842. He said that nothing proves more difficult to reconcile the old and new theories than this necessity admitted by Graham of considering mercury cyanide and potassium cyanide as two substances containing different radicals.¹²⁹ This telling-criticism appeared to invalidate the molecular theory as Graham first presented it.

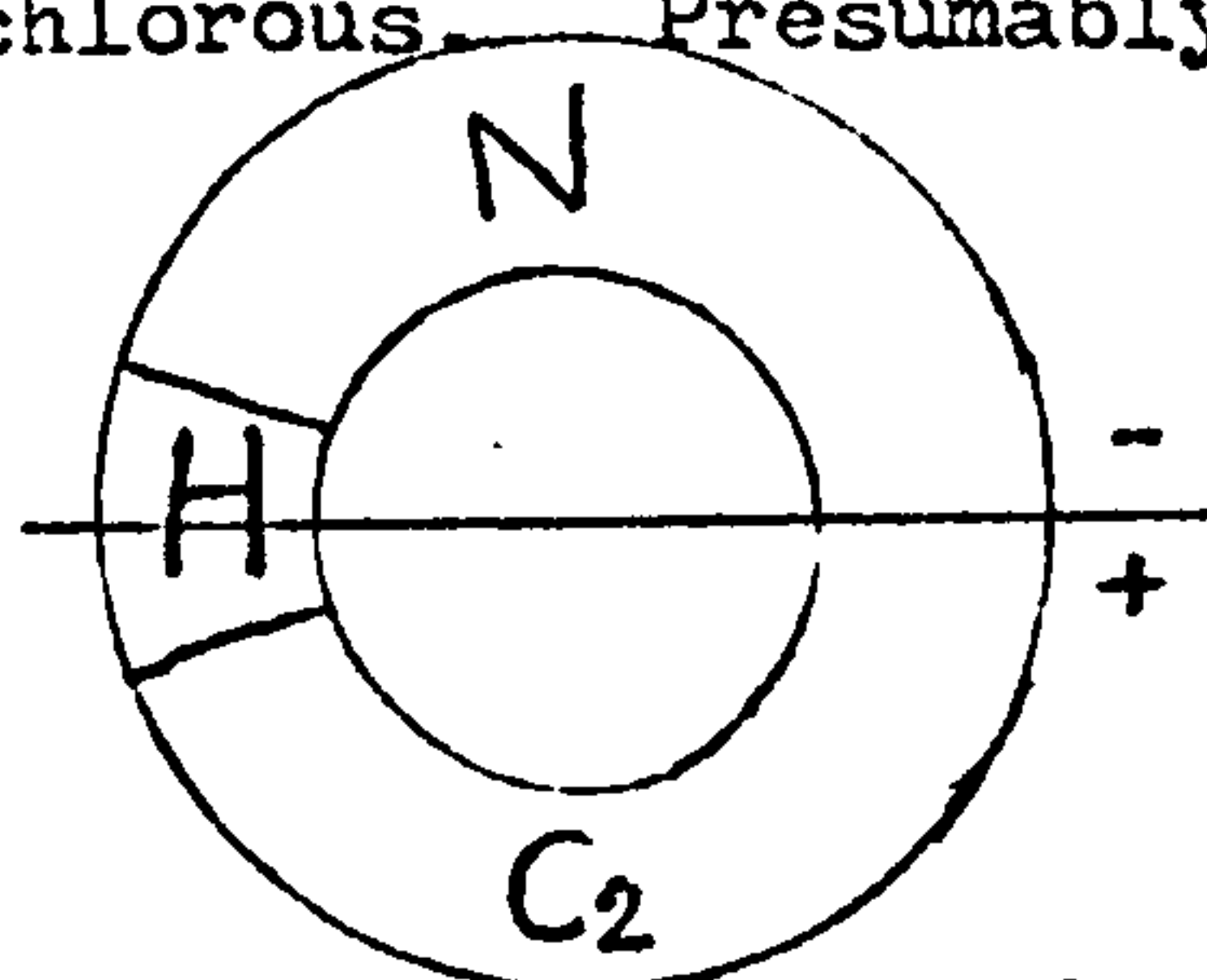
130. Graham, Elements of Chemistry (London, 1842) - an annotated and interleaved edition which belonged to Graham is in University College Library, London. These diagrams of polar formulae appear opposite p 731. They are in Graham's handwriting. Presumably this annotated text was used as a revision for the 2nd edition. Earlier annotations suggest that this is probable. However Graham did not finish the 2nd edition and the organic section was omitted by Henry Watts, who edited Vol.2 of the 2nd edition in 1857. The annotated edition of Graham's Elements of Chemistry is in two volumes: The first volume contains pp 431-696 and the second volume pp 697-1088 of the 1st edition (1842). The earlier part pp 1-430 is not recorded in the catalogue of Graham's library which was presented to University College in 1879 by his nephew J.C.Graham.
131. V. Regnault, Ann.de Ch. 59 'Recherches de chimie organique,' (1835) 358-375.

When Graham wrote the second edition of his textbook he suggested that the hydrogen in hydrocyanic acid was just on the limit between basylous and halogenous character. Also, in an annotated copy of the first edition of his textbook, Graham drew out polar formulae literally as voltaic circles¹³⁰ showing hydrogen on the limit between basylous and halogenous character e.g.:-



Regnault had shown that $C_4H_4Cl_2$ lost a molecule of HCl, when it reacted with an alcoholic solution of potash, to give C_4H_3Cl or vinyl chloride.¹³¹

Graham must have realised that this reaction showed that hydrogen could not be entirely chlorous. Presumably he would have drawn hydrocyanic acid as follows



showing the neutral position of hydrogen in the revised version of his polar formulae.

Graham found polar formulae useful both in his thermochemical researches and as a teaching aid. They allowed him to clarify certain difficulties which conventional formulae failed to do. For example he was able to show the isomerism of urea and ammonium cyanate, by drawing them as different polar molecules e.g. urea $\frac{N \cdot O_2 \cdot N}{C_2 H_2 \cdot H_2}$; ammonium cyanate $\frac{NO_2 \cdot N}{C_2 H \cdot H_3}$. He argued that polar formulae showed the attractions of the ultimate elements for each other in a way which did not use any contested theory of constitution. Thus, in the decomposition of oxalate of ammonia by phosphoric acid, water was removed because it was more strongly attracted to phosphoric acid, and so oxamide and cyanogen were produced. Graham emphasised that there was no alteration in the original polar

132. Graham, Elements of Chemistry 2nd.edn. vol.1 (London, 1848) part 2
207.

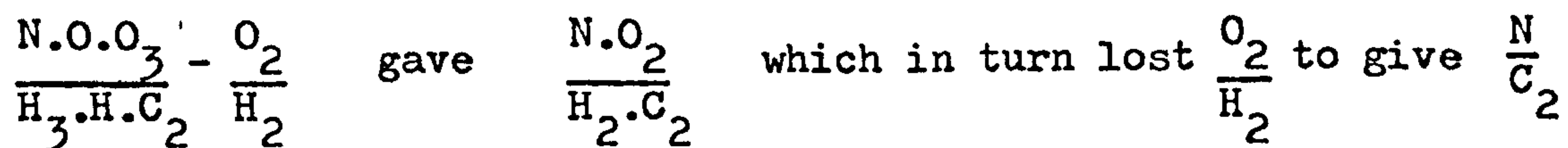
133. Berzelius, Rapport Annuel trans. by Plantamour (1843) 182-183.

relations of the elements in this natural division e.g.

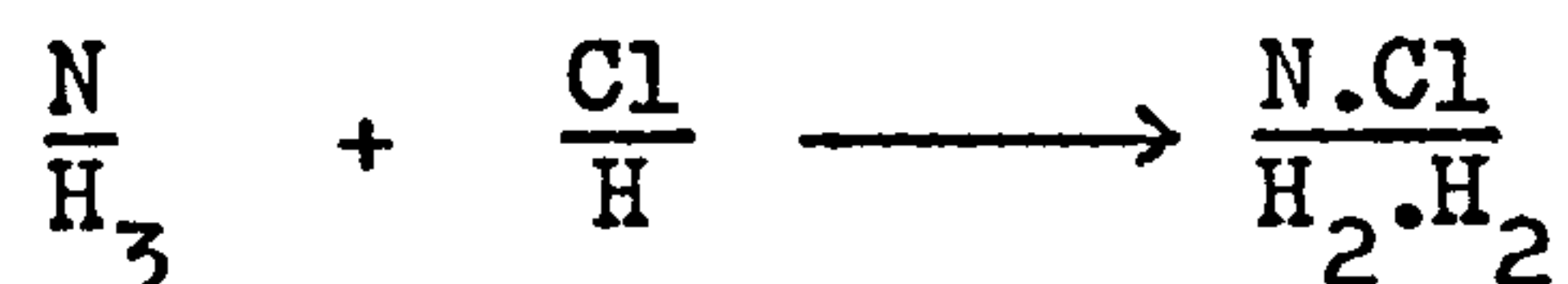
oxalate of ammonia

oxamide

cyanogen



Another valuable feature of polar formulae was their ability to reveal the reason why certain chemicals were bases or acids.¹³² To show why ammonia was a base, consider the formation of ammonium chloride



The highly negative chlorine shared or assumed entirely the attraction of the third equivalent of hydrogen in ammonia. This hydrogen was less powerfully held by the nitrogen and was less neutralised by nitrogen than the other two equivalents of hydrogen. The reasoning behind this statement was that one atom of nitrogen was equivalent to two atoms of oxygen ($\text{N} \equiv 2\text{O}$) and therefore $\frac{\text{N}}{\text{H}_2}$ was equivalent to $\frac{\text{O}_2}{\text{H}_2}$, and so NH_2 had the same polar neutrality as two molecules of water. Furthermore, the analogy between cyanogen $\frac{\text{N}}{\text{C}_2}$ and carbon monoxide CO or C_2O_2 , that is $\frac{\text{O}_2}{\text{C}_2}$, convinced Graham that $\text{N} \equiv 2\text{O}$. Therefore it was possible to understand why the third equivalent of hydrogen gave ammonia the basylous or positive character of a base. Indeed, in metallic oxides there was generally an excess of basylous character, and in acids there was a greater negative or chlorous character from the excess of oxygen. For example in sulphuric acid, SO_3 or $\text{SO}_2.\text{O}$, the third atom of oxygen was more feebly united than the other two, giving an acid character to the molecule.

Graham appears to have been attempting to reconcile the electro-chemical theory of Berzelius with the theories of substitution and types put forward by Dumas. Although Graham may have been satisfied with his theory, it does not seem to have claimed much support, or even attention.

However, Berzelius did review the theory in his Jahresbericht for 1843.¹³³ He noted that Graham's views completely ruled out the idea of compound radicals. He wrote that Graham's method of considering and

134. Berzelius, 'Opinions relating to the composition of organic substances' Taylor's Scientific Memoirs 4 (1846) 661-682 (p 672) from Pogg. Ann. 68 (1846) 161.
135. Berzelius, *ibid.* 673.
136. A. Baudrimont, 'Complaint from M. Baudrimont relating to a passage read by Laurent in the previous session', Comptes Rendus 20 (1845) I 960-961.
137. A. Baudrimont, Traité de Chimie (Paris, 1844) Vol. 1 pp 125, 143 and on bismuth p 719. Also Baudrimont, 'Sur la détermination des poids atomiques et en particulier sur une loi relative aux chaleurs spécifiques', Comptes Rendus 2 (1836) 530.

expressing the compositions of compounds was like book-keeping. There were simple methods of book-keeping, which showed at a first glance clear and comprehensible results for every one to see, but Graham's particular method was so complicated and muddled that it was difficult to give an account of it. His dismissive attitude was not softened when he wrote in 1846 that: "Graham assumes that the simple atoms of every fundamental principle combine with each other according to certain types consisting of a definite number of atoms in a fixed and unchangeable order. When fundamental principles unite with each other, the atoms are exchanged from the types by a sort of double decomposition, and when organic compounds are produced, carbon atoms are exchanged from the carbon type for hydrogen, nitrogen or oxygen atoms from their types, the places of these latter being filled by carbon atoms. In this manner it is clear that anybody who undertakes to explain the rational composition of organic compounds and does not feel satisfied with what his predecessors have done, may fabricate or invent a new view of his own; nor is there any reason why this should have a limit, until some rule is sought for, to guide us in the mode of proceeding which ought here to be followed."¹³⁴

The rule referred to, was the analogy principle, that the constitution of organic compounds should be derived from the analogous known-combinations of inorganic compounds. He added: "We must then be satisfied with the empirical composition, and defer establishing the rational until our knowledge is sufficiently ripe to enable us to do so To increase, in the meantime, the number of imaginative theories is only to retard instead of advance the progress of science."¹³⁵

Baudrimont referred to Graham's theory in 1845 when he criticised Laurent for not acknowledging that he had been anticipated in developing theories of the polymeric nature of elements in order to explain their different equivalents.¹³⁶ Baudrimont argued that he had discussed the molecular state of elements both in the account he had given of bismuth in his Traité¹³⁷ and in some notes which he had sent to the Académie des

138. A. Laurent, Chemical Method trans. by W. Odling (London, 1855) 222.

139. Samuel Brown (1817-1856), 'On the preparation of cyanogen in large quantities and on the isomerism of cyanogen and paracyanogen' communicated by Dr. Christison on February 15th 1841 and May 3rd 1841. Trans.R.S.E. 15 (1844) 165-176 and 229-249.
For biographical details concerning Brown, see: D.N.B. article, 'Recollections of Prof. Masson', Macmillan's Magazine 12 (1865) 74-86 and 'Dr. Samuel Brown' North British Review 26 (1856-7) 384-406.

140. J. F. W. Johnston, 'On the present state of knowledge in regard to dimorphous bodies', British Association Report 1837 (1838) 163-215.

Sciences in 1836 and 1840. He added that Ampère had always admitted the divisibility of atoms and in addition one could consult Graham's recent letter to Dumas.

Like Berzelius, Laurent was critical of Graham's polar formulae, although the main thrust of his criticism was directed at Hofmann for wrongly-attributing his opinions on the salts of Gros and Reiset to Graham. He complained: "thus according to Graham the atoms of the succeeding compounds would be disposed as follows:-

Wöhler's white precipitate $\frac{\text{Cl.N}}{\text{Hg.H}^3}$ $\frac{\text{negative elements}}{\text{positive elements}}$

Black precipitate ... $\frac{\text{Cl. N}}{\text{Hg}_2 \cdot \text{H}_2 \text{Hg}_2}$ or $\frac{\text{ClHg. N}}{\text{Hg}_2 \cdot \text{H}_2 \text{Hg}}$

What relation, I ask, is there between these formulae, and that of chloride of ammonium even when represented as $\frac{\text{Cl N}}{\text{H}_4}$?" ¹³⁸

Graham understandably became more cautious in his espousal of polymerism and molecular theories of organic chemistry. Although he had speculated freely on the polymeric nature of elements and on molecular theories of compounds he was very reticent with regard to stating an opinion on the unitary theory of matter. Indeed, he was rightly cautious about some of the more extreme suggestions claiming that it would be possible to perform transmutation experiments on the elements if all matter was indeed uniform.

Another possible reason for Graham's increasing reluctance to develop both polymerism and molecular theories of compounds was the turn of events which took place in Scotland in 1841. In that year, Samuel Brown claimed that he had transmuted the element carbon into silicon. ¹³⁹

The origins of this claim can be traced back to 1837 when James F. W. Johnston had delivered a report on dimorphism to the British Association in which he had foreshadowed transmutation. ¹⁴⁰ He had pointed out the analogies which existed between dimorphism and isomerism. As Dumas had previously suggested, isomerism involved more extreme changes in

141. Johnston. *ibid.* 212.

142. The Athenaeum (1837) p 747. In a lecture given on June 10th 1836, Faraday discussed the nature of elements and indicated that elements might be complex substances. He wrote: "Thus either present elements are the true elements, or else there is the high probability before us of obtaining some more high and general power of nature even than electricity; which at the same time might reveal to us an entirely new grade of the elements of matter, now hidden from our view, and almost our suspicion. This is the high prize set before the chemico-physical philosopher of the present day by the present state of our scientific knowledge." H.Bence Jones, Life and Letters of Faraday 2 (London, 1870) p 86.

properties than dimorphism. Isomerism required changes of chemical properties in addition to the changes of physical properties which were found in dimorphism. Certain cases of isomerism also involved polymerism. Here, Johnston quoted the examples of: the conversion of cyanogen into solid paracyanogen; the conversion of cyanuric acid crystals ($3\text{Cy} + 6\text{O} + 3\text{H}$) into solid cyanuric acid $3(\text{CyO} + \text{HO})$; and the polymerism of hydrocarbons. He also believed that it was possible for the elements carbon and sulphur to exist in isomeric forms. Indeed, Berzelius was to develop this idea when he introduced the concept of 'allotropy' in 1840. Johnston pointed out that the radical cyanogen behaved like chlorine and bromine and therefore it was possible that the latter might be compounds. Graham, as we have seen, believed in the compound nature of chlorine and presumably of all the other halogens. Johnston was inclined to believe that the elements were truly complex. He wrote: "are the elementary substances isomeric? is another form of the question are the received elements really compound? in as much as it indicates the desire to diminish the number of simple substances; but it is a very different question with regard to the way. maybe in some brighter moment we shall show that substances considered elementary are yet mutually convertible without decomposition. Are the received elements isomeric? is thus a preliminary question to are they compound? and in the case of some of them may receive the earlier answer." ¹⁴¹

Graham, Liebig, Faraday, Whewell, Kane and Sir William Hamilton all attended this meeting. In the discussion which followed Johnston's report, Faraday joined Whewell, Hamilton and Kane in opposing atomism. It was reported that: "Dr. Faraday also objected to the use of the word 'atom' in Chemistry as he conceived that atoms were not only hypothetical but that their existence was obviously disproved even by the report of Professor Johnston. Dr. Faraday emphatically stated that he was not an atomic chemist." ¹⁴² At this same meeting Liebig was requested to report back on organic chemistry and the problem of isomerism.

143. Dumas, 'Lettre de M. Dumas à M. Ampère, sur l'isomérisation', Ann.de Ch.
47 (1831) 324-335.

144. Dumas, Leçons sur la Philosophie Chimique, from lectures given by
Dumas delivered in 1836 and written down by M. Bineau (Paris, 1837)
317-320.

Was Johnston influenced by Dumas's earlier suggestions of the
complexity of the elements?

145. R. Kane, Elements of Chemistry (Dublin, 1841) 377-378.

George Wilson thought he had made a compound of sulphur and iodine
in March 1838 and he wrote to his brother concerning it; "The
compound I have got is a very curious one, and throws very great
light on the constitution of a supposed element, bromine, which I am
at present trying to decompose." In October 1838 Wilson told Graham
of these speculations and "he smiled, as all older and wiser heads
do." J.A.Wilson, Memoir of George Wilson (Edinburgh, 1860) 132-4, 161.

146. Brown, op.cit. (139) Trans.R.S.E. 15 (1844) 165-176, 229-249.

Iron had an atomic weight of 27.18 and rhodium had an atomic weight
52.2 so presumably Brown imagined that two atoms of iron were con-
verted into one atom of rhodium. Although $2 \times 27.18 = 54.36$ not
52.2.

The speculations of Dumas on isomerism undoubtedly influenced Johnston's deliberations on this subject. In 1831 Dumas had supposed that those metals whose atomic weights were either equal, or had a simple relation to each other, might be isomeric, or polymeric modifications of the same elements.¹⁴³ He listed several groups of isomeric metals, for example: cobalt and nickel; platinum and iridium; molybdenum and $\frac{1}{2}$ tungsten. This speculation was repeated by Dumas in 1836 when he suggested that there were two kinds of elemental isomerism: either atoms contained the same number of molecules differently arranged, for example Pt and Ir; or one atom of an element contained two atoms of another element joined together, for example Bi=2Pd, which was an example of polymerism. Graham had admitted that Dumas might be correct in assuming that there was a simple relation between a certain small number of elements and their equivalents as we have noted previously. Dumas concluded, in 1836, by saying that transmutation of elements was not impossible but no one had yet achieved it.¹⁴⁴ Kane also believed that the elements were complex. From the analogy between chlorine and cyanogen he inferred that the elements were probably compound substances. He also accepted the notion that the metals might be isomeric.¹⁴⁵

At this time of speculation on the nature of elements and their possible transmutation it is not surprising that experiments were made to test out these ideas. Thus, on May 3rd 1841 a memoir was read to the Royal Society of Edinburgh, on behalf of Samuel Brown, in which Brown claimed to show that carbon could be transmuted into silicon. He began by showing that paracyanogen was N_2C_4 and that on heating a decomposition took place producing silicon and nitrogen.¹⁴⁶ The four atoms of carbon (atomic weight 6) were converted into one atom of silicon (atomic weight 22.2). He coupled this claim with another in which he said that iron could be converted into rhodium by transmutation.

The first reaction of Graham to this claim was communicated in a letter which he wrote to Lyon Playfair on May 11th 1841. He said:-

147. MS. letter from Graham to Playfair, dated May 11th 1841.
Playfair correspondence letter no.316, Imperial College Library,
London.

148. S. Brown, Lectures on the Atomic Theory and Essays Scientific and Literary. Vol.1 (Edinburgh, 1858), Critical lectures on the atomic theory (1843) 1-80, see pp 64-69. These lectures were delivered in Edinburgh during April 1843.

"rumours had reached us here respecting Brown's supposed discoveries. That he has deceived himself in one and all of them I have not the smallest doubt, and regret the exhibition which is being made at Edinburgh, both on his account (for I believe him a discerning person), and for the sake of English Science, which has certainly suffered lately by the aberrations of its cultivators. It would be useless to speculate on the results of such experiments as Brown appears to make, judging from the one you particularly mention, but the activity of cementation has probably been overlooked - 20 grs. of silicon from the iron of his crucible would account for everything. Why too use an iron and not a platinum crucible, unless predetermined to mistify [sic] himself. Without considerable experience of the conduct of parties of Brown's stamp, it is also difficult to conceive how grossly they will mislead if not positively deceive others by their statements, although of sound principles in other matters." ¹⁴⁷

Brown adopted certain arguments which Graham had himself used on polymerism. According to Brown, paracyanogen was polymeric, it was a neutral combination of two cyanogen atoms, like the neutral hydrocarbon polymers. Paracyanogen, because of its neutral state, was not decomposed by heat, electrolysis, or reagents. The concept of chemical affinity defined by Boerhaave as the attraction between dissimilar particles was extended and identified with the attraction of cohesion between similar particles. All this Graham would have found to be unobjectionable, but then Brown continued along more controversial lines. He said that the isomerism of cyanogen and paracyanogen was a practical foundation for a likely hypothesis on the constitution of the elements. The elements might form an isomeric series, for example two atoms of oxygen ($O = 8$) might conceivably be converted into one atom of sulphur ($S = 16$). Brown explained his view of atoms in a series of lectures which he gave in April 1843. ¹⁴⁸ The particle of matter was a molecular nucleus. He used this name, to distinguish it from either the point of infinite repulsion defined

149. Berzelius, Berzelius Bref. by H. G. Söderbaum Vol.6 (Uppsala, 1932) p 265, letter from Berzelius to Mitscherlich dated September 3rd 1841. and Berzelius, Rapport Annuel. trans. by Plantamour 5 (1845) 3
Dumas, Traité de Chimie Appliquée aux Arts. Vol.7 (Paris, 1844) p 587. "M. Brown has announced that paracyanogen at a high temperature could be transformed into silicon. This extraordinary result, to which the author called the attention of chemists, has not been confirmed by experiments repeated in Germany and in England. These experiments have only furnished negative conclusions."
150. M. A. Sutton, 'Sir John Herschel and the development of spectroscopy in Britain' B.J.H.S. 7 (1974) 42-60, see p 57, where Sutton mentions that although Herschel and Fox Talbot were sceptical about Brown's claims they expressed support for the general concept of complex elements. Sutton refers to Royal Society MSS. J.F.W.Herschel: Vol. 17. letter 306 Talbot to Herschel, April 6th 1841, and 306a Herschel to Talbot, April 6th 1841.
151. 'Transactions of Section B' B.A. Report (Plymouth, 1841) 54 and The Athenaeum report of B.A. meeting of August 2nd 1841, p 647. Liebig also added in his letter to Playfair: "This man [Brown] must be very confused in Chemistry, especially in analysis ... It is all completely stupid stuff," but this was not reported. See MS. letter Liebig to Playfair, July 22nd 1841, Lyon Playfair correspondence, letter no.425, Imperial College Archives, London.

by Boscovich or the solid nucleus suggested by Newton,^{and} to show that chemists do not deal with ultimate atoms. There were five polar spheres of force surrounding the molecular nucleus which were alternately repulsive and attractive like Boscovich's force curve from which they were probably derived. The first sphere was repulsive and it was never further penetrated in chemicals; the second was an attractive sphere of chemical affinity; the third was a repulsive sphere which corresponded to the resistance to compression of solids; the fourth was an attractive sphere of solidity, and the fifth a repulsive sphere of 'gasiformity'. If two particles of oxygen revolved around each other on the first sphere of repulsion they would be transmuted into one compound particle of sulphur. Likewise, two atoms of cyanogen, rotating on the first sphere, united to form paracyanogen. By a similar synthesis two particles of carbon might unite to produce one of boron ($B = 10.9$); two borons might produce one silicon; or four carbons might combine to produce one silicon. Whether Graham would have rejected these speculations with their Boscovichean basis we do not know; all that is certain is that Graham was convinced that Brown's experimental results were false.

Graham's scepticism about Brown's experimental claims was shared by Dumas, Berzelius,¹⁴⁹ Herschel and Fox Talbot; although the latter two scientists did accept that chemical elements might possibly be complex.¹⁵⁰ At the meeting of the British Association in August 1841, Playfair read out a letter he had received from Liebig, which included the following passage: "We have repeated all the experiments of Dr. Brown on the production of silicon from paracyanogen but we have not been able to confirm one of his results. What our experiments prove is, that paracyanogen is decomposed by a strong heat into nitrogen gas, and a residue of charcoal which is exceedingly difficult of combustion."¹⁵¹ Immediately following this statement Graham's student, E. A. Parnell, announced that he too had repeated Brown's experiments without being able to verify any one of his results. In September 1841, a further denial of

152. R.H.Brett and J.Denham Smith. 'Experiments on the alleged conversion of carbon into silicon' Phil.Mag. 3 Ser.19 (1841) 295-305; 'Reply by Dr. S.M.Brown' Phil.Mag. 3 Ser.19 (1841) 388-391; Brett and Smith 'Additional remarks' Phil.Mag. 3 Ser.20 (1842) 24-32.
- 152a. T.G.Tilley, 'On the alleged transformation of carbon into silicon and of iron into rhodium', Liebig Ann. 39 (1841) 321-327. Liebig wrote to Playfair saying that "Mr. Tilley has repeated the experiments of Brown, it is nonsense, this man does not know the principles of analysis, his rhodium is iron and his paracyanogen contains silica, that is bits of glass from the tubes." Letter from Liebig to Playfair, August 14th 1841, Lyon Playfair correspondence, letter no.426, Imperial College Archives, London.
153. G.J.Knox, 'On the compound nature of nitrogen', Proc.R.I.Acad. 2 (1840-4) 171-3. [Brown attempted unsuccessfully to have his experiments confirmed; Faraday and Thomas Thomson both refused to witness his experiments.]
154. D.M.Knight, D.Phil.Thesis (1964,Oxford) 'The problem of the chemical elements, from Humphry Davy to Benjamin Brodie the younger.' See particularly pp.236-248.

the validity of Brown's results was given by J. Denham Smith and R. H. Brett in Philosophical Magazine. These authors included full details of their experiments.¹⁵² Understandably, Brown replied with a protest which was in turn answered by the two authors. Also, in Germany, Liebig had asked his research student, Thomas George Tilley, to investigate Brown's experiments. Tilley found a number of experimental mistakes in Brown's work and he was unable to substantiate any of the claims for transmutation. This work was published at Liebig's request in his Annalen.^{152a} in the Autumn of 1841.

However, all was not lost for Brown, because in November 1841 G. J. Knox communicated via Kane a paper on transmutation to the Royal Irish Academy. This paper was inspired by Brown's experiments and by Davy's former speculations on the complex nature of nitrogen.¹⁵³ Knox had heated potassium amide with pure iron and he claimed that he had produced silicon. He challenged Brown's own interpretation of transmutation saying that it was more likely that, nitrogen was itself a compound, which had been reduced by carbon to give silicon and hydrogen. A detailed discussion of these experiments and others on the complexity of the elements can be found in Dr. Knight's excellent thesis,¹⁵⁴ however, he has not discussed Graham's role in this debate.

The events which followed Brown's claims encouraged Graham to take a more active part in this controversy. In August 1843, Charles Hope resigned his Chair of Chemistry at Edinburgh University and Samuel Brown put his name forward as a candidate for the Edinburgh Chair. When it became evident that Brown was a front-runner in the election Graham felt that he could not afford to stand by as a passive observer. This occasion was noticed by Alexander Bain in his autobiography. He wrote that whilst Graham was: "careful to avoid giving offence, he could be courageous when the occasion demanded it. This was shown in his famous letter to Bailie Gray [I think the councillor concerned, was in fact, J. Macfarlan] of Edinburgh, at the time when the Chair of Chemistry was

155. Alexander Bain, Autobiography (London, 1904) edited by W.L.Davidson, p 128.

156. The Scotsman September 20th 1843.

Mr. J. F. MacFarlan had obtained the diploma of the Royal College of Surgeons of Edinburgh. In early life, he had practised medicine, but he soon became a manufacturing chemist and druggist, in Edinburgh. He was well known for the manufacture of alkaloids and chloroform. In 1822, he became President of the Royal Medical Society of Edinburgh. Also, he was a Fellow of the Chemical Society, (he was elected in December 1842). He took an active interest in public matters for over 40 years and was engaged in many important movements for the political and social benefit of his fellow-citizens. He died in 1860. (Information from his obituary notice found in J.Chem.Soc. 14 (1862) p 349).

157. Liebig, Familiar Letters on Chemistry and its Relation to Commerce, Physiology and Agriculture, edited by J. Gardner, 1st.edn. (London, 1843) 53 and also 3rd.edn. (London, 1845) 47-56.

about to be conferred on Samuel Brown (surnamed the Alchemist)." ¹⁵⁵

The candidates for this election, which was controlled by the patrons Edinburgh Town Council, were: J. F. W. Johnston, D. B. Reid, A. Connell, John Murray of Hull, F. Penny, W. Gregory, L. Playfair, A. Fyfe, ^{Dr. Anderson} and, of course, S. M. Brown. The election was scheduled for September 26th 1843.

Graham wrote a remarkable letter on September 16th 1843 to Councillor Macfarlan who supported Gregory's candidature. It read as follows:-

"The important influence on the progress of Chemistry in Scotland, which the appointment the Town Council are about to make of a Professor of that Science in their University may exert, is my only motive for troubling you at present with a few words respecting the pretensions of one of the candidates who, I am astonished to hear, is receiving such support as is supposed to render his election not improbable - I mean Dr. Samuel Brown - whose claims are founded on experiments of utter worthlessness of which chemists entertain but one opinion. The unbiased decision of Professor Liebig upon these researches you will find at page 53 of the printed paper enclosed - a proof of which passed through my hands with the rest of a work in the press by the Professor and which you will find advertised for publication during the present month. I feel it a most painful duty to assume the responsibility of making that statement, affecting so deeply the scientific reputation of one of your candidates, and to give my consent at the same time to any public use being made of it which you may deem proper." ¹⁵⁶

The excerpt referred to is found in Liebig's Chemical Letters, ¹⁵⁷ in letter V on isomerism. Liebig used an interesting argument to deny the isomerism of elements: it was that isomorphous compounds, like sulphuric and selenic acid, were so closely related in their properties that there was insufficient difference to suppose that sulphur and selenium were isomeric. He then wrote: "We have not, I believe, at present the remotest ground to suppose that any one of these substances which chemists regard as elements can be converted into another. Such a conversion,

158. Liebig, *ibid.*, 1845 edn., p 56.

159. The Scotsman, September 20th 1843.

indeed, would presuppose that the element was composed of two or more ingredients, and was in fact not an element; and until the decomposition of these bodies is accomplished, and their constituents discovered, all pretensions to such conversions deserve no notice. Dr. Brown of Edinburgh thought he had converted iron into rhodium, and carbon or paracyanogen into silicon. His paper upon this subject was published in the Transactions of the Royal Society of Edinburgh, and contained internal evidence, without a repetition of his experiments, that he was totally unacquainted with the principles of chemical analysis. But his experiments have been carefully repeated by qualified persons, and they have completely proved his ignorance: his rhodium is iron and his silicon an impure incombustible coal." ¹⁵⁸

When Brown heard of Graham's letter he wrote to the Lord Provost with a request that this letter should be considered openly. He wrote:- "This is an attempt not only to crush me as a candidate for your favour by the weight of two names, but by protracting the angry scepticism of the chemists of Europe, to defer my hopes as an acknowledged discoverer. I urge the consideration that Liebig and Mr. Graham have not themselves repeated my experiments and that consequently to them, rejecting as they do the results to which my researches conducted, I must of necessity appear to be ignorant in the extreme. Mr. Graham, I have the best of reasons for believing prejudged my views before they were through the press; and this is not to be wondered at, for they aim at the root of some of his own published speculations." ¹⁵⁹ This last sentence is crucial. If Graham was arguing from a fundamental unstated belief in the unity of matter, in his discussions of polymerism and the nature of metals in voltaic circles, then he would have been very sensitive to the development of Brown's theories. They seemed to be very close to Graham's own speculations but the experimental claims for transmutation went too far. Thus Graham was driven to intervene in an uncharacteristic way in this contest. In turn, he was forced to be much more restrained in

160. Brown, op.cit. (136) Trans.R.S.E. 15 (1844) 176.

161. Brown, The Scotsman, September 20th 1843.

162. *ibid.*

163. The Scotsman, September 23rd 1843.

163a. Letter to the Lord Provost, the Magistrates and the Town Council of Edinburgh from S.M.Brown, September 21st 1843, included in the printed collection of pamphlets entitled: Chemistry Chair (Edinburgh, 1843) O.S.5404/2, Edinburgh University Library.

his own speculations on molecular theory and in particular with regard to the unitary theory of matter. Brown had indeed put forward the hypothesis that "the various elements may all be isomeric forms of one truly elementary substance," ¹⁶⁰ in his paper on transmutation.

The letter from Brown continued with a criticism of Liebig's role as an umpire in this question, because "he was subject to a sinister influence of the same kind, inasmuch as my doctrine when established will materially modify the theory of compound radicals with which he has achieved so much for the chemistry of organic bodies." ¹⁶¹ At the Council meeting of September 19th 1843, both ^{of} the letters from Graham and Brown were read out. Brown's supporters responded angrily to Graham's intervention. ¹⁶² On the following day, Professor Christison, in whose laboratory Brown had carried out his researches, wrote to the Scotsman about the 'extraordinary predicament' in which Brown was placed by Graham's letter. He wrote that "the very embarrassment has arisen which I dreaded" and he advised Brown to have his statements and experiments checked in a full personal trial by a chemist of celebrity. ¹⁶³ Brown complained to Councillor Macfarlan that Graham had written to Walter Crum in 1841 expressing himself very strongly against his experiments, after they had been read to the Royal Society of Edinburgh, before they had even been printed. Furthermore, he added that Dr. Anderson had stated that Graham believed that the rhodium, Brown had obtained was a sample, which had been purchased five years previously on his visit to Russia. However, his most interesting criticism of Graham came next, when he wrote: "if my views regarding carbon and the constitution of metals be correct, Mr. Graham's conjecture regarding the arrangements of the metallic elements of a voltaic circle falls to the ground." ^{163a}

Graham offered no comments on this last extraordinary statement. He did, however, write to Macfarlan on September 21st 1843 saying that his assistant Parnell had translated Liebig's letter to Playfair for the Plymouth meeting of the British Association. Also, he denied that he had

163b. Letter from Graham to Councillor J.F. Macfarlan, September 21st 1843, included in the printed collection: Chemistry Chair (Edinburgh, 1843) O.S.5404/2, Edinburgh University Library. Graham wrote:

"I have just received your favour of the 18th, on returning to town from the country today. In regard to the work containing Professor Liebig's opinion of Dr. Brown's scientific attainments, I beg to say, that it is quite recent, consisting of a series of letters which were lately published, and widely circulated over Germany, in the Allgemeine Zeitung. They are translated by Dr. Gardner, under the Professor's revision, and published by Taylor and Walton. The letter from Professor Liebig to Dr. Playfair, containing a similar opinion, I have nothing to do with; it merely passed through my hands, but was translated and made use of by Mr. Parnell (then my assistant), in a communication to the British Association at Plymouth, which he attended. I can however state, that Liebig's opinion was not misrepresented on that occasion.

I may add, that, so far from prejudging Dr. Brown's researches, as he complains in his letter to you, my opinion was formed after his paper in the Edinburgh Transactions was in my hands, and after devoting several weeks to an experimental examination of the extraordinary allegations it contains. The conclusion to which I came, and upon the truth of which I willingly stake my scientific reputation, is, that the paper referred to is a tissue of gross mistakes (if not wilful misrepresentations), inexcusable in the merest chemical tyro, and painfully discreditable to English Chemistry, as appearing in a publication of such high authority as the Transactions of the Royal Society of Edinburgh.

I was quite prepared for such remarks as Dr. Brown makes in his letter to you. I have no hostile feeling towards him, - and you are well aware how contrary it is to my habits to interfere in such matters. But being at a distance from the scene of contest, and not personally interested in it, I thought it my duty to convey such an opinion to a gentleman - himself a Chemist - and respectfully to urge farther inquiry before the appointment is made."

164. The Scotsman, September 23rd 1843. See: The Revenue in Jeopardy from Spurious Chemistry Demonstrated in Researches upon Wood-spirit, by Andrew Ure, (London, 1843), analytical chemist to the board of customs (London, James Ridgway)

See the discussion of this incident in E. Frame, 'Thomas Graham - a centenary account', Philosophical J. 7 (1970) 116-127. Graham's failure to recognise the presence of alcohol in a sample of crude naphtha led to a scathing attack by Andrew Ure, who referred to eminent professors, who have good incomes and well-appointed laboratories, who had performed a faulty analysis and then failed to retract publicly his statements. Ure reminded the importers who had described Graham as one of the first chemists of Europe that such chemists as "Faraday, Berzelius, Gay-Lussac, Thenard, Mitscherlich, Liebig, Gmelin, Dumas, Pelouze etc. are in existence, with each of whose names such important discoveries are associated, as have changed the main features of the science, and constitute a legacy of invaluable truths to all future generations. Nothing will give me greater delight than to see Prof. Graham [whom he later described as the 'autocrat of British Chemistry'] produce chemical researches, entitling his name to be emblazoned in that brighter galaxy. But, as an older, if not a better, chemist, let me caution him against such precipitancy and dogmatism, as he has displayed in his naphtha certificate", p 18, of Ure's pamphlet. Ure's personal abuse of Graham undoubtedly weakened the criticism. Graham had succeeded Ure as Professor of Chemistry at the Andersonian University in 1830 after the latter had been manouvered out of his position and this may explain his extraordinary animosity towards Graham. See W.V. Farrar,

cont...

prejudged Brown's paper, adding that he had spent several weeks investigating his experiments and had found them full of gross mistakes.^{163b}

Brown was, however, not short of support. The physiologist Andrew Combe wrote to the Scotsman referring to the 'detestable attack' on Brown's character by Professor Graham. "The little I know of Graham was favourable to his skill as a chemist, but now his own letter conveys to my mind an impression of its writer which I am truly sorry to receive. Even if you were so ignorant as he declares of the first principles of chemical analysis, he was surely the last man in Britain who had a right to twit you with it, if Dr. Ure's narrative of his analysis of the Custom-house naphtha be at all correct, and as yet I have seen no counter-statement. If Graham failed to detect any alcohol in a liquid of which it formed by far the largest constituent and persisted in his error after being warned, is he the man to denounce another as deficient in analytic skill!"¹⁶⁴ The editorial comment in the Scotsman, whilst professing neutrality, continued "We cannot help condemning in strong terms the unhandsome conduct of Professor Graham in transmitting the letter published in our last. Dr. Brown's experiments whether conclusive or not at least come before the world in a form which entitled them to something better than the summary and disdainful judgement applied to them by Dr. Graham. This, we must say, was making a very unwarrantable use of the reputation he has acquired."¹⁶⁵

Understandably this cause célèbre attracted much discussion and on the date of the appointment for the Chair, September 26th 1843, the public gallery was filled to capacity. D. B. Reid suggested that the election should be delayed for two weeks so that Brown could demonstrate his experiments and Graham's former pupil, George Wilson, submitted a letter strongly supporting Brown's candidature regardless of the transmutation experiments. The discussion was soon concluded, however, when the council accepted the Lord Provost's plea to delay the election until the end of the session in April 1844.¹⁶⁶

164. cont...
'Andrew Ure, F.R.S. and the Philosophy of Manufactures'. Notes and Records R.S. 27 (1973) 299-323, for a useful account of Ure.
165. The Scotsman, September 23rd 1843.
166. The Scotsman, September 27th 1843. T. S. Traill lectured for the time being in place of Hope.
167. Letter from Dr. S. M. Brown withdrawing his candidature. Edinburgh Town Council Minutes, February 27th 1844.
168. G. Wilson and J. Crombie Brown, 'Account of a repetition of Dr. Samuel Brown's process for conversion of carbon into silicon', read April 1st 1844, Trans.R.S.E. 15 (1844) 547-559. See also J. A. Wilson: Memoir of George Wilson (1860) 310-314 and the useful review by G. Wilson, 'On isomeric transmutation, and the views recently published concerning the compound nature of carbon, silicon and nitrogen' Edin.N.Phil.J. 51 (1844) 1-21.
169. The Scotsman, May 15th 1844.
170. North British Review 26 (1856-7) 392. Hope and Christison had both read Brown's transmutation paper before its presentation; amongst the scientists who refused to act as referees were Faraday (see letter of December 26th 1842 to Brown in: Bence Jones, Life and Letters of Faraday (London, 1870) 2 170) and Thomas Thomson, September 12th 1843, letter to Brown, *op. cit.*(163a), p7.

Meanwhile Brown had to demonstrate the truth of his experiments if he was to survive as a candidate. He made a number of applications to potential referees who might oversee his experiments and, if they were successful, make a public declaration of that fact. Eventually, in December 1843, Dr. Kane agreed to act as referee. Brown then went to Dublin where he worked for seven weeks without success and incidentally without having experimented with Kane at all!¹⁶⁷ At the same time George Wilson was repeating Brown's experiments in an attempt to show that there was a quantitative conversion of carbon into silicon but, despite a great deal of hard work, he was unable to substantiate the transmutation experiments.¹⁶⁸ Samuel Brown took the honourable course whilst his experiments were unproven and withdrew his candidature. When the election finally took place on May 14th, 1844 there were only two candidates left in the contest: William Gregory and Andrew Fyfe. Gregory won by twenty votes to thirteen.¹⁶⁹

There is a certain irony in Gregory's appointment. He had been the only chemist, in 1841, prepared to witness the repetition of Brown's experiments after his paper had been published. However, before further arrangements could be completed by Brown, Gregory was "seized with a severe and prolonged illness."¹⁷⁰ Gregory, himself, later admitted that the elements were complex. In 1856, the year in which Brown died, Gregory wrote: "At the meeting of the British Association in Ipswich, M. Dumas drew the attention of the association to the extraordinary analogy between homologous groups of organic compounds and certain small groups of elementary bodies The best example is that of chlorine, bromine, and iodine, which differ from each other precisely as do three contiguous homologous compounds that is, in properties In affinity, bromine is intermediate between chlorine and iodine, as it is in atomic weight Now, although M. Dumas may have been the first to point out strongly in public the remarkable analogy between the elementary groups chlorine, bromine, iodine; potassium, sodium, lithium etc. and

171. W. Gregory, Handbook of Organic Chemistry (London, 1856) 26-27.

172. Gregory, *ibid.*, p. 27.

173. Gregory, *ibid.*, p. 28.

174. *ibid.*

175. Gregory, *ibid.*, p. 28.

176. See D. M. Knight, *op.cit.* (154), 249-261.

homologous organic groups, such as methylamine, ethylamine and propylamine the author of the present work has for several years pointed it out in his lectures; nay, the late Dr. Turner and other teachers, including the author, constantly drew the attention to the analogy between chlorine, bromine, and iodine, as furnishing an argument for their being truly compound." ¹⁷¹ Gregory then explained that, however, they took a different view to Dumas in regarding Cl, Br, and I as elements having "the same base or substratum, with a different addition in each case." ¹⁷² Gregory then discussed the transmutation of elements: "it was supposed that, by a new arrangement of the same atoms, a different although elementary substance might be obtained." ¹⁷³ He attributed this to allotropy, where an element in different allotropic forms had similar chemical properties, "whereas carbon and silicon, even in the alleged results of Dr. Brown cannot be made to yield the same products." ¹⁷⁴

Gregory did not deny that transmutation might be possible, but he said it would be difficult to accomplish, because it would require some very great and unusual force. "It is, we conceive, much more probable that chlorine, bromine and iodine are really homologous compounds, and not elements; and if we can discover their common difference (their C_2H_2 so to speak), we may hope to transmute them into each other. And so of all similar groups." ¹⁷⁵

During this period of Graham's life, from 1837 to 1844, most chemists were sceptical about both Daltonian atomism and the extension given to atomism by Berzelius in his electrochemical or dualistic theory. Likewise, the majority of chemists favoured the view that the elements were complex. As we have seen Graham was quite prepared to accept speculation about the elements provided that it did not lead to false claims such as the experimental verification of transmutation. Graham's reticence with regard to unitary theories of matter must be seen in the context of the claims of actual transmutation made by Samuel Brown and the more extreme speculations made by Low and Rigg. ¹⁷⁶ In Britain, during this period,

177. C. Daubeny, An Introduction to the Atomic Theory, 2nd.edn. (London, 1850) 440-443.
178. M. A. Sutton, 'J. F. Daniell and the Boscovichian Atom' Studies in the History and Phil.of Science 2 (1971) 277-292; See Daniell: An Introduction to the Study of Chemical Philosophy, 2nd.edn. (London, 1843) p 8.
On Hope, see D. F. Larder, 'Prout's hypothesis - a reconsideration' Centaurus 16 (1970) 44-51.
179. R. Fox, The Caloric Theory of Gases from Lavoisier to Regnault, (Oxford, 1971) 291-2, 319-20.
180. Graham, Elements of Chemistry 1st.edn. part 2 (London, 1838) 121.

Thomson at Glasgow was presumably still convinced of Prout's hypothesis; Hope at Edinburgh may have discussed Boscovich's theory and Gregory accepted the complex nature of Elements. Kane in Ireland rejected Daltonian atomism and believed in the complexity of the elements. Likewise, in England, Faraday claimed he was not an atomic chemist and in 1844, he announced that he subscribed to Boscovich's theory. Daubeny at Oxford believed in a unitary theory of matter.¹⁷⁷ Johnston at Durham accepted the complexity of the elements and Daniell in London discussed Boscovich's theory.¹⁷⁸

On the continent Liebig, Magnus, Henry Rose, Wohler and L. Gmelin, decided in 1838 to reject atomic weights because they were hypothetical and therefore they turned to equivalents in the belief that they were less hypothetical.¹⁷⁹ Graham also preferred to work in terms of equivalents and he argued that in the atomic theory the "terms atom and atomic weight may be used as synonymous with equivalent, equivalent quantity and combining proportion."¹⁸⁰ In France, Dumas was never a simple Daltonian atomist; instead he believed that 'atoms' were in reality molecules and in 1840 he proposed a planetary model of the 'atom'. Also, with the re-determination of the atomic weight of carbon in 1840, the whole question of Prout's hypothesis came back into the forefront of chemical discussion.

During this period Graham speculated freely. His studies on the voltaic circle were influenced by Faraday's electrical researches. These researches convinced Graham that chemical affinity was the unifying force which joined together both similar and dissimilar atoms. From his own work on the constitution of salts and Liebig's theory of compound radicals Graham saw combination in terms of binary molecules. These molecules were linked to one another by chemical affinity in polymeric chains. Indeed, the existence of polymerism was seen by Graham as an important phenomenon, in the constitution of elements, compounds, and radicals. He believed that polymerism occurred far more widely than

chemists had previously supposed.

In molecules, polarity, or the existence of zincous and chlorous affinities was in some way related to combined heat rather than to electricity. Likewise the quantity of combined heat was important for explaining some examples of apparent isomerism. Combined heat was also released during polymerism, in those cases, where ignition was observed. When Graham suggested that there was an attraction between a zinc atom, and an atom of chlorine in hydrochloric acid, he envisaged changes occurring in the chemical affinity of the individual atoms, so that chlorine might leave the hydrogen atom to which it was attached and join to the zinc. The details behind these changes of chemical affinity remained obscure in Graham's writings. Presumably, he must have contemplated some alteration in the quantity of combined heat associated with the atoms of hydrogen and chlorine in HCl, as the affinity of the zinc for chlorine increased and finally became dominant.

Behind these studies, there appears to be an underlying belief in the unity of matter, which Graham was reticent to express openly. Indeed, if he was not guided by such a theory, it is difficult to account for some of his conclusions: for example that the equivalents of elements were multiples of half an atom of hydrogen; that elements could be integrated in a natural series or classification; and that chlorine and polymeric elements were complex.

Chapter 6

THE LIQUID STATE

AND

MOLECULAR MOTION IN SOLUTION

1. Graham, Wellcome manuscripts 2580 (old no.3390) 'On the liquid condition of matter' (undated)
This is probably the manuscript of the evening lecture with the same title read by Graham to the Chemical Society on March 6th 1854.

"I take up [the liquid condition of matter] because [it is] less attended-to and indeed less known than the two [other] conditions of gas and solid, although it is not inferior to either of the latter subjects in interest and importance. It has indeed a special interest to the chemist as the condition which above all promotes chemical affinity To the physiologist also, for while bones and muscles are the solid framework and elastic bands of the animal machine, the circulating fluids are the true source of its force. The liquid is decidedly an intermediate condition, a composite of the two others, although probably not destitute of characters of its own." ¹

These words reveal the importance of the liquid state to Graham, for whom it became a central focus connecting solvent action, osmosis, colloids and molecular motion. Graham was dissatisfied with the model of the liquid state developed by Laplace in terms of material caloric. Therefore he proposed a new model based on polymeric liquid molecules. Inspired by an analogy put forward by Gay-Lussac, Graham took up the study of liquid diffusion. Gay-Lussac had suggested that the spreading out of a salt into water was similar to the evaporation of a liquid. Graham tried to develop an analogy between gaseous and liquid diffusion favouring the view that diffusion occurred by a repulsive force. The origin of this repulsive force appeared to be the intrinsic molecular motion found in both gaseous molecules and polymeric liquid molecules. The analogy between gas and liquid diffusion was imperfect because as Graham discovered there was no simple diffusion law for liquids although the same weights of some chemicals did diffuse equally.

Having completed the first detailed study of liquid diffusion, Graham turned his attention to osmosis. He correctly recognised the features of osmosis which required explanation. He stumbled initially producing an inadequate electrochemical theory to explain osmosis. His first explanation of osmosis was rejected but his experiments on osmosis and liquid

diffusion were recognised to be valuable. Thus he was forced to re-examine his ideas on osmosis and this led to his discovery of dialysis. This in turn led him to make a new division of solutions into colloids and crystalloids, which were seen to shade naturally into one another. Crystalloids differed from colloids in terms of both molecular mobility and molecular complexity but an essential continuity was evident in these states of matter.

Once Graham had appreciated the distinction between colloids and crystalloids he was able to give a more satisfactory explanation of osmosis. This was based on two principles: firstly, liquid diffusion and secondly, differences in the chemical affinity of water for colloids and crystalloids. His conception of colloids was limited to true solutions. Consequently, he overlooked the earlier work of some of his predecessors on suspensions. As we shall see, Graham's studies on the liquid state proved to be influential in Biology, particularly for Herbert Spencer.

Graham's model of the liquid state differed from the prevailing Laplacian model. He developed a model in which liquid molecules were assumed to be polymeric. The number of molecules in such a liquid polymer decreased as the temperature was raised. This model was derived partly from his own researches on electrolysis in which polymeric liquid molecules were assumed to exist and also from Gay-Lussac's study of chemical force. In the Laplacian model of the liquid state, the particles of matter were surrounded by material caloric particles. Three forces were assumed to be necessary in this theory to explain the different states of matter. They were:- the attraction of particles for one another; the attraction of particles for the heat which surrounded neighbouring particles; and the repulsion between adjacent heat particles. In the liquid state the dominant force was that of attraction for the heat which surrounded neighbouring particles. The liquid particles were free to move around inside the body of the liquid. These liquid particles

2. Graham, Elements of Chemistry, 2nd.edn. Vol.1 (London, 1846) p 68; also see J.J.Berzelius, Traité de Chimie translated by A.J.L.Jourdan (Paris, 1829) 1 85 and P.S.Laplace, 'Sur l'attraction des corps sphériques et sur la répulsion des fluides élastiques', Ann.de Ch. 2 Ser.18 (1821) 181-190, 273-280.

3. Graham, op.cit. (1)

4. Gay-Lussac, 'Considerations on chemical force', Ann.de Ch. 70 (1839) 407-434.

5. Graham, op.cit. (1) and for a similar reference see Graham, 'On osmotic force', The Bakerian lecture of June 15th 1854, Phil.Trans. 144 (1854) p 184 [N.B. This paper is omitted from Graham's Chemical and Physical Researches, edited by R.A.Smith, (Edinburgh, 1876).]

were held inside the interior of the liquid but at the surface the repulsive force of heat could cause evaporation.²

Graham rejected this view of the liquid state when he wrote (ca.1854) that "the physical representation of a liquid which was accepted by Berzelius and his contemporaries is that proposed by Laplace But it is impossible to rest satisfied with such vague generalities. Gay-Lussac [has] pointed out that the volatility of solids does not appear altogether compatible with this view that at all events, an abrupt fall in the vapour tension of a liquid should take place on freezing. He examined the effect of freezing upon the vapour tension of water at 32°F and he found that it was insensible"³

A fall in vapour pressure when water was frozen to produce ice would have been expected from Laplace's caloric model but experiment had disproved this. Gay-Lussac had attempted to overcome this difficulty by suggesting that vaporisation was not connected with cohesion or chemical affinity as we shall see presently.⁴

Graham chose water as the example to illustrate his new model of the liquid state which was designed to replace the Laplacian model. He wrote that: "the idea of aggregation due to chemical affinity has been had recourse to, and water is viewed as a more compound molecule than steam: vapour HO, liquid water H_nO_n and solid H_mO_m . Ice is probably a still higher polyatomic molecule or homologue [than liquid water]. The resistance to ebullition exhibited by water and other liquids is thus explained by the vaporisation being preceded by a chemical decomposition or catalysis of the liquid molecule but probably the liquid molecule is not constant at different temperatures but is variable becoming a less considerable aggregate at higher temperatures."⁵ This concept of polymeric water molecules marked an important advance in the understanding of the nature of the liquid state. A change of state from ice to water and from water to steam required a reduction in the complexity of the molecular aggregates.

6. Graham, 'On the absorption of gases by liquids,' Ann.Phil.N.S. 12 (1826) 69-74, also in Researches.pp 1-6.
In 1826 Graham gave a lecture 'On liquidity' to the Hunterian Society of Edinburgh.

7. Graham, 'On the exceptions to the law that salts are more soluble in hot water than in cold water; with a new instance', Phil.Mag. 2 (1827) 20-26 and also in Researches.303-309.

8. Graham, op.cit. (5) p 185.

In his first researches of 1826, Graham had emphasised the force of affinity existing between liquid molecules in order to explain the absorption of gases by liquids.⁶ A gas was first condensed to produce a volatile liquid which was then held in solution by the attractive force exerted by the less volatile solvent molecules.

Certainly, Graham recognised that it was not adequate to consider water merely as an inert solvent. In 1827, he examined the anomalous changes in solubility of certain compounds in water as the temperature was raised. He emphasised the importance of hydration in solubility and demonstrated that changes in the degree of hydration could alter the solubility dramatically; indeed hydrates were always more soluble than anhydrous compounds.⁷

During the 1830s Graham showed that water played an important role in the chemical properties of acids and salts, as we have seen. Later in 1854 he wrote that when "considering the action of chemical affinity between bodies in solution, we are apt to confine our attention to the principal actors in the combination, and to neglect entirely their associated water of hydration. Yet both acid and base may have large trains of water attached to them by the tie of chemical union. Sulphuric acid certainly evolves heat with the fiftieth equivalent of water that is added to it, and probably in dilute solution that acid is capable of having a still greater number, indeed an indefinitely large number of equivalents of water combined with it. In fine there is reason to believe that chemical affinity passes in its lowest degrees, into the attraction of aggregation."⁸

From the beginning of his researches in 1826, Graham had examined the role which water played in the process of solution. The prevailing view of solution, in 1826, was derived from the writings of Berthollet. He had suggested that, when a salt was dissolved in water, a weak chemical combination was formed between the salt and the water. Thus the degree of solubility of a salt was determined by two opposed forces: the force

9. C.L.Berthollet, Essai de Statique Chimique 1 (Paris, 1803) 34-36,59, 412,428. See also the MS. Chemistry lecture notes of Graham's teacher, T.C.Hope (written between 1797-1798), which are in the Chemical Society Library. Hope explained the process of solution in a similar manner to Berthollet. Solution was a process of attraction between particles of salt and water. Salt was attracted to layers of water until they became saturated and so on in succession until the salt was uniformly diffused through the water. Hope demonstrated the slow nature of liquid diffusion by pouring a blue solution through a funnel so that it was carefully placed under a layer of water. Uniform diffusion took 28 days; the slowness of this process was explained by Hope as being due to the very small differences in the attractive force of different layers for one another and also because chemical attraction only operated at small distances.
10. Graham, 'Effects of animal charcoal on solutions,' Quart.J.Sci. 1 (January - March 1830) 120-125 and also in Researches.630-634.
11. A.Payen, 'Miscellaneous intelligence — chemical science', Quart.J.Sci. 15 (1823) p 384.
12. Graham, op.cit. (10) Researches. p 631.

of cohesion which held salt particles together and the force of affinity by which water was attracted to the salt.⁹

Graham was led to question this view. There was a marked difference between the attraction of a salt for solvent water and the attraction of chemical affinity inside chemical compounds. The solute-solvent force was a very weak force when it was compared to the relatively strong force of chemical affinity. Graham recognised this in 1830 when he examined the action of animal charcoal on different solutions.¹⁰ Earlier studies of charcoal had been concerned with the removal of colouring-matters from solution. Payen had noticed, when lime water was boiled with animal charcoal, that all the lime was removed.¹¹ Graham confirmed this and examined several other examples of adsorption, thereby, hoping to obtain a clearer understanding of the state of combination of substances in solution. The doctrine of definite proportions, he observed, did not apply to solutions. He continued: "if a solid body, such as carbon, destroy such a combination [of salt and water], and take down the saline matter attached to its surface, we may conclude that there is an analogy between the combination of the salt with the water, and the combination of the salt with the charcoal, and that the former as well as the latter processes have something of a mechanical character."¹²

Therefore, by 1830, Graham had recognised two important principles, firstly, that hydration was an important consideration in the process of solution of many salts and secondly, that the solute-solvent force was an extremely weak force of chemical attraction resembling the force of adhesion between charcoal and dissolved substances. These initial studies paved the way for Graham's later conception of the diffusion processes in solution. However, in liquid diffusion another significant feature had to be taken into account: the inherent motion of the molecules. Molecular motion was seen to be a more important influence, in the dispersion of a solute through a solvent, than the attractive force between the solute and solvent. Boscovichian interpretations of the processes of

13. Graham, MS. Notebook B (July 1832 - August 1834) 450 pp.
Andersonian Library, University of Strathclyde, p 47.

14. Graham, *ibid.* pp 277-278.

solution and liquid diffusion involving rather static attractive and repulsive forces must have seemed inappropriate to Graham. In these processes molecular motion was the key factor. Graham may have abandoned any former interest in the Boscovichian theory, when his attention was drawn to problems of molecular motion by the study of gaseous diffusion. Graham was also prepared by his studies of gas diffusion to look favourably on Gay-Lussac's later interpretations of the processes of change of state and solution.

During the 1830s Graham recorded a few isolated references to the problem of liquid diffusion in his laboratory notebooks. In 1832 he suggested that volatile liquids probably mixed with water by a species of vaporisation. He found that when carbonate of ammonia was added to one side of a corked U-tube containing water, the ammonia diffused downwards and was detected in the other limb fifteen hours later.¹³ The only other reference to liquid diffusion in his surviving notebooks of the 1830's, was written in 1834. He recorded a number of interesting questions:- "would a mixture of muriate of ammonia and muriate of potash, of iodide of potassium and chloride of potassium exhibit any disposition to separate? [Are] iodide of sodium or potassium found in the sea at great depths only? Curious inquiry - if they diffuse with different velocities into pure water? Use diaphragms of cloth, felt, or blotting paper. Discs of cloth packed on each other (to be traversed - would prevent currents.)

Grand object to find the diffusion volumes. Then we could learn whether to halve or double atomic weights. So learn the real atomic weights of sugar, alum, oxalate of potash and iron, quadroxalate of potash. Bichromate of potash whether it contains a 'double atom' of chromic acid ($\overset{\cdot\cdot}{\text{Cr}}\overset{\cdot\cdot}{\text{Cr}}$) or 'half-atom' potash. Connect shorter tubes perpendicularly by coupling boxes. Interpose diaphragm."¹⁴ Whether Graham took up these interesting suggestions is uncertain. Unfortunately, he found out later that there was no simple relationship between the speed

15. Gay-Lussac, op.cit. (4).

Stuart Pierson has suggested that Gay Lussac's views on cohesion were developed between 1812 and 1820. Apparently Gay-Lussac had discovered that the vapour pressure of ice did not differ from that of water. Gay-Lussac 'Note sur la fixité du degré d'ébullition des liquides' Ann.de Ch. 2 Ser.7 (1817) 307-313. On page 311, Gay-Lussac wrote "Moreover, it is certain that the vapour of a body in the liquid or solid state, but at the same temperature, like water and ice at zero, has in these two circumstances, exactly the same elastic force." See Stuart Pierson, 'Gay-Lussac and Berthollet's theory', 12th Congrès International de l'Histoire des Sciences (Paris, 1968) Vol.6 pp 82-86.

of liquid diffusion and molecular mass. At this time he clearly entertained the hope that there would be a diffusion law for liquids analogous to that found for gases. With this anticipation of a liquid diffusion law, Graham hoped to be able to resolve some of the uncertainties relating to molecular mass, which he had come across in his studies of the constitution of salts.

The analogy between gaseous and liquid diffusion which guided Graham's researches on liquid diffusion was supported by Gay-Lussac's discussion of chemical force in 1839.¹⁵ Gay-Lussac questioned a number of opinions which Berthollet had put forward concerning the influence of cohesion on both change of state and solution. Berthollet had suggested that the force of cohesion diminished considerably when ice was melted to form water. However, Gay-Lussac observed that the vapour pressures of both ice and water at 0°C were identical. There appeared to be no change in vapour pressure when a solid was melted and so Gay-Lussac proposed an alternative explanation for this change of state. The cohesion or molecular attraction of ice did not change when ice was melted, instead, changes in volume and caloric gave rise to a considerable alteration in the molecular constitution of ice as it turned into water. Likewise, Gay-Lussac argued that cohesion did not play a major part in the process of solution. He suggested that there was an analogy between the process of solution and the vaporisation of a liquid. For example when a solution was diluted, cold was produced because the salt molecules expanded into the added water, like a compressed gas admitted into an extra space. Both vaporisation and solution were temperature-dependent processes. A fall in the temperature caused both condensation of a vapour and precipitation of a salt from a saturated solution. The only difference which Gay-Lussac could see between the two processes was that, with a vapour, the repulsion between the gaseous molecules was sufficient to keep them in a given space, whereas in a liquid some account must be taken of the affinity between the solvent and solute although he

16. Graham, 'On the diffusion of liquids', (1849) Researches. 444-445.

17. Graham, 'On the diffusion of liquids', (Bakerian lecture) received on November 16th 1849 Phil.Trans. 140 (1850) 1-46, 805-836; 141 (1851) 483-494; read on December 20th 1849; received on May 2nd 1850 and read on June 20th 1850; and received on March 27th 1851 and read on May 22nd 1851; respectively. See also in Researches. 444-544. Graham, 'On the application of liquid diffusion to produce decompositions' J.Chem.Soc. 3 (1851) 60-67 and in Researches. 544-551, Graham 'On liquid diffusion' B.A.Report (1851) Chemical Transactions p 47. Graham lectured to his University College students on liquid diffusion in October 1848. His lecture notes show that most of his important conclusions had been reached by this time. See Wellcome MS. University College Lecture Notes (1838-48) New No.2579 (Old No.3202).

18. Graham, op.cit. (16) p 445.

presumed that the self-repulsive nature of the solute molecules was the predominant force. Furthermore, a lowering of the temperature affected the repulsive force to a greater extent than the solute-solvent affinity. Additional evidence for this analogy was that heat was rendered latent in both the vaporisation of a liquid and the solution of a hydrated salt.

Graham acknowledged the influence of Gay-Lussac's analogy on his own thoughts when he wrote:- "Gay-Lussac proceeds upon the assumed analogy of liquid to gaseous diffusion in the remarkable explanation which he suggests of the cold produced on diluting certain saline solutions ...," and continued that "the phenomena of solubility are at the same time considered by that acute philosopher [Gay-Lussac] as radically different from those of chemical affinity, and as the result of an attraction which is of a physical or mechanical kind. The characters of these two attractions are strongly contrasted. Chemical combination is uniformly attended with the evolution of heat, while solution is marked with equal constancy by the production of cold."¹⁶ Thus Graham introduced his first paper on liquid diffusion in 1849.

The main aim of Graham's researches on liquid diffusion, published between 1849 and 1851,¹⁷ was to compare the speeds of diffusion of different substances through liquids. There had been no previous detailed experimental study of liquid diffusion so Graham began by accumulating the data for a study of the diffusion of substances in water. These results in themselves were an important contribution to the study of solutions. Liquid diffusion had been mentioned in earlier studies of osmosis, but, as Graham remarked, the process of diffusion was obscured by the imbibing action of membranes.

An important consideration in liquid diffusion was the question of solubility and Graham commented on this question initially.¹⁸ Both starch-iodide and hydrochloric acid were quantitatively very soluble in water, but these substances were held in solution by very unequal forces. Starch-iodide was only weakly-held in solution, because it was very easily

precipitated from its solution by either potassium acetate or charcoal; hydrochloric acid, on the contrary, was held in solution by a very strong force and therefore it resisted precipitation. Graham suggested that the rapidity of diffusion might be a measure of the force of attraction between the solute and solvent. This was later to be important in Graham's distinction between crystalloids and colloids by dialysis.

He found that the assumed analogy between gas and liquid diffusion was only partially correct. Liquid diffusion was a much slower process than gas diffusion taking days rather than minutes. Also, liquid diffusion was promoted to a much greater extent than gas diffusion by an increase in the temperature. On the other hand, the analogy held for both interdiffusion and the diffusive separation of mixtures. For example sodium carbonate diffused away at the same speed into both water and sodium chloride solution, and with mixtures, the more diffusive component was observed to escape more rapidly than it did on its own just as in the case of mixed gases. For example sulphate of potash diffused more rapidly from the sulphate of alumina in alum than it did on its own in water.

The major defect of the analogy was the absence of a simple relation between the diffusion speed and the molecular mass of the solute or the density of the solution. Liquid diffusion was, however, a regular process. Using dilute solutions of sodium chloride in an open jar, placed in a large container of water, Graham found that the diffusion product was directly proportional to the percentage weight of salt in the water. But, when the diffusion speeds of solutions of the same density were compared, there were no obvious relations between them except that albumen and gum arabic diffused much more slowly than did saline solutions.

He then examined the diffusion of solutions containing equal weights of different substances. Simple relationships were not always observed, for example equal weights of sugar and magnesium sulphate both diffused at the same speed although they were chemically very different and their

19. The ratio of solution densities for potash to soda salts was 2 to 3. The times of equal diffusion of both nitrate and carbonate of soda were related like those of the nitrate and carbonate of potash or as the square roots of 1 to 2, i.e. 1 to 1.4142.

20. Graham, op.cit. (16) Researches.495.
In the Royal Society manuscript MS.37.1 of Graham's paper originally entitled 'On liquid diffusion' but later crossed out and altered to 'On the diffusion of liquids', Graham attempted to explain his results. This passage was deleted from the printed version of the paper. Although Graham crossed it out, it is worth recording as it indicates his thoughts on his results from liquid diffusion. He wrote: "this result may be conceived in the following manner. In the diffusion experiments we have equal weights of the carbonate and nitrate in solution. Let the carbonate of potash be supposed to exist as one volume of a gas of density 2, and the nitrate of potash as two volumes of a gas of density 1. Then according to the recognised laws of gaseous diffusion, the times in which equal weights of the two gases would escape by diffusion would be as $\sqrt{2}$ to 1 i.e. in conformity with the actual times of equal diffusion of the two salts."

solutions possessed markedly different densities. More significantly, however, certain pairs of salts were found to be isodiffusive, for example potassium nitrate and ammonium nitrate; magnesium sulphate and zinc sulphate. The same weights of these salts, taken in grams, but not in chemically equivalent quantities, diffused equally in a given time. On closer examination, Graham discovered two classes of isodiffusive potash salts; the first class included: potassium chloride and potassium nitrate; and the second class: potassium carbonate and potassium sulphate. For each class he worked out the square of the diffusion time observed for the same weights of each salt to diffuse equally. A comparison between these two classes gave a simple numerical ratio, of one to two, and this could be expressed as:-

$$\frac{\left(\text{Time for a given diffusion of 1\% potassium nitrate}\right)^2}{\left(\text{Time for an equal diffusion of 1\% potassium carbonate}\right)^2} = \frac{1}{2} = \frac{\text{Solution density of potassium nitrate}}{\text{Solution density of potassium carbonate}}$$

Similar numerical relations were found to exist for the corresponding soda salts, and also when the soda and potash salts were compared.¹⁹

These results suggested by analogy with gases, the existence of a limited diffusion law for liquids. Graham related the square of the time for equal diffusion to a new kind of 'solution density'. He observed that the relationship appeared to give an experimental support for Gerhardt's suggested division of potash and soda salts into two classes: the monobasic nitrate class and the bibasic sulphate class.

One important problem remained, what were these new solution densities and how were they related to atomic weights, if at all? Graham admitted that he could not answer this question. For he wrote: "liquid diffusion thus supplies the densities of a new kind of molecules, but nothing more respecting them."²⁰ The relations did not depend on atomic weights or chemical equivalents but rather on equal weights of substances measured in grams. Graham considered that such relations, based on an

21. Graham, *ibid.*

22. Report of Graham's lecture to the Chemical Section of the British Association meeting at Liverpool in 1854 entitled 'On the concentration of alcohol by Sömmering's experiment'. B.A.Report.(1854) part 2 p 69. Also see the report in The Athenaeum (1854) p 1208 from which these quotations are taken. This discussion was omitted from the official B.A.report and from Graham's collected researches.

23. Graham, *ibid.* The Athenaeum (1854) p 1208.

equality of weight, were more fundamental than Daltonian atomic weights; they reached "to the very basis of molecular chemistry."²¹ This new class of large molecules of equal weight or of simply related weights were formed from a large number of chemical atoms grouped together. In other words, isodiffusive molecules were polymers of equal weight and as such they were more simply related to one another than Daltonian atoms. These polymeric molecules were involved in the phenomena of liquid diffusion and solubility; Daltonian atoms did not appear to be involved in these processes.

Comparative relations between the diffusion speeds of different salts remained a difficult problem to resolve until diffusion processes were treated mathematically, and until the presence of independent hydrated ions was recognised. The conclusion which Graham drew from his experiments on liquid diffusion appeared to suggest that there was a relation between molecular diffusive motion and equality of mass. The theory of primary matter may have derived some support in Graham's mind from these experiments. Certainly, Graham pursued the theory of primary matter later in his speculative paper of 1863.

It is interesting to examine Graham's view of liquid diffusion at this stage, because liquid diffusion was to play an important part in his subsequent researches on osmosis and colloids. Graham accepted Gay-Lussac's explanation that salt molecules expanded into water like a compressed gas admitted into an additional space. Having established a partial analogy between gaseous and liquid diffusion, he explained his vision of liquid diffusion at a meeting of the British Association in September 1854: "... liquids diffuse mechanically by a kind of repulsive force of the same nature as that exhibited by gases"²² Faraday asked Graham at this meeting to explain why he believed that liquids diffused as a result of the force of repulsion between liquid particles, adding the question: "might not the attraction of the surrounding medium be wholly or partly the cause?"²³ Graham replied that it was possible

24. Graham, *ibid.*

25. Graham, 'On osmotic force', Phil.Trans. 144 (1854) p 177.

to explain diffusion either in terms of attractive or repulsive forces. However, liquid diffusion was analogous to gas diffusion having the same intensity of action. For example when alum solution was diffused, sulphate of potash separated out first, leaving sulphate of alumina behind. Also, sulphurous acid and common salt could be boiled together and no hydrochloric acid was released, but when the same mixture was diffused, hydrochloric acid did separate out by diffusion leaving behind sulphite of soda. So Graham concluded that he saw: "every reason to consider that since gaseous diffusion, can be most clearly explained by the repulsive view, liquid diffusion so analogous to it should be likewise expressed." ²⁴

The nature of the repulsive force which activated diffusive motion was probably the inherent molecular motion existing in both gas and liquid molecules. When a layer of salt solution was covered by a layer of water, diffusion occurred producing ultimately a uniform mixture of salt and water. Graham explained this process: "the molecules of salt have the liquid condition when in solution as well as those of water itself, and we have in the experiment the contact of two different liquids, which must of necessity diffuse through each other, the molecules of a liquid being self-repellent, or subject to a force the same in kind but less in degree as that which gives to gases their elasticity and diffusibility." ²⁵

From his thermometric researches Graham had observed that the process of solution was usually accompanied by a fall in temperature unless it was masked by the heat released from the hydration of the solute. On dissolving, the solute changed from the solid to the liquid state absorbing heat from the solvent in a latent form. This latent heat caused the expansive motion of the solute particles. Liquid salt molecules were polymeric aggregates with an intrinsic molecular motion. If two liquid salt particles collided they would be thrown apart by their diffusive motion which thus gave rise to an essentially mechanical repulsive force in liquid diffusion.

26. Graham, op.cit. (1). Also Graham had written to Thomas Andrews in 1856: "I have long been of the opinion that diffusion; transpiration of both gases and liquids will never have an explanation except from the motion theory of heat." Letter dated November 25th 1856 in Andrews' collection, Queen's University, Belfast.

26a. Translation of a letter from J.Liebig to A.W.Hofmann, dated 21st October 1850. I am grateful to Dr.W.H.Brock for supplying me with this draft translation from his forthcoming edition of the Liebig-Hofmann correspondence.

When Graham actually dispensed with the concept of material caloric is not clear. Certainly he had replaced the concept of material caloric by heat as motion in his speculative paper of 1863; and he had previously expressed discontent with Laplace's interpretation of the states of matter in terms of material caloric. The latter rejection is contained in his unpublished paper on the liquid condition of matter, presumably written in 1854.²⁶ Therefore it is probable that Graham was thinking of heat as motion in 1854. It is also possible that Graham might have believed that the elements were constructed from primary matter when he was carrying out his researches on liquid diffusion. On this theory, atoms of all elements were identical in mass, but the atoms of different elements were distinguished from one another by possessing unalterably different amounts of motion. Salt molecules were polymers of simple molecules which in turn contained primary atoms united together in a simple volume combination. These polymeric salt molecules were the oscillating molecular complexes involved in liquid diffusion. Equality of diffusion speed occurred in certain cases when equal weights of salt were used. Graham noticed that equality of diffusion speed was often related to isomorphous groupings of elements in salts. However, this relationship between isomorphism and diffusive motion was not investigated in detail by Graham.

The response to Graham's papers on liquid diffusion came mainly from scientists interested in the relevance of this work to the problems of physiology. For example in October 1850 Liebig wrote to A.W.Hofmann: "I have now studied Prof. Graham's work more closely and find the results he obtained very remarkable. I want to take them complete for the Annalen and would like you to ask him on some occasion whether he wants to add any results. It is a pity his style is so dry."^{26a} In 1853, C.G.Lehmann also referred to Graham's 'remarkable discoveries' in relation to dissolved substances saying that: "even now Graham is devoting his energies to the elucidation of the numerous effects of diffusion, and we

26b. C.G. Lehmann, Physiological Chemistry Vol. 3 (London, 1854, translated by George E. Day from the 2nd. German edition published in 1853), p 167. Carl Gotthelf Lehmann (1812-1862), was Professor of Physiological Chemistry at Leipzig from 1843 to 1857 and then from 1857-1862 he was Professor of Chemistry at Jena. His textbook of physiological chemistry (which first appeared from 1842-1845 (1st.edn.); followed by a second edition 1851-1853) was an influential work.

27. A. Fick, 'On liquid diffusion' Phil. Mag. 4 Ser. 10 (1855) 30-39. Adolph Fick (1829-1901) took a medical degree with maths. at Marburg in 1851; he became assistant in Anatomy and Physiology at Zurich in 1852 under his former teacher, Carl Ludwig, who was responsible for Fick's interest in diffusion studies. Fick's paper 'On liquid diffusion' was first published in Pogg. Ann. 94 (1855) 59-86 and also in a modified form in Zeit. für rationelle medicin 6 (1855) 288-301. See the article on 'Fick's diffusion law', by H.J.V. Tyrell in J. Chem. Ed. 41 (1964) 397-400, for a discussion of Fick's work. Tyrell is perhaps too critical of Graham's failure to discuss liquid diffusion mathematically and he underestimates Graham's achievements in accumulating a body of experimental knowledge for further research. For Fick's papers see A. Fick. Gesammelte Schriften., Verlag (Wurzburg, 1903-4) Editor R. Fick, Volume 1.

28. A. Fick, 'On liquid diffusion', Phil. Mag. 4 Ser. 10 (1855) 30-39, See p 30.

scarcely yet possess any solid bases for our views of the phenomena which are termed endosmotic. Yet the few certain conclusions which we have drawn from our experiments on diffusion and endosmosis have already largely augmented our knowledge of many of the processes in animal life."^{26b}

Graham's researches on liquid diffusion provided the stimulus for Adolph Fick to develop a mathematical theory of diffusion in 1855. He expressed his regret "that in such an exceedingly valuable and extensive investigation [of liquid diffusion by Graham] the development of a fundamental law, for the operation of diffusion in a single element of space, was neglected."²⁷ Fick accordingly supplied this omission. For a chemist of Graham's training it would have been unthinkable for him to have used calculus in developing a theory of liquid diffusion. Like Davy and Faraday, Graham did not want to introduce higher mathematics into chemistry. He sought laws that could be inferred from careful experiments undertaken in the exploration of chemical phenomena and like most British chemists of this period he probably regarded the use of calculus as being more suitable for investigations in mathematics or natural philosophy.

But Fick, who had been trained in mathematics, did produce a mathematical theory of diffusion basing it on the previous mathematical treatments given by Fourier and Ohm concerning the diffusion of heat and electricity respectively. Fick stated his fundamental diffusion law thus: "the transfer of salt and water occurring in a unit of time, between two elements of space filled with differently concentrated solutions of the same salt, must be, other things being equal, directly proportional to the difference of concentration and inversely proportional to the distance of the elements from one another."²⁸ This law was confirmed by Fick in one instance. He allowed some saturated salt solution in a cylinder to diffuse into pure water. When equilibrium had been reached, the measured concentrations of salt were found to decrease in an arithmetic progression as the cylinder was ascended. From this experiment, Fick calculated the

29. Fr.Beilstein, 'On the diffusion of liquids', Liebig Ann. (1856) 99 165-197. See also H.Watts' supplement to Graham's Elements of Chemistry 2nd.edn. Vol.2 (London, 1857) 610-613, or H.Watts, Dictionary of Chemistry 3 (London, 1865) 705-711, for a summary of Beilstein's work.
30. A. Fick, 'A reply on some points in the paper "On the diffusion of liquids" by Fr.Beilstein', Liebig Ann. 102 (1857) 97-101.
31. Graham, op.cit. (16) Researches p 496.
32. Graham, Chemical Reports and Memoirs (London, 1848) published by the Cavendish Society, London. Graham was the editor and G.E.Day translated the foreign papers. Graham was concerned that there should be a Society devoted to the translation of foreign chemical memoirs and he was instrumental in helping to set up the Cavendish Society for this purpose, becoming its first and only President in 1846.
33. Graham, *ibid.* 'On the law according to which the mixing of fluids and their penetration into permeable substances occurs, with special reference to the processes in the human and animal organism', by Julius Vogel, see pages 85-117.

diffusion coefficient, or the constant of proportionality, in his law and the value he obtained agreed with his theory.

In 1856, Beilstein criticised Fick's law, by pointing out that Fick had not fully investigated the effect of varying the salt concentration. Using an apparatus designed by Jolly, Beilstein examined liquid diffusion experimentally. He believed that it was preferable to relate the transfer of salt in unit time to the square root of the concentration differences,²⁹ but this was incorrect as Fick pointed out later.³⁰ Beilstein was correctly convinced, however, that his experiments supported Graham's conclusion that the amount of salt diffusing into water in unit time was directly proportional to the concentration of the original salt solution.

Graham does not appear to have referred to the mathematical elucidation of liquid diffusion, presumably because he was reluctant to engage in mathematical discussions. The natural sequel to Graham's researches into liquid diffusion was an examination of the related problems of osmosis. He expressed this logical progression in 1849 as follows: "when the diffusibility of the salts in a liquid is known, the compound effect presented in an endosmotic experiment may be analysed, and the true share of the membrane in the result be ascertained."³¹

Graham's interest in osmosis must have been aroused by this time. In 1848 he had edited the first volume published by the Cavendish Society which contained translations of foreign papers.³² One of these papers was an article by Julius Vogel on the mixing of liquids and osmosis.³³ Vogel wanted more research to be undertaken on liquid mixture and the related problem of osmosis; he called for both detailed observations on volume changes, and the analysis of liquids before and after osmosis. Was Vogel's appeal answered by Graham? Certainly, Graham began his researches into liquid diffusion at this time and then proceeded to study osmosis. Another probable influence on Graham was the study of osmosis published by his friend Liebig in 1848. This study was translated into

34. J. Liebig, Researches on the Motion of the Juices of the Animal Body, edited by W. Gregory, (London, 1848) from a manuscript by the author:- Untersuchungen über einige Ursachen der Säftebewegung im thierischen Organismus. (Brunswick, 1848).
A French account of this work appeared in Ann.de Ch. 3 Ser.25 (1849) 367-447. In his July 1848 preface to: Chemical Reports and Memoirs (London, 1848), Graham wrote: "the attention of chemists and physiologists has lately been recalled to the subject of endosmose by the researches of Liebig on the motion of juices in the animal body."
35. K. Vierordt's article 'Transsudation et endosmose', in Rudolph Wagner's Handwörterbuch der Physiologie Vol.3 (Braunschweig, 1849)
Wellcome MS. old no.3396, new no.4937 (22 ll.) - a French translation of this article from the original German, with a few annotations by Graham.
36. Georg Wiedemann, 'On the motion of liquids in the current of the closed galvanic battery', Pogg. Ann. 87 (1852) 321-357 or the summary in Phil. Mag. 4 Ser.3 (1852) 546.
A full translation of this article, from Pogg. Ann., appeared in Taylor's Scientific Memoirs N.S. Natural Philosophy (1852) 232-256.
Wellcome MS. No.5000 (This is an English translation from Pogg. Ann.)
37. The Athenaeum, September 18th 1852, page 1013. Report of the Chemical Section of the British Association meeting at Belfast.
There is no written account in the official 1852 B.A. Report of Graham's address given on Monday, September 13th 1852.
38. The Literary Gazette, No.1861, September 18th 1852, page 715.
39. For useful accounts of the history of osmosis see:-
Henri Milne-Edwards, Leçons sur la Physiologie et l'Anatomie Vol.5 (Paris, 1859) 99-175.
Emmanuel Doumer, M.D. Thesis, (Bordeaux, 1881) entitled: Étude sur l'Osmose des Liquides au Point de Vue Historique, Physique et de ses Principales Applications
and for Dutrochet's contribution see:-
J. V. Pickstone, Ph.D. Thesis (1973) London, Chelsea College entitled The Origins of General Physiology in France with Special Emphasis on the Work of R. J. H. Dutrochet. See particularly Chapter 7.
J. V. Pickstone, 'Vital actions and organic physics: Henri Dutrochet and French physiology during the 1820s', Bull. of the History of Medicine Vol.50 No.2 (1976) pp 191-213.
J. and T. Schiller, Henri Dutrochet (Henri du Trochet 1776-1847) (Paris, 1975). See particularly Chapter 6.

English by William Gregory and given the title: Researches on the Motion of the Juices of the Animal Body.³⁴

Two manuscripts survive which show that Graham prepared himself carefully for his study of osmosis: they are an annotated French translation of Karl Vierordt's article 'Transsudation et endosmose', published in 1849³⁵ and George Wiedemann's article 'On the motion of liquids in the current of a closed galvanic battery', translated from the German in 1852.³⁶

Graham first described his investigations of endosmose (osmosis) in an address given to the chemical section of the British Association in September 1852. It was entitled:- 'On the principle of the endosmose of liquids'. The reporter from The Athenaeum noted that this was an "oral exposition with experiments of the various laws adverted to. Professor Graham recapitulated the researches of Dutrochet, Porrett, Magnus, Matteucci, Liebig and others to explain the movement of fluids in the cells and vessels of plants and animals." ³⁷ The Literary Gazette commented: "Graham gave some valuable notices of experiments on the endosmose of liquids. He described an instrument called an osmometer by which he measured the diffusion of salts through porous membranes into water, and he had arrived at several curious results, not least among which was the almost entire abnegation of the action of exosmose. He classified solutions of salts and other liquids according to their diffusibility through membranes; among the most diffusible being a combination of the alkalies with vegetable acids - a curious fact when we consider the presence of these salts in the sap of plants." ³⁸

In 1854 Graham gave his Bakerian lecture 'On osmotic force' to the Royal Society. Not only was this an important link, between liquid diffusion and colloids; it was also a valuable contribution to the study of osmosis. To understand Graham's contributions in the field of osmosis, it is necessary to review the main developments of the subject before Graham.³⁹

The first detailed studies of osmosis were made between 1826 and 1837

40. R. J. H. Dutrochet, L'Agent Immédiat du Mouvement Vitale Dévoilé dans sa Nature et dans sa Mode d'Action Chez les Végétaux et Chez les Animaux. (Paris, 1826) p 114 etc.

41. R. J. H. Dutrochet, 'Recherches sur l'endosmose et sur la cause physique de ce phénomène', Ann.de Ch. 49 (1832) 411-437, see pp 412-414. It is interesting to note that Wollaston had constructed a primitive kind of endosmometer for his studies of the action of electricity on animal secretions. W. H. Wollaston, 'On the agency of electricity on animal secretions', Phil.Mag. 1 Ser.33 (1809) 488-490.

42. J. V. Pickstone, op.cit. (39) . Ph.D.Thesis, see pp 235-240.

by Dutrochet. He had first observed osmosis in 1809 with a capsule of fish fungus; but his attention was drawn to the subject in 1826 by a second observation of osmosis occurring through the sperm sacs of snails. Dutrochet then reproduced the process by enclosing milk or gum in an intestine placed in water. Two currents appeared to be visible which he called 'endosmose' and 'exosmose'.⁴⁰ Water passed into the more dense solution contained in the sperm sac or intestine; this was the stronger current or endosmose. The weaker current, or exosmose, was directed from the milk or gum to water. Initially, Dutrochet used the term 'endosmose' to designate the current towards the membrane regardless of the strength of this current. But, by 1832, Dutrochet had altered his nomenclature; 'endosmose' was thereafter the name given to the stronger current and 'exosmose' was the weaker current. He constructed an 'endosmometer' to measure the force of endosmose.⁴¹ This was a tube ending in a bell shape with a membrane tied over it; the force of endosmose was estimated by the measured ascent of the liquid in the tube. Initially, Dutrochet used membranes made from animal and vegetable matter for endosmose. However, in 1827, Dutrochet discovered that certain inorganic solids, for example baked clay, could be used as partitions in endosmose experiments. The latter discovery ruled out any vitalistic explanation of endosmose.

J. V. Pickstone has recently given an important account of the initial reactions of the members of the French Academy to Dutrochet's discovery of endosmose.⁴² In these discussions, as well as in those which followed, four major explanations of endosmose were put forward. The explanations were based on electricity; viscosity; capillarity; and imbibition or absorption. Until 1840, Dutrochet was the only serious experimenter on osmosis and his experiments enabled him to assess the various explanations of osmosis.

To begin with, in 1826, Dutrochet explained endosmose by an electrical theory. He suggested that there was an analogy between the two opposite

43. R. Porrett, 'Curious galvanic arrangements', Ann.Phil. 8 (1816) 74-76 and also Ann.de Ch. 2 (1816) 137-140.
44. R. J. H. Dutrochet, L'Agent Immédiat etc. (Paris, 1826) op.cit. (40), pp 126-139. See for example page 139: "Ces résultats nous font déjà pressentir que l'impulsion qu' éprouvent les liquides dans ses expériences, dépend d'un courant électrique déterminé par le voisinage de deux fluides de densité ou de nature chimique différentes, fluides que sépare imparfaitement une membrane perméable. Cette membrane ne joue évidemment aucun rôle propre dans cette circonstance...."
45. J. & T. Schiller, Henri Dutrochet (Paris, 1975) op.cit. (39), Chapter 7 p 87 'Notice of my life and work', a late unpublished MS. by Dutrochet (ca. 1840-6)
46. R. J. H. Dutrochet, 'Nouvelles recherches sur l'endosmose et l'exosmose', Ann.de Ch. 37 (1828) 191-201.
See also the book of the same name written by Dutrochet and published in Paris (1828) and R. J. H. Dutrochet, 'Recherches sur l'endosmose et sur la cause physique de ce phénomène', Ann.de Ch. 49 (1832) 411-437.
47. A. M. Ampère, J. de Chimie Medicale 3 (1827) 153, see Pickstone, op.cit. (42) p 237.
For Dulong's views see J. & T. Schiller, op.cit. (45) p 96.
48. G. Magnus, 'Sur quelques phénomènes de capillarité', Ann.de Ch. 51 (1832) 173-182, translated from an earlier article found in Pogg. Ann. 10 (1827) 153-168.
Berzelius accepted the interpretation of endosmose given by Magnus, [see J. J. Berzelius, Traité de Chimie 7 (Paris, 1833) 133-137], but Liebig rejected the explanation given by Magnus.

currents of endosmose and exosmose and the two current theory of electricity, in which positive and negative electricity flowed in opposite directions. This analogy was derived from Porrett's observation that water moved in electrolysis through a bladder, or sheet of coagulated albumen, from the positive to the negative pole.⁴³ Dutrochet argued that an electric current was produced when two liquids, of different density or chemical nature, came into contact. The electric current drew the less dense liquid into the more dense liquid.⁴⁴ This electrical theory was supported by his observations that water gave a stronger endosmose towards the more dense solutions of gum, whereas acids gave a stronger endosmose to water. Dutrochet soon rejected the theory when he found a number of inconsistent experimental facts. The electrical theory, as Dutrochet himself later recognised, was not generally well-received.⁴⁵ He had found that the density gradient was less decisive than he had supposed; for example water gave a stronger current through a bladder towards the less dense alcohol. By 1828, Dutrochet had also discovered that his earlier observation on acids was incorrect; indeed, he had discovered that there was an endosmose from water towards dilute acids. Consequently, he modified his explanation of endosmose, by suggesting that the primary cause was the mutual attraction of different liquids. The action of electricity was then relegated to a secondary role in endosmose.⁴⁶ In a similar manner, Graham gave an electrochemical explanation of osmosis which he also abandoned at a later date.

Both Ampère and Dulong attributed endosmose to differences in the viscosity of liquids rather than to electricity. Two liquids, for example water and gum, were attracted to one another, but the less viscous liquid, water, travelled more quickly through the membrane thus producing endosmose.⁴⁷ A more detailed exposition of the viscosity theory was put forward by Magnus in 1827.⁴⁸ He suggested that the intermolecular forces in a salt solution were greater than those in pure water, and furthermore that these forces were stronger in more concentrated

49. S. D. Poisson, J. de Physiologie expérimentale (Magendie) 6 (1826) 361-366 and also: 'Note on effects which can be produced by capillarity and affinity of different substances', Ann.de Ch. 35 (1827) 98-102; 'Mémor on the equilibrium of fluids', 39 (1828) 333-335; 'New theory of capillary action', 46 (1831) 61-70.
50. R. J. H. Dutrochet, 'New observations on endosmose and exosmose and on the cause of this double phenomena', Ann.de Ch. 35 (1827) 393-400.
51. R. J. H. Dutrochet, op.cit. (46) Ann.de Ch. 49 (1832) 411-437.
52. R. J. H. Dutrochet, 'De l'endosmose des acides', Ann.de Ch. 60 (1835) 337-368.

salt solutions. Therefore, endosmose was directed from water to salt solution because water experienced less resistance than salt solution when it passed through the pores of a membrane. Dutrochet objected to the viscosity theory because it did not provide for the two opposite currents of endosmose and exosmose. He successfully combatted the theory with several contrary experiments, for example the direction of endosmose between alcohol and water depended on the nature of the separating partition and not on the viscosity of the liquids.

An alternative theory which Dutrochet almost came to accept, was the capillarity theory advocated by Poisson. The physicist, Poisson, developed this theory in a number of papers without any experimental support.⁴⁹ He argued that two different liquids separated by a membrane should experience unequal capillary attraction. One of the liquids, only, would pass over into the other until the excess pressure prevented this flow. The liquid which passed through the membrane was the one which was most strongly attracted by the membrane capillaries.

This theory still left Dutrochet with the problem of explaining the double current.⁵⁰ In 1832, Dutrochet was prepared to admit that the force of endosmose was proportional to the difference in capillary rises of the two liquids,⁵¹ but further experiments led him to question this opinion. In endosmose experiments with animal membranes, he discovered that dilute acids above a certain concentration changed their direction of flow.⁵² This new problem was difficult to explain on any of the existing theories of endosmose.

In 1837, Dutrochet concluded his researches by rejecting all of the theories of endosmose based on differences in density, viscosity, or capillarity. This retreat from earlier theories left a lacuna which was filled by subsequent researchers who produced more adequate explanations of osmosis; Graham played his part in this development as we shall see. Although Dutrochet rejected the capillarity theory of endosmose he did accept that different liquids had an affinity both for one another and

53. R. J. H. Dutrochet, Mémoires pour Servir a l'Histoire Anatomique et Physiologique des Végétaux et des Animaux, 2 volumes. (Paris, 1837)
See Vol.1 pages 1-99 for Dutrochet's final account of endosmose, particularly pages 96-99.
54. Graham, Notes and Drafts for University College Lectures 1838-1848. Wellcome MS. New No.2579 (Old no.3202) (154 ll). The notes referred to appear to have been written in 1838.
55. J. V. Pickstone, op.cit. (39) Ph.D.Thesis pp 235-236. See report of discussion in Le Globe November 2nd 1826 pp 182-183 and in Bull.des Sciences Naturelles 9 (1826) 336-337.

for the partition. He concluded that the liquid with the greatest affinity for the partition was the one which gave the endosmose current. For example alcohol gave an endosmose towards water through a rubber partition because alcohol possessed a greater affinity for rubber than did water; whereas with bladder the current was from water to alcohol because water had more affinity for bladder than did alcohol. Dutrochet accepted that the acting affinities were essentially electrical in origin but he considered that their detailed-action was obscure.⁵³ For somewhat different reasons Graham also rejected capillary explanations of osmosis.

Graham commented on Dutrochet's researches, in his University College lecture notes of 1838, saying that in osmosis, much depended on the power possessed by a membrane to absorb or imbibe a given liquid. Graham insisted that the power of imbibition was essentially chemical and not mechanical; membranes were not like sponges and liquids were not forced out of them by pressure. He noted that some liquids were absorbed in greater quantities than others, for example bladder absorbed more water than alcohol, and this resulted in a separation of these liquids. He added that: "Dutrochet has neglected this power of imbibition - he is eclectic - his endosmose and exosmose are complex."⁵⁴ Graham was quite correct to point out Dutrochet's neglect of absorption differences. Although, ironically, Graham appears to have neglected this very power of imbibition in his own 1854 account of osmosis. Instead, he placed too much stress on the chemical decompositions occurring in the porous partitions. He corrected this imbalance later in 1861.

Theories of imbibition or absorption had been advanced before Graham referred to them. In 1826, Magendie, a leading physiologist, led the discussion which followed Dutrochet's announcement of the discovery of endosmose at the Académie des Sciences. Magendie claimed that endosmose was very similar to imbibition, which he had previously shown to depend on the texture of membranes.⁵⁵ The botanist, F. V. Raspail, also argued that a membrane absorbed water more rapidly than gum because the membrane

56. J. V. Pickstone, *ibid.* pp 237-238.
F. V. Raspail, Revue Médicale 24 (1826) 471-473 and for his subsequent views 'Sur l'endosmose de M. Dutrochet', Bull. des Sciences Naturelles 14 (1828) 364-365 or F. V. Raspail, Nouveau Systeme de Chimie Organique (Paris, 1833) pp 81-83.
57. J. K. Mitchell, 'On the penetrativeness of fluids', Amer. J. Med. Sci. 7 (1830) 36-67, also in Journal of the R.I. 2 (1831) 101-118, 307-321.
58. Ernest Wilhelm Brücke, (1819-1892), was taught by Johannes Müller in Berlin and became his assistant in 1843. Brücke belonged to the group of researchers who tried to apply physics to physiology; this group included Ludwig, Helmholtz, Magnus and Du Bois Reymond. Brücke's research thesis: De Diffusioni Humororum per Septum Mortua et Viva was published in 1841.

had a greater affinity for the water. He assumed that water was forced up into the gum by a decomposition of the membrane surface. This was an interesting anticipation of Graham's later theory that chemical decomposition in membranes was essential in osmosis. Raspail later modified his views possibly following Dutrochet's discovery that inorganic partitions could also be used for endosmose. Thus, Raspail abandoned his theory of membrane decomposition arguing that endosmose occurred simply because gum attracted and imbibed the water.⁵⁶ In 1830, J. K. Mitchell also discussed Dutrochet's work. He rejected Dutrochet's first theory of the electrical origin of endosmose and argued instead that liquids possessed 'different degrees of penetrativeness' for membranes and this accounted for endosmose.⁵⁷

The importance of absorption in osmosis was emphasised in the 1840s. The German physiologist E. W. Brücke⁵⁸ explained absorption in terms of capillarity and his explanation was widely accepted in Germany. Brücke's explanation was used by Carl Ludwig and his pupil Adolph Fick, but it was rejected by Graham, who dismissed all theories based on capillary action. Brücke suggested that an animal membrane contained capillary channels which exerted an unequal force of attraction for different liquids. When water was separated from brine by a membrane, the water was more strongly attracted than brine to the walls of the capillary channels. Hence the water was drawn along the capillary walls to meet the brine. A capillary channel would therefore contain a lining of water around its walls and a mixture of salt and water at its centre; the salt concentration would decrease from the centre of the capillary channel to the walls. This salt water gradually progressed to mix with the pure water. In the opposite direction the endosmose current of water was strongly drawn along the capillary walls and propelled into the brine. To demonstrate the water movement, Brücke poured a solution of potassium dichromate into a tube closed with bladder and dipped it into a solution of lead acetate saturated with sugar to increase its concentration. The solutes penetrated into the bladder forming a yellow precipitate of lead chromate inside; and

59. E. W. Brücke, 'A contribution to the theory of diffusion of liquids through porous partitions', Pogg. Ann. 58 (1843) 77-94, see page 89.
60. Ch. Matteucci and A. Cima, 'Mémoire sur l'endosmose', Ann. de Ch. 3 Ser. 13 (1845) 63-86.
61. Graham, 'On osmotic force', Phil. Trans. 144 (1854) pp 186-187.
62. J. Liebig, Researches on the Motion of the Juices of the Animal Body, edited by W. Gregory (London, 1848) op.cit. (34).
Similar views to those of Liebig were expressed at the same time by Matteucci, "The endosmose current is in general determined by the liquid which has the greatest affinity for the interposed substance and by which it is imbibed with the greatest rapidity. In fact it is evident that the membrane imbibes the two liquids unequally; and that the one which is imbibed with the greatest facility ought to mix with, and augment the volume of the other." from Carlo Matteucci, Lectures on the Physical Phenomena of Living Things, (London, 1847) English translation by Johnathan Pereira, page 39.
63. Chevreul had noticed in 1821, that tendons and ligaments absorbed different quantities of liquids. He found that, of all the liquids, water was absorbed in greatest quantity, next came salt water and finally oil was hardly absorbed at all.
M. E. Chevreul, 'On the influence of water on several azotised substances', Ann. de Ch. 19 (1821) 32-57, see p 52.

a strong endosmose current was observed from potassium dichromate to lead acetate. Water alone was transferred in the endosmose because there was no observed orange colouration of the lead acetate solution. With this elegant demonstration of osmosis, Brücke claimed that he had clearly shown that water could be separated from a solution by capillary action.⁵⁹

The action of different membranes was studied very carefully in 1845, by Matteucci and Cima.⁶⁰ They observed definite variations in the endosmose between water and solutions depending upon which particular surface of the membrane faced the water. Later, Graham revealed both how these differences arose and how they could be avoided, thereby simplifying the experimental study of osmosis. He explained that irregular osmotic results were caused by the outer muscular coating of a bladder becoming putrescent and then releasing a large quantity of salts and other soluble material. Graham recommended the removal of the muscular coating from bladders because he found that the remaining serous membrane was much more active in osmosis and in addition, it gave osmotic results of a much greater regularity in successive experiments.⁶¹

In 1848, Liebig described his researches on osmosis.⁶² These researches probably influenced Graham to take up the study of osmosis. Initially, Graham did not accept Liebig's explanation of endosmose, but after further study he revised his own explanation of osmosis and produced a theory resembling that given by Liebig.

Following Chevreul,⁶³ Liebig showed that membranes, and to a lesser extent baked clay, absorbed unequal quantities of different liquids. He found that the order of decreasing absorption of liquids was: water, brine, alcohol and oil. He observed that bladders absorbed large volumes of water and became swollen. Whilst, on the contrary, brine or alcohol were found to contract a moist bladder. Liebig explained endosmose by suggesting that a greater quantity of one of the liquids was absorbed, because it was more strongly attracted to the bladder; for example if water and brine were separated by a bladder, water would be more strongly

64. Karl Vierordt (1818-1884) studied medicine at Heidelberg, Berlin, Göttingen and Vienna. His teachers included Gmelin, Bischoff, J. Müller etc. He obtained his doctorate in medicine at Heidelberg in 1841. In 1843, he showed that less carbon dioxide was expired during rapid respiration. He wrote articles on respiration and endosmose in Rudolph Wagner's Handwörterbuch der Physiologie. In 1849, he became Professor of theoretical medicine at Tübingen, where he gave accounts of an accurate method of counting red blood corpuscles and a pulse recorder. For his biography, see 'K. von Vierordt', Ann.Med.Hist. 10 (1938) 463-473 and for his work on endosmose see:- Pogg. Ann. 73 (1848) 519-531 and 'Transsudation und endosmose' in Wagner's Handwörterbuch Vol. 3 (Braunschweig, 1849).

attracted to the bladder and so it would be absorbed in greater quantity. The bladder would swell on the water side and contract on the brine side. As the two liquids mixed inside there were alternate contractions and expansions of the membrane, which gave rise to a form of mechanical pressure forcing water into brine thus generating the endosmose current. Liebig maintained that all attractions were caused by chemical affinity. Salt was attracted to water; brine and water were attracted to the solid bladder, all, by chemical affinity. He even quoted Graham's experiments on the removal of salts from solution by adhesion to charcoal as examples of the operation of chemical affinity between salts and charcoal. He explained the final formation of a uniform mixture in the osmosis of water to brine through a bladder, by assuming firstly, that water and brine were absorbed until they met in the bladder and secondly, that the salt was attracted into the water. This gave diluted brine which in turn attracted more salt from the strong brine; this process continued until the salt was uniformly spread throughout the water.

Liebig's views were not radically different from those of Brücke except that Liebig placed more emphasis on differential absorption than on superior capillary attraction. To predict the direction of endosmose Liebig referred to the chemical affinity acting between the liquids and bladder instead of referring to the force of capillary attraction. He had only examined the osmosis of a small number of different liquids; so the full range of different solutions still remained to be examined.

Also in the 1840s, Karl Vierordt took up the quantitative study of endosmose.⁶⁴ He pointed out that although Dutrochet had made numerous comparative experiments on endosmose, his experimental techniques had been faulty. He showed that Dutrochet had not allowed for changes, either in the pressure, or in the size of the membrane, which usually swelled during endosmose. Vierordt avoided these errors by designing an endosmometer which overcame them. He then tested Dutrochet's conclusion that the difference in the velocities of endosmose and exosmose, between water and

65. J. Liebig, op.cit. (62).

66. Philipp Johann Gustav von Jolly, (1809-1884), studied physics and technology at Heidelberg and Vienna. He concentrated on physics and mathematics, later, whilst he was at Berlin and gained his doctorate in 1834. Jolly was appointed to the Chair of Physics at Heidelberg in 1846 and became a well-known experimental physicist. At Heidelberg, he was often consulted by J. R. von Mayer. During this period, Jolly was concerned with questions about osmosis and he helped to elucidate its nature. For his experimental researches on endosmose, see:- P. Jolly, 'Experimental researches on endosmose', Henle and Pfeufer's Zeit für Rationelle Medecin 7 (1849) 83-148 or P. Jolly: Pogg. Ann. 78 (1849) 261-271 and Liebig Ann. 68 (1848) 1-15.

67. K. Vierordt, op.cit. (35).

a solution, was directly proportional to the concentration of the original solution and found that it was incorrect. He found that more dilute solutions of salt or sugar gave a relatively greater endosmose; but with more concentrated solutions, relatively less water was transferred by endosmose and more salt escaped than would be expected.

The exchange of salt and water had also been examined by Liebig. He wondered whether water was simply exchanged for salt during osmosis. Unlike Graham, he rejected this possibility when he calculated that one atom of salt was exchanged for 15 atoms of water, whilst from solubility data, one atom of salt required at least 18 atoms of water for its solution.⁶⁵ A more detailed study of this exchange process was made by Jolly in 1848.⁶⁶ He placed a solution of known concentration in a tube closed with pig's bladder. Then, he immersed it just below the surface of a large volume of water which was renewed continuously. The experiment was performed at constant pressure and it was stopped when all the salt had escaped, having been replaced by water. This stage was reached when the tube no longer changed in weight. Jolly then calculated the 'endosmotic equivalent' for each salt, or the weight of water which had replaced one gram of salt. His results were averaged values because successive experiments gave slightly different figures. The largest endosmotic equivalents were given by alkalies, followed in order by neutral salts, acid salts, and finally acids which gave the lowest values. This order was supported by Graham's experimental results of 1854. Jolly concluded that the amount of substance passing out in unit time, under the same conditions, was proportional to the concentration of the solution. This conclusion was reported by Vierordt in his review article: 'Transsudation and endosmose' and Graham wrote at the side of the conclusion: "Is diffusion?"⁶⁷ We see that Jolly's conclusion was confirmed by Graham in his 1849 liquid diffusion paper and it supported the view which Graham adopted, that, in osmosis, salts simply escaped by liquid diffusion.

Liebig recognised that Jolly's researches had again raised the problem

68. Liebig and Kopp, Annual Reports of Chemistry for 1847 and 1848,
Volume 1 (London, 1849) p 13.
69. C. Ludwig, 'On the endosmotic equivalent and the theory of endosmose',
Pogg. Ann. 78 (1849) 307-326. See pp 321-325 and also in Henle and
Pfeuffer's Zeit. für Rationelle Medecin 8 (1849) 1-52.
70. Liebig and Kopp, Annual Reports of Chemistry for 1849 2 (London, 1850)
6-7.
71. M. Harzer, Roser und Wunderlich's Archiv für Physiologische Heilkunde,
15 (1856) 202-.
Also see the summary in H. Milne-Edwards: Leçons.5, op.cit.(39), pp 155-
156, 159.

of the exchange of water and salt and Liebig's comments on this research, possibly provided Graham with a research programme in osmosis. Liebig wrote:- "It would be very important to confirm, by a more extensive series of experiments the two laws resulting from Jolly's researches; viz., firstly, that the amount of salt permeating the membrane in the unit of time, is proportional to the density of the solution; and secondly, that, quite independently of the density, the quantity of salt eliminated in a certain time is replaced by the passage of an endosmotically proportional amount of water. Such a confirmation, when more general, would be an important support of the view - that from the saline solution, salt molecules only pass into water, whilst the latter sends particles of pure water only into the salt solution." ⁶⁸

Before turning to Graham's clarification of the relation between diffusion and endosmose it will be helpful to look at some of the criticism which followed Jolly's work. Carl Ludwig showed experimentally that endosmotic equivalents were far from constant. Factors which altered the values of these equivalents were: the concentration of the salt solution; the duration of the experiment; and the age of the membrane. Ludwig favoured Brücke's theory of endosmose; and in support of this theory he quoted the following experiment. A dry bladder was placed in a 10% solution of salt, and it absorbed a liquid containing 7% salt. This result supported Brücke's opinion that the liquid in the capillary channels should contain more water than the outer liquid. ⁶⁹ However, Liebig commented on Ludwig's result that it was well known that animal membranes, at first, chiefly absorbed water from saline solutions. ⁷⁰ The permeability of membranes used in endosmose was also examined by Harzer, a physiologist from Dorpat, who compared membranes which were chemically treated to alter their permeability. ⁷¹ He found that a membrane treated with chromic acid gave an endosmose which was six times greater than that given by a membrane treated with dilute sulphuric acid. Clearly it was important to use a fresh membrane in osmosis if

72. Graham, The Bakerian lecture: 'On osmotic force', Phil.Trans. 144 (1854) 177-228 read on June 15th 1854. Curiously, this important paper was omitted from Researches. by R. A. Smith. It was also not discussed by: Smith, Thorpe, Ramsay, Williamson or Chandlers Roberts in their reviews of Graham's work, although it was mentioned by: Hofmann, Odling, Lord Neaves (R.S.E.) and James Bryce (Glasgow Phil.Soc.) in their obituary notices of Graham.
73. Graham, ibid. p 178. Graham mentioned another new term in an MS. note found in the Wellcome MS. volume of Graham's letters and correspondence. This term was not included in his papers; this term was used as a name for the permeable partition which he called an 'osmiferous septum'. Graham also used the verb 'osmify' in another MS. note in which he expressed his intention to 'diffuse and osmify solutions of perchloride of tin'. He also intended at an earlier stage in his investigation to call this paper 'Inquiries respecting the osmotic force', or 'Inquiry into electric osmose of salts and mixtures'. The term 'osmosis' was not used by Graham. This Latinate form of the word osmose first appeared in 1867, in J. Hogg, Microsc.I. iii 206 and later in 1876 in Foster Phys.I iv (1879) 122.

comparable results were to be obtained.

When Graham began his investigation of osmosis it seemed clear that the prevailing opinion was, that osmosis could be explained by a mechanism of preferential absorption. When water and brine were placed on opposite sides of a bladder, water would be preferentially absorbed either because of its greater chemical affinity for bladder or from the superior capillary attraction exerted by the bladder. Jolly's researches appeared to show that there was a constancy in the exchange of water and salt and also that salts escaped simply by diffusion. Osmosis would cease when solutions of equal concentration were established on both sides of a bladder. However, the exchange of salt and water could become a more complicated problem if concentrated salt solutions were used or if there were alterations in the permeability of the bladder caused by chemical actions on the bladder. However, in his first explanation of osmosis, Graham did not have recourse to the view that osmosis was caused by preferential absorption instead he gave an electrochemical interpretation of the phenomenon.

Graham opened his paper, 'On osmotic force' in 1854 by proposing a new nomenclature for the subject.⁷² He found that the weight of salt which escaped from a jar of salt solution into water was the same whether the jar was open, or covered with a thin bladder. Therefore liquid diffusion occurred in osmosis but the diffusion of liquid salt molecules was not the same as Dutrochet's exosmose because: "it is not the whole saline liquid which moves outwards, but merely the molecules of salt, their water of solution being passive. The inward current of water, on the other hand, appears to be a true sensible stream or a current carrying masses. The passage outwards of salt is inevitable, and being fully-accounted for by diffusibility, requires no further explanation. It is the water current which requires consideration, and for which a cause must be found. This flow of water through the membrane I shall speak of as osmose, and the unknown power producing it as the osmotic force."⁷³

74. Graham, 'On the liquid condition of matter', op.cit. (1).
It is interesting to note that, in 1853, Pouillet had reached a similar conclusion when he wrote that: "capillary force was insufficient to explain endosmose."
C.S.M.Pouillet, Éléments de Physique Expérimentale.6th.edn. (Paris, 1853) Vol.2, p 17.

Graham's new nomenclature which also included the name 'osmometer' for Dutrochet's 'endosmometer' was generally accepted.

Graham had clearly demonstrated that Dutrochet's endosmose and exosmose were really osmose and liquid diffusion. This important clarification enabled Graham to ask the correct questions about osmosis. He began by asking whether diffusibility could be used to explain both osmose and liquid diffusion. He observed that water diffused four times faster than alcohol, and four to six times more rapidly than the less diffusive salts. Graham thought it was possible that the small osmose, shown by both neutral salts and slowly-diffusing organic substances, could be explained by diffusive exchange of the solute for water. Examples of such substances were sodium chloride; magnesium sulphate; alcohol; and sugar. But there were many substances where the large osmose could not be accounted for by diffusive exchange. The superior diffusibility of water could not be used to explain how, in osmose, one part of a certain salt could be exchanged for several hundred parts of water.

A new explanation was needed for the large number of chemicals which gave a high osmose. Was capillarity the answer? Graham referred to capillarity as: "the only intelligible explanation offered by Dutrochet, Magnus and Poisson,"⁷⁴ but he concluded that this hypothesis was untenable because he found that the measured capillary rises in glass tubes, of many solutions, were almost identical to the value found for pure water. The only alternative theory which he could offer at this time for explaining the movement of large masses of water was one of chemical or electro-chemical action in the membrane.

Graham performed many experiments to measure the osmose and corresponding diffusate of different solutions. The partitions which he used were either clay pots or membranes. He took care to avoid Dutrochet's experimental errors by equalising liquid levels during osmose and by using varnished zinc mesh supports for the membranes to prevent any swelling. Graham had obviously heeded Vierordt's advice.

75. Graham, *op.cit.* (72), page 225.

Using baked clay pots, Graham found that, the most osmotic chemicals were dilute solutions having acidic or basic properties. During the osmose these chemicals acted on the silicates of lime and alumina in the clay. Indeed, the corrosion of the clay seemed to be a necessary condition for osmose because clay and lime were invariably found in solution after osmose. One major problem occurred with the use of clay pots; it was difficult to remove all soluble matter before use and unless this was done the osmose varied.

Graham therefore turned to more suitable partitions. He used either natural animal membrane, or artificially-prepared albuminated calico, made by coagulating an albumen solution on calico with steam. Both natural and artificial partitions gave a remarkably large osmose with potassium carbonate solution; 500 parts of water replacing one part of this salt. This experiment led Graham to conclude that osmose could not be caused by membrane contractions because the same result was given with both natural and artificial organic structures. This ruled out the possible action of a vital force and appeared to cast doubt on Liebig's explanation of osmose which involved membrane contractions and expansions.

Membranes lost between 20 and 40% of their original weight during use which suggested that chemical actions were occurring inside them. Graham was able to generalise Dutrochet's observation that acids at a certain concentration gave negative osmose from acid to water by showing that all acids gave a negative or very low positive osmose. Alkalies or alkaline salts showed the greatest positive osmose; water flowed very strongly into alkaline solutions. These observations indicated to Graham that different chemical actions were taking place at the inner and outer surfaces of membranes. He supposed that there was an alkaline action at the inner surface of an albuminous membrane facing the solution and an acidic action at the outer surface facing the water. Osmose experiments showed that water always accumulated at the alkaline surface of albumen.⁷⁵ Graham assumed that there was an analogy between the passage of water to

76. Graham, op.cit. (72), page 184.

77. Partington has observed that $H_{m+1}O_m$ is analogous to the hydroxonium ion in modern terms.
Partington, History of Chemistry 4 (London, 1964) 652.

78. Graham, Elements of Chemistry 2nd.edn. part 2 (London, 1848) pages 266-267.

the alkaline side of a membrane and the passage of water and hydrogen through a diaphragm to the negative pole in water electrolysis.

The electrochemical theory of osmose proposed by Graham was developed from his own explanation of Porrett's electrical endosmose, in which, during water electrolysis, there was a transport of water and hydrogen through a porous diaphragm from the positive to the negative pole. A polymeric water molecule, written as n times HO or $H_n O_n$, underwent a molecular decomposition in a voltaic circle. This binary fission produced a large positive radical or basyl $H_{m+1} O_m$ and also an oxygen atom which was the negative or chlorous radical, O. The binary fission was written $H_n O_n = (H_{m+1} O_m) + O$.⁷⁶ Graham reasoned that a polymeric water molecule was decomposed much more easily than a single water molecule because the positive radical contained proportionately-less, excess hydrogen in a polymer and so held on to oxygen less well. For example a positive radical $H_{101} O_{100}$ would have much less affinity for an oxygen atom than say $H_3 O_2$ would have. The positive radical $H_{m+1} O_m$,⁷⁷ in Porrett's experiment, moved to the negative pole where Graham suggested that it decomposed, releasing hydrogen H, and setting free a large volume of water mHO .⁷⁸ This explained the large transport of water noticed by Porrett in his experiment. This water transport was also confirmed by Wiedemann in his experiments of 1852.

To explain ordinary osmose Graham examined first the strictly neutral monobasic salts of the alkali metals, like NaCl, which gave little or no osmotic action. Assuming that similar polymeric molecules were present, which could assume a binary form, as in electrochemistry, Graham wrote:- "We may imagine, the formation within the thickness of the septum of a polar circle, one segment of which (composed of the binary molecules of the salt) presents a basic molecule to the albumen at the inner surface of the septum, and an acid molecule to the albumen at the outer surface, the circle being completed through the substance of the septum which forms the second segment. Both surfaces of the septum would be acted upon, but at

79. Graham, op.cit. (72), page 190.

one side we should have combination of the albumen with an alkali, on the other side with an acid." ⁷⁹ Graham admitted that this was an ideal view of the septum in osmose, adding that it was not possible to prove that the septum was polar by using a galvanometer, because polarisation would be induced by the instrument. Graham was not explicit about the details of the movement of water from the acidic to the basic surface of the septum. However, it is possible to infer that a polymeric water molecule would decompose in a voltaic circle, forming the positive radical $H_{m+1}O_m$. This radical would then decompose at the basic surface releasing a large volume of water into the saline solution; this was the osmose.

Polybasic salts produced a greater positive osmose and the extent of this osmose seemed to depend on the instability of the salt. Both the sulphate and oxalate of potash, being relatively stable salts, gave a small positive osmose. However, unstable salts such as aluminium acetate, ferric nitrate and aluminium chloride gave a large positive osmose. In the former case, he assumed that the bibasic salts were partially resolved into a free alkaline base and an acid salt. In the latter case, the unstable salts decomposed to give a basic salt and a free acid. In both cases, the free alkaline base or basic salt combined with the albumen producing a distinctly basic inner surface and the acid or acid salt diffused away.

Graham was reticent about supplying details of the water movement with more active salts but his notes suggest a possible interpretation. He wrote: "Examine for decomposition the salts of high osmose. This may well be the case with acetate of alumina etc. Does the acetic acid always take a polyatomic water homologue after leaving the alumina? An action of mass. A large mass of water entering the membrane to take the place of the alumina. Does carbonate of potash decompose into hydrate of potash and bicarbonate? So, of all the bibasic salts which appear to be the most osmotic? Is a decomposable salt such as sulphate of alumina protected from decomposition by the presence of other salts? Or have

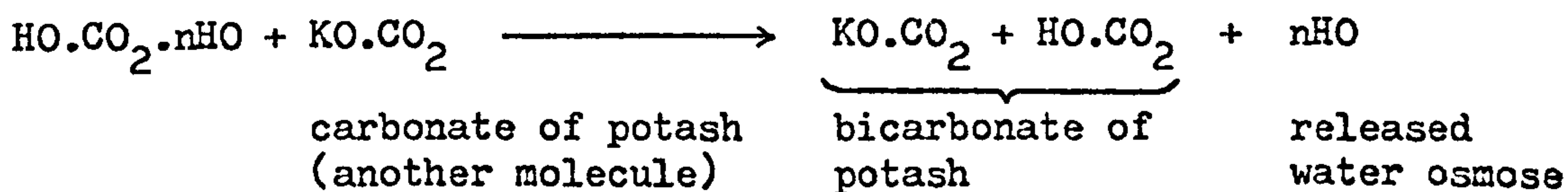
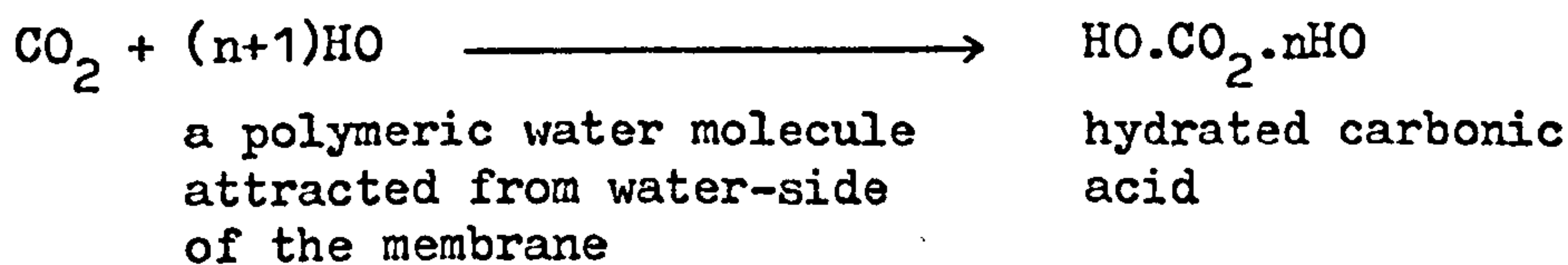
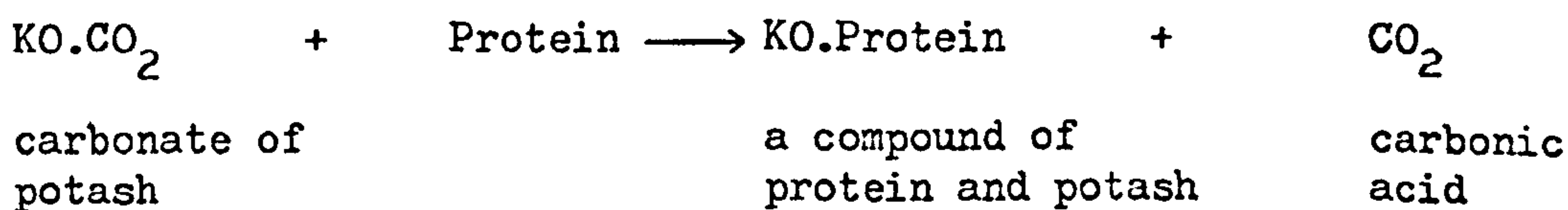
80. Graham, MS. note in: Graham's Letters and Correspondence, at the Wellcome Library.

81. Graham, *ibid.*

any added salts, on the contrary, a catalytic influence on sulphate of alumina?"⁸⁰ Graham's comments on aluminium sulphate were based on his discovery that trace amounts of saline impurities could change the results of osmose experiments remarkably. For example a small amount of sodium chloride added to potassium carbonate solution reduced the positive osmose markedly; on the other hand, a small amount of sodium chloride added to hydrochloric acid increased the osmose making it positive. Graham attributed these effects to obscure chemical changes in the membrane but as we shall see a more convincing explanation was suggested later by Milne-Edwards. Graham continued his unpublished notes:- "... With hydrochloric acid and other acids, may combination be first formed with the substance of the membrane and the decomposition of this compound be the source of the osmose, a decomposition determined by the disposition of the acid to diffuse into water. With carbonate of potash may the potash combine with the protein and the CO₂ go back carrying water with it to combine with carbonate of potash to form bicarbonate of potash?"⁸¹

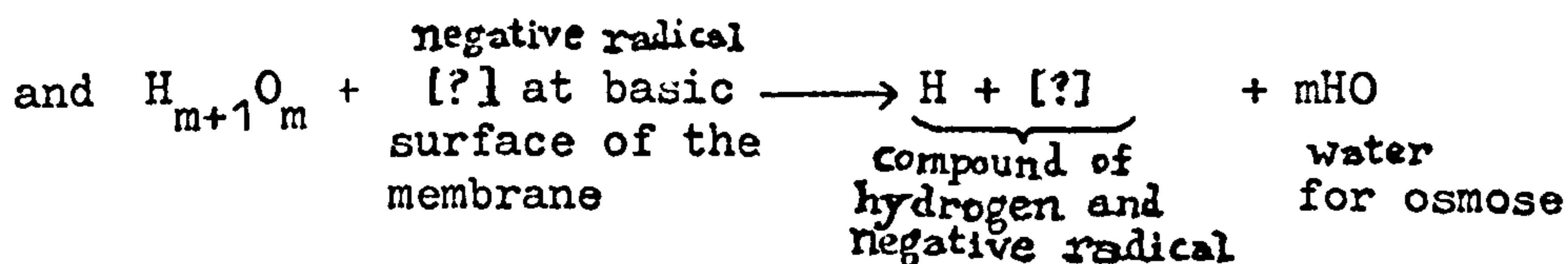
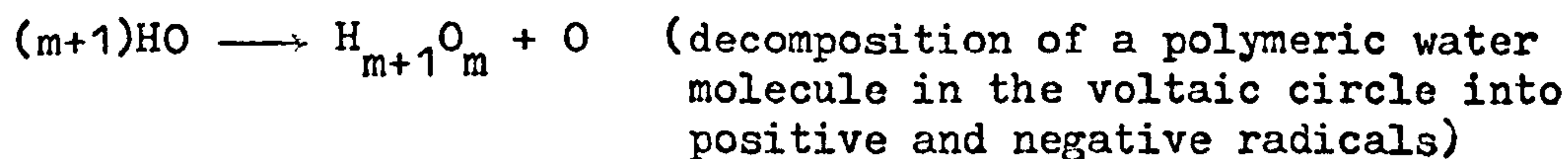
From this evidence it is possible to reconstruct Graham's electro-chemical theory of osmose. Unstable salts which gave a large positive osmose, for example aluminium acetate or potassium carbonate, decomposed at the membrane surface. The base alumina or potash combined with the protein to give a basic surface whilst the acids were released. The free acetic or carbonic acid combined with a large polymeric water molecule, which took the place of the released base, alumina or potash, just as sulphuric acid was known to combine readily with a polymeric water molecule. These acid hydrates were then decomposed releasing a large volume of water which constituted the positive osmose. In the case of hydrated carbonic acid, Graham suggested that there was a secondary reaction in which the carbonic acid combined with potassium carbonate to form potassium bicarbonate, thereby releasing the combined water.

A possible reaction scheme for carbonate of potash might be:-



In all cases, there was an attachment of a polymeric water molecule, either to an acid, or a salt, followed by a binary decomposition of the polymeric water molecule to form a positive radical and oxygen. The positive radical finally underwent electrochemical decomposition at the negative or basic surface of the membrane.

These decompositions might be written:-



Graham was reluctant to give clear details of these decompositions in his published paper. Perhaps he did not want to speculate too widely; or maybe he was still uncertain of the exact mechanism of the processes and so preferred to delay publication of his thoughts until he had made a more thorough study of osmosis.

Electrical interpretations of osmosis had been put forward by several researchers before Graham. Dutrochet had suggested an electrical interpretation in 1826 and he did not entirely reject such a view in his final discussion of osmosis in 1837, when he argued that osmosis was caused by three affinities: the affinities of the two liquids for each other and for

82. R. J. H. Dutrochet, op.cit. (53) pp 86-99.

83. A. C. Becquerel, Traité Expérimental de l'Électricité et du Magnétisme Vol.4 (Paris, 1836) 192-202.

Antoine César Becquerel (1788-1878) was an experimental physicist who was particularly interested in electrochemistry; his explanation of electrochemical decomposition was similar to that given by Ampère. Becquerel became Professor of Physics at the Muséum d'Histoire Naturelle in 1837.

84. J. W. Draper, 'A physical theory of endosmose', Amer.J.Med.Sci. 22 (August, 1838) 302-323. This paper is also found in the appendix to his book: A Treatise on the Forces which Produce the Organization of Plants, (New York, 1844) Appendix pp 57-72.

the separating partition. Dutrochet supposed that the action of these affinities could give rise to electrical currents which were somehow involved in the progress of osmosis, but he omitted to give details because he believed that the science of electricity had not developed sufficiently.⁸²

One explanation which Dutrochet did consider was A. C. Becquerel's suggestion that electrical impulsion could affect the process of osmosis. Becquerel accepted the theory of Magnus, which stated that, when water and brine were separated by a membrane, water was preferentially absorbed; Becquerel added that electricity played a secondary role in this process.⁸³ From the theory of two electricities brine took positive electricity and water, negative electricity. The recomposition of the two electricities took place via the solid membrane. The positive current, which was known to be superior in overcoming obstacles, made the poor conductor water travel more rapidly towards brine enhancing the endosmose. This mechanism was ^{sometimes} reversed when a membrane separated water from an acid. The acid took positive electricity and the water negative electricity and as a result the dominant electric current was from water to acid. Becquerel recognised that this was not generally true, the endosmose could be from acid to water in opposition to the electrical impulsion, so he gave electrical impulsion a secondary role in osmosis. Dutrochet was impressed by Becquerel's reasoning on the role of electricity in osmosis but he was critical of certain details. For example Dutrochet noted that Becquerel had considered that electric currents originated from the affinity between two liquids but he had neglected to mention the possibility that electric currents might be formed between the membrane and each liquid and therefore this led to some obscurity in Becquerel's electrical interpretations.

In 1838, J. W. Draper commented that the first investigators who saw osmosis as an electrical action were not far wrong. He believed that endosmose was a manifestation of capillary action and this in turn was an electrostatic phenomenon.⁸⁴

Graham's electrochemical theory of osmose was based on an analogy

85. Robert Porrett, 'Curious galvanic arrangements', Ann.Phil. 8 (1816) 74-76. Porrett was chief clerk in the Ordnance Department of the Royal Mint; he discovered electrofiltration in 1815. Wollaston had previously observed the separation of sodium hydroxide from a weak solution of sodium chloride, when the former crossed a bladder proceeding from the negative to the positive pole. Wollaston, 'On the agency of electricity on animal secretions', Phil.Mag. 1 Ser. 33 (1809) 488-490.
86. F. F. Reuss apparently discovered electrical osmose in 1807. See Partington, History of Chemistry 4 (1964) 737. An account of his discoveries is also given in a review article written in: Ed.Med. and Surg.J. 30 (1828) 222, which would have been available to Graham, but he never referred to Reuss. The article was abstracted from: Commentationes Soc. Physico Medico Mosquensem, II (1821) ii 327, which contained a paper read by Reuss to the Physico-Medical Society of Moscow in October 1817. Here Reuss referred to the power of galvanic electricity to move water from the positive to the negative pole. He observed particles of copper oxide travelling in water to the negative pole from the positive copper pole. The phenomenon was seen much more clearly when two platinum wires in water were sandwiched between two glass plates; the water travelled from the \oplus to \ominus wire and particles of chalk were seen to stream in this direction and were then trapped on the glass. He also showed that water moved from a \oplus to a \ominus platinum wire when the wires were placed into two tubes of water dipping into clay or into a U tube containing sand inside with water on top.
For further experiments on electrical osmose, see F. Raoult, 'Cause of electric endosmose', Comptes Rendus. 36 (1853) 826-830.
87. G. Wiedemann, op.cit. (36).
88. J. Poiseuille, 'Experimental researches on the movement of liquids in tubes of very small diameter', Comptes Rendus 11 (1840) 961-7, 1041-1050 and 'Report on Poiseuille's memoir', Ann.de Ch. 3 Ser. 7 (1843) 50-74.
89. F. Verdet, 'Extract from Wiedemann's memoir', Ann.de Ch. 3 Ser. 52 (1858) 224-250.
90. The British and Foreign Medical Review, 15 (January 15th 1855), page 102.
91. M. L'Hermite, 'Researches on endosmose', Ann.de Ch. 2 Ser. 43 (1855) 420-431; see also his shorter notes in Comptes.Rendus. 39 (1854) 1177-1180 and in Phil.Mag. 4 Ser. 9 (1855) 544-546.
In another account, which is very similar, L'Hermite discusses Matteucci's researches, repeating a misquotation given in the faulty French translation of Matteucci's lectures. See L'Hermite, Ann.des Sciences Nat. Parties Botanique. 4 Ser. 3 (1855) 73-84, also see the reply from Matteucci on p. 388 of the same journal.
L'Hermite adds the point "one sees opposition between Graham and Matteucci; for Graham there is no endosmose without decomposition of the membrane and for Matteucci when putrefaction occurs there is no endosmose." page 74. The only information I can find regarding L'Hermite is that he was a Licentiate of Sciences and a Member of the Pharmaceutical Society of Emulation. Sturgeon Annals of Electricity and Magnetism 7 (1841) 417 (from J.de Pharm.) 'Notice on the indication of capillarity of some liquids'.

between ordinary osmose and Porrett's electrofiltration or 'voltaic endosmose' as Graham referred to it. Porrett had observed the flow of water through a bladder, or a filter paper coated with coagulated albumen, from the side of the voltaic cell containing the positive wire to the negative wire.⁸⁵ This phenomenon had also been discovered independently in 1807 by F. F. Reuss⁸⁶; but Graham's attention was particularly drawn to voltaic endosmose by the work of Georg Wiedemann in 1852. Wiedemann had shown that the volume of liquid transferred in voltaic endosmose was directly proportional to the current intensity.⁸⁷ He pointed out that this was analogous to the pressure flow of liquids in capillary tubes which had been investigated by Poiseuille.⁸⁸ Graham related the volume of liquid transferred in ordinary osmose to the degree of chemical action on the membrane which was analogous to current intensity. Also, in his first experiments on osmosis, Graham used porous earthenware pots and here he was presumably following Wiedemann's example.

Graham's electrochemical theory of osmose was not well-received, but his experimental results were accepted as a valuable contribution to the study of osmose. F. Verdet in a translation of Wiedemann's second paper on electrical osmose wrote of Graham's "rather complicated explanation,"⁸⁹ referring readers to the original paper. The reviewer of Graham's paper in the British and Foreign Medical Review commented that there was still no satisfactory theory of endosmose.⁹⁰

A more serious criticism of Graham's electrochemical theory was made by Michel L'Hermite in 1855.⁹¹ He argued that Graham was incorrect to attribute osmose to a chemical decomposition of the membrane or porous pot. He chose the example of oxalic acid solution which passed more rapidly than water through a membrane, giving an osmose from oxalic acid solution to water. From Graham's arguments, oxalic acid should decompose a membrane more rapidly than water, but L'Hermite found that, when a membrane was kept separately for three months in these two liquids, the membrane decomposed in water, but not in oxalic acid. He even went as far as

recommending anatomists to store organic tissues in oxalic acid solution rather than in water because they would keep better. L'Hermite also attacked Graham's generalisation that the progression of osmose was from acid to base. Graham had suggested that in osmosis, an acid moved to water (the water acting as a base); and water moved to a base because water behaved as an acid, relatively speaking. The surfaces of a membrane differed, according to Graham, one surface being acidic and the other basic and the osmose was always directed from the acidic surface to the basic surface. L'Hermite suggested that Graham had been too hasty in his generalisation and to prove this he quoted a contradictory experiment. He enclosed a solution of sulphuric acid dissolved in alcohol, in an osmometer closed with gold beater's skin, which was dipped into a solution of caustic potash in water. The osmose was from base to acid and not as Graham would have predicted from acid to base. L'Hermite explained that he believed that acids, in general, moved across membranes more quickly than bases because acids moistened membranes better.

L'Hermite maintained that osmose was due to affinity if this could be extended to include capillary action; essentially this was an extension of Poisson's theory of capillary action. The liquid which moistened the partition most successfully, filtered through more easily and gave the osmose current. He disagreed with both Dutrochet and Graham on capillary attraction by insisting that there were considerable differences between membranes, containing a huge number of fine pores, and glass tubes in which differences in the capillary rises were not pronounced. He assumed that a membrane acted like a solvent, preferentially dissolving the liquid which produced the osmose current. In his 'solution theory of membrane action' L'Hermite compared a membrane to the central liquid in a column of three immiscible liquids. For example with ether, water and chloroform; the water was analogous to the membrane. Ether, unlike chloroform, was slightly soluble in water, and therefore ether passed through water and dissolved in the chloroform layer, thus completing the analogy with osmose.

92. E. Doumer, M.D.Thesis Bordeaux (1881), op.cit. (39), pp 158-159.
93. Henri Milne-Edwards, (1800-1885), studied medicine in Paris. He undertook a vast programme of research on invertebrates, particularly crustaceans, gaining the prize in experimental physiology from the French Academy in 1828. In 1832, he became Professor of Hygiene and Natural History at the École Centrale; he was elected to the Zoology Section of the French Academy in 1838; in 1841, he became Professor of Entomology, etc. at the Museum of Natural History. In 1861 he transferred to Mammalogy and at the same time became Professor and later Dean of the Faculty of Sciences. He gathered his lectures into a 14-volume publication: Leçons Sur la Physiologie et l'Anatomie Comparée de l'Homme et des Animaux, written over a period of 20 years. (Paris, 1857-1881). In 1858, he published his law of the division of labour within organisms. He was for many years the leading French naturalist.
94. H. Milne-Edwards, Leçons sur la Physiologie et l'Anatomie Comparée de l'Homme et des Animaux, Vol. 5 (Paris, 1859) 37-41, 101-175.
95. H. Milne-Edwards, *ibid.* p 117.
96. A. Cima, 'On the evaporation and the transudation of liquids across animal membranes', [1851]. Mém. de l'Académie de Turin, 13 (1853) 267-288.

Another cogent objection to Graham's conclusion that acids travelled towards the basic side of a membrane was raised much later by Doumer.⁹² How, he asked, could Graham explain the observation of Magnus that there was an osmose through a membrane from a dilute solution to a more concentrated solution of the same solute, potassium acetate? Clearly, it was impossible to regard dilute and concentrated solutions of the same chemical as relatively acidic or basic.

In 1859, the French Zoologist, Henri Milne-Edwards⁹³ published a major survey of osmosis in which he reviewed all the previous studies made in this field.⁹⁴ He wrote that: "the more recent researches of Brücke, Ludwig and Graham have provided me with the principal views touching the play of forces which coincide with capillary attraction, adhesion or affinity of heterogeneous liquids to produce the effects which accompany endosmose. I should add however that Graham does not seem to take enough account of the role of capillarity in the production of these phenomena, and I would not want to adopt his theoretical views relative to the entirely chemical origin of osmotic force."⁹⁵

So while Milne-Edwards accepted Graham's interpretation of osmose as a process of the exchange of a diffusing salt for an osmose of water, he believed that Graham had neglected the phenomena of capillary attraction in membranes. For example he mentioned that Cima had noticed that the forced filtration of different liquids through membranes took place in different times; the liquids in order of decreasing filtration speed were ammonia, water, brine and alcohol.⁹⁶ Milne-Edwards explained these differences by saying that there were variations in the extension of the membrane which affected both capillary attraction and liquid absorption. He used this explanation to interpret successfully Graham's discovery that trace impurities could influence osmose. Graham had observed that a small amount of hydrochloric acid actually increased the osmose when it was added to sodium chloride solution instead of reversing it which would happen if hydrochloric acid was used on its own. Milne-Edwards suggested that

97. H. Milne-Edwards, *op.cit.* (94), p 154.

98. *ibid.* p 157.

hydrochloric acid diminished the contraction which salt would normally produce on organic tissues. The flow of water was therefore made easier giving a greater osmose. Conversely, when a little sodium chloride was added to a solution of sodium carbonate there was a reduction in the osmose because the added salt caused a contraction of the membrane tissues.

Graham was also taken to task for neglecting to point out the variations in the endosmotic equivalents when membranes of differing hydrostatic pressure were used. The hydrostatic pressure, or the resistance of a membrane, was the time which elapsed between the fall of two successive drops of distilled water from the membrane surface. Milne-Edwards noted that Graham had used a 10% solution of sodium carbonate in two albumen osmometers of resistance 12 and 6 respectively. In the first case the same quantity of salt was replaced by 14 volumes of water and in the second case it was replaced by 8 volumes of water.⁹⁷ A further shortcoming, he pointed out, was Graham's failure to comment on the relative fall in the diffusion product, compared with the received osmose, when the solution concentration was increased. Milne-Edwards wrote:- "I am astonished that M. Graham has not been struck by it, for it is obvious in several series of results contained in the work of this useful chemist. I will limit myself to quoting one example. By using a solution of magnesium sulphate of varying concentrations, one part of this salt escapes while the instrument gains:- 5.16 volumes of water for a 2% solution, 5.76 volumes for a 5% solution, 6.01 volumes for a 10% solution and 6.57 volumes for a 20% solution."⁹⁸ He appended the interpretation which Graham should have realised. During the osmose there was an attack of the membrane by the active salt, which widened the capillary passages. This gave an increase in the diffusate compared with the osmose as the solutions were made more concentrated. Certainly, Graham's experimental results supported this conclusion.

Finally Milne-Edwards considered Graham's electrochemical theory:-

"Graham, one of the most distinguished English chemists, after having made

99. *ibid.* pp 170-171.

a detailed study of these questions has even been led to think that the play of affinities was an essential condition for the development of osmotic power. This opinion does not appear to be founded to me; but it seems to have some connection with the great display of force and the realisation of some chemical work." ⁹⁹ He thought Graham had shown that there was a certain coincidence between the development of osmotic power and the attack on the partition used. However, he complained that Graham had not adequately explained the relation between the different chemical actions on the two surfaces of the membrane and the play of the electrical forces.

Graham's complete table of the comparative osmotic powers of different substances was quoted by Milne-Edwards with the comment that one could not fail to be struck by the facts that acids gave a large negative osmose and alkaline salts gave a large positive osmose whereas the more stable neutral salts gave only a small positive osmose. Clearly, Graham's experimental results were recognised to be a valuable contribution to the study of osmosis but his theoretical explanation of osmosis was unconvincing.

Milne-Edwards stated his own view of osmosis. It was the result of the physico-chemical attraction of two liquids for one another, and of the repulsive force which tended to produce the uniform diffusion of particles in solution. The inequality of exchange was determined by the relative ease of passage of the two liquids through the interstitial cavities in the partition. This passage depended upon the nature of the partition; the nature of the two liquids; and the diameter of the capillary passages. Finally, to cover all possibilities, he added that heat, electricity, and the play of chemical forces could modify the osmotic effects produced.

Graham was forced to reconsider his explanation of osmosis in response to his critics and so he continued with his experiments. He was then able to develop a new theory of osmosis and his new studies led him to the discovery of dialysis and an appreciation of the fundamental distinction between crystalloids and colloids.

100. Graham, 'On the concentration of alcohol in Sömmering's experiments', B.A. Report (Liverpool) 1854 part ii page 69, and in Researches. 551-552.

Another report which contains more information is given in The Athenaeum (October 7th 1854) p 1208. Graham's talk was given on Saturday, September 30th 1854.

101. Graham, ibid. Researches. 552.

S. T. Sömmering's work can be found in Bayerische Akademie der Wissenschaften Denkschriften, Munich iii (1811-12) 273-292, read 1809; v (1814-15) 137-150 and also in 'Ueber das Verdünsten des Weingeists durch thierische Häute und durch Kautschuck', Ann. der Physik. 61 (1819) 104-110.

S. T. Sömmering (1755-1830) was Professor of Surgery and Anatomy in Cassel (1779); Professor of Medicine in Mainz (1784-1795) and he was later a physician in Frankfurt and Munich (1804-1820). See Partington, History of Chemistry. 4 (London, 1964) 651.

In September 1854, Graham described his latest researches to the meeting of the British Association at Liverpool.¹⁰⁰ He had been investigating the experiments of Sömmering, who, in 1809, had found that a bladder bag filled with dilute alcohol and suspended in air would decrease in volume. Apparently this phenomenon was caused by water passing outwards through the membrane and evaporating to leave behind a more concentrated solution of alcohol. This was a curious observation because only water had escaped from the membrane, and not the more volatile alcohol. The membrane clearly interfered with the normal diffusion processes of water and alcohol. Graham confirmed this fact and then he compared the diffusion of alcohol and salt from aqueous solutions through a bladder into water. With salt, the diffusion increased as the percentage of salt in the solution was raised, but, surprisingly, with alcohol there was no increase in the alcohol diffusing out when the percentage of the alcohol in water was raised from 5 to 20%.

Graham varied Sömmering's original experiment. Sömmering had mentioned that the action of the membrane was improved by coating it with isinglass (pure gelatine). Graham dispensed with the bladder and painted cotton calico with an isinglass solution. The new gelatine septum was just as effective as a bladder for concentrating alcohol. In order to elucidate the process, he simplified the technique by placing some dry gelatine in an alcoholic solution. He found that the weight of the gelatine rose by 11% and the remaining solution was richer in alcohol. He wrote: "there can be no doubt, therefore, that gelatin per se separates water from alcohol, and the colliferous tissues possess the same property."¹⁰¹ This was the important clue for his new explanation of osmosis and this can be detected in the following report of his talk:- "The phenomenon indicates a sifting or separating power to reside in the membrane and has introduced a third element in addition to diffusion and osmose into the discussion of porous septa. The author believed Sömmering's experiment was an instance of arrested diffusion when more than 5% alcohol was present. The action

102. Graham, op.cit. (100), The Athenaeum. (1854) p 1208.

103. Graham, 'Liquid diffusion applied to analysis', received May 8th 1861 and read on June 13th 1861, Phil.Trans. 151 (1861) pp 183-224 and in Researches. 552-600, see pp 598-599.

has some resemblance to the separating and secreting power of cells in the living organism and may prove of great physiological interest particularly if the action should be found to extend to albumen and other organic substances." 102

The development of Graham's researches appears to have been delayed by his appointment as Master of the Mint in April 1855. However, by 1857, his notebooks show that he was again examining osmose and in 1861 he published a short final note containing his new views on the mechanism of osmose. This note appeared at the end of his paper: 'Liquid diffusion applied to analysis'.

Graham now emphasised the importance of changes in hydration during osmosis. He explained that the water movement in osmose: "is an affair of hydration and dehydration in the substance of the membrane or other colloid septum, and that the diffusion of the saline solution placed within the osmometer has little or nothing to do with the osmotic result, otherwise than it affects the state of hydration of the septum." 103

Colloids like gum gave a particularly large osmose and yet they did not diffuse except in trace quantities through highly hydrated membranes. The degree of hydration of a membrane was markedly influenced by the liquids which were in contact with it. A membrane placed in pure water, hydrated and swelled much more than it did when placed in a neutral salt solution. Therefore, with a neutral salt solution inside a membrane osmometer, dipping into pure water, the outer surface in contact with water became much more hydrated than the inner surface. The pure water swelled the outer surface by a considerable degree of hydration, whereas the inner surface was contracted by the salt solution. As water penetrated from the outer to the inner surface, it received a check because the hydration of the gelatine had been lowered. Here the salt had set free water for the osmose and had left less-hydrated gelatine. The salt solution in the membrane 'catalysed' the decomposition of the more hydrated gelatine; indeed the diffusion of salt through the membrane

104. In a letter to his sister Miss Margaret Graham dated May 16th 1861, Graham says: "I was able to send in a paper to the R.S. last week, [op.cit. 103], which contains two or three years work, and has cost no small effort to get up amid my other distractions. I need only describe it as 98 folio pages in length. I expect to hand in two short ones, all but ready, before the recess. This is an unspeakable relief to me for nothing depresses me more than to fall behind in my scientific career, consequently upon my official engagements; but I hope to recover in some considerable degree my place in the race by these papers."

This letter is quoted in R. A. Smith, Life and Works of Thomas Graham (1884), p.52. Only one, of the 'two' short papers referred to, was presented to the R.S.; it was: 'On the capillary transpiration of liquids in relation to chemical composition', Phil.Trans. 151 (1861) 373-386, received on June 20th 1861 and read on June 20th 1861. See also Researches. 600-617. The next paper published by Graham was 'On the molecular mobility of gases', received by the R.S. on May 7th 1863. It would appear, therefore, that this was not the 'short' paper promised for the R.S. in 1861, and therefore it is possible that the MS. paper in the Wellcome library (undated) and entitled 'Of gelous hydration' was written at this time, but remained unread, and unpublished. A possible alternative view, however, is that Graham rejected his paper 'Of gelous hydration' and appended a short summary of his views on osmose at the end of his paper 'On liquid diffusion applied to analysis'. This alternative would mean that Graham delayed the publication of his paper 'On the molecular mobility of gases', for almost two years, from May 1861 to May 1863. The latter paper originally contained Graham's 'speculative ideas respecting the constitution of matter'. This latter view may be more likely, because Graham wrote to Schönbein, on January 9th 1862 saying that: "I have been clearing off some of my old work lately, and besides a paper on Liquid Transpiration, of which you may have observed a preliminary notice in Comptes Rendus., I have an investigation closed on gas diffusion." MS. letter 483 Graham to Schönbein, Universitäts Bibliothek, Basel.

105. Graham, MS. notebook 24, Wellcome No. 2575 (old no.3202) labelled by Graham, Book No.5. See entry 'Experiments on osmose' circa. June 1864.

106. Graham, Wellcome manuscripts No.2580 (old no.3390). MS. No.6 of an unbound collection with the title 'Of gelous hydration' (undated 9 11.).

tended to reduce the osmose by equalising the state of hydration of the gelatine. Colloids such as gum did not suffer from this disadvantage because they did not penetrate into the membrane.

The hydration of membranes could be increased still further by using very dilute acids or alkalis. These chemicals were known to swell protein substances, such as fibrin, albumen and membranes, to a greater extent than pure water thus giving more hydrated colloids. The highly hydrated septa produced by very dilute acids or alkalis were even more sensitive in osmose experiments; the water in these hydrates was held by a very feeble force and this water could be increased or decreased very easily by catalysis. Graham did not give details of these changes or of the catalytic process. However he subscribed to Liebig's view of catalysis as the transfer of molecular motion. Presumably the molecular motion of diffusing saline particles, or the increased molecular motion resulting from the decomposition of unstable salts, was transmitted to a gelatinous hydrate causing it to dissociate into a lower gelatinous hydrate, thereby setting water free for osmose.

Graham may have planned to complete a more-detailed paper on osmose, later in 1861, but it was not published.¹⁰⁴ This paper: 'Of gelous hydration' is amongst the Wellcome manuscripts. The reason for its non-publication is perhaps that Graham was still continuing with his investigations into osmose; his notebooks show that he was still working on osmose in 1864.¹⁰⁵ Alternatively, he may have lacked the time to finish the paper. During 1861, he was heavily-engaged in his work at the Royal Mint arising from the introduction of the bronze-coinage.

In his unpublished paper,¹⁰⁶ Graham began by discussing how organic substances were converted into the 'gelous condition' during the formation of jellies. An organic colloid first combined weakly with water producing a liquid which gradually solidified to give a jelly. The process by which a liquid changed into a solid jelly did not just involve a change in the physical condition; it changed the chemical nature of the substance.

107. *ibid.*

108. *ibid.*

109. Graham, *ibid.* .

It seemed that the degree of hydration was probably lowered in the transformation of a liquid into a solid jelly. The definite capacity which gelatine had for taking up water and becoming more hydrated was a manifestation of chemical affinity and not of mere solvent attraction. The evidence for this view was that gelatine removed water from 46% alcohol, which was "a definite chemical combination $C_2H_6O + 3H_2O$,"¹⁰⁷ so chemical affinity must be effective even in the feeble hydration of gelatine. Graham explained his view of the role of chemical affinity in hydration when he wrote that: "gelous hydration does not appear to be regulated by obviously definite or atomic proportions. On the contrary, steps of progression or limits of any kind are not discernible in the gelous hydration; the proportions of 'gelogenous' water capable of uniting with a 'geliform' substance may be, it appears, indefinitely small or indefinitely great. With a certain increase in the proportion of water the combination may indeed become liquid and lose all gelous aggregation, as happens with animal size, starches and other soluble 'gelides'. With smaller proportions of water the ready divisibility and tremulous character of the jelly may disappear and be replaced by toughness and great aggregation and ultimately by a vitreous brittleness as with size and fibrin."¹⁰⁸

The true basis of osmose was in Graham's opinion to be found in the influence of minute quantities of acid and saline substances on gelous hydration. When fibrin and other protein substances were allowed to remain in pure water, they increased in weight until eventually they might pass into solution. Fibrin appeared to be passing through a series of molecular changes, "attended with increasing hydratability and terminating in perfect liquefaction."¹⁰⁹ The progress of this hydration was stopped at an early stage if the water contained the smallest trace of mineral impurities, for example it could be halted by the impurities found in river or well water. Conversely, minute proportions of dilute acids, particularly acetic, hydrochloric, or nitric acids, produced a marked increase in the degree of hydration of fibrin. To demonstrate these facts Graham

110. Graham, *ibid.* It is interesting to note that Bouchardat and Sandras had observed that water, weakly acidified with hydrochloric acid, made fibrin, albumen, casein, gluten and gelatinised animal tissues swell so that they became translucent and sometimes even dissolved. Although fibrin expanded greatly it did not dissolve completely. See 'Report on a memoir by MM. Sandras and Bouchardat by J. B. Dumas,' Comptes.Rendus. 16 (1843) 254.
111. Graham, *op.cit.* (106).
112. Graham, Wellcome Manuscript notebook 21, No.2572 (old no.3197). This notebook was labelled by Graham: 'Experiments on osmotic force' - Notebook No.2 (overwritten as No.6), December 1859 - February 1864. 1859-60 -1862 -1863 -1864
The experiments referred to are undated but they precede a new section, entitled 'Experiments on colloids' 1863 dated 31st August 1863. Therefore, it is probable that the experiments on bladders were carried out in 1862 or 1863.

left gaps in his 'gelous hydration' manuscript for experimental figures which he hoped to fill in later. He suggested that there was no reason to suppose that the acids actually combined with the fibrin. He explained: "it is an action of contact like that of mineral acids upon starch, leading to the conversion of that substance into dextrine." ¹¹⁰

The hydration of fibrin was also promoted by alkalies such as the carbonate of potash; but salts in general had a "retrogressive action upon highly hydrated fibrin. They diminish the hydratability and appear to reverse the direction of the molecular changes in the fibrin." ¹¹¹ Very small amounts of salt were remarkably effective in reducing hydration, for example even as little as 0.001 g. of sulphate of potash acted on 5 g. fibrin reducing its hydration. He also noticed that fibrin jelly shrivelled up in the presence of concentrated acids.

The experiments which supported these views of gelous hydration were probably carried out in 1862; they appear in Graham's laboratory notebook under the entry: "Action of dilute acids and alkalis on bladder." ¹¹² He left 20 g. of ox-bladder in different solutions for a day and then recorded the final weight of the bladder. His results were:-

Bladder left in:-	<u>Water</u>	<u>0.25% potassium carbonate</u>	<u>0.25% HCl</u>	<u>0.25% oxalic acid</u>	<u>1% solutions of acetic, formic, citric, tartaric or oxalic acids</u>
Average weight in grams after 1 day:-	22.5	27.7	34.7	45.8	38 to 45

In all cases the bladder had swollen and increased in weight in the dilute solutions of acids and alkalis to a greater extent than in pure water. He then allowed these swollen bladders to diffuse for one day in pure distilled water, followed by a final day in a 0.25% solution of potassium sulphate. His results were as follows:-

113. Graham, op.cit. (106).

<u>Bladder swollen with:</u>	<u>Original weight of the bladder</u>	<u>Weight after 1 day in distilled water</u>	<u>Weight after 1 day in 0.25% potassium sulphate</u>
0.25% HCl	100 g	177 g	91 g
0.25% oxalic acid	100 g	145 g	79 g
0.25% potassium carbonate	100 g	118 g	95 g

Bladders treated with dilute acids increased considerably in their hydratability when left in pure water; a smaller increase was observed for bladders treated with a dilute solution of the alkali, potassium carbonate, and there was a marked decrease in hydration when all of these bladders were left in neutral saline solutions, such as potassium sulphate or sodium chloride. Graham found when he left 20 g. of bladder in solutions of common salt of different strengths that the change in weight was negligible and any increases could be accounted for by the diffusion of salt into the bladder. His results were:-

<u>Solution used:</u>	Water	1% NaCl	2% NaCl	5% NaCl	10% NaCl	20% NaCl
<u>Weight in grams of bladder after 1 day:</u>	21.25	20.70	21.05	21.90	22.15	20.05

These results show that dilute solutions of NaCl do dehydrate the bladder slightly. Analysis of a bladder revealed that it contained 86.4% water and 13.6% of dry organic matter.

Graham summarised his new views on osmosis at the end of his paper on gelous hydration:- "The osmose of Dutrochet appears to be the result on the jelly of these contrary actions of water and a saline solution on the opposite sides of a membrane or other gelous septum. The pure water on the one side tending to hydrate (increase the hydratability) and the salt on the other tending to dehydrate (diminish the hydratability of) the substance of the septum." ¹¹³

Graham's revised view of osmosis was well-received. Liebig commented that the explanation given by Graham, of the volume change of liquids in the

114. J. Liebig, Liebig Ann. 121 (1862) 78-82.
Liebig had added some notes here, entitled 'On the theory of osmose',
to the translation of Graham's paper 'Liquid diffusion applied to
analysis'.

115. Liebig, *ibid.*

116. Graham also wrote in his preface to, Chemical Reports and Memoirs
of the Cavendish Society (London, 1848): "The attention of chemists
and physiologists has lately been recalled to the subject of endos-
mose by the researches of Liebig on the motion of the juices in the
animal body."

process of diffusion of salt solutions through porous partitions, was identical to his own explanation.¹¹⁴ He recalled that in his book, On the Motion of the Juices, he had concluded that the volume change of two liquids, and their mixture through a partition, were two processes which were not directly related. The diffusion of salt was the result of the affinity between the salt particles and the liquid particles; whereas the volume change was caused by the unequal attraction between the partition and the two liquids on different sides. He compared Graham's explanation with his own, juxtaposing the two accounts to remove any doubt about their agreement. Liebig explained his position by saying that osmose was the result of an unequal hydration, or attraction, of the membrane. When a tube of water was closed with a bladder and placed in salt water or alcohol, the side of the bladder in contact with the salt or alcohol was altered in quality. As the salt or alcohol became mixed with water in the open pores of the bladder, it developed a reduced power for water absorption. Therefore, water flowed to the alcohol, or salt, side of the bladder. The shrinkage of the salt side of the bladder caused a state of unequal contraction on the two sides of the bladder, and gave rise to a continual motion of water towards salt water until concentration differences were equalised out by the diffusion of salt.

Generously, Liebig remarked "there can of course be no question of a quarrel about priority between myself and my friend Graham. I am completely sure that he arrived at his explanation independently and without knowing of my work."¹¹⁵ Graham clearly did know of Liebig's work. It was mentioned in Vierordt's article and also by Graham, himself, in his British Association lecture of 1852; furthermore, Graham possessed a copy of Liebig's book, On the Motion of the Juices, in his own library.¹¹⁶

However, the views of Liebig and Graham were not identical. Graham explained diffusion by repulsive rather than attractive forces. Although Graham shared Liebig's view of hydration and dehydration of membranes, he did not accept the unequal contraction mechanism; instead Graham regarded

117. H. Milne-Edwards, Leçons sur la Physiologie et l'Anatomie etc. Vol.7 (Paris, 1862) 461-462.

118. R. Buchheim, 'Beitrage zur lehre von der Endosmose', Archiv für Physiologische Heilkunde 12 (1853) 217-243. For a summary of Buchheim's osmose theory see: H. Milne-Edwards, Leçons sur la Physiologie et l'Anatomie etc. Vol.5 (Paris, 1859) 121-122. Rudolph Buchheim, (1820-1879), was a leading German pharmacologist. He studied medicine at Dresden (1838-1841) and continued his studies at Leipzig, where he became an assistant to the physiological chemists, C. G. Lehmann and E. H. Weber, who introduced him to the chemical aspects of medicine. Buchheim obtained his M.D. in 1845 with a dissertation on the behaviour of egg white, pepsin and mucin towards different reagents and also with a study of the elimination of ferrous sulphate mixed with protein. He became Professor of Pharmacology and the Practice of Medicine at Dorpat in Estonia (1847) and remained there until 1866, when he moved to Giessen.

See 'Rudolph Buchheim and the beginning of pharmacology as a Science', by E.R.Habermann, Annual Review of Pharmacology 14 (1974) 1-14.

Buchheim's work is referred to by his teacher, C. G. Lehmann, in his textbook: Physiological Chemistry, translated from the second edition, for the Cavendish Society, London (1851-4). See Volume 3 (1854) p 262. Presumably, Graham who was consulted during the translation, by G. E. Day the translator, would be familiar with this work.

In his paper on the contributions to the theory of endosmose (referred to above), Buchheim recognised the importance of Graham's work on liquid diffusion (p 218). He emphasised that it was necessary to distinguish between the processes of solution and hydrate formation, as Graham had shown. Gay-Lussac had originated the idea that heat was evolved when substances were condensed, for example in hydration, a process of chemical combination. Conversely, heat was absorbed in expansion, for example during the diffusion of a salt through a liquid (p 218). The affinity of salts for water had been demonstrated by both Carl Schmidt, (Charakteristik der Cholera (Mitau, 1846) pp 22-28), and Schwede ('Experiments on hygroscopicity', Inaugural dissertation, Dorpat 1851). Schwede found that dry salts possessed differing powers of absorption for water and Buchheim noted that the salts which diffused most rapidly were those which attracted water most strongly (pp 221-225). He did not think that Brücke's theory of endosmose had been confirmed by Ludwig (pp 226-229). Thus, Buchheim put forward his own explanation of endosmose. He believed that water attracted salt and membranes by chemical affinity and not by adhesion (p 229). Salt water separated, by a bladder, from pure water gave an endosmose. He explained that salt, by its attraction for water, removed hydrated water from the bladder material. The bladder became rehydrated, by attracting water from the side facing pure water, thus giving rise to the endosmose. Salt slowly diffused through the capillary channels. This theory was described on (pp 233-234) of Buchheim's paper.

Interestingly, Wm. Sharpey, Prof. of Physiology at University College and Graham's colleague, possessed a copy of the journal containing this article.

osmose as the result of the dissociation of water from molecules of gelatinous hydrates. The feeble force binding gelatinous water could be easily overcome by molecular motions transmitted from the diffusing salt particles. Graham preferred this view instead of one postulating unequal contractions of the membrane. It would seem that Graham's hydration mechanism had its origin in his studies of Sömmerring's experiment; although, Liebig's researches cannot be entirely dismissed as a guiding influence.

The question of the originality of Graham's final explanation of osmose was also raised by Henri Milne-Edwards in 1862 when he wrote:- "According to Graham, the progression of a liquid or any crystalline body in jelly or in the thickness of a non-porous membrane arises from a series of chemical reactions analogous to those which occur in cementation. His views on this subject do not appear to differ from those of Buchheim of Dorpat. I would add that the non-penetration of colloids in a jelly or in the substance of a dialytic sheet of the same nature would explain itself, because these bodies cannot decompose the hydrates of bodies of the same kind, whilst crystalloids can seize water of combination and spread themselves." ¹¹⁷

Rudolf Buchheim ¹¹⁸ had come closer than Liebig to an anticipation of Graham's explanation when he discussed osmosis in 1853. Buchheim distinguished between the solid parts and the porous or hollow parts in the tissue of an osmotic membrane. He thought that the imbibition of liquids was not a phenomenon of capillarity. Rather it was the result of the chemical combination between water and the constituent substance of the membrane tissue. The molecules of the hydrate, thus formed, at the surface in contact with the saline solution, would be decomposed. The membrane hydrate would give up part or all of its constituent water to the salt which was avid for water. The decomposed hydrate would reconstitute at once by combining with molecules of water drawn from the layer of hydrate underneath. This process was continued by a succession of such

119. See the article by Karl Sollner, 'The basic electrochemistry of liquid membranes', Historical review in: 'Diffusion Processes' from The Proceedings of the Thomas Graham Memorial Symposium held at Strathclyde University, by J. N. Sherwood et al., published by Gordon and Breach, London 1971, in 2 volumes.

120. Graham, Wellcome Manuscript notebooks. Notebook No.17, December 1857 - February 1858, No.2568 (old no.3193).

changes starting from the surface of the membrane in contact with salt solution and proceeding through to the surface in contact with water. This latter surface would then rehydrate at the expense of the external water. Therefore, a current of water or an osmose would be established. The water would pass through the substance of the membrane, from the water side, into the saline solution. An opposite current also occurred as the salt molecules diffused through the pores of the membrane. Buchheim explained that this diffusion current existed because salt, unlike water, could not form a chemical combination with the membrane tissue.

Whether Graham knew about Buchheim's explanation of osmose is uncertain but there is a remarkable resemblance between their explanations, except that Graham does not seem to refer to pores or passages for salt diffusion.

Even if Graham's ultimate explanation of osmose was not particularly novel his experimental findings in the fields of liquid diffusion and osmose were significant; the development of this work led to the important discoveries of dialysis and colloids. The nature of osmose was later shown to be a complex problem of the diffusion of electrolytes, which gave rise to electromotive forces, along with an accompanying osmotic flow of solvent. To understand these problems of osmosis required the development of the physical chemistry of electrolyte solutions and a theory of ionisation.¹¹⁹ To simplify the study of osmosis, not only was the advancement of chemical theory required, but also the discovery of semi-permeable membranes. These membranes were introduced in 1867 by Traube as a direct result of further discoveries which were made by Graham: dialysis and colloids.

The keynote to Graham's work on colloids is the discovery of dialysis, which arose from his extended studies of osmosis. His notebooks show that between December 1857 and February 1858 he investigated the use of parchment paper as a partition for osmometers and found it was a very suitable substance.¹²⁰ Parchment paper had been patented in 1853 by W. E. Gaine

121. Rev. J. Barlow, 'On some modifications of wood fibre and their applications', read April 3rd 1857, Proc. of the R.I. 2 (1854-1858) 409-413.
122. A. W. Hofmann, 'Report on vegetable parchment', August 12th 1858, for Thomas De La Rue & Co. Pharm.J. 18 (1858-9) 272-278, see p 273.
123. Graham, Wellcome Manuscript, No.2571 (old no.3196)
Notebook 20, labelled Notebook III by Graham, Experiments 'on osmotic force' September 6th 1859 - December 16th 1859.
See the experiments made between December 12th and 16th 1859.

and it was first made commercially, in 1857, by Thomas De La Rue and Company. It was prepared by drawing unsized paper through a mixture, of two parts of concentrated sulphuric acid and one part of water, and then immediately washing it to remove all the acid. The properties of this paper were described in 1857, by Barlow at the Royal Institution; he reported that it absorbed water without allowing the water to percolate through it.¹²¹ In 1858, A. W. Hofmann observed that water could cross parchment paper "like an animal membrane by endosmotic action."¹²²

Graham compared a number of different osmometers at the end of 1859 and found that most of them were able to concentrate alcoholic solutions by the 'sifting' power of the septum (porous partition). He used osmometers with partitions made of calico coated with one of the following substances: mucus, gum tragacanth, albumen, and starch; and he also used parchment paper partitions. The latter proved to be the best material for partitions because it gave the greatest osmose and diffusate.¹²³ The parchment paper was either tied to the base of a small bell jar or to a wooden hoop and it was used both for studying osmose and particularly for Graham's new dialysis experiments.

Dialysis is the separation, by diffusion through a gelatinous partition, of small highly-diffusive molecules from slowly-diffusing molecules of much larger molecular mass. The origins of dialysis in Graham's work can be traced back to his studies of 1849 on liquid diffusion when he recognised the existence of considerable differences in the diffusive mobility of substances. By liquid diffusion he found that the masses in grains of different solutes, which diffused into water in the same time, were:

<u>Albumen</u>	<u>Gum Arabic</u>	<u>Cane Sugar</u>	<u>Magnesium Sulphate</u>	<u>Sodium Nitrate</u>	<u>Sodium Chloride</u>	<u>Sulphuric Acid</u>
3.08	13.24	26.21	27.42	51.56	58.68	69.32

These solutions, which contained 20 salt to 100 water, were allowed to diffuse for 8 days into water at 60.5°F. Graham commented on these results: "... the most remarkable result is the diffusion of albumen, which

124. Graham, 'On the diffusion of liquids', (1849) Researches. pp 453-454.

125. Willibald G. Schmidt, Wellcome Manuscript 1717, (from Graham's papers) "Experiments on the velocity of filtration of various liquids through animal membrane," An English translation made from Schmidt's original paper in Pogg. Ann. 89 (1856) 337-388, dated November 16th 1856. See also E. Hatschek, 'Early experiments on ultrafiltration', Nature 120 (1927) 515, on Schmidt's paper.

126. Graham, Wellcome Manuscript. op.cit. (123).

is low out of all proportion when compared with saline bodies chloride of sodium appears 20 times more diffusible than albumen ..., but the disparity is really greater; for nearly one-half of the matter which is diffused consisted of inorganic salts.... Nor does albumen impair the diffusion of salts dissolved together with it in the same solution, although the liquid retains its viscosity." ¹²⁴

The next step was to compare the rates of passage of different solutions through membranes. In 1854 Graham studied the passage of salts, acids, and alkalis through membranes in osmosis experiments but he did not extend his studies to albumen; this extension was made in 1856 by W. Schmidt and Reinhardt. Graham possessed an English translation of the latter study and so it may be inferred that he made use of their discoveries in the subsequent development of his technique of dialysis. Schmidt and Reinhardt found that solutions of sugar, or different salts, filtered through animal membrane under pressure without any change in concentration. However, this was "not so with solutions of gum arabic and albumen, which both gave a filtrate, not so concentrated as the original solution, although the solutions were filtered beforehand several times through calico and paper." ¹²⁵

Graham's notebooks show that he examined the osmose and diffusate from solutions of gum arabic and albumen in mid-October 1859; both gave a large osmose, but virtually no diffusate. On November 4th 1859, he recorded an experiment which appears to be his first example of dialysis:- "50 g. of a solution containing 5% gum and 5% cane sugar was put in it [a mucus osmometer]. The osmometer was then placed as usual in distilled water. After 4 days the diffusate was 0.990 g. consisting of sugar only." ¹²⁶. A more detailed example was recorded on November 30th 1859 in which a solution of 10% gum arabic was mixed with 1% sulphuric acid and placed in both mucus and parchment paper osmometers. The respective diffusates after one day were: 0.354 g. sulphuric acid, 0.050 g. gum; and 0.530 g. sulphuric acid, 0.065 g. gum; the osmose was 5.3 and 5.4 mm. respectively. By this technique Graham had demonstrably separated gum from sulphuric acid. He

127. Graham, Wellcome Manuscript. op.cit. (112).
H. Milne-Edwards commented on dialysis "animal membranes, in general, as well as thin sheets which form the walls of secretory cells are made of colloid materials and so the water, salts, urea and other crystalloid materials found in the blood plasma, which bathes one of the surfaces of these tissues should tend to penetrate them and expand into the liquid on the opposite side. So these substances should tend to escape from serum, whilst albumen and other colloids which accompany these matters in blood do not follow them and remain in the circulation. The separation is thus performed and Graham calls it dialysis which is very much like that which occurs in the renal glands and it appears very probable to me that the elimination of urinary principles depends on a phenomenon of a similar kind." He continued^{ly}, referring to Graham's experimental dialysis of urine and recommended it to the attention of physiologists.
See H. Milne-Edwards, Leçons sur la Physiologie et l'Anatomie.etc. (Paris, 1862) 462.
Liebig also referred to the extreme importance of dialysis in the separation of organic compounds and for the analysis of animal secretions; he quoted Graham's extraction of urea from urine and described his own extractions of creatin from meat broth and of a jelly-like mucous containing alloxan from the bowels during diarrhoea.
Liebig Ann. 121 (1862) 80-82.

128. MS. letter from Graham to Lyon Playfair, dated May 10th 1860, from Playfair MSS. collection at Imperial College Library, London - letter no.329.

continued to try out further examples of dialysis, separating sulphuric acid from indigo; arsenious acid from gum or albumen; sodium hydroxide from albumen; and on January 28th 1860 he separated urea from urine,¹²⁷ obtaining very pure white urea crystals by extracting them with alcohol. Modern experiments with dialysers for artificial kidney machines have used a technique similar to Graham's.

By March 1860 Graham was using sized paper for dialysis and in May 1860 he wrote to his former pupil, Lyon Playfair, describing his work:- "The following is an experiment in what I call 'osmolysis'. Pour in a soup plate 8 ounces of distilled water. Lay a sheet of the thinnest sized paper (foreign post) upon the surface of the water - the margin of the paper projecting all around beyond the edge of the plate. Take 4 ounces of defibrinated blood (as received from the butchers) and add to it 0.2 grains of arsenious acid in solution. Pour the last liquid upon the surface of the paper and leave the whole for 24 hours. Thereafter in the soup plate below, you will find a colourless liquid containing $\frac{1}{2}$ at least of the arsenious acid, which may be precipitated by SH [sulphuretted hydrogen] as freely as from pure water and weighed."¹²⁸ This experiment was an example of the possible use of dialysis in poison-testing.

Presumably, between May 1860 and May 1861, Graham replaced the term 'osmolysis' by 'dialysis' and also developed his hoop dialyser for they both appear in his 1861 account of dialysis. In this paper, Graham gave a clear explanation of the mechanism of dialysis. He referred to the dialysis of a mixture of 5% cane sugar and 5% gum arabic. After only one day this gave a diffusate containing three-quarters of the cane sugar used with only a trace of gum in it. He wrote that: "the sized paper has no power to act as a filter. It is mechanically impenetrable, and denies a passage to the mixed fluid as a whole. Molecules only permeate this septum, and not masses. The molecules are moved by the force of diffusion. But the water of the gelatinous starch is not directly available as a medium for the diffusion of either the sugar or gum, being in a state of

129. Graham, 'Liquid diffusion applied to analysis', op.cit. (103), Researches. p 555.
Henri Saint-Claire Deville gave a slightly different explanation of dialysis in his Chemistry lectures of 1864-5. H. St-C. Deville, 'Affinity and heat', Phil.Mag. 4 Ser. 32 (1866) 365-378. (This is a translation of Deville's lectures on dissociation - Chapter 1). Deville argued that the latent heat stored up in the process of the solution of a substance caused diffusion and sometimes partial decomposition or dissociation of a salt. If aluminium chloride solution was floated in a dialyser on a large quantity of pure water then the aluminium chloride would penetrate the top of the membrane to form a thin layer. Water would also penetrate from the underside of the membrane to give a much thicker layer. The layer of aluminium chloride decomposed, when it was in contact with water, by a process of 'indefinite diffusion', an effect of heat, whereby hydrochloric acid would be carried away by the water, leaving a layer of hydrated alumina on the upper surface in the form of colloidal particles. This upper layer, he argued, would be a true filter and decomposition would continue in the interior. He suggested that decomposition by diffusion would always be incomplete, because it depended on the quantity of water in contact with the aluminium salt and this would decrease as the water contained more hydrochloric acid. Furthermore, a little aluminium chloride would always pass through the membrane and therefore colloids and crystalloids could never be entirely separated by diffusion. Deville had here developed an analogy between dialysis and the dissociation of gases by heat.
130. C. Ludwig, 'Nieren und Harnbereitung' (Kidneys and urine production) an article in Rudolph Wagner's Handwörterbuch der Physiologie 2 (Braunschweig, 1844) 628-640; this extract is from a translation of pages 637-638 made by L. G. Wilson.
See: Selected Readings in the History of Physiology. 2nd.edn. (Springfield, 1966), by J. F. Fulton and L. G. Wilson, pages 360-361. Ludwig's anticipation of dialysis has been discussed in papers by N. S. R. Maluf:- 'The centenary of Bowman's exposition of the renal unit', Ann. of Medical History 3 Ser. 4 (1942) 427-449 and also in 'How a physiologist anticipated a physical chemist', Bull.Hist.Med. 14 (1943) 352-365.
131. L. Miahle, 'Memoir on the physiological state of albumen in the economy', Comptes Rendus. 33 (1851) 450-454 and also L. Miahle, Chimie Appliquee a la Physiologie (Paris, 1856) p 139.
132. A. Morin, Mem. de la Soc. d'Histoire Nat., Geneva 13 (1854) 251-278 or 'Nouvelles expériences sur la perméabilité des vases poreux et des membranes desséchées par les substances nutritives', [1852] J.de Pharm. 24 (1853) 100-112. See also H.Milne Edwards, op.cit. (39) pp 168-170.

true chemical combination, feeble although the union of water with starch may be. The hydrated compound itself is solid, and also insoluble.

Sugar, however, with all other crystalloids, can separate water, molecule after molecule, from any hydrated colloid, such as starch. The sugar thus obtains the liquid medium required for diffusion, and makes its way through the gelatinous septum. Gum, on the other hand, possessing as a colloid an affinity for water of the most feeble description, is unable to separate that liquid from the gelatinous starch, and so fails to open the door for its own passage outwards by diffusion."¹²⁹ Thus, the process of dialysis was clearly defined by Graham.

Dialysis had been observed before Graham, but few had so far been able to give a clear description of the process. An anticipation of dialysis can be seen in Carl Ludwig's explanation of urine secretion from the glomerulus in the kidney. Ludwig put forward the hypothesis that the vessel walls of the glomerulus possessed a characteristic power by which only water and the soluble constituents of the blood contained inside, were allowed to pass through, "while none of protein substances, fat (and mineral constituents occurring in combination with them) are allowed through. This, at first glance somewhat daring, hypothesis loses its recklessness when one considers the interesting experiment of Brücke in which the egg shell membrane, in its endosmotic flow, is independent of the albumen"¹³⁰ The action of an egg shell membrane was also studied by Louis Miahle in 1851.¹³¹ He observed that egg membranes were perfect osmometers and that albumen (egg-white serum) never crossed the membrane. As an explanation, he suggested that albumen existed in the form of globules suspended in the liquid medium like casein, starch and fibrin; these globules were unable to pass through membranes until they were modified by a ferment such as pepsin. Another example of selective diffusion through membranes was given by Morin in 1854.¹³² He placed milk in the mucous tunic of the duodenum, suspended in water, and observed that only sugar escaped because casein, oils, and gum were unable to cross

133. A. Dubrunfaut, 'Note sur l'osmose et ses applications industrielles', Comptes Rendus. 41 (1855) 834-838.

134. Graham, op.cit. (103).

135. J. Stefan, 'On the diffusion of liquids', Wien Akad.Ber. 79 (1879) 161-214. For a summary see: W. Ostwald, Solutions (London, 1891, translation by M.M.P.Muir) pp 130-131.

the membrane. In the same year, Dubrunfaut used an osmotic separation to remove the salts from molasses, a process, in which the colouring matter of the molasses did not escape through the animal membrane.¹³³

This was a dialytic separation although, as we shall see later, Dubrunfaut did not recognise this fact at the time.

In 1861, by the use of dialysis and jar diffusion, Graham distinguished two different states in solution: the 'colloid' and the 'crystalloid'.¹³⁴ Although these states were usually distinct, Graham recognised that there were instances when they shaded into one another. Jar diffusion was used to study the speeds of diffusion of different substances in solution. A layer of the solution to be diffused was pipetted beneath the surface of a large volume of water, in a glass cylinder, taking great care to avoid any mechanical mixture. After 14 days of diffusion, portions of the mixture were siphoned off and analysed. The detailed results provided later workers like Stefan with the necessary information to calculate diffusion coefficients.¹³⁵ Graham compared the times taken for substances to undergo equal diffusion. These times showed clearly that the substances caramel, gum and albumen diffused much more slowly than sugar or salts. Graham believed that these diffusion times were of fundamental importance. He found that sodium chloride diffused at the same speed through both water and gelatine, whereas gum was almost entirely stopped by gelatine or starch. This observation led Graham to distinguish two classes of matter in solution. One group consisted of highly diffusive substances, most of which could be crystallised, for example potassium sulphate; sodium chloride; sugar and even alcohol. These he called 'crystalloids'. The second group of substances had a very low diffusive power. These substances did not crystallise and they possessed softened outlines. This group included: hydrated silica; alumina when soluble; starch; dextrin; gums; caramel; tannin; albumen; and gelatine. These he called 'colloids'.

Apart from possessing a low diffusibility, colloids were also found to

136. Graham, op.cit. (103) Researches. p 598.

This quotation appears to have originated, in part, from John Leslie's writings. Leslie wrote: "But after a certain accumulation of heat, the balance [between attraction and repulsion] is destroyed; and as nature admits only gentle transitions, we may reasonably conclude that the attractive power increases regularly at a slower rate than the repulsion." See J. Leslie, 'On heat and climate', Ann.Phil. 14 (1819) 12. The second part of the quotation was a theme in Graham's very first paper:- "...that in the physical states of gas, liquid and solid, there is nothing of absolute permanency, and that any body may assume consecutively all these forms." Graham, Ann.Phil.NS 12 (1826) 69, or Researches. page 1. This paper was recalled by E. W. Brayley who claimed that Graham's researches on fluids supported his own views on fluids: "...the distinction of the latter into aeriform and liquid being still however retainable with propriety as a matter of convenience, though there seems every reason to believe it a distinction that has no real existence." E. W. Brayley, 'On the rationale of the formation of the filaments and mamillary varieties of carbon; and on the probable existence of but two distinct states of aggregation [solid and fluid] in ponderable matter'. Ann.Phil.NS. 12 (1826) 196.

be high molecular weight substances which formed gelatinous hydrates. Colloids were usually soluble in water but they were only held in solution by a very weak force. The weakness of the force of affinity between colloid molecules and water, allowed crystalloids to remove water from them by an exchange process, as they diffused through these gelatinous colloidal hydrates. The colloidal state, unlike the crystalloidal state, was a dynamical state in which change could occur easily although the speed of any such change was usually slow. For example liquid colloids like hydrated albumen or silica could change into a curdled or pectous form, probably by a reduction in their hydration. This process, which Graham called 'pectisation', could result in the formation of a jelly. All liquid colloids appeared to have a pectous form, which could be rapidly produced by the addition of salts.

Graham suggested that colloids might be formed by the polymerisation of crystalloids. This process was similar to the observed polymerisation of silica, alumina and ferric oxide which Graham had described in the 1830s. The resulting high molecular weight colloid molecules lacked any marked chemical properties; they were either chemically inert or possessed feeble acidic or basic properties. The gradual transition from colloid to crystalloid was also a possibility; Graham remarked that natural crystalline quartz might have evolved gradually from colloidal silica. Ice appeared to exist in both crystalloid and colloid varieties; for example ice made from frozen snow or frost was crystalline, but ice formed from water was homogeneous and showed its colloidal properties in regelation and glacier flow. Albumen, a well-known colloid, had also been observed to form crystalline contours in blood. The distinction between colloids and crystalloids was not well-defined or as Graham succinctly expressed it: "In nature there are no abrupt transitions and that distinctions of class are never absolute."¹³⁶ Colloid molecules also contained a considerable amount of stored energy which allowed them to undergo change. Above all, the colloidal condition, with its store of inherent

137. Graham did not explain his choice of the word 'colloid'. Henry Watts explained, in his Dictionary of Chemistry 3 (London, 1865) p 711, that the word was derived from the Greek word (κολλα) meaning glue. Graham chose the substance gelatine as the typical colloid and it is probable that he chose the word 'colloid' from the pathological term. This term is defined, in Robert Todd's Cyclopaedia of Anatomy, Vol.1 (London, 1836) p 515, as "colloid or scirrhus - a solid matter deposited in cases of chronic inflammation - an effusion of intercellular tissues ... a white or grey matter of lardaceous homogeneous appearance ... doubtful whether it consists of fibrin, albumen or some newly-formed material ... can lead to a chronic abscess which contains a serum mixed with flaky matter." In the same work, Vol.5 (1859) p 591, there is a more appropriate description of colloid - "a cancer of the ovary characterised by the gelatinous content of the cells. The cell walls contain fine white fibrous tissue and follicles, often like a thin-walled trembling jelly. These cysts are filled with a viscid mucous-like material resembling half-jelly and half-opaque masses as found in jelly-like blancmange or cream." It is probable that Graham was acquainted with the pathology of colloid cancer because his colleague at University College, W. H. Walshe, the Professor of Medicine, had studied colloid cancer. Graham did refer, in 1854, to 'colliferous' tissues which like gelatine could separate water from alcohol. B.A.Report (1854) part ii p 69.

138. S. G. Mokrushin, 'Thomas Graham and the definition of colloids', Nature 195 (1962), page 861.

energy, could be the primary source of force in living matter.

Graham had given a remarkably vivid description of the colloidal state.¹³⁷ He did not restrict his description to a few examples instead he showed that it was possible to obtain a whole new range of liquid colloids by dialysis.

The process of dialysis was used to separate colloids from crystalloids. Only crystalloids were able to pass through membranes or parchment paper. Graham made use of this property to produce his new colloidal solutions. Even substances, previously considered to be insoluble in water were turned into solutions by dialysis. He was therefore able to extend his earlier studies on hydrated oxides, which had been abandoned in the 1830s, by making their colloidal solutions. Thus, for example he obtained a solution of pure ferric hydroxide by dialysis which removed all the crystalloid hydrochloric acid.

It is important to realise that Graham regarded solutions of colloids as true solutions and not suspensions. Therefore, he did not acknowledge, in his papers on colloids, the earlier researches of Selmi on pseudo-solutions and of Faraday on gold suspensions, presumably, because he believed that these previous studies were concerned with suspensions and not with true solutions. It was only in the twentieth century that Freundlich and Wolfgang Ostwald redefined colloids as substances in the dispersed state; this definition brought together Graham's 'true' colloidal solutions and the suspensions discovered by earlier researchers.¹³⁸

According to Graham a colloidal solution contained liquid colloid molecules which underwent liquid diffusion. He did not extent the property of liquid diffusion to suspensions and hence his vision of colloidal solutions was a restricted one. This can be seen from a letter which he wrote to Sir George Stokes, in reply to an enquiry about the observed opalescence of colloidal solutions. Graham wrote: "The liquid condition of all such bodies [colloidal solutions], it is to be remembered is not permanent. Now in silicic acid the transition to the gelatinous

139. Péan de Saint-Gilles, 'On soluble metaperoxide of iron', Comptes Rendus. 40 (1855) 568-570.
140. MS. letter from Graham to Stokes, Cambridge University Library, Stokes Correspondence, Add. MS.7656, G394; see also an inaccurate transcription of the same letter from Graham to Sir G.G.Stokes dated July 6th 1861, quoted in: Memoir and Scientific Correspondence of the late Sir George Gabriel Stokes, by Joseph Larmor (Cambridge, 1907) Vol.2 pp 73-74.

(solid) form is visibly preceded by a faint opalescence of the liquid. This gradually increases during a few hours or even days and is sometimes very beautiful. But it is sure to end sooner or later in the somewhat sudden solidification of the mass. The previous opalescence may very well be due to suspended solid matter, like Faraday's highly-divided gold as your theory supposes. It is however the effect of an incalculably minute amount of suspended matter, and does not touch the great mass of colloidal matter present. In short the opalescence may be due to suspended matter although the colloid is truly liquid. Indeed one or two per cent [solutions] of such substances generally produce a firm jelly, on passing from the liquid condition, while the solutions operated upon were perfectly limpid with from three to ten per cent of substance in solution.

That colloids are really in solution appears also to follow from the fact that they are diffusive. They possess the property, and of several the rate has been accurately observed. They may be twenty or fifty times less mobile than any crystalloid; but there appears to be nothing liquid that is absolutely non-diffusive. A liquid colloid also, such as caramel, is found to diffuse through jelly, as well as in pure water.

I have only further to add that the permanent or nearly permanent opalescence seen in ferrocyanide of copper is by no means a common property of colloidal liquids. Indeed the salt named and the metaperoxide of iron are the only liquids of the class in which it has been yet observed. The property is particularly decided in the last solution, as was first observed by Péan de St. Gilles.¹³⁹ It seems hazardous, therefore, to infer much respecting the constitution of colloidal liquids from what appears to be an inessential character.

At the same time the solution of a colloid must be something very different from ordinary solution as we know solution in the case of crystalloids. It would be interesting to know whether the difference in the two forms of solution is marked by any optical distinction between them."¹⁴⁰

141. Francesco Selmi (1817-1881) was Professor of Chemistry at Liceo, Reggio and then reader in Chemical Physics, at the Collegio Nazionale, in Turin. Selmi's papers on 'colloid' chemistry were translated by Emil Hatschek and are found in E. Hatschek, Foundations of Colloid Chemistry (London, 1925). His papers are:- 'What emulsions and demulsions are', Nuovi Ann.de Scienze Naturali di Bologna. Series II t IV (1845) p 146. 'Some facts of physiological chemistry' Nuovi Ann.... Feb. 1846, 'A study of pseudo-solutions of Prussian blue and of the influence of salts by destroying them', Nuovi Ann Series II t VIII (1847) p 401. 'On the products of the decomposition of sulphuretted hydrogen and sulphurous acid in aqueous solutions', (1849). For a summary of this paper read by, A. Sobrero and F. Selmi, see Ann.de Ch. 28 (1850) 210.

It would appear that Stokes had suggested that all colloid solutions might be suspensions, but Graham did not accept this view. It is worth noting that Stokes had been recently studying fluorescence and the effect of light on chemicals in solution.

The success of Graham's paper on colloids can be seen from the recognition which it received. The Académie des Sciences awarded Graham the Prix Jecker, for his researches on molecular diffusion applied to analysis, and the Royal Society gave him their highest award, the Copley Medal, for his work on liquid diffusion, osmose and particularly for his paper on liquid diffusion applied to analysis. This success can be attributed to three important advances. Firstly, Graham had suggested a new terminology for his investigations which was important for obtaining a clear appreciation of the phenomena under consideration. This new language can be likened to Faraday's new terminology for electrolysis; it added a precision to the study of the subject matter. The new words introduced by Graham included 'colloids', 'crystalloids', 'dialysis' and 'pectisation'. These were followed by the terms 'peptisation', 'hydrosol', 'hydrogel', and 'synaeresis' in 1864. Secondly, the distinction between colloids and crystalloids was clearly established by marked differences in their speeds of molecular diffusion. Graham was thus able to give a precise description of colloidal substances although he restricted the concept of colloids to true solutions and thus excluded suspensions. Thirdly, he developed the technique of dialysis and so produced a considerable number of pure colloidal solutions for the first time. Dialysis was immediately recognised to be a very useful practical technique in chemical analysis.

The success of Graham's researches tended to obscure and overshadow earlier approaches to the understanding of the nature of the colloidal state and of dialysis. Between 1845 and 1849 the Italian chemist, Francesco Selmi, had made a careful study of emulsions or 'pseudo-solutions' of silver chloride, prussian blue, and sulphur.¹⁴¹ These emulsions would now be called colloids although it is probable that Graham would have

142. Alexandre Édouard Baudrimont, (1806-1880), was in turn a pharmacist in Paris, (gaining his M.D. in 1831), physician in Valenciennes, préparateur in Chemistry at the Collège de France, assistant professor in the Medical Faculty, and finally Professor of Chemistry in Bordeaux (1848).

Baudrimont wrote a textbook: Traité de Chimie Générale et Expérimentale, avec les Applications aux Arts, à la Médecine et à la Pharmacie, in two volumes, (Paris, 1844 and 1846). He described 'particulate or non-crystalline organic substances' on pages 842-850 of volume 2 which was published towards the end of 1846. Wilder D. Bancroft has given a translation of this section in his article: 'Baudrimont as colloid chemist', J.Phys.Chem. 23 (1924) 256-262.

143. Graham referred to "Baudrimont's excellent Traité de Chimie" in 1846. See Graham, Elements of Chemistry 2nd. edn. Vol.1 p 156 (London, 1846). The reference is to atomic weight determinations and not to the section on 'colloids'. Graham possessed a copy of both volumes of Baudrimont's, Traité de Chimie, in his own library.

regarded them as suspensions rather than true colloids.

Selmi accepted Gay-Lussac's explanation of true solutions in which the solute molecules were spread out as far as possible from one another in the solvent; the process being analogous to the admission of a gas into a vacuum. He suggested that emulsions, or pseudo-solutions, differed from true solutions because they contained groups of solute molecules dispersed in the solvent. In 1847, Selmi described the appearance of the particles found in a pseudo-solution of basic prussian blue. The particles consisted of molecular aggregates which were swollen and subdivided to give thin membranes, flakes, or vesicles. He also referred to the transparent pseudo-solutions of silica and alumina which were studied later by Graham. On standing, pseudo-solutions contracted and eventually gave either an insoluble precipitate or a jelly. This process was accelerated by the addition of inert foreign substances like salts; Selmi explained their action by the extra vibration or increased motion which occurred when a salt was added. He also anticipated Graham's observations that there was a noticeable incorporation of water when a solid formed a pseudo-solution, and that there was no change of temperature when a pseudo-solution was formed, in contrast to the case of 'true' solutions. Therefore, Selmi had described many of the properties of colloids in his studies of pseudo-solutions.

Another anticipation of the elucidation of colloids is seen in the second volume of Alexandre Baudrimont's, Traité de Chimie,¹⁴² published in 1846. Graham probably knew of Baudrimont's work since he referred to his Traité in a different context.¹⁴³ Baudrimont classified organic substances into three groups:- crystalline compounds of fixed proportions; particulate or non-crystalline compounds of indefinite proportions; and the organised structures found in tissue, nerve or muscle. The class of 'particulate substances' appear to extend from suspensions to colloids. He described them as "formed of particles visible under the microscope and having no definite axes. When left to themselves, the particles either

144. A. E. Baudrimont, op.cit. (142), Traité de Chimie. 2 p 842.

145. Baudrimont, *ibid.*

146. M. Faraday, 'Experimental relations of gold (and other metals) to light', Phil.Trans. 147 (1857) 145-182 and in Faraday, Chemical and Physical Researches (London, 1859) pp 391-443. For a discussion of this paper see: L. Pearce Williams, Michael Faraday, (London, 1965) 471-474 and E. Hauser, 'Historical background of colloid chemistry', J. Chem.Ed. 27 (1950) 264-266.

147. Graham, 'On the properties of silicic acid and other analogous colloidal substances', read to the Royal Society on June 16th 1864 and published in Proc.R.S. 13 (1864) 335-341, where it was referred to as a 'preliminary notice' - but nothing further was added. See also J. Chem. Soc. 17 318-327 and Researches. 618-625 for the same account.

remain free and take the form of a liquid, like albumen, or they agglomerate and form tuberculous masses like the gums and the resins." ¹⁴⁴

The particles appeared to be spheroidal in shape; liquid in form; and varied in their diameter from $\frac{2}{100}$ th mm. to 1 mm. They were "formed under the influence of forces peculiar or inherent in them." ¹⁴⁵ He also noticed that particles like starch would swell in water but they were not truly soluble, although they appeared to be so, because their special structures allowed the particles to slide over one another rather like the dispersion of one liquid in another. Finally, Baudrimont noticed that, when the viscosity of solutions of starch, gelatine, or gum increased, the non-crystalline particles adhered to form a jelly. He also observed that precipitation could occur when foreign substances were added to these solutions. Both Selmi and Baudrimont had described many of the properties of the colloidal state before Graham.

Faraday also described many of the features of colloids in his paper on gold suspensions published in 1857. ¹⁴⁶ He observed that gold suspensions could deteriorate spontaneously, on standing, to deposit gummy or mucous-like masses. These suspensions differed: in colour, from blue to ruby-red; in particle-size and stability; and in their power to scatter light. Faraday supposed that either some kind of repulsive force held these gold particles in solution or that the gold particles were surrounded by an envelope of water. It is interesting to see that Faraday appeared to be following Graham by suggesting a repulsive view of liquid diffusion in the former explanation. Particularly noteworthy in Faraday's study is the effect of added substances on gold suspensions; many salts were found to cause precipitation but, in contrast, organic substances had little effect. Graham failed to acknowledge the analogy between his own studies on colloids and those of Faraday, Selmi and Baudrimont.

Between 1861 and 1864, Graham extended his studies on colloids and he read his final paper on this subject ¹⁴⁷ to the Royal Society in June 1864. He found that the solubility of silicic acid appeared to depend upon the

148. Graham, 'On the capillary transpiration of liquids in relation to chemical composition', read June 20th 1861. Phil.Trans. 151 (1861) 373-386, or Researches. 600-615.
The experiments for this paper were performed mainly between October 1858 and May 1859. They are recorded in Wellcome Notebook No.17, MS. number 2569, (old no.3164) entitled 'Molecular movement of liquids.'
- 148a. A copy of the MS. letter from Graham to Thomas Andrews, November 25th 1856, Andrews' papers, Queen's University, Belfast.

extent of its hydration. The method of preparation of silicic acid influenced both its solubility and the amount of water which was found in the jelly formed from this acid. During pectisation, silicic acid solution became increasingly viscous and this could be detected by measuring the rate of flow of the solution through a capillary tube. This technique of 'liquid transpiration' had been developed by Poiseuille and it was used by Graham in his 1861 paper on capillary transpiration. Graham found that there was a relationship between chemical composition and liquid transpiration: the solution which flowed most slowly through a capillary tube was usually a definite hydrate of the acid or alcohol used. He explained that the slowest capillary transpiration was either due to the increased viscosity, because hydrates were larger molecules, or, alternatively, because the hydrate might be molecularly decomposed by friction with a resultant loss of its impelling force.¹⁴⁸

At the beginning of his studies on liquid transpiration, in 1856, Graham wrote to Thomas Andrews and made the following interesting comments on his work: "I have at present very wild ideas respecting the cause of these anomalies of transpiration - such as referring the retardation to a mechanical decomposition of the hydrates, a change which would require absorption of heat. Force is converted into heat, and hence the retardation! Generalize this assumption and it will be allowed that mixed liquids may be in a decomposed condition while in a state of movement, which will combine when at rest, and a theory upon it of the coagulation of blood! But seriously I have long been of the opinion that diffusion; transpiration of both gases and liquids will never have an explanation except from the motion theory of heat."^{148a} It is possible to see in these ideas an anticipation of Graham's eventual theory of the catalytic decomposition of gelatinous hydrates in osmosis and dialysis.

In 1864, Graham suggested a new method for distinguishing between colloids and crystalloids, this was to compare their rates of transpiration through capillary tubes. Colloids transpired much more slowly

149. August-Pierre Dubrunfaut, (1797-1881), studied Chemistry under Désormes, Dulong and Gay-Lussac. He was interested in:the industrial chemistry of grain distillation and the refining of beet sugar. From 1830,he developed these industries considerably. He opened several sugar refineries and he began the treatment of beet molasses. In 1854, he used the phenomenon of osmose to extract sugar from molasses and he constructed an apparatus for this purpose which he called the 'osmogene'. Dubrunfaut believed he had served Science well so he presented himself as a candidate for the French Academy, in 1868, but he was brushed aside, much to his regret.
(Dictionnaire de biographie française, 1965-7, article on A. P. Dubrunfaut).

150. A. Dubrunfaut, 'Note sur l'osmose et ses applications industrielles', Comptes Rendus. 41 (1855) 834-838 (November 12th 1855).

than crystalloids especially when peptisation was approached and so they could be distinguished easily by measuring their rates of transpiration. He referred to his capillary tube apparatus as a 'colloidoscope'. The tendency of colloid particles to adhere and contract near peptisation was followed by a contraction of the jelly itself in which water separated out. He called the latter process: 'synaeresis'. Graham named the liquid and gelatinous hydrates of silicic acid, the 'hydrosol' and 'hydrogel' respectively (later contracted to 'sol' and 'gel'). He showed that water, which was only weakly retained by colloids, could be exchanged for alcohol; ether; glycerine; sulphuric acid; benzole; or carbon disulphide. Finally, he observed the useful process of 'peptisation' in which silicic acid jelly was made soluble by the addition of a trace of alkali. Using peptisation, Graham was able to extend further the number of colloidal solutions which he could prepare. Thus, he made new solutions of the previously insoluble substances: stannic, titanitic, tungstic and molybdic acids.

Graham's studies of osmosis, colloids, and dialysis were criticised by the French industrial chemist, Auguste-Pierre Dubrunfaut.¹⁴⁹ In 1855, Dubrunfaut claimed that he had anticipated Graham by discovering that osmose could be used to bring about a more or less complete separation of mixtures of salts or other water-soluble substances. He alleged that this discovery was made in April 1854, three months before Graham's paper on osmotic force.¹⁵⁰ Dubrunfaut explained how he had used his discovery to purify beet molasses for sugar extraction. Beet molasses contained a mixture of sugar with organic, and inorganic salts, amongst which were potassium nitrate and potassium chloride. He poured the molasses into a Dutrochet endosmometer which was then placed in water. There were two currents: a strong current from the water to the molasses and a weak current in the opposite direction. He wrote that: "this latter current carries away organic and inorganic salts of the molasses into the water leaving, in the endosmometer, diluted sugar with colouring matter and a

151. Dubrunfaut, *ibid.* p 838.

152. Translation of a letter from Graham to the Editor of Mondes, in reply to Dubrunfaut's alleged anticipation of the discovery of dialysis, (published on August 11th 1864). Graham's letter was forwarded on August 15th but its publication was delayed for three weeks. Chem. News 10 (September 24th 1864) p 156. See Dubrunfaut's English patent description in: B. Woodcroft, Patents for Inventions, Abridgements of Specifications Relating to Sugar AD 1863-1866. (London, 1871) p 329. Dubrunfaut registered his patent no. 2053 on August 18th 1863, it was entitled 'an improved method of, and apparatus for, treating molasses, syrups, saccharine juices and other products'. He refers to his adaptation of endosmose using parchment paper. Mondes was a weekly paper published by L'Abbé Moigno: Mondes Revue Hebdomadaire des Sciences et de leurs Applications aux Arts à l'Industrie, Année 1-11 (tome 1-33) Paris 1863-73. Moigno wrote in Mondes tome 5 (August 11th 1864) pp 670-671: "Extraction of Sugar from Molasses by Dialysis. On the 1st April 1854, M. Graham had not yet definitely attached his name to dialysis, at that time our countryman and friend M. Dubrunfaut took out a patent in which he declared in formal terms that he saw first (1) that when one put water and molasses in contact across an organic membrane, there was a double osmotic current, the strong current from the water to the molasses, the weak current from the molasses to the water, (2) that the strong current carried away with it the salts of molasses to the water in such a way that the salts left, and the sugar of the molasses remaining, would crystallise without difficulty. This patent (1) indicated therefore clearly the possibility of extracting sugar from molasses rendered crystallisable by the elimination of salts, which is not dialysis in the proper sense admitted by M. Graham; (2) affirmed the identity of the effects of endosmose and diffusion which, to our knowledge, the previous works unpublished by M. Dubrunfaut have perfectly established. Let us add that M. Graham gave his Bakerian lecture on the osmose on the 15th June [1854]; that his lecture was published in The Athenaeum on the 24th June; announced in our Cosmos of the 30th June and analysed by us in July, three months after the patent of M. Dubrunfaut. The process of the extraction of sugar from molasses by endosmose was stifled in the cot by the much more brilliant process of extraction through barytes; and it is only on the 22nd June 1863 that M. Dubrunfaut has patented in his name the osmogene apparatus, a complete apparatus, of cells separated by vertical membranes of parchment paper ... Let us add that a first osmose or dialysis separates the salts from one another and gives, crystallised separately, potassium nitrate and potassium chloride." Graham's reply was printed in Mondes tome 6 (September 1864) pp 53-54. He wrote: "As an assiduous reader of Mondes I could not miss noticing in a recent number the description of a new process invented by M. Dubrunfaut and patented by him, the 22nd of June 1863, for the extraction of sugar from molasses by dialysis." etc.

fraction of the salts which, in a first trial, escape from the reaction."¹⁵¹
The molasses had then lost its bad taste and could be used for sugar production; whilst the water contained both potassium salts and organic salts. It could be argued that this was an anticipation of dialysis, in the sense that, crystalloid salts were separated from the colloidal colouring matter; but the sugar had not been separated and the intention of Dubrunfaut's experiment was simply to remove the unpleasant-tasting salts from sugar by osmosis.

Initially Graham ignored Dubrunfaut's claim that he had anticipated the analytical use of osmose. Subsequently in June 1863 Dubrunfaut patented what he called a new process to extract sugar from molasses by dialysis and followed this with an English patent in August 1863. Graham could ill-afford to ignore this latest challenge which was reported in the weekly French paper: Mondes on August 11th 1864. Therefore, he wrote to Mondes replying to Dubrunfaut's alleged anticipation of dialysis and this reply was reprinted in Chemical News.¹⁵² Graham wrote "I have little doubt that by dialysis through parchment paper M. Dubrunfaut might succeed in separating gum and a portion of colouring matter from molasses, but the earlier process of the same chemist, patented on April 1st 1854, appears to be different in principle and intended to effect a separation of crystalline salts, but not gum and colloid colouring matters, from sugar - an effect which, as you justly observe, is not dialysis. For neither animal membrane nor parchment has any effect in separating different crystalline substances from one another. All such bodies, when in solution pass through membrane with the same facility. The separation of salts from sugar which was observed by M. Dubrunfaut could only be very partial and I may be allowed to say that it is simply the effect of the greater rapidity of diffusion in water possessed by potash salts than by the crystalline sugar contained in the molasses. In fact, as is proved directly in my memoir of 1854, that the interposed membrane goes for nothing in the phenomenon. A great number of separations by diffusion

153. *ibid.*

154. *ibid.* Was S.S., Simeon Stoikowitsch, Graham's assistant in his laboratory in the Royal Mint at this time?

155. A. Dubrunfaut, 'Note on diffusion and endosmose', Comptes Rendus: 63 (1866) 838-840. (November 12th 1866).

156. Graham, 'On endosmose and dialysis', Comptes Rendus. 63 (1866) 937-939. (December 3rd 1866).

of artificial and natural mixtures of salts (e.g. sea water) are described in my memoir which is printed in Annales de Chimie for May 1850 29 197." ¹⁵³

A note was added to this translation of Graham's letter by S. S. [?] who wrote: "it is to be observed of Dubrunfaut's first patent of April 1st 1854, that it does not effect a dialysis, but the separation (very partial) of crystalloids by diffusion which had been previously exemplified in great detail in Mr. Graham's original paper on 'liquid diffusion' published in Phil.Trans. 1850 or 4 years before. Again the second patent of M. Dubrunfaut dated June 22nd 1863 is manifestly founded on Mr. Graham's paper on dialysis published a year earlier in 1862, from which the use of parchment paper has been borrowed by the patentee." ¹⁵⁴

The controversy was not ended by Graham's letter. For in 1866, Dubrunfaut wrote to the editor of Comptes Rendus claiming that dialysis was only a special case of osmotic analysis which he, Dubrunfaut, had pioneered in 1854. ¹⁵⁵ He argued that diffusion and osmose were essentially identical processes and that diffusion was apparently caused by an attractive force between adjacent particles, analogous to gravitational attraction.

Immediately, Graham replied to this note, in a typically restrained manner, answering Dubrunfaut's claim of partial anticipation of the principle of dialysis. ¹⁵⁶ Graham began by suggesting that endosmose could not be identified with dialysis. Osmose was simply the addition of water to a salt solution in an osmometer. The motive force of osmose was the attraction of the membrane for water which was greater than the attraction of the membrane for salt solution. He regarded the best examples of osmose to be, those in which the solute did not escape, for example gum and albumen, the substances which Dutrochet had preferred for endosmose; or even better, tungstic acid which, as Graham had discovered, gave the greatest osmose. Dialysis was the separation of a crystalloid from a colloid and was thus a quite different process. Dubrunfaut's separation of potassium salts from sugar was simply due to the differences in the

157. A. Dubrunfaut, 'Observations on dialysis and endosmose', Comptes Rendus. 63 (1866) 994-998.

158. A. Dubrunfaut, 'Memoir on diffusion, endosmose, molecular movement etc.', Comptes Rendus. 66 (1868) 354-359.

speeds of liquid diffusion of these crystalloids. This process could have been carried out by liquid diffusion in open jars as Graham had demonstrated in 1849. The use of a bladder by Dubrunfaut was inessential. As Graham had shown in 1854, salts diffused equally well out of vessels with, or without, a bladder. Therefore, Dubrunfaut had not discovered a new principle, although Graham admitted that the use of a bladder, or better still of parchment paper, gave a better industrial process. Here Graham allowed the matter to rest presumably feeling that he had made his views clear.

Dubrunfaut was not satisfied, however, and he continued to criticise Graham. He protested that he had not identified osmose with dialysis. Instead, Dubrunfaut maintained that both processes had a common origin in diffusibility, although he accepted that there were 'distinct nuances' of difference between them.¹⁵⁷ He argued that Graham had not appreciated the similarity between diffusion and osmose until he, Dubrunfaut, had published his first paper in 1855. He reminded Graham that he had attributed osmotic force to electrical origins which resulted from the incessant alterations of the membrane. On the contrary, he, Dubrunfaut, had championed diffusibility as the cause of osmose. However, Dubrunfaut weakened his argument by insisting that there were two liquid currents in osmose, the endosmose and exosmose of Dutrochet. He also attempted to weaken the distinction which Graham had drawn between colloids and crystalloids by referring to the example of liquid sugar which did not crystallise and yet was perfectly diffusible.

In 1868, Dubrunfaut expressed further criticism of Graham,¹⁵⁸ by concluding that diffusion was due to molecular attraction and so there was no evidence for Bernoulli's theory of molecular motion explaining diffusive mixture. This was a view which Graham certainly did not share. Dubrunfaut regarded osmose as a process of unequal diffusion in which one of the two currents was dominant. The dominant current was produced by the action of the membrane which diminished the diffusibility of the two

159. A. Dubrunfaut, 'Note on supersaturation and superfusion and solutions', Comptes Rendus. 68 (1869) 916-920, (1218-1222). Even after Graham's death and Dubrunfaut's rejection as a candidate by the Académie des Sciences, Dubrunfaut was determined to justify his alleged priority. He wrote a textbook: L'Osmose et ses Applications Industrielles, (Paris, 1873), in which he gave his version of this regrettable polemic. In the introduction he described how he had read Dutrochet's Mémoires. of 1837 (op.cit.53), whilst on holiday in 1853. This work had led him to try out endosmose for purifying the sugar from molasses, (L'Osmose.XI). Dubrunfaut argued that Graham's dialysis was "in all respects a disguised borrowing, unworthy of an eminent and illustrious savant. It was in reality plagiarism." (L'Osmose.XXVI). He continued: "The conduct of Graham in this circumstance has no excuses; and he could not allege ignorance of a publication printed in 1855, in the Comptes Rendus, with a title which did allow any ambiguity 'Applications industrielles de l'osmose'. He could no more make excuses for the omissions of the names of Dutrochet and his endosmometer, when he had taken from them so slavishly his dialyser and his diffusimeter." *ibid.* (XXVI). Finally he commented: "We have not waited for the death of M. Graham to make these remarks, and if we had been less polite and less respectful of the works of the illustrious savant, we would have declared, what is our personal conviction, that Graham has stolen from us the principle of our invention and that to hide his theft he has invented this luxury of neologism, of which he is so lavish in all his works. The dialysis, we will repeat to repletion is only a particular case of osmose it has been borrowed slavishly by him in his principles and his means." L'Osmose. p 37.

currents unequally. Graham correctly did not accept his view of osmose in which there were two liquid currents of endosmose and exosmose, rather he believed that there was an osmose current and an accompanying diffusion of salts in the opposite direction. Dubrunfaut insisted that Graham's dialyser was based on his osmotic analysis and that the dialyser was simply a metamorphosed Dutrochet endosmometer. Even Graham's atmolysis was quoted as an extension of Dubrunfaut's osmotic analysis.

Finally, in 1869, Dubrunfaut repeated his complaint that Graham had based dialysis on his process of osmotic analysis. He conceded that liquid sugar was probably a solution of sugar in a modified state; possibly it could be in a different state of hydration which Graham had 'improperly' called the colloidal state.¹⁵⁹ It is interesting to see that Graham's work did not lack contemporary criticism. Dubrunfaut felt that his own work had not been adequately recognised and this led him to overstate his case. Graham does not appear to have had any recourse to Dubrunfaut's experiments when he was developing the technique of dialysis.

Graham's researches on colloids and dialysis had a significant influence on the thought of Herbert Spencer, who was working, in 1862, on his evolutionary Principles of Biology. Spencer realised that Graham's colloids could be fitted into a natural scheme in which the colloidal molecules were developed from highly diffusive crystalloid molecules by aggregation. He extended Graham's vision of crystalloids and colloids to show how the molecular mobility of the constituent parts of organic colloids was revealed in the characteristic properties of these slow-moving, unstable molecules. He wrote that: 'Professor Graham's all-important investigations respecting the colloid and crystalloid forms of matter, well-exemplified the need for transcending the limits of pure chemistry for the further advance of chemistry. The contrasts he draws between colloids and crystalloids - the instability of the one, and the stability of the other, between the consequent energia of the former and the quiescence of the latter, have important implications of many kinds, especially biological.'

160. D. Duncan, Life and Letters of Herbert Spencer (London, 1908), Appendix B, p 556. This appendix was a sketch-plan of the intellectual history of Spencer's own ideas, called 'the filiation of ideas'. It was the basis for his Synthetic Philosophy, which included the Principles of Biology. Spencer wrote the sketch-plan in February 1899 but omitted it from his Autobiography. He left the plan for the use of his biographer.
161. Graham, 'Liquid diffusion applied to analysis', op.cit. (103) Researches. p 554.
162. H. Spencer, The Principles of Biology. Vol. 1 (London, 1864), Chapter 1, Organic Matter.

But, not being guided by the relevant biological ideas, there is a corollary which he did not reach. Had he looked at the vital changes from the physiological point of view, and observed that while the wasted tissues are continually being rebuilt the waste-matters have continually to be carried away; he would have seen that it is because the tissues are formed of colloids while the waste matters are crystalloids that the vital processes are possible. From the small molecular mobility of the large colloid molecules and the greater molecular mobility of the small crystalloid molecules, it results that these last can rapidly diffuse through the first and escape into the channels which carry them out of the body." ¹⁶⁰

Spencer correctly suggested that Graham had not fully-developed the consequences of the role of colloids in organic life-processes, although it is fair to notice that Graham had stated that the energy in colloids was the "probable primary source of force appearing in the phenomena of vitality." ¹⁶¹ In his discussion of organic matter, Spencer argued that all combinations must possess the resultant of the properties of their components as a consequence of the principle of conservation of force. ¹⁶² Organic compounds often contained the four elements carbon, hydrogen, oxygen and nitrogen. These elements had sharply contrasted properties; carbon was immobile whereas the gases hydrogen, oxygen and nitrogen were extremely mobile. He admitted that large organic molecules possessed a low degree of molecular mobility because of their large mass. However, this low molecular mobility allowed changes to occur more easily in large organic molecules and, in addition, the varied properties of the constituent elements produced a chemical tension. In colloids, the low degree of molecular mobility indicated that the vibrations of the atoms, inside the colloid molecules, were small. But these atoms possessed a high degree of individual mobility which explained the observed polymerism and isomerism of these molecules. The large size of colloid molecules also reduced the effects of polar attraction of the constituent atoms giving chemically inert, spherical molecules, which were unable to crystallise.

163. The term 'molecular mobility' was introduced by Spencer.
The Principles of Biology (London, 1864) Vol.1 pp 3-4.
In Graham's library there were the successive instalments of
H. Spencer's System of Philosophy, in 22 unbound parts 1860-1866,
which would have included The Principles of Biology.

164. H. Spencer, The Principles of Biology, Vol.1 (London, 1864) pp 3-4.

Spencer believed that organic tissues were more complex, because they contained soluble and insoluble colloids permeated by crystalloids such as oxygen, water and salts. Crystalloids of high molecular mobility were capable of decomposing complex colloids to give diffusible colloids which allowed for the elimination of waste matter and the processes of vital activity. Nitrogen had a special role in organic compounds, it was easily released and was therefore a constant cause of molecular disturbance and of vital motions. This idea was drawn from the fact that nitrogen had a feeble affinity for other elements and that nitrogenous substances were used artificially to promote change, for example in explosives and in fermentation. Spencer realised that Graham's colloids had just the required compromise between fluidity and solidity for the construction of living organisms. Consequently, living matter was formed by a transformation of the nutrients, followed by polymerisation to produce colloids, or the still larger molecules found in the fundamental physiological units of life.

Graham was an original subscriber to Spencer's Synthetic Philosophy and in January 1863 he must have received the first instalment of Spencer's book: The Principles of Biology, in which his own work on colloids was discussed. There can be little doubt that Spencer's work had in turn some influence on Graham. He chose Spencer's terminology for the title of his next paper, 'On the molecular mobility of gases', which was written between March and April 1863.¹⁶³ Spencer had written: "one of the leading properties of each substance is its degree of 'molecular mobility'; and its degree of molecular mobility more or less sensibly affects the molecular mobilities of the various compounds into which it enters. Hence we may infer some relation between the gaseous form of three out of the four chief organic elements, and that comparative readiness displayed by organic matters to undergo those changes in the arrangements of parts which we call development, and those transformations of motion which we call function."¹⁶⁴

Graham concurred with the view that the properties of the constituents manifested themselves in more compound structures. He had deduced the

165. Graham, 'Speculative ideas respecting the constitution of matter',
Phil.Mag. 27 (1864) 81-84, or Researches. page 300.

166. Graham, *ibid.* Researches. 301-302.

isomorphism of compounds from the presence in these compounds of isomorphous elements and in 1863 he speculated that "the gaseous molecule must itself be viewed as composed of a group or system of the preceding inferior atoms, following as a unit laws similar to those which regulate its constituent atoms The gaseous molecule is then a reproduction of the inferior atom on a higher scale. The molecule or system is reached which is affected by heat, the diffusive molecule, of which the movement is the subject of observation and measurement. The diffusive molecules are also supposed to be uniform in weight, but to vary in velocity of movement, in correspondence with their constituent atoms." ¹⁶⁵

In blurring the distinctions between the different states of matter Graham went even further than Spencer who had referred to colloids containing the appropriate compromise between fluidity and solidity. Graham wrote that "in the general properties of matter we have, indeed, to include still further (1) the remarkable loss of elasticity in vapours under great pressure, which is distinguished by Mr. Faraday as the Caignard Latour-state, after the name of its discoverer, and is now undergoing an investigation by Dr. Andrews, which may be expected to throw much light upon its nature; (2) the colloidal condition or constitution, which intervenes between the liquid and crystalline states, extending into both and affecting probably all kinds of solid and liquid matter in a greater or less degree. The predominance of a certain physical state in a substance appears to be a distinction of a kind with those distinctions recognised in natural history as being produced by unequal development. Liquefaction or solidification may not therefore involve the suppression of either the atomic or molecular movement but only a restriction of its range." ¹⁶⁶

Graham recognised the existence of an essential continuity in the states of matter. There were no sharp divisions between the different states which often coexisted. Graham had held this view of continuity consistently from his earliest researches on the absorption of gases by liquids. In this early research he had blurred the clear distinction

167. Graham, 'On the properties of silicic acid and other analogous colloidal substances', op.cit. (147), Researches. 619-620.

168. Graham, Wellcome MS. No.2580 (old no.3390). Unbound file Item (5) 'Notes on gases', dated 21/3/68, containing 5 ll.

between the gaseous and liquid states. The evidence for this view was drawn from the researches of Faraday and Caignard-Latour. The same vision was still retained by Graham in his last paper on colloids, of 1864, when he said "bearing in mind that the colloidal phasis of matter is the result of a peculiar attraction and aggregation of molecules, properties never entirely absent from matter, but greatly more developed in some substances than in others it is not surprising that colloidal characters spread on both sides into the liquid and solid conditions. These characters appear in the viscosity of liquids, and in the softness and adhesion of certain crystalline substances. Metaphosphate of soda, after fusion by heat, is a true glass or colloid; but when this glass is maintained for a few minutes at a temperature some degrees under its point of fusion, the glass assumes a crystalline structure without losing its transparency. Notwithstanding this change, the low diffusibility of the salt is preserved, with other characters of a colloid." ¹⁶⁷

In an unpublished manuscript note, dated 1868, Graham outlined his ideas on the continuity of matter by considering matter as a hierarchy of increasing molecular complexity. The simplest molecules were those present in gases. More complex molecules were found in liquids and colloidal solutions, whilst the most complex molecules were those found in crystalline solid structures. The note recorded "condensed descriptions of successive forms of construction of chemical substances:

areo-molecular	atmo-molecule	
liqui-molecular	hydro-molecule	
colli-molecular	colli-molecule	
crystallomolecular	crystallomolecule	" 168

Thus Graham divided matter into four states still assuming a basic continuity: gas; liquid; colloid; and crystalline. These states were distinguished from one another by their different degrees of molecular mobility. Presumably he intended to develop this new nomenclature in a paper which was never written.

Graham had begun his studies on the liquid state at a time when little was known about the subject. His important studies on liquid diffusion, which had been inspired by Gay-Lussac's analogy between solutions and gaseous diffusion, showed that there were considerable variations in the diffusive mobility of different substances. This study was extended to osmosis where Graham clearly defined the process as one of osmose and the liquid diffusion of a salt. Finally, Graham was led by dialysis to distinguish colloids from crystalloids through their differences in both affinity for water and molecular motion and thereby he was able to give a clearer explanation of osmosis. Graham undoubtedly showed by his experimental studies on the molecular motion of liquids that it was possible to make progress towards an understanding of the liquid state. His work on colloids, couched in a new terminology, gave a new status to the study of colloid chemistry, as it is now called, and established a multi-disciplinary study which embraced chemistry, physics, biology and physiology. There is indeed some justice in the later descriptions of Graham as 'the father of colloid chemistry'.

Chapter 7

SPECULATIVE IDEAS CONCERNING
THE CONSTITUTION OF MATTER

1. Graham, undated MS. note marked page 4 in: Volume of MS. letters and correspondence etc. of T. Graham in the Wellcome Library.

SPECULATIVE IDEAS CONCERNING THE CONSTITUTION OF MATTER

"The different 'elements' are the same atom with different amounts of motion. The higher the degree of mobility, the more volume does the same weight of matter occupy, and consequently, when equal volumes are compared the less is its atomic weight. But perhaps it would be better to avoid entirely the idea of atom, and to view matter as a homogeneous fluid or medium with the capacity for possessing weight and capable of undulations or vibrations of that minute character description which is considered molecular. These vibrations are in their nature perpetual, although greatly influenced by temperature. The only origin that can be assigned to these vibrations is a first impulse to be compared to the primordial impulse which moves the planets causing them to move in orbits with different velocities and counteracts the direct influence of gravity tending to bring them to a common cubic distance from the sun." ¹

This short note is possibly a preliminary sketch of Graham's speculative ideas on the constitution of matter. As the note shows Graham proposed two alternative conceptions of the nature of matter. On one view, all the elements were constructed from the same primary material atoms. The atoms of one element were distinguished from those of other elements by possessing different unalterable motions. Thus copper and sulphur contained the same primary atoms; but the degree of motion of a copper atom was fixed and it differed quantitatively from the degree of motion found in a sulphur atom. Alternatively, Graham proposed a theory of matter which was analogous to the wave theory of light. If a continuous homogeneous fluid medium was allowed to exist, then 'atoms' would correspond to different unalterable vibrations of this fluid. To explain the properties of gases Graham found it easier to use the theory of primary material atoms rather than the alternative wave theory.

As Robert Angus Smith wrote "one may almost say that it was the object of Graham's life to find what the movement of an atom was Graham avoids picturing the most primitive motion in all its character,

2. Robert Angus Smith, 'Graham and other atomists' Preface (dated November 1875) to: Chemical and Physical Researches by Thomas Graham, Edinburgh (1876) p xvi. In this Preface, Smith gives the wrong date, 1868, when he quotes from Graham's 'Speculative ideas' paper; it should have been 1863. See Researches. Preface p xix.

but he seems to indicate one of revolution as he brings in the similarity to the orbit of a planet, and in this way with Davy connects in an interesting manner the very first speculations on the eternal motion of the heavens with those movements the smallest conceivable of atoms." ²

Although Smith was correct to say that Graham devoted much of his research work to an attempt to discover the motions of atoms and molecules it is important to recognise that Graham was very reluctant to speculate on the detailed nature of this motion. Although he had been examining diffusion for more than 30 years he had refrained from giving a full explanation of its mechanism, because he had not been clear what meaning should be given to his experimental results. However, by 1863 Graham was ready to speculate on his results. We have seen that he had rejected all previous explanations of diffusion in 1831 when he had been unable to account for the observed differences between the speed of diffusion of a gas and its speed of passage into a vacuum. Until he had completely resolved these differences he did not attempt to give a mechanism for diffusion.

Between 1846 and 1849 Graham established that effusion and transpiration of gases were different processes but he was unable to deduce a simple quantitative law for transpiration. Finally, in 1863, as a response to Bunsen's criticism of the diffusion law, Graham distinguished clearly between the three different modes of gas motion: diffusion; effusion; and transpiration. Effusion and transpiration involved the flow of a mass of gas; whereas diffusion was a quite different phenomenon caused by the inherent motion of gas molecules. The recognition of inherent molecular motions in diffusion led Graham to speculate on the nature of all matter.

This chapter will be concerned with the possible origin and nature of these speculations; and also with their impact on his contemporaries and later writers.

As we have seen, Graham's teachers, Thomson, Hope and Leslie, believed in primary matter. Thomson's views on primary matter were also

3. T. Thomson, System of Chemistry, 1st.edn. Vol.1 (Edinburgh, 1802) p.386. This is repeated in the 2nd.edn. (Edinburgh, 1804), 3rd.edn. (Edinburgh, 1807) and in the 4th.edn. (Edinburgh, 1810) Vol.1 p 631.

4. H. Davy, Elements of Chemical Philosophy (London, 1812) p 182.
"Matter may ultimately be found to be the same in essence, differing only in the arrangements of its particles; or two or three simple substances may produce all the varieties of compound bodies."

5. W. Prout, Chemistry, Meteorology and the Function of Digestion Considered with Reference to Natural Theology, 1st.edn. (London, 1834), being Volume 7 of the Bridgewater Treatises, pp. 28-64, 553-554.
A later version of the molecular theory is given in fuller detail in the 3rd.edn. of Prout's Bridgewater Treatise (London, 1845) pp.35-43, 84-104, 152-163, 499-502. See also the useful discussion of Prout's molecular theory in W. H. Brock, Ph.D. Thesis: The Chemical Career of William Prout, Leicester University, 1966. Chapter 8 pp.361-394.

adopted by Herapath in 1821. Thomas Thomson wrote that "indeed it has been the opinion of many distinguished philosophers of all ages that there is only one kind of matter; and that the differences which we perceive between bodies depend on the variety in the figure, size and density of the primary atoms when grouped together."³ Although Thomson later advocated Dalton's atomic theory he was also convinced of the truth of Prout's integral multiples hypothesis. This allowed him to retain a theory of primary matter. Likewise, Davy was drawn towards a theory of primary matter.⁴ It is therefore not surprising to see that Graham believed in primary matter.

The motion of matter was insisted upon by Davy when he stated that gas particles vibrated and rotated about their axes. These views probably influenced Prout when he constructed his molecular theory of matter.⁵ This molecular theory would have interested Graham, because Prout discussed Graham's work on gaseous diffusion from the viewpoint of his new theory. Prout assumed that matter consisted of spherical molecules which revolved about their axes. The constant velocity of axial rotation of a molecule was inversely proportional to its mass and this motion gave rise to a fixed repulsive force in a molecule. In addition, Prout introduced a force of attraction between molecules which was directly proportional to their masses. The most interesting connection which is to be found between Prout's theory and Graham's speculations concerns the explanation of chemical combination. Prout suggested that, when two different molecules were aligned correctly according to their polarities, then they could combine by uniting their motions. He wrote that: "two dissimilar molecules may unite statically at those moments when the two motions of the two molecules are coincident; e.g. two molecules, the one moving twice as fast as the other, may unite at every revolution of the slower molecule, which will be coincident with every second revolution of the quicker. Hence the more simple the relation between the weights and motions of two molecules, the more readily will they unite, and the more

5a. W. Prout, Bridgewater Treatise., 3rd.edn. (London, 1845) p 501.

6. W. H. Brock, op.cit. (4) p 375.

7. J. B. Dumas, Leçons sur la Philosophie Chimique, (Paris, 1837)
Sixième Leçon. 21st May 1836. pp 234-235.

8. J. B. Dumas, 'Première Mémoire sur les types chimiques', Ann.de Ch.
2 Ser.73 (1840) p 73.

stable will be their union." ^{5a} As Brock has pointed out, these simply related motions were more likely to be produced when their weights were also simply related by Prout's integral multiples hypothesis. ⁶ Similarly, Graham stressed that individual motions could be combined to produce simply-related compound motions when different gaseous atoms or molecules were united together.

Another possible influence on Graham's thoughts about the nature of matter was the planetary theory of matter suggested by Dumas as an alternative to Dalton's atomic theory. The first intimation of the use of this theory by Dumas was given in 1836. He looked forward to a time when the innermost molecular movements of bodies might be calculated in order to predict the properties of matter in the same way that Newton had made quantitative calculations for the heavenly bodies. ⁷ In 1840, these ideas were developed into a planetary theory of matter which was used by Dumas to introduce his concept of chemical types. He wrote that "if one envisages different chemical compounds as so many planetary systems formed from particles retained in position by different molecular forces whose resultant force is chemical affinity, one no longer sees the need for the universal application of the dualistic law admitted by Lavoisier. These particles would be more or less numerous; they could be simple or compound; they would play the same role in the constitution of bodies as the simple planets such as Mars and Venus or the compound planets like the Earth with its moon, and Jupiter with its satellites play in our planetary system." ⁸ He added that it would be possible to replace certain particles by others without much change of property in the same way that a planet might be exchanged for a body with the same gravitating mass.

Particles of matter were distinguished into two kinds by Dumas: physical and chemical atoms. By a physical atom, he meant a particle, or what is now called a molecule, which was not divisible by heat but which could be divided by chemical forces. The constituent parts of a physical

9. J. B. Dumas, Traite de Chimie Appliquee aux Arts, Vol.1 (Paris,1828), Introduction XXXIX-XL and also J. B. Dumas, Leçons sur la Philosophie Chimique, (Paris,1837) p 270.

10. Graham, 'Speculative ideas respecting the constitution of matter', (1863) Researches. p 300.

11. C. Daubeny, An Introduction to the Atomic Theory, 2nd.edn. (London, 1850) pp 276-279.

atom were chemical atoms; the latter being the smallest particles which took part in chemical reactions. Dumas did not state that chemical atoms were indivisible; only that they had not yet been divided.⁹ In Graham's speculations, there is a correspondence between his diffusive molecules and the physical atoms of Dumas. Also, Graham's ultimate atoms might correspond to the chemical atoms of Dumas. Like Dumas, Graham was prepared to concede that the "advance of science may further require an indefinite repetition of such steps of molecular division."¹⁰

In 1850 Graham's friend, Charles Daubeny, noted that Dumas thought that the particles of solid matter were like the different suns with their attendant planets and satellites. Daubeny then attempted to extend this analogy.¹¹ The celestial bodies were held in position by the mutual attraction of gravitation just as atoms were held together by the force of cohesion. He suggested that our solar system when it was seen from a distance might appear to be blended into one compact mass. Being one of many such solar systems, when viewed by a distant observer, there was an analogy between widely-spaced solar systems and the atoms in a crystal. Like Dumas, he argued that in a gas, the particles might be divisible into smaller ones by chemical affinity and even the latter particles might be composed of groups of atoms rather than single atoms. Now it was possible that every one of these particles within its own little world might undergo an alteration in the position of its constituent parts, which might alter its properties without loss of material. Significantly, Daubeny then wrote that: "it is quite allowable to suppose, that the atoms of a simple body, although they may be unsusceptible of the smallest change in point of size from the beginning to the end of time, should nevertheless differ materially from those of every other. And this would be a necessary inference, if we assume that the force of gravitation is common to all matter as such, as a property, not varying in degree according to the nature of the substance itself, but determined by the quantity of matter comprised within a given compass. Hence supposing

12. C. Daubeny, *ibid.* pp 278-279.

13. *ibid.* pp 430-431 footnote.

14. C. Daubeny, *ibid.* p 140.

that all bodies were of the same specific gravity, the atomic weight of each would represent the relative size of atoms, or in other words, its atomic volume." ¹²

In this passage, Daubeny was approaching but not entirely reaching Graham's later position that since the force of gravitation was uniform in its action on matter, then it was possible to construct the different elements from the same primary atoms by endowing them with different degrees of motion. The motion of a primary atom would sweep out a fixed volume in space producing matter of a particular density.

Again, when Daubeny discussed organic matter he took the Proutian view that it might be constructed from gradual modifications of one primary matter. In support of this he cited Leibniz's law of continuity (which Boscovich had used) whereby natural changes occurred by minute and imperceptible gradations. Like Graham, Daubeny referred to the fact that "Cagniard de la Tour's work gives considerable confirmation of the idea of continuity, his research shows that as the solid condition passes imperceptibly to the liquid, so does the liquid into the aeriform; whilst the recent researches of Faraday suggest that the property of existing in the gaseous state is the exclusive condition of none." ¹³

Inspired by Prout's hypothesis, Daubeny explained his views on the creation of the elements: "The only way, indeed, in which I can conceive the formation of such bodies, is by supposing that their component particles which on this hypothesis, may just as well be assumed to consist of one kind of matter, as of more - clustered together, when first formed, by the force of cohesive attraction in various groups consisting of different numbers of the same, and that some of these groups, owing to mechanical conditions, arising out of the arrangement of their component atoms, become indissolubly connected. These might constitute the bodies we regard as elements, since the difference in chemical properties which they present, might result from the mode of collocation of their atoms Thus hydrogen might consist of 10 of these primary atoms, oxygen of 80 and carbon of 60 and so on." ¹⁴

15. W. S. Jevons, MS. note 'Theory of heat', March 24th 1853 page 1, The Jevons MSS., The John Rylands Library, Manchester.

16. In his 1854 [?] lecture on the 'liquid condition of matter' Graham wrote about the molecular condition of gases: "Even when the mass is at rest, the molecules are in motion, exchanging places with each [other] a balanced movement which involves no loss of force and may therefore be perpetual. The force at work is the same in a cubic inch of every gas and is measured by the elasticity. But where the gas is light (like Hydrogen) the particles are moved more rapidly than where the gas is heavy as in oxygen." Wellcome MSS. Miscellaneous notes and oddments on Chemistry, etc. Graham's holograph MSS. No.2580. Unbound in pamphlet case. Item (6) On liquid condition of matter. See also the letter from Graham to Thomas Andrews, dated November 25th 1856, in which Graham says: "I have long been of [the] opinion that diffusion, transpiration of both gases and liquids will never have an explanation except from the motion theory of heat." Andrews' Papers Queen's University, Belfast.

Some of Graham's ideas are found in the earlier work of Dumas and Daubeny; but Graham's theory was distinguished by the idea that the difference between atoms was due to varying quantities of motion in the prime matter rather than different numbers of primary atoms.

A further interaction of ideas can be seen in the early speculations of William Stanley Jevons who studied under Graham and was awarded the gold medal for Chemistry in 1853. In this year, Jevons began to speculate on the nature of heat. He wrote that "the particles of all matter are supposed to be perfectly elastic, without which, motion cannot be indestructible Heat is caused by a vibratory motion of atoms, which is different in solids, liquids and gases. This motion is a simple rectilinear one but from the atoms continually meeting each other it becomes either a vibratory one, the atom remaining in the same relative position or more free so as to cause intermingling of atoms." ¹⁵ He proceeded to assert, like Herapath, that equality of temperature was caused by equality of momentum and that the repulsive property of heat was a result of atoms requiring a certain space for their vibrations. As we have seen, Graham accepted the motion theory of heat at this time ¹⁶ and it is possible that Jevons might have discussed his ideas with his teacher Graham.

An even more interesting speculation, made by Jevons, and inspired no doubt by his studies with Graham in 1852 and 1853, was developed whilst Jevons was an assayer at the Sydney mint in Australia. It is found in a letter which he wrote to H. E. Roscoe in 1855. It is even conceivable that Jevons talked over his ideas with Graham when he met him again on his return to England in 1859; but, like Jevons' own theory, this is pure speculation. Jevons admitted to Roscoe that "through the whole of science there is nothing I should like to follow up more, and spend my whole life on than the atomic theory and theoretical chemistry, but my road seems to lie another way. Lately however a sublime idea (as I think it) occurred to me for the foundation of an atomic system, which

17. R. D. Collison Black (editor), Papers and Correspondence of William Stanley Jevons, Volume 2, Correspondence 1850-1862, (London, 1973) pp 159-160. Letter 66. from W.S.Jevons to H.E.Roscoe, Sydney, July 11th 1855.

would altogether beat Williamson's ideas; it is to suppose that the ultimate atoms of bodies (small spheres perfectly elastic and similar whatever element they form) are subject only to the force of gravitation which is thus made quite universal. Two spheres under the influence of each other's attraction would approach and revolve (like double stars) round each other forming a compound atom of the first degree of complexity. Instead of two we may have any larger number, as in compound stars, of atoms revolving around the common centre of gravity, thus producing the different elements and explaining the curious relations of the equivalents. Next, two of these compound atoms may revolve around each other, as wholes, like the planets accompanied by their satellites revolve round the Sun, and these atoms of the second degree of complexity may combine (i.e. revolve round each other) and form atoms of third degree and so on. You will easily see that this system would admit of an almost infinite number of combinations of compounds, while the variations of the speed of revolution and of the actual free motion of gaseous atoms, would correspond to the quantities of combined and sensible heat, and the increase of the orbits of atoms by increased speed would give the dilation by heat Of course atoms must come against each other sometimes which is rather awkward, and I have got no idea of what would take place in solids and liquids. In gases I believe two compound atoms meeting would appear to pass through each other but probably composed of different ultimate atoms which had been exchanged in contact. The mechanical properties, diffusion, dilatation, specific heat etc. etc. of gases I am sure could be easily worked out mathematically on the supposition of these atoms freely scampering about each other in all directions under nothing but the force of gravitation. This is enough of my theory which I only tell you because it is tiresome to think of things without a soul here to communicate them to." ¹⁷

It is significant to observe that Jevons, like Graham, begins with primary matter in order to construct his atoms. The small elastic spheres

18. H. Spencer, Principles of Biology, Volume 1 (issued in parts, London, 1863) pp 3, 14-15.

19. R. Chambers, Vestiges of the Natural History of Creation, 4th. edn., (London, 1845) p 28.

which revolve round one another constitute the atoms of elements.

Presumably, the number of elastic spheres in an 'atom' is the characteristic property which distinguishes any one 'atom' from another. Unlike Graham, Jevons does not give each atom a fixed degree of motion. With this model, Jevons had developed his ideas on heat to include circular motion for the combined heat and possibly vibratory or rectilinear motion for the sensible heat. Did Graham have similar notions about heat?

We do not know.

I have already suggested that Graham's paper on the molecular mobility of gases might have been influenced by his reading of the first part of Herbert Spencer's, Principles of Biology, which he had received in January 1863. Spencer emphasised the importance of motion stressing the word 'mobility'. He pointed out that compounds were formed by uniting together elements, with different atomic mobilities. The resultant molecular mobility was one of the leading characteristics of a substance; in general, as the mass of a substance was increased then its molecular mobility was correspondingly decreased.¹⁸ However, Spencer did not make any detailed statements until later about the creation of the atoms of elements. This is in marked contrast to another evolutionist, Robert Chambers, the author of: Vestiges of the Natural History of Creation. Like Spencer, he believed in the nebular hypothesis according to which the creation of the stars was caused by the aggregation of diffused nebulous matter. Chambers could see no difficulty in the view that different chemical elements were merely modifications of primordial matter formed under suitable conditions. He wrote: "analogy would lead us to conclude that the modifications of primordial matter, forming our so-called elements, are as universal, or as liable to take place everywhere, as are the laws of gravitation and centrifugal force."¹⁹ It may be significant that this passage was written immediately after Samuel Brown had described his controversial experiments on transmutation. Speculative ideas analogous to those proposed by Graham were very much in the air in

20. Graham, 'On the molecular mobility of gases', Phil.Trans. 153 (1863) 385-405. The original MS. of this paper, lacking the section marked 'Speculative ideas', is held by the Royal Society. MS. no.P.T.69.2.
21. Graham, 'Speculations respecting the constitution of matter', Proc. R.S. 12 (1863) 611-623 or Researches. pp 299-302.
22. Graham, Wellcome MS.2584 (old no.3394) 'On the molecular mobility ['diffusive movement' superscribed and crossed through] of gases'. Copy with holograph corrections and additions 44 ff. 1863 [?]. The section entitled 'Theoretical considerations' is found from p 38 to p 43 of the MS.
23. Graham, Researches. pp 299-300. In his draft MS., op.cit. (22), Graham added "Such views of the constitution of matter being admitted by Newton the transmutation of metals and other elements would not fail to appear to him, as we know it did, a legitimate subject of enquiry."

mid-Victorian Britain and some of Graham's speculations can be found in the works of these earlier writers.

Having examined some of the earlier speculative attempts to explain the constitution of matter let us now examine Graham's own views. As a fitting conclusion to his paper 'On the molecular mobility of gases', presented to the Royal Society in 1863, Graham added a theoretical appendix entitled 'Speculative ideas respecting the constitution of matter'. It was published separately from the rest of the paper as a result of criticisms made both by the Royal Society's referees and its Secretary. The main paper appeared in Philosophical Transactions²⁰; but the 'speculative ideas' appeared in the Proceedings of the Royal Society.²¹ In addition to these published papers, a draft copy of the whole paper still exists in the Wellcome Library's collection of manuscripts and notebooks written by Graham.²² The section entitled 'Theoretical Appendix' in this draft paper contains some significant differences from the published paper.

In his published speculative ideas on matter, Graham argued that differences in motion caused changes in the properties of matter. He explained that "it is conceivable that the various kinds of matter may possess one and the same ultimate and atomic molecule existing in different conditions of movement. The essential unity of matter is an hypothesis in harmony with the equal action of gravity upon all bodies. We know the anxiety with which this point was investigated by Newton, and the care he took to ascertain that every kind of substance, 'metals, stones, woods, grain, salts, animal substances etc.' are similarly accelerated in falling, [to the earth] and are therefore all equally heavy."²³

The unity of matter was an ancient hypothesis, advanced by Leucippus and Democritus, favoured by Davy and recently revived by Prout. Graham had previously commented on the atomism of Democritus in a review of chemical history which he had prepared for his University College lectures

24. Graham, 'Notes and drafts for University College lectures', (1838-1848)
154 ll. Wellcome Library MS. no.2579 (old no.3202).

25. Graham, op.cit. (21) Researches. p 300.

in 1838. He wrote that "the ideas [of Democritus] on atoms are in accordance with the speculations of modern philosophers, but they scarcely belong to Chemistry and have had no influence on its progress." ²⁴ By 1863, Graham was led to revise his opinion as a result of his experiments on gaseous motion.

To illustrate his views Graham chose the simplest form of matter: that found in gases. Primary matter was present in all substances and if it was at rest all substances would be identical. But this was not the case; in the real universe, motion was always present. The ultimate atoms of matter were all alike in size and weight but the atoms of different elements were distinguished from one another by possessing different unalterable degrees of motion. A primordial influence endowed an ultimate atom with a particular invariant motion. All atoms of the same element possessed an identical motion which differed quantitatively from the motions of atoms of other elements. This motion of a primary atom gave rise to a characteristic atomic volume. As Graham expressed it: "the more rapid the movement, the greater the space occupied by the atom, somewhat as the orbit of a planet widens with the degree of projectile velocity. Matter is thus made to differ only in being lighter or denser matter." ²⁵

On this view different inconvertible elements must contain atoms of different density. One major difficulty with these speculations was Graham's insistence that the motion of a primary atom should be unchangeable and unceasing. Motion might be unceasing but it is difficult to envisage any real motion which could not be altered by heat or collision. This objection was raised by G. G. Stokes as we shall see.

Having distinguished primary atoms, by differences in motion, Graham next turned to the nature of the diffusive molecules found in gases. These diffusive molecules were polyatomic molecules formed by joining together primary atoms. Diffusive molecules were themselves uniform in weight but, unlike the ultimate atoms, their velocities were affected by

- 25a. The importance of the inherent motion of ultimate molecules was recognised by Redwood in a lecture which he gave to the Pharmaceutical Society. He wrote that: "we derive from the study of the phenomena connected with the diffusion of liquids, an additional indication that the molecules of matter are active not quiescent, - that their normal condition is that of motion, not of rest." See: Theophilus Redwood, 'On dialysis, or liquid diffusion applied to analysis, the preparation of medicines etc.' A lecture delivered at the Pharmaceutical Society on March 19th 1862. Pharm.J. 2 Ser. 3 (1862) 515-528. See p 527.
26. Graham, 'On the molecular mobility of gases', Researches. pp 211-212.
27. Graham, ibid. p 211.
28. J. Herapath, 'A mathematical inquiry into the causes, laws, and principal phenomena of heat, gases, gravitation etc.' Ann.Phil. 2 Ser. 1 (1821) 273-293, 340-351, 401-416, see p 281 and J. Herapath, Mathematical Physics, (London, 1847) Vol. 1 Introduction XX and pp 4-5.

heat. We have seen that Graham had proposed the existence of polyatomic molecules both in the solid metals found in voltaic circles and in the molecules existing in the liquid state, particularly those studied in experiments on liquid diffusion. It is even possible that Graham may have been led to speculate that polyatomic molecules were composed of primary atoms from his observation that, in liquid diffusion, equal weights of different substances diffused in the same times. Graham believed that motion was a more fundamental and characteristic property^{25a} than atomic weight. Indeed, the motion of a diffusive molecule was simply a reproduction on a larger scale of the constituent motions of the primary atoms.

The motion observed in gaseous diffusion could be deduced from the kinetic theory of gases. Graham wrote that "the sole motive agency appears to be that intestine movement of molecules which is now generally recognised as an essential property of the gaseous condition of matter. According to the physical hypothesis now generally received, a gas is represented as consisting of solid and perfectly elastic spherical particles or atoms, which move in all directions, and are animated with different degrees of velocity in different gases. Confined in a vessel, the moving particles are constantly impinging against its sides and occasionally against each other, and this contact takes place without any loss of motion, owing to the perfect elasticity of the particles."²⁶ In a footnote he attributed the physical hypothesis to D. Bernoulli, J. Herapath, Joule, Krönig, Clausius, Clerk Maxwell and Cazin adding that "the merit of reviving this hypothesis in recent times and first applying it to the facts of gaseous diffusion, is fairly due to Mr. Herapath. See Mathematical Physics, in two volumes, by John Herapath Esq. (1847)."²⁷

In his earlier writings Herapath had favoured a theory of primary matter and he continued to entertain this theory in 1847.²⁸ He regarded heat to be a vibratory motion of the particles of matter. Temperature was not just a measure of the velocity of a particle but it was an average measure of the individual momentum of a particle. With a rise in

29. H. Davy, Elements of Chemical Philosophy, (London, 1812) p 95.

30. J. Clerk Maxwell, 'On the dynamical theory of gases', Phil.Mag.
4 Ser. 19 (1860) p 19. Maxwell repeated these views in his article
'Atom' in the 9th edn. of Encyclopaedia Britannica (Edinburgh, 1875).

31. Graham, op.cit. (21) Researches. 301.

temperature the vibratory motion increased and so expansion occurred; this was caused either by an increase in the number of vibrations per second or by longer vibrations. Herapath accepted the possibility that particles could be compounds and that an inferior order of vibrating particles might constitute a compound-particle. Davy had previously suggested that fluids contained particles which vibrated and rotated on their axes,²⁹ but Herapath could not see any necessity to assume an additional rotary motion. Maxwell in his first paper on the dynamical theory of gases proposed two possible alternative views of the particles in gases. Either they were hard, spherical, elastic particles or they were centres of force whose action was insensible except at very small distances from the centres when a very strong repulsive force suddenly appeared. This latter alternative was Boscovichian point-atomism.³⁰

Graham did not give a detailed view of the motion which he required in atoms. He may have accepted Herapath's view that atoms had a vibratory motion or like Davy he might have admitted that both vibration and rotation occurred in gaseous atoms. Indeed, some kind of revolutionary motion is hinted at in Graham's analogy between the gaseous molecule, and the sun, with its planets and their satellites.

As we have seen, Graham also proposed an alternative theory of primary matter similar to the wave theory of light, but he did not develop this theory to include diffusive molecules. He thought that a fluid medium might exist which could be made to undulate. He then explained that "a special rate of vibration or pulsation originally imparted to a portion of the medium enlivens that portion of matter with an individual existence, and so gives rise to a distinct substance or element."³¹

In his draft manuscript Graham did not distinguish between ultimate atoms and molecules. Instead, he referred to molecules throughout. One significant paragraph was omitted entirely from the earlier draft. This paragraph was probably added in order to clarify the distinction between ultimate atoms and gaseous molecules so that only the latter were

32. Graham, op.cit. (21) Researches. 300.

33. Graham, op.cit. (22) p 40 of the MS. Initially Graham wrote the last paragraph: "Heat appears to have an 'opposing but similar' influence to gravity, 'changing equally' the velocities of the different molecules without altering the relation of these molecules to each other." He deleted the words given in single inverted commas from his own draft.

affected by heat. Thus, Graham was able to bury the primary atoms inside the gaseous molecule so that they were unaffected by the motion of heat. The additional paragraph is worth quoting in part. He wrote: "What has already been said is not meant to apply to the gaseous volumes which we have had occasion to measure and practically deal with, but to a lower order of molecules or atoms. The combining atoms hitherto spoken of are not therefore the molecules of which the movement is sensibly affected by heat with gaseous expansion as the result. The gaseous molecule must be viewed as composed of a group or system of the preceding inferior atoms, following as a unit laws similar to those which regulate its constituent atoms. We have indeed carried one step backward, and applied to the lower order of atoms, ideas suggested by the gaseous molecule, as views derived from the solar system are extended to the subordinate system of a planet and its satellites Accordingly molecular volumes of different elementary substances have the same relation to each other as the subordinate atomic volumes of the same substances." ³²

The other major difference between the draft paper and the final published version of his 'speculative ideas' is that two paragraphs were omitted from the original draft paper. In order to assess Graham's views on matter fully it will be helpful to consider these two paragraphs. He wrote: "this molecule of varying velocity continues, as matter, under the influence of the force of gravity. The attraction of gravitation must modify that absolute and no doubt assignable degree of velocity, which the molecule possesses; as analogically the weight of the Sun influences the width of the orbits which the planets assume under a direct projectile force.

Heat appears to have an antagonistic influence to gravity, augmenting the velocities of the different molecules without altering the relation of these molecules to each other." ³³

A fundamental difficulty remained in these earlier drafts: how could the motions of primary molecules be unaffected by changes in the

34. R. A. Smith, The Life and Works of Thomas Graham, (Glasgow, 1884) p 59.
"I had an evening occupation for the last two months which has nearly excluded everything else, correspondence in particular. It is the composition of a paper for the R.S., embodying several years work - the subject, the Gases - which I was very anxious to get off my hands. It has cost more work (I mean investigation) than the dialysis, but is necessarily a little mathematical, and consequently less interesting. I am glad that it is now off my hands, having been delivered in fairly copied only last evening."
35. Graham sent his paper to the Royal Society on May 7th 1863 via the Assistant Secretary of the R.S., Mr. White, to whom he wrote:
"In sending the accompanying paper I have to apologise for the absence of the usual abstract. The latter however is in the course of preparation and will follow in a few days."
G. G. Stokes Correspondence, Cambridge University Library, MS.7656, R.S.377.
36. Minutes of the Committee of Papers, Royal Society, Volume III.
The committee referred the paper on June 11th 1863, and postponed a decision regarding its publication on June 18th 1863. The committee on June 11th included: President Sabine, Dr. Carpenter, Mr. De La Rue, Captain Galton, Mr. Godwin Austen, Mr. Lubbock, Mr. Clerk Maxwell, Dr. W.A. Miller, Prof. W.H. Miller, Dr. Sharpey, Prof. Stokes, Prof. Sylvester, Prof. Wheatstone, and the Rev. R. Willis.
37. Royal Society Referee's Report 5.83. by W. Allen Miller on Graham's paper: 'On the molecular mobility of gases' dated July 10th 1863.

temperature? In the final published version, primary atoms were buried inside the diffusive molecules; but the problem was not solved and this may explain Graham's reluctance to be precise about the unalterable motion which he envisaged for a primary atom. Was it a vibrational motion? Or was it rotation about an axis? Or was it a revolutionary motion about some central point in the same sense as a planet moves around the sun? He only hinted by using an analogy with the solar system that he was thinking of some kind of revolutionary motion.

Further information on these difficulties can be obtained by following the progress of the paper from the stage of its composition through to its reception by the Royal Society referees and finally to its publication. On May 9th 1863, Graham wrote to his sister saying that he had spent two months writing his paper on gases during the evenings.³⁴ Thus it would appear that the paper was written during the months of March and April of 1863. Graham sent his paper to the Royal Society on May 7th.³⁵ The paper was first referred to the Committee of Papers on June 11th and then again on the day when Graham read his paper to the Royal Society, June 18th 1863. The Committee decided to postpone a decision on its publication.³⁶ Presumably, it was necessary to obtain referees' reports on the paper before its publication. The two referees chosen were William Allen Miller, Daniell's successor at King's College, London, and Alexander W. Williamson, Graham's successor at University College, London.

Miller wrote that "the paper concludes with some bold speculations on the constitution of matter. It is well worthy of publication."³⁷ On the other hand, Williamson, 'after careful and repeated perusal of the theoretical appendix', was less happy with its contents. He wrote: "In looking repeatedly at the theoretical appendix I have failed to discover any connection between it and the substance of the paper. Its conclusions are moreover so much at variance with the best-established works of chemico-physical enquiry that they require far more explanation. I cannot recommend the publication of the appendix in its present form

38. Royal Society Referee's Report 5.84. by Alexander W. Williamson on Graham's paper: 'On the molecular mobility of gases' dated July 29th 1863.
39. For Williamson's views on atomism, see: D. M. Knight, Atoms and Elements, 2nd. impression, (London, 1970) pp 3, 34, 105-106, 115-121, 125-126.

although I cordially recommend the rest of the paper. I should recommend that Mr. Graham be requested to give more development to the views stated in the appendix of this paper, or to defer publishing them until more simple explanations can be given." ³⁸ As we know Williamson favoured a simple chemical atomism and he did not have much sympathy with discussions on the ultimate structure of matter. ³⁹

A more serious criticism was made by the Secretary of the Royal Society, G. G. Stokes, who had seen Graham's paper before it was read to the Society on June 18th. On receiving Williamson's report, Stokes decided to write to the Officers of the Royal Society: "having read Graham's paper with much interest I have formed my opinion of it independently of the referees With reference to the bold speculations as to the ultimate constitution of matter with which the memoir concludes my feeling was that one who has done so much excellent work has a right to speak if he pleases; but that it would be better for the author's reputation if this part were omitted. [My] chief objection I should not have felt in the same way but I cannot help regarding the speculations as crude as well as bold. It is now generally believed and Mr. Graham shares in the view that the thermometric heat is molecular disturbance. But the amount of heat in a given portion of matter is capable of increase and decrease in a continuous manner. That is according to the view admitted by both parties, the amount of heat constituting molecular disturbance is liable to increase or decrease. There is nothing here like the fixity of properties which distinguishes hydrogen, sulphur, or gold etc. from one another. What sort of motion then can we conceive to belong to the ultimate molecules of matter which shall remain unchanged even in the processes of the chemist's laboratory? The only kind I can conceive is that of a swinging [? - this word is difficult to decipher] body round an axis (not necessarily fixed in the body or in space) hopping [sic] through it, or a circulatory motion like that of the solar system and even the latter resting on the condition that

40. Royal Society Referee's Report 5.85. Report by G. G. Stokes to the Officers of the Royal Society on Graham's paper: 'On the molecular mobility of gases'. July 29th 1863.
41. Stokes Correspondence, Cambridge University Library, MSS.7656 R.S.409. Letter from E. Sabine to G. G. Stokes, dated August 1st 1863: "Your letter with the enclosures concerning Graham's paper reached me just $\frac{1}{2}$ hour before I entered the carriage for the train to come here [Llandoverly]; and I immediately sent it then on to Dr. Sharpey. I name this lest you should hear that I left London on Friday evening, and be afraid that your letter should have missed me."
42. William Sharpey Correspondence, University College, London, MS.Add.227, letter no.148 from G. G. Stokes to Wm. Sharpey, dated August 10th 1863.
43. Stokes Correspondence, Cambridge University Library, MSS.7656 R.S.410 letter from Graham to Stokes, dated August 11th 1863.
44. Royal Society MS. of Graham's paper, 'On the molecular mobility of gases'. P.T. 69.2.
45. The 'Speculative ideas' paper appeared in:-
The Athenaeum No.1867, August 8th 1863, in which there is a report of the Royal Society meeting of June 18th 1863. 'The speculative ideas respecting the constitution of matter' are found on pp 182-183.
Chemical News 8 (1863) 91-93 (August 22nd 1863).
J.Chem.Soc. 2 (1864) 368-371.
Proc.R.S. 12 (1863) 611-623, see pp 620-623.
Phil.Mag. 4 Ser.27 (1864) 81-84 (February 1864).
Ann.de Ch. 4 Ser.2 (1864) 457-460 (May 1864).
Liebig Ann. 131 (1864) 147-152.

the distances between molecules are quasi-infinite compared with the dimensions of the molecules. But I can't see that these kinds of motion would help us in the least towards the explanation of the phenomena of diffusion. The difficulty I have mentioned with reference to the nature of heat has been touched on by Mr. Graham but dismissed I think too summarily. In short, I doubt if Mr. Graham has formed a clear idea in his mind of the part of motion which would suit his purpose, and so regard these speculations as crude. I recommend that Mr. Graham be asked whether these speculations contain too many difficulties and [be told] that they are in too immature a form for publication at present I would like to know the views of the other officers." ⁴⁰ This note by Stokes is dated July 29th 1863.

Stokes sent his report to both President Sabine and William Sharpey.⁴¹ On August 10th 1863 Stokes informed Sharpey: "I have written to Mr. Graham suggesting the omission for the present of the last few pages containing his speculations, which are quite distinct from and hardly connected with the body of the paper." ⁴² Graham replied to Stokes on August 11th commenting on his suggestion: "you have anticipated me, for I had intended when the paper again came before me to strike out the theoretical part, which is more suitable for a journal or the Proceedings (where indeed it receives sufficient publicity) than the Transactions. I had made this excision in a French version of the abstract for the Comptes Rendus [which he had sent to Dumas on July 7th 1863]. With many thanks for your letter." ⁴³ Thus, on August 12th 1863, Stokes sent Graham's paper, with the 'Speculative ideas' crossed out, to the printers Taylor and Francis.⁴⁴

Undoubtedly, Graham wanted to publish his speculations and indeed they had already appeared in print on August 8th 1863 in The Athenaeum; and afterwards they appeared in: Chemical News; the Philosophical Magazine; the Proceedings of the Royal Society; and in the Annales de Chimie et de Physique etc. ⁴⁵ When the Royal Society Committee of Papers

46. op.cit. (36). The committee on October 15th 1863 included: Babington, Buckton, Carpenter, Galton, Hooker, Lubbock, Maxwell, W.A.Miller, W.H.Miller, Sharpey, Stokes, Sylvester, Wheatstone and Willis.

47. See the letters, written between Stokes and William Thomson, of 1854, in G. G. Stokes, Mathematical and Physical Papers, edited by J. Larmor (Cambridge, 1880-1905) Vol. 4 pp 367-376; and a letter from Stokes to Lockyer written in 1879:- Stokes wrote that: "the question observe is not, Are the elements compound bodies? But has any satisfactory evidence been now obtained that they are compound bodies? You would, I imagine, find plenty of chemists from Prout downwards, who would regard it as most probable that they were compounded. I must say that, in common I suppose with multitudes of others, I have long supposed for my own part that they were." from J. Larmor, Memoir and Scientific Correspondence of the Late Sir George Gabriel Stokes, Vol. 1 (Cambridge, 1907) p 406.

48. Graham, 'On the molecular mobility of gases', Researches. p 224.

met again on October 15th 1863 they reported that the paper by Graham:
"on the molecular mobility of gases was to be printed with the omission
of the 'appendix which the author withdraws.'" ⁴⁶

Graham did not advance any further comments on the nature of the unalterable motion of atoms in answer to Stokes's criticism. From his studies on spectrum analysis, it is evident that Stokes favoured the idea that elements were compound bodies. ⁴⁷ But he believed that Graham had not described sufficiently the exact nature of the motion of atoms or molecules, nor had he explained adequately how this motion was related to heat or molecular disturbance.

In his speculations Graham dealt with two other major themes: the chemical combination of gases and the continuity of matter. He regarded the chemical combination of gases to be firstly "an affair of volume." When equal volumes of two elementary gases combined, their movements were also combined. The new compound would possess the whole, or half, or some simple proportion of the original motion and consequent volume. Therefore chemical affinity was related to motion and therefore to volume. These combining volumes of gases were related to the density and specific gravity of the gas. This was a view of chemical combination based on motion; atomic weight was not important on Graham's view. Motion was the principal property of combining atoms; next came volume. This emphasis on motion, as the basis of affinity and diffusibility, was stressed by Graham. He wrote that diffusibility was not "determined or caused by specific gravity. The physical basis is the molecular mobility. The degree of motion which the molecule possesses regulates the volume which the gas assumes, and is obviously one, if not the only, determining cause of the peculiar specific gravity which the gas enjoys. If it were possible to increase in a permanent manner the molecular motion of a gas, its specific gravity would be altered, and it would become a lighter gas. With the density is also associated the equivalent weight of a gaseous element, according to the doctrine of equal combining volumes." ⁴⁸

49. Cagniard de la Tour, 'An account of some results obtained by the combined action of heat and compression upon certain fluids, such as water, alcohol, sulphuric ether and rectified oil of petroleum', Ann.Phil. 5 (1823) 290-294 from Ann.de Ch. 2 Ser.21 (1822) 127-132, 178-182. This paper is dated Paris, August 12th 1822. Charles Cagniard de la Tour was born at Paris in 1777 and died there in 1859. He was an attaché in the Ministry of the Interior and a member of the French Academy. His researches in physics were mainly devoted to acoustics. However, his most important discovery was, what was later described as, the concept of critical temperature.
50. Graham, Referees Report for the Royal Society RR 6. 15 on Thomas Andrews' paper, 'On the continuity of the gaseous and liquid states of matter' published in Phil.Trans. 159 (1869) 575-590. The referees report is dated July 19th 1867.
51. Graham, *ibid.*

In the final part of his speculative paper, Graham considered the continuity of matter. He argued that the predominance of a given physical state was produced by an unequal development of molecular motion. The liquid and solid states did not involve the complete extinction of the gaseous state but they were an addition to that state. Indeed it was possible that all three states co-existed in every liquid or solid although one state prevailed over the other two. A restriction in the range of motion caused the change from a gas, to a liquid or solid, and Graham again referred to the important observation made by Gay-Lussac that both ice and water at 0°C emitted water vapour with precisely the same pressure.

Graham believed that, between the three main states of matter, there were intermediate states which were difficult to classify. The intermediate states of matter possessed properties shared by both of the states which bounded them and this showed that there was an essential continuity between all the states of matter. Between gases and liquids, there was a condition which Faraday had called the Cagniard-Latour state. In 1822, Cagniard-Latour had found, by heating liquids in sealed tubes, that there was a fixed temperature at which a liquid turned into a compressed vapour.⁴⁹ Above this temperature, compression alone did not cause liquefaction. Thomas Andrews later investigated this state in his experiments on the liquefaction of carbon dioxide and Graham was appropriately chosen, in July 1867, as the referee for this paper. Graham pointed out that Andrews had made a significant observation that there was a "peculiar appearance of moving and flickering striae through the entire mass [of compressed carbon dioxide gas], when the pressure was lowered"⁵⁰ below the critical point. Here again was a condition intermediate between liquid and gaseous carbon dioxide. Graham thought that Andrews' experiments, on the continuity of the liquid and gaseous states, were on too small a scale to be conclusive, but he conceded that "they were probably the best which the subject admits."⁵¹

52. Graham, op.cit. (21), Researches. p 301.

Another intermediate region in the states of matter was the colloidal condition. This region was first distinguished clearly by Graham. He believed that the colloidal condition "intervenes between the liquid and crystalline states, extending into both and affecting all kinds of solid and liquid matter to a greater or lesser degree." ⁵² Atomic or molecular motion was evident in all the states of matter. This motion was more restricted in liquids than gases and was most limited in the solid state. Generously, Graham remarked that Williamson had used the hypothesis of molecular movements in liquids to explain the process of etherification and molecular exchange reactions in solution.

Let us now turn to the reception of Graham's speculative ideas. It seems to be true that they were not widely commented upon in print by his contemporaries. Most writers, who mentioned them, did so without comment; and this is particularly true of Graham's obituarists. However, this is not the case with Joseph Bayma who, in 1866, discussed Graham's speculations in his book: The Elements of Molecular Mechanics. Bayma was a Jesuit teacher, being Professor of Philosophy at Stonyhurst College in Lancashire. He did not accept the view that motion was the only active power of matter nor did he believe that motion was indestructible. He was critical of the introduction of molecular vortices in explanations of matter, because he argued that they were simply designed to replace the repulsive power of matter by the centrifugal force of a revolving atom. He believed that matter must possess both attractive and repulsive powers. If a revolving atom was placed in an elastic medium, motion must be transmitted to this medium and so a conservation of vortex motion was not possible. If, on the other hand, a vortex was placed in a vacuum this might allow a conservation of motion but it still raised the problem of action at a distance and hence attractive and repulsive powers must be introduced in such a theory. He regarded Graham's speculations as 'another theory of molecular vortices' but he did not see how the motion of primary atoms could be indestructible.

53. Joseph Bayma, The Elements of Molecular Mechanics, (London, 1866) pp 41-42.

Bayma also noted that both J. Mayer and Graham held motion to be indestructible. He added: "We dare to say that these two men are no authority. Surely, they make wondrous assertions; but the more wondrous the assertions, the more we are entitled to be favoured with reasons in their support. Now, Mr. Graham asserts simply what he cannot prove; and, in fact, he does not pretend to have proved his assumption." p 24.

54. A. Bain, Logic, Volume 2 (London, 1873) Chapter 13 p 128.

Alexander Bain (1818-1903) was mainly interested in the development of experimental psychology. He had attended Thomas Clark's lectures on Chemistry at Aberdeen and in 1842 he was introduced to Graham whom he considered to possess a scientific intellect second to none in his generation. For Bain's comments on Graham see A. Bain, Autobiography, (London, 1904) pp 104-5, 128. Bain was Professor of Logic at Aberdeen University from 1860 to 1880. He helped J.S. Mill with his system of logic. Bain attempted to correlate physical processes with psychological bases. He was a utilitarian. Bain advised Herbert Spencer that Graham had suggested the word 'molar' to him for describing mechanical forces as opposed to molecular forces. Thus, Bain had used this word in his subsequent writings.

Concerning Graham's theory he wrote: "I do not see, by what mechanical principles Mr. Graham would be able to account for the motion of his atoms. Is their motion progressive or vibratory? Is it curvilinear or rectilinear? If simply rectilinear, how can it give rise to volume? and how is it to be compared with the orbits of planets? If curvilinear, what and where is the cause of its curvature? Are we to suppose that curvilinear motion can be the effect of a simple 'primordial impulse' which is essentially rectilinear? We must therefore assume that there is an agent which urges each atom to abandon its rectilinear path. Mr. Graham has neglected to inform us what this agent is: and wisely too. For the motion of his atoms being 'inalienable' and 'inconvertible', it would have been improper to suppose that there is a cause capable of working that change. If, lastly, the motion is assumed to be vibratory, the velocity of each atom will become = 0 at the limit of each vibration. Now is there anything that checks a motion 'inalienable' and 'inconvertible', and reduces it to zero? And, when motion has been reduced to zero, how is it restored? We think it is evident that Mr. Graham's view cannot be reconciled with the known principles of mechanics; and therefore any ulterior remark, on our part is quite superfluous." ⁵³

Bayma's criticism was valid; Graham had not given details of the unalterable motion which was required for his primary atoms. However, Graham's speculations were not generally the subject of criticism. Interestingly, his speculations were used by Alexander Bain, Professor of Logic at Aberdeen University, in his textbook on logic published in 1873.⁵⁴ Bain believed that Graham's speculative ideas were a sound example of an hypothesis. He defined the word: hypothesis as the suppositions, suggestions, or guesses about any matter unknown which might lead to experimental or other operations for its possible proof or otherwise. He recognised that hypotheses concerned with the minute structure and motions of bodies were by their very nature incapable of direct proof. Their only merit lay in their suitability for expressing

55. A. Bain, *ibid.* p 128.

56. J. C. Maxwell, 'On the dynamical theory of gases', read May 31st 1866, Phil.Trans. 157 (1867) 49-88 or Maxwell Papers, (Cambridge, 1890) Volume 2 pp 26-78.

57. J. N. Lockyer, 'The Bakerian lecture', read on November 27th 1873 'Researches on spectrum analysis', Phil.Trans. 164 (1874) 479-494, see p 491, and also the report of the British Association meeting held at Belfast in September 1873, Chemical News 28 (1873) 175-176.

58. D. Duncan, The Life and Letters of Herbert Spencer, (London, 1908) p 434.

59. Graham, *op.cit.* (2).

phenomena; they were representative fictions. All theories of the constitution of matter were hypothetical and as Bain remarked their value arose from their aptness to represent phenomena. In his examination of the assumptions of Graham's hypothesis he identified as the leading parameter: the density or specific gravity of matter. This was assumed from the postulate that "the greater the energy or swing of the primordial and inalienable movement of the ultimate atoms, the lighter the mass These ultimate molecules, whose primitive movement gives the specific gravity, are supposed to be made up in groups, each group having a further movement, vibratory or other, which second super-induced movement represents the gaseous molecule affected by heat, and leading to gaseous expansion. This Graham also calls the diffusive molecule." ⁵⁵ He pointed out that the special feature of this hypothesis was the assumption of motions within motions, like primary and secondary planets. Finally, Bain suggested that the somewhat different hypothesis of molecular motions proposed by Clerk Maxwell in 1866⁵⁶ could be 'super-added to Graham's hypothesis'.

In the same year, 1873, the attention of chemists was again directed towards the problem of the complexity of the elements by Lockyer's dissociation hypothesis. Lockyer argued from spectroscopy that the elements on the Sun might be dissociated into simpler elements.⁵⁷ Later, Herbert Spencer claimed that "Lockyer's speculations concerning the compound nature of the elements, as shown by the changes of the spectra, were pursuant on a remark I made to him expressing that belief."⁵⁸ These speculations may have induced later writers to look back approvingly on Graham's suggestion that elements were constructed from primary matter. This can be seen in the responses to the posthumous publication of Graham's Chemical and Physical Researches in 1876. In his preface to this work Robert Angus Smith wrote a short introductory essay on 'Graham and other atomists'.⁵⁹ Smith saw Graham as one of a chain of writers on the unity of matter and atomic motion stretching backwards to the writings of

60. W. Crookes, 'Review of Graham's Chemical and Physical Researches', Chem.News 35 (January 26th 1877) 40-43, see p 42. Crookes was an admirer of Graham's researches. In 1869 he had reviewed Graham's work and had drawn attention to the fact "that gases have initial movements as one of their original properties and that the speed of these movements severally may be their main distinction. This would take them out of the region of Chemistry proper, and bring them into physics, but physics and chemistry are after all fundamentally one." Chem.News. 20 (October 15th 1869) p 187. Crookes included Graham as a precursor in the belief that the elements were really compound in his lecture given to the British Association in 1886. See B.A.Report (1886) p 558. Crookes strongly advocated the award of a baronetcy to Graham for his chemical researches when he reported, in 1866, that this honour had been conferred on Fergusson of King's College, Simpson of Edinburgh and on the geologist Murchison. See Chem.News 13 (January 12th 1866) p 24 and the British Medical Journal 1 (1866) p 137. However, Graham was not made a baronet. Perhaps this was because a certain degree of disquiet was felt with regard to Graham's administration of the Royal Mint. See G. F. Ansell, The Royal Mint, 3rd.edn. (London, 1871) for a partisan discussion of the running of the Royal Mint during this period.
61. J. B. Stallo, The Concepts and Theories of Modern Physics, 2nd.edn. (London, 1882) pp 21-39, 294-295.
62. Stallo, *ibid.* p 35.

Leucippus and Democritus. He suggested that Graham was attempting to discover the true motion of atoms and that his immediate predecessor in this attempt was Davy. Graham's own comments on the work of Democritus however suggest that the writings of the ancients did not influence his thoughts on atomic motion to any real extent. Certainly, this publication drew attention to Graham's thoughts on matter. In a review, William Crookes wrote that "as a piece of speculative reasoning his paper on the constitution of matter will always be read with admiration. It appears in some sort to be a confession of faith on the part of the writer In this paper we cannot help being astonished at the boldness and closeness of the reasoning, although some may demur to the conclusions drawn therein." ⁶⁰

As we have seen not all discussions of Graham's speculations were free from criticism. This can be seen in the examination of his speculations by a principal opponent of atomism, J. B. Stallo, in 1882.⁶¹ He argued that the assumption of primary matter endowed with specific motions for all elements was in direct conflict with Avogadro's law. He explained that there was no reconciliation between Avogadro's law and Graham's hypothesis because the latter "accounts for differences of density by attributing to equal primordial atoms unequal volumes resulting from their occupancy of unequal spaces by virtue of differences in the velocities of movement with which the several kinds of atoms are supposed to be inalienably endowed. It accounts for inequalities in the volumes of equal masses, not for inequalities in mass of equal volumes, and cannot serve as an explanation of the latter, unless it is supplemented by the further assumption - to which, indeed, it lends little, if any, aid - that some, if not all, of the molecules are compounds or aggregates of different degrees of complexity." ⁶² In addition to this criticism he advanced an even more cogent physical argument: the "attribution of inalienable energy or motion to a given mass" must be rejected because it is "repugnant to the fundamental postulate [of the mechanical theory] of the absolute

63. *ibid.* p 39.

64. *ibid.* pp 294-295.

65. W. V. Farrar, 'Nineteenth century speculations on the complexity of the chemical elements', B.J.H.S. 8 (1965) pp 297-323, see p 312.

indifference of mass to motion no motion can inhere essentially in distinct and separate masses." ⁶³ He concluded "there is no doubt a large class of bodies whose constitution is molecular; but from this it does not follow that the molecules composing them are primordial unchangeable units, existing independently and in advance of all physical action, and therefore absolutely exempt from change." ⁶⁴ As a positivist thinker Stallo was determined to base physical science on experiment and rid it of all hypothesis.

Finally let us consider what recent commentators have to say about Graham's speculations. W. V. Farrar underlines the originality of the view that the matter in chemical atoms must be uniform because of the uniform action of gravity. He adds that Graham was even more original in his vision of atoms "as the seat of the indestructible motion of sub-atomic particles, or, in modern terms, a packet of energy; and his final throw away remark that this energy might be regarded alternatively as a standing wave. There is more of Boscovich than of Dalton in Graham's atomism, and the reputation of Boscovich was beginning to wane; little attention was attracted by these remarkable paragraphs." ⁶⁵ As we have seen Graham's speculations did receive some attention. Certainly the ascription of unalterable motions to distinguish the different primary atoms from one another was an imaginative and appealing idea. However it is not easy to visualise how Graham could have superimposed a revolutionary motion on a Boscovichean point atom. It is more likely that he believed that the primary atoms possessed a finite size if they underwent some form of revolutionary motion.

D. M. Knight observes that what is unexplained in Graham's theory is how the atoms retain their original motion unchanged. He says that it seems probable that his hypothesis resembles the theory of gases of Newton or Davy; the particles are not in rapid translational movement, always colliding and gaining or losing energy at each impact, and do not come into contact with one another. They are running on the spot, rather than

66. D. M. Knight, Atoms and Elements, (London, 1967) pp 80-81 and also Knight, Natural Science Books in English 1600-1900, (London, 1972) p 153.

67. M. D. Swords, Ph.D.Thesis, The Chemical Philosophy of Thomas Graham, 1973, Case Western Reserve University, pp 84-87.

rushing hither and thither as envisaged in the kinetic theory of gases. The theory is incompatible, he suggests, with the collisions required by the kinetic theory.⁶⁶ The most difficult problem with Graham's model of matter was exposed by Stokes. How could heat affect the motions of diffusive molecules and yet leave the motions of ultimate atoms undisturbed? D. M. Knight has rightly drawn attention to the difficulty of reconciling the collisions between gas molecules and the unalterable motions of primary atoms. Likewise, Bayma had also drawn attention to this problem when he asked what motion Graham could envisage for an atom which would be unalterable. It would seem that Graham was thinking in terms of a revolutionary motion rather than a vibratory motion as Knight seems to suggest. This allowed Graham to have a more flexible theory even if it was necessarily less precise. Graham was more circumspect than Jevons when he explained the relation which existed between motion and heat. He could not forego the unalterable motions of primary atoms or transmutation would have been a distinct possibility and as Graham had shown by his comments on Samuel Brown's experiments he was not prepared to countenance transmutation.

Most recently, M. D. Swords has seen these speculations as a natural outcome of Graham's career devoted to the search for the true motion of atoms.⁶⁷ The ultimate atomic core possessed a primordial motion and Swords assumes that different atoms moved with varying revolutionary motions, creating different atomic volumes and different specific gravities; that is different chemicals. These primitive or combining atoms could be grouped together in small numbers to generate a diffusive molecule. Diffusive molecules were affected by changes in temperature and pressure causing alterations in their volumes or densities, without altering the constant primordial motions of the atomic units. And yet, the motion of a gaseous molecule was definitely related to the motions of its constituent atoms, and so the atomic properties were constantly asserting themselves at a molecular level. The blending of primordial

68. Newton took two pendulums, as nearly as possible identical in shape and size, on which two equal rounded wooden boxes were suspended. He filled one box with wood and the other with an equal weight of gold. The pendulums were then equal in both weight and size and so they experienced the same air resistance. On setting the pendulums simultaneously into motion Newton found that they moved with equal oscillations. The experiment was repeated using silver, lead, glass, sand, common salt, water, and wheat, in place of gold with the result that the motion was always identical. Thus, the force of gravitation was unaffected by substances of different chemical natures, provided that the same mass was taken; all masses were therefore equally accelerated by gravity.
- I. Newton, Philosophiae Naturalis Principia Mathematica (London, 1687) Book 3, Prop. VI.
- See The Mathematical Principles of Natural Philosophy translated by A. Motte (London, 1729) Vol. 2, p 220.

69. R. A. Smith, 'Graham and other atomists', Researches. (1876) Preface XV.

motions and volumes gave new volumes, new molecular motions, and therefore new chemicals. This combination of motions only occurred in the simple proportions indicated by the law of gaseous volumes. This interpretation of Graham's speculations seems to be sensible but Swords is more definite than Graham was, in assuming that the motion of an atom was revolutionary.

When Graham began his researches on the diffusion of gases he was presented with a major difficulty if he wanted to assume that molecules were themselves constructed from primary matter. In 1825, his teacher, Thomas Thomson, had attempted to demonstrate that the atomic weights of the elements were integral multiples of the atomic weight of hydrogen. This was the hypothesis of Prout, who believed that all atoms were aggregates of primary matter. Turner and Berzelius showed that Thomson had been too eager in his support of Prout's hypothesis. Thomson had used rounded-off atomic weights which were based to some extent on faulty experiments. For this reason Graham did not choose a dubious argument based on atomic weights to justify his belief in primary matter. Instead, he based his belief on Newton's experimental proof that gravity acted uniformly on all matter, regardless of its chemical nature. Therefore all primary atoms must have the same size and weight,⁶⁸ when at rest. As Farrar has suggested, this appears to have been an original argument used by Graham to justify his recourse to primary matter.

Like Dalton, Graham believed that there was a different kind of atom for each particular element. In this sense R. A. Smith was correct when he stated that Graham was "as strict an atomist as perhaps could be found."⁶⁹ Dalton distinguished atoms by their different atomic weights; Graham distinguished them by their different unalterable motions. This novel and imaginative hypothesis allowed Graham to predict that all elements would contain atoms of identical size and weight if they were at rest. But, in reality, atoms of any two elements differed, because they were endowed with different primordial, fixed quantities of motion. This change of emphasis from atomic weight to motion explains why Graham was

70. Graham, Wellcome MSS. No.2580 (old no.3390)
Unbound file, Item (5) Notes on gases dated 21/3/68 containing 5 ll.
A note in this file gives "condensed descriptions of successive
forms of construction of chemical substances
 areo-molecular atmomolecule
 liqui-molecular hydromolecule
 colli-molecular colli-molecule
 crystallomolecular crystallomolecule."

not particularly concerned with Prout's hypothesis, as such. Therefore, Graham did not assume that the ultimate atoms were polymers of primary matter, as Prout and Daubeny had done, instead, he invested the primary atoms of various elements with different unalterable degrees of motion.

In Graham's view, chemical affinity was also based on motion. Thus the combination of primitive atomic motions gave rise to new simply-related compound motions. Here Graham appears to have been following the path taken by Prout in his molecular theory of matter.

The relationship between diffusive molecules and the ultimate chemical atoms in Graham's speculations closely resembled the distinction which Dumas had drawn between physical and chemical atoms. Possibly Graham drew on these ideas when he made these distinctions.

A fundamental concern with motion was central to Graham's beliefs about matter. From differences in the degrees of motion of matter he was able to make distinctions between colloids and crystalloids; solids, liquids, and gases; diffusive molecules and the ultimate atoms themselves. Indeed, as we have seen previously, Graham probably intended to extend his ideas on the continuity of matter to provide a hierarchy of increasing molecular complexity.⁷⁰ Gases; liquids; colloids; and crystalline substance were all distinguished by their different degrees of molecular mobility, giving at least four identifiable states of matter.

APPENDIX 1

An explanatory note on the symbols used by Graham in his researches on the phosphates.

Graham adapted the symbols devised by Berzelius. For anhydrous phosphoric acid, Graham wrote $\overset{\cdot\cdot}{\text{P}}$ or PO_5 in his 1833 paper. He explained that he intended this symbol to stand for a double atom of phosphoric acid (P = 62.768, O = 8). Berzelius wrote $\overset{\cdot\cdot\cdot}{\text{P}}$ or P_2O_5 for anhydrous phosphoric acid (P = 31.384, O = 8). The five dots placed above the symbol were used by both Berzelius and Graham to represent five atoms of oxygen. Graham wrote one atom of water as $\overset{\cdot}{\text{H}}$ or HO (H = 1, O = 8), whereas Berzelius wrote $\overset{\cdot}{\text{H}}$ or H_2O . An underlined symbol represented two atoms of the element concerned. Berzelius used the atomic weights (H = 0.5, O = 8).

Graham's formulae for the phosphoric acids and their salts

Modern equivalents
using present day atomic weights

(Atomic weights used by Graham H = 1, P = 62.768, O = 8, Na = 23, Ag = 108)

(Atomic weights H = 1, O = 16, P = 31, Na = 23, Ag = 108)

Common phosphoric acid = $\overset{\cdot\cdot\cdot}{\text{H}}\overset{\cdot\cdot\cdot}{\text{P}}$

or $3\text{HO},\text{PO}_5$

$3\text{H}_2\text{O} + \text{P}_2\text{O}_5 = 2\text{H}_3\text{PO}_4$

Pyrophosphoric acid = $\overset{\cdot\cdot\cdot}{\text{H}}\overset{\cdot\cdot\cdot}{\text{P}}$

or $2\text{HO},\text{PO}_5$

$2\text{H}_2\text{O} + \text{P}_2\text{O}_5 = \text{H}_4\text{P}_2\text{O}_7$

Metaphosphoric acid = $\overset{\cdot\cdot\cdot}{\text{H}}\overset{\cdot\cdot\cdot}{\text{P}}$

or HO,PO_5

$\text{H}_2\text{O} + \text{P}_2\text{O}_5 = 2\text{HPO}_3$

Common phosphate of soda = $\overset{\cdot\cdot\cdot}{\text{Na}}\overset{\cdot\cdot\cdot}{\text{HP}}$

or $2\text{NaO},\text{HO},\text{PO}_5$

Sodium phosphate or disodium monohydrogen phosphate

$2\text{Na}_2\text{O} + \text{H}_2\text{O} + \text{P}_2\text{O}_5 = 2\text{Na}_2\text{HPO}_4$

Pyrophosphate of soda = $\overset{\cdot\cdot\cdot}{\text{Na}}\overset{\cdot\cdot\cdot}{\text{P}}$

or $2\text{NaO},\text{PO}_5$

Sodium pyrophosphate

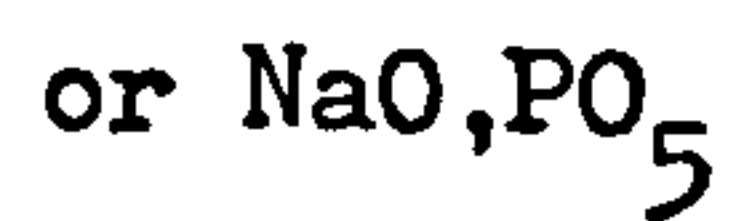
$2\text{Na}_2\text{O} + \text{P}_2\text{O}_5 = \text{Na}_4\text{P}_2\text{O}_7$

Cont...

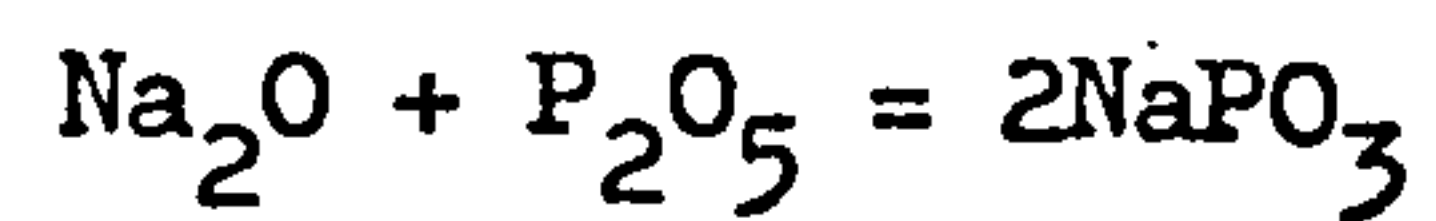
Graham's formulae cont...

Modern equivalents

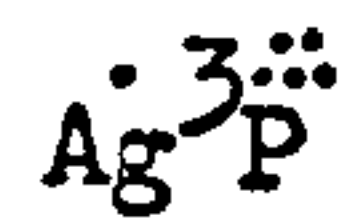
Metaphosphate of soda



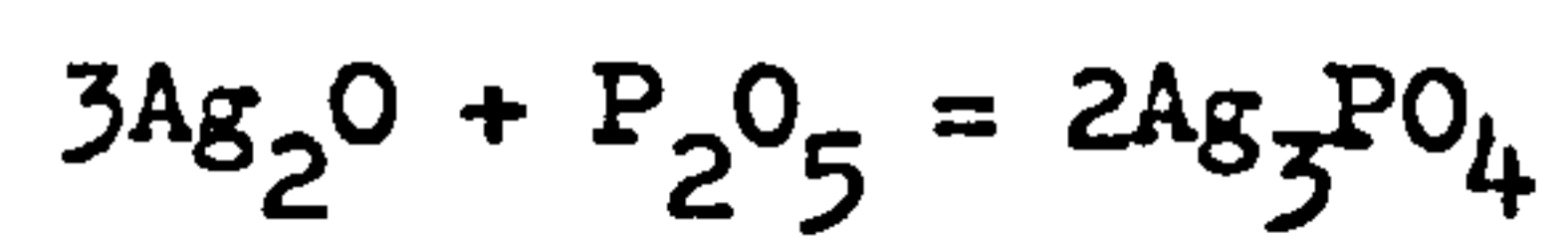
Sodium metaphosphate



Phosphate of silver

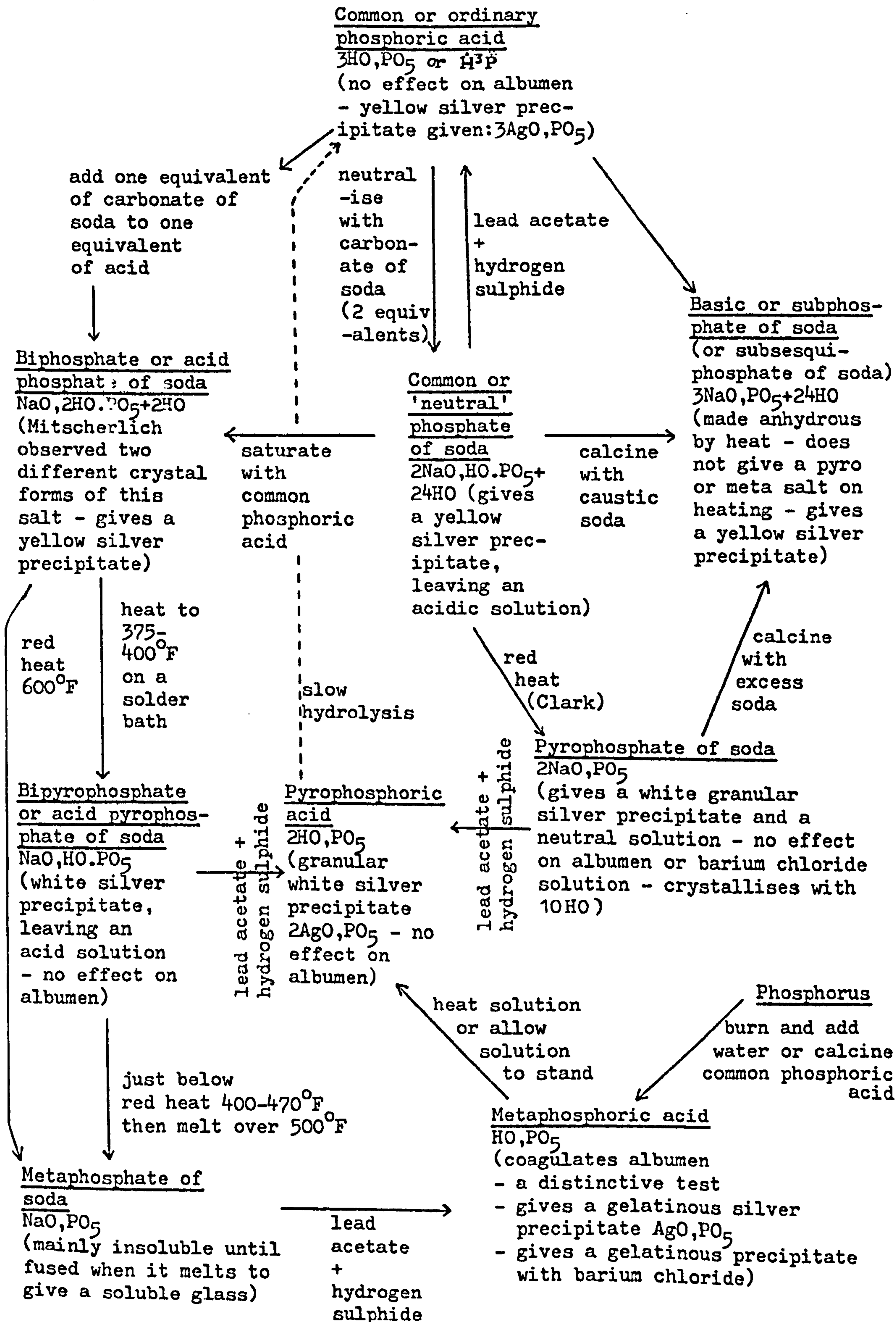


Silver phosphate



Appendix 1 continued:-

A summary chart of the more important formulae and reactions of the phosphates established by Graham.



APPENDIX 2

Graham's Contributions to Physiology

1. Graham, 'On the law of diffusion of gases', 19th December 1831, Researches, 44-70, see pp 67-68.

2. Graham, 'Notice of the singular inflation of a bladder', Quart. Journ. of Sci. iii (October, 1829) 88-89 or Researches, 40-41.

3. J. K. Mitchell, 'On the penetrativeness of fluids', Amer. J. Med. Sci. 7 (1830) 36-67 or the Journal R.I. 2 (1831) 101-118, 307-321 and 'On the penetration of gases', November 1833, Amer. J. Med. Sci. 13 (1833) 100-112.

Graham's Contributions to Physiology

Graham, like most chemists of his time, was educated in a medical school. He retained a close interest in physiology and pointed out the application of his researches to medicine. The contributions which he made to physiology vary from relatively minor examples to some quite significant additions to the knowledge of the subject. His investigations undoubtedly had an influence on physiologists and they illustrate his own interest in the application of chemistry to physiology.

In 1831, Graham suggested that his gaseous diffusion results could be used to explain the inflation of the innermost tubes and air-cells of the lungs.¹ Carbon dioxide diffused out of the lungs more slowly than oxygen entered. He produced evidence for this view from the volumes of these gases which diffused in equal times. 95 volumes of oxygen were exchanged for 81 volumes of carbon dioxide according to the law of gaseous diffusion and therefore the inner tubes of the lungs would remain inflated by the excess of oxygen which entered them. Graham must have assumed that the walls in the lungs through which gases diffused were analogous to stucco in terms of their porosity. This was a curious over-simplification for him to make because he had found that carbon dioxide passed more rapidly than air through a moist bladder. He had explained this anomaly in 1829² by suggesting that this was a case of liquefaction and not of simple diffusion. Carbon dioxide was more easily liquefied than air and so a partially inflated moist bladder suspended in carbon dioxide became fully inflated by liquefaction of carbon dioxide in the water of the membrane. The liquefied carbon dioxide passed to the inside and evaporated freely into the air inside the bladder. Had Graham overlooked this earlier work or did he believe that a bladder did not resemble the air cells in the lungs? - presumably the latter view is correct.

J. K. Mitchell made a clear distinction between the passage of gases through membranes and through porous plugs, stressing the effect of pore size on the penetration of gases through barriers.³ Surprisingly Mitchell's

4. J. W. Draper, 'On the physical theory of capillary attraction', February 1838. See Appendix to J. W. Draper, A Treatise on the Forces which Produce the Organization of Plants, (New York, 1844) 57-72.
5. C. A. Culotta, 'German Biophysics, objective knowledge and romanticism'. Hist. Studies in Physical Science 4 (1974) 3-20. See also the more detailed paper: C.A. Culotta 'Respiration and the Lavoisier tradition: Theory and modification, 1777-1850' Trans. Amer. Phil. Soc. 62 (1972) part 3 pp 3-41, particularly 25-26, 33-38.
6. G. Valentin and C. Brunner 'On the ratio of carbon dioxide eliminated to that of oxygen taken up in human respiration', Archiv fur Physiologische Heilkunde 2 (1843) 373-417 and Valentin, Lehrbuch der Physiologie des Menschen, (Braunschweig, 1844) 1 507-580. The results obtained by Valentin and Brunner are reported in J. F. Simon, Animal Chemistry (London, 1845) 1 pp 131-132. From Graham's diffusion law, the respiratory coefficient, i.e. volume of carbon dioxide exhaled ÷ volume of oxygen inhaled, should be 1 to 1.17585 (or 0.8504 to 1) and Valentin and Brunner found it was 1 to 1.1742 (or 0.8516 to 1). This was an error in their experiments of only 1 part in 170. In man, the respiratory coefficient is normally below one, being 0.82 on average.
7. G. Valentin, Grundriss der Physiologie. (Braunschweig, 1851) p 263 and G. Valentin, A Textbook of Physiology (translated and abridged from 3rd German edn. by William Brinton) (London, 1853) pp 249-250.
8. C. Ludwig, 'Some comments on Valentin's theories of respiration and blood circulation', Zeit. für rationelle medicin 3 (1845) 147-164; 'Reply to Valentin's criticism' of the preceding paper, 4 183-190. See also H. Milne-Edwards Leçons (1857) 1 468.
9. J. Reed, 'Respiration', an article in R. B. Todd: Cyclopaedia of Anatomy and Physiology 4 (London, 1847) 363.
10. H. V. Regnault and J. Reiset: Recherches Chimiques sur la Respiration des Animaux, (Paris, 1849) page 11 or an extract in Ann. de Ch. 3 Ser. 26 (1849) 299-519, see p 408.

pupil, J. W. Draper, remarked that Graham's theory of respiration was probably correct.⁴ Yet Draper had noticed that the passage of gases through membranes depended on their absorption by the membrane rather than on simple diffusion.

Culotta has pointed out recently that Graham's work on gaseous diffusion was especially important for the German physiologists.⁵ For example Valentin and Brunner found that there was a good agreement between their experiments on respiration, from which they determined the exchange volumes of oxygen and carbon dioxide, and Graham's diffusion law. This close agreement led them to suggest in 1843 that a living membrane could be compared to a porous inorganic screen.⁶ Following criticism, Valentin later emphasised that he did not intend to suggest that respiration could be explained by Graham's diffusion law, but merely to point out the close coincidence between the figures for oxygen and carbon dioxide exchange and the relative diffusion volumes.⁷

Valentin's over-simplified view of respiration was attacked by a number of his contemporaries. Ludwig could not accept this simple interpretation of respiration in terms of diffusion and he pointed out that carbon dioxide was not free in blood, instead it was joined to soda as bicarbonate of soda.⁸ Like Ludwig, J. Reed in England, commented that carbon dioxide and oxygen were not found in the same condition in the lungs as they were in Graham's stucco diffusion experiments.⁹ For example oxygen was a free gas in the lungs but carbon dioxide was in solution. Therefore, the volumes of gases exchanged were far from constant because the humid membrane in the lungs was different in its nature to stucco.

Regnault and Reiset made extensive experiments on animal respiration and they showed conclusively that the exchange volumes were not constant. Between 0.62 and 1.04 volumes of carbon dioxide were exhaled for every one volume of oxygen inhaled by the same animal.¹⁰ They were the first to define the term 'respiratory coefficient', that is the volume of carbon dioxide exhaled divided by the volume of oxygen inhaled.

11. K. Vierordt, 'Respiration' an article in R. Wagner's Handwörterbuch der Physiologie 2 (Braunschweig, 1846) 900. See Culotta op.cit. (5) Trans.Amer.Phil.Soc. 62 (1972) 35-38.
12. The first suggestion that carbonaceous deposits could cause a blackening of the lungs was made by an English Physician, George Pearson (1751-1831), in 1813. See 'On the colouring matter of the black bronchial glands', Phil.Trans. 103 (1813) 159-172.
13. J. C. Gregory, 'On the cause of a peculiar black infiltration of the whole lungs resembling melanosis', Ed.Med. and Surg.J. 36 (1831) 389-394. Gregory was a physician at the Royal Infirmary in Edinburgh. He asked R.Christison to examine the black matter. Christison concluded that the black matter was very different from that produced in melanosis and that, the small sample he used, gave on heating products which resembled coal distillation. However, there was insufficient material for a conclusive analysis.
14. Graham, 'On the existence of charcoal in the lungs', Ed.Med.and Surg.J. 42 (October 1834) 323-334.
15. W. H. Walshe, Professor of Medicine at University College, London. 'On adventitious products - melanic deposits:(a) introduction of black-coloured deposits from without' in R. B. Todd's Cyclopaedia of Anatomy & Physiology 4 (London, 1852) 117 and also W. H. Walshe: A Practical Treatise on the Diseases of the Lungs 3rd.edn. (London, 1860) 227-229.
16. Graham, Elements of Chemistry 1st.edn. (London,1842) Preface page vi (November 1841).

Vierordt also examined respiration. He believed that a diffusion process was operating in respiration although his results did not strictly conform to Graham's law. He referred to this process as 'parenchymatic diffusion' to distinguish it from simpler forms of gaseous diffusion.¹¹ Physiologists, therefore, recognised that the gaseous diffusion law had to be taken into account in their explanations of respiration.

Following his researches on gaseous diffusion, Graham was asked by local doctors to investigate the black-colouring matter which appeared in the lungs of coal-miners.¹² The doctors wanted to know whether the black substance was an organic secretion or whether it was just coal dust as J. C. Gregory and R. Christison had inferred in 1831.¹³ Graham discovered that it was neither an organic secretion nor coal dust.¹⁴ The black substance when heated gave a fawn ash and a gas. However, the gas which was released, differed in composition from coal gas and there was no noticeable production of tar or ammonia. Thus, Graham concluded that the black substance was charcoal, or lampblack. Furthermore, he explained the true origin of charcoal in this industrial disease. The miners had inhaled the charcoal from the ill-trimmed oil lamps which were attached to their foreheads. This discovery was incorporated in later works on lung disease, along with the recommendations: that there should be free ventilation in pits and that substitutes should be found for the oil in miners' lamps.¹⁵

In 1841, Graham finished the first edition of his textbook, and his introductory comments clearly show his interest in physiology, for he recognised:- "It was now obvious that the science [of organic chemistry] was sufficiently advanced to be applied to the elucidation of the great questions of vegetable and animal physiology. A condensed view is given of the new discoveries in the former department, and also of the important conclusions respecting the animal functions of respiration and digestion, results which are entirely new, and now enter for the first time into a systematic work on Chemistry."¹⁶

17. MS. letter from Graham to J. Liebig, dated August 16th 1842, from collection of Graham-Liebig correspondence in Munich State Library, Liebigiana 58.

18. Graham, Elements of Chemistry, 1st.edn. (London, 1842) 1017-1018.

Graham's interest in physiology was extended when he read Liebig's book Animal Chemistry. Thus Graham wrote to Liebig in 1842: "I have been much delighted with your Animal Chemistry, which contains I believe a greater body of profound and well considered speculations than was ever presented before at one time to the Chemical world, and I have been planning an extension of some of your experimental inquiries for my winter occupation." ¹⁷

However, these inquiries were delayed for a year following the death of Graham's father on September 16th 1842. After completing his studies on thermochemistry Graham began an investigation of diabetes during the winter of 1843-1844. He continued his investigations until 1845. At the same time he also studied the conditions for the coagulation of casein and albumen. During this period Graham was Dean of the Medical Faculty of University College, London and this may explain his interest in medical problems.

To study diabetes, Graham had to consider carefully the related phenomena of respiration and digestion. In his textbook of 1841, Graham presented the explanations of J. B. Dumas for both of these processes. Thus, Graham wrote that the theory of respiration proposed by Dumas and Boussingault "has a high degree of probability. Under the influence of oxygen absorbed, the soluble matters in the blood are supposed to be converted into lactic acid, an acid which has been observed in the blood by Mitscherlich, Boutron-Chalard and Fremy. The lactic acid itself becomes lactate of soda, and undergoing a true combustion from combination with oxygen is converted into carbonate of soda. The last salt is decomposed in its turn by a new portion of lactic acid, and the carbonic acid set free, with which the venous blood becomes charged in the lungs. The conversion of farinaceous matters into lactic acid, ... is a fact well understood The large production of lactic acid in the blood, and its conversion into carbonic acid may therefore be admitted." ¹⁸

Again he quoted Dumas in his description of digestion which was taken

19. J. B. Dumas, 'Leçon sur la statique chimique des êtres organisés' Ann.Sci.Nat. 16 (1841) 33-61 or Dumas, Essai de Statique Chimique des Êtres Organisés, (Paris, 1842) 2nd.edn. p 43.
This theory of respiration was a slight modification of the theory put forward by E.Mitscherlich, L.Gmelin and F.Tiedemann in 1833 in their 'Researches on blood', Liebig Ann. 12 (1834) 346-354. They found that blood released carbon dioxide by treatment with acetic acid. Thus, the blood contained alkali carbonates. Oxygen combined with blood releasing acetic acid; this acid released carbon dioxide which was stored in blood as a bicarbonate. Dumas substituted lactic acid for acetic acid because it was a known constituent of blood, muscle and urine. He made the theory more elegant by deriving sodium carbonate from sodium lactate in the blood. See F. L. Holmes, Claude Bernard and Animal Chemistry (Harvard, 1974) p 19.
20. Graham, op.cit. (18) p 1021 from Essai de Statique Chimique des Êtres Organisés 2nd.edn. (Paris, 1842) pp 40-41.
21. Graham, Wellcome notebook. (old no.3186) new no.2561.
Graham notebook No.10 dated August 1843-June 1844. 'Notes on Chemistry, diabetes, diet etc.'
22. Graham, Wellcome notebook. (old no.3187) new no.2562.
Notebook 11 (1844) - see notes dated July 1st 1844 entitled diabetes.
23. A. Bouchardat, 'New researches on the nature of the malady known as diabetes', Comptes Rendus. 6 (1838) 337-338.
24. Robert Macgregor (or M'Gregor) 'An experimental inquiry into the comparative state of urea in the healthy and diseased urine and the seat of the formation of sugar in diabetes mellitus' - An essay submitted to the Faculty of Physicians and Surgeons when candidate for admission in 1836.
See also R. Macgregor London Medical Gazette 20 (1837) 270 or T. Thomson Chemistry of Animal Bodies (Edinburgh, 1843) 482-488 for a summary of Macgregor's work.
25. Graham, op.cit. (21).

from Dumas's recently published paper: 'Leçon sur la statique chimique des êtres organisés'.¹⁹ Graham wrote that "digestion is a simple function of absorption. The soluble matters pass into the blood, for the most part unaltered; the insoluble matters arrive in the chyle sufficiently divided to be aspired by the orifices of the chyliiferous vessels Thus amylaceous matters are converted into gum and sugar; the saccharine matters formed are absorbed The neutral azotised matters, the fibrin, albumen and casein, first dissolved, then precipitated, pass into the chyle highly-divided or dissolved anew."²⁰

To study diabetes, Graham compared the ingesta and egesta of diabetic patients. He continued this daily examination, without interruption, in two cases for several months, and with several other cases for a few days at a time. His notebooks²¹ show that, in February 1844, he compared his own: respired carbon dioxide; diet; change in weight (Graham was just under 8 stone); urine volume and specific gravity, as well as its sugar content; and the quantity of faeces passed. All of these observations were compared with those of diabetic patients. To understand diabetes Graham began by asking the question: was the sugar in a patient's urine more than accounted for by farinaceous food?²² In June 1844, he concluded that there was an exact proportionality between the sugar in the urine and the saccharisable matter of the food. This result confirmed a similar conclusion which had been reached by A. Bouchardat²³ in 1838.

The next problem, a most important one, was to account for the presence of sugar in diabetic urine. Graham referred to an earlier study of diabetes made by Robert Macgregor an apothecary at Glasgow Royal Infirmary.²⁴ This study was made in 1836 whilst Graham was himself a Professor in Glasgow.²⁵ Macgregor had found that sugar was present in the blood, saliva, digestive organs, and faeces, as well as in the urine of diabetic patients. Macgregor then analysed diabetic urine and found that the quantity of urea present was not at all diminished. Therefore, the sugar had not replaced the urea in diabetic urine. Finally, Macgregor

26. F. Tiedemann and L. Gmelin: Recherches Expérimentales, Physiologiques et Chimiques, sur la Digestion, translated by A.J.L.Jourdan, 2 Vols. (Paris, 1826-7) pp 201-202.

27. A. Bouchardat, Revue Médicale (1839) p 321.

28. Graham, op.cit. (22)

29. R. Macgregor, 'Carbon dioxide from lungs', British Association Report (1840) p 87.

30. Dr. Malcolm, London and Edinburgh Monthly J. of Medical Science page 1, quoted in: J. F. Simon, Animal Chemistry (London, 1845) 1 127.

31. Graham, op.cit. (22) See note dated April 22nd 1845. Graham compared the amounts of oxygen inhaled to carbon dioxide exhaled. With amylaceous foods, like cane sugar ($C_{12}H_{11}O_{11}$ according to Graham), all the oxygen would be used to burn the carbon, water being merely separated from the carbohydrate. With an animal diet which contained protein ($C_{48}H_{36}N_6O_{14}$ according to Liebig), oxygen was used to burn both carbon and the excess hydrogen (e.g. 48 atoms of carbon and 22 atoms of hydrogen were burned and 14 atoms of water already in the protein would be separated). The respiratory coefficient was lower in the latter case because a given volume of oxygen was used for burning both the carbon and hydrogen and not just the carbon as in the case of amylaceous foods.

observed that sugar was found in the blood of healthy persons who were fed on a vegetable diet. This result had been observed previously by Tiedemann and Gmelin²⁶ and was also noticed by Bouchardat in 1839.²⁷

Graham recognised that sugar in urine had come from the blood but he was unable to detect any diseased organs. Therefore he decided that there was an "entire want of a power The blood seems at fault or the sanguinous circulation at some point. The oxidation of the sugar is not taking place as it should do in the circulation. A diseased condition of the blood vessels? Examine them. Affords a case for transfusion or would repeated small bleedings with a properly regulated diet effect the necessary change in the blood corpuscles Could anything be given with sugar that would facilitate its digestion?, spices? " ²⁸

Further studies convinced Graham that diabetes was a more complex disease. He examined the respiratory coefficient of a diabetic patient, that is, the volume of carbon dioxide exhaled, divided by the volume of oxygen inhaled. Formerly, Macgregor²⁹ and Malcolm³⁰ had observed changes in the respiratory coefficient in a number of diseases but they did not detect any changes in cases of diabetes. However, Graham did expect to find differences in the respiratory coefficient of a diabetic patient, fed on animal diet, compared to the value found for a healthy person. He reasoned that because there was a lower intake of carbon in an animal diet, then less carbon dioxide would be exhaled, and this would give a lower respiratory coefficient. Whereas, with an amylaceous diet the only combustible element was carbon and this would give a higher coefficient. To his surprise, Graham found that the respiratory coefficient of a diabetic patient fed on an animal diet was quite normal.³¹

This normal respiratory coefficient suggested to Graham that diabetes was not a disease of either the blood or the respiration. He concluded that it was caused by a want of separating power or tone in the intestines or by a general loss of assimilating power. A report on Graham's 'very interesting experiments performed on patients at University College Hospital

32. W. H. Walshe (Professor of Medicine, University College, London) wrote: 'Adventitious products - sugar', an article, which appeared in R.B.Todd's Cyclopedia of Anatomy and Physiology 4 (London, 1847). See pp 99-100 for an account of Graham's work; and A.B.Garrood (Lecturer on Materia Medica and Therapeutics, University College, London):- 'Lectures on the chemistry of pathology and therapeutics showing the application of the science of Chemistry to the discovery, treatment and cure of diseases - Lecture 32 Results of Professor Graham's experiments on diabetic patients' The Lancet Vol.2 (December 2nd 1848) p 597.

33. *ibid.*

34. *ibid.* W. H. Walshe's article.

appeared in an article printed in 1847 in Todd's Cyclopaedia of Anatomy and Physiology. This report was again quoted, in the lectures of A. B. Garrod, which appeared in the Lancet for 1848.³² Graham summed up his results as follows:- "The quantity of saccharine matter found in the urine never exceeded the starch and sugar in the food. On the other hand, the sugar and starch in the food were accounted for in the urine to within $\frac{1}{4}$ or $\frac{1}{5}$ th of the whole quantity. As there was also sugar, besides, in the faeces, in a sensible although not inconsiderable quantity it appeared to follow that sugar and substances convertible in the stomach into sugar, are, in diabetic patients, nearly, if not entirely, indigestible; that is they pass through the blood without being burned and thrown off in the form of carbon dioxide and water, as they are in the healthy state. The idea of any portion of the saccharine matter found in the urine being formed from the protein or azotised protein of the food, was entirely excluded the protein compounds are only partially digested in the system of a diabetic patient. The assimilating power appears, indeed to be generally deficient." ³³

W. H. Walshe, the Professor of Medicine at University College, London, summed up the problem: "in consequence of deficient oxidation of sugar in the respiration process, that substance (which in the normal state of things is burned off as quickly almost as it mixes with the circulating fluid) accumulates to a greater or less extent in the blood and its elimination from this fluid is partially effected through the secretions, especially the urine. This [Graham's account] is a most plausible and clear view of the chemical mechanism of sugar-disease but [it is] a quid ignotum - the cause of the deficient oxidising power - remains in the background mysterious and impenetrable." ³⁴

It is probable that Graham had completed his studies on diabetes by April 1845 but he does not appear to have published the results of them himself. Perhaps he thought that his results were not of sufficient significance or maybe he wanted to avoid any controversy. The latter

35. A. Bouchardat, 'New researches on diabetes or glucosury', Comptes Rendus. 13 (ii) (1841) pp 942-952, see p 944.
36. F. L. Holmes, Claude Bernard and Animal Chemistry (Havard, 1974) p 75. This reference to Dumas's lectures is taken from Holmes's account of Dumas's lecture of June 10th 1843 on glucose (Dumas MSS. 1946 Bibliothèque Mazarine, Institut de France, --as quoted by Holmes).
37. L. Miahle: 'Memoir on diabetes' read to French Academy of Sciences on April 15th 1844. Ann.de Ch. 3 Ser.12 (September 1844) 120-122.
38. For an account of this priority dispute see F.L.Holmes: Claude Bernard and Animal Chemistry (Havard, 1974) pp 228-237.
39. A. B. Garrod, op.cit. (32).

view is suggested because a priority dispute was being waged in the French Academy at this time between Louis Miahle and Apollinaire Bouchardat. In 1841, Bouchardat had noticed that the normal acid secretion of the skin did not occur in diabetes and he assumed therefore that the chemistry of the digestive system was altered in diabetes, acids replacing the alkalies normally found there.³⁵ In 1843, Dumas, who was assisted by Miahle, had suggested that some illnesses might be due to incomplete combustion caused by insufficient supply of alkali. When glucose entered the blood it underwent a slow combustion under the influence of the alkalies present in the blood. Dumas was uncertain whether glucose itself passed into the blood, or, whether it was first transformed into lactic acid.³⁶

In 1844, Louis Miahle extended Dumas's argument when he declared that sugars did not oxidise in diabetic patients because the blood was no longer alkaline in diabetes.³⁷ He explained that the reason why the blood was no longer alkaline in diabetes was that acids did not escape in sweat as normal. In the following year, Bouchardat discussed the question of the necessity of alkalinity in the oxidation of carbon and hydrogen. He referred to the earlier work of Chevreul, who had suggested that substances, normally resistant to oxidation, could be oxidised in the presence of alkali. This led to an unfortunate priority question on the role of alkalinity and the ease of oxidation processes in the blood.³⁸ It is quite possible that Graham did not want to become embroiled in this argument with the publication of his own results. Although Graham did not refer to the question of alkalinity, Garrod did comment that he was not aware that the blood was less alkaline in diabetes than in health; and certainly alkaline salts had been given repeatedly to diabetic patients, [Graham had prescribed subphosphate of soda], without diminishing the quantity of sugar in the urine.³⁹ Graham's experiments do not appear to have been noticed by later writers. His work was almost certainly overshadowed by the important researches of Claude Bernard which

40. J. Scherer, 'Chemical-physiological researches', Liebig Annalen. 40
(1841) 1-64 or Phil.Mag. 20 (1842) 314-319, 412-417.

41. J. Liebig, Animal Chemistry.trans. W. Gregory, (London,1842) pp 51-52.

42. Graham, Elements of Chemistry 1st.edn. (London,1842) p 1028.

contributed to a much clearer understanding of the nature of diabetes.

Between June and September 1844, Graham, assisted by Dugald Campbell, examined the coagulation of milk and egg albumen. It had been suggested by J. Scherer that casein in milk was only a modification of albumen, produced by its combination with alkaline bases.⁴⁰ Liebig wrote that Mulder was correct when he suggested that casein was identical in composition to fibrine and albumen. However, casein could be distinguished from fibrin and albumen by its greater solubility and by the failure of casein to coagulate on heating. From a chemical examination of casein, Liebig noticed that it contained a larger quantity of earth of bones [calcium phosphate] than was found in blood.⁴¹ The apparent similarity in chemical composition of albumen, casein, and fibrine tended to mask the complex nature of their protein structures and so it was difficult to make much progress with the study of proteins in the mid-nineteenth century.

Graham's studies of casein and albumen were interesting but again he does not appear to have published them. These studies gave him practical experience in the complexities of animal chemistry and an early insight into the properties of colloidal substances. Initially Graham examined the coagulation of casein, in milk, which had been allowed to stand. He reasoned that the casein was acting as a ferment, probably being affected by the air. The ferment action caused the conversion of the milk sugar, lactose, into lactic acid. The lactic acid then combined with the casein and coagulated it.⁴² Casein appeared to coagulate instantly when the acidity had reached a certain point and this process was accelerated by heat. When egg albumen was added to milk, Graham noticed that the casein could be coagulated by warming. The albumen was not itself coagulated but it appeared to communicate the power of coagulation to the casein. The filtrate, from some casein which had been coagulated by albumen, was found to be alkaline. Therefore, acidity was not responsible for the coagulation of casein by albumen. But acidity did cause casein to

43. These experiments on casein, albumen, pepsin, rennet etc. were made between June 22nd and September 18th 1844. They are found in Wellcome Notebook 13 (old no.3189), new no.2564, June-Sept.13th 1844 and in Notebook 14 (old no.3190), new no.2565, Sept.17th 1844-1845.

coagulate in other cases. When milk was allowed to stand lactic acid was formed and this acid did coagulate casein; also when either dilute acids or an acidic solution of pepsin were added to milk, the casein was precipitated.

Albumen, itself, was coagulated by boiling but this could be prevented by adding an excess quantity of alkaline sodium subphosphate. When Graham heated this mixture to 100°C no coagulation occurred, but on cooling, a highly transparent jelly was formed. On addition of acetic acid to albumen, precipitation occurred because small amounts of acid neutralised the albumen. However with excess acetic acid, albumen formed a jelly, if it was heated to 65°C , and at higher temperatures it coagulated incompletely.⁴³

These experiments and others prompted Graham to write down a number of speculative observations in his notebook. They are worth quoting as an illustration of the problems and difficulties facing a chemist who investigated the nature of proteins and enzymes at this time:-

"1. In the coagulation of milk by rennet proper, albumen appears not to be involved from the matter always remaining in whey being coagulable by heat

2. If the curd of milk (by rennet) does not carry down true albumen does it carry down sulphate of lime? protosulphate of iron?

3. Does egg albumen contain any casein, either before only, or both before and after being neutralised by acetic acid? It is true that acetic albumen is not affected by rennet. But may not a very large excess of such albumen prevent the action of rennet on milk?

4. How far does the thickening of casein by rennet resemble the spontaneous coagulation of blood? Would blood involve a little milk in its coagulation? Do substances which prevent the coagulation of blood prevent the action of rennet on milk also? Is there anything like a polar condition in the blood vessels, consequent upon the chemical action going forward in the capillaries? Place milk with rennet or fluid blood

44. Graham, Wellcome MS. notebook 14 (old no.3190), new no.2565.
Observations dated Sept.22nd 1844.

45. Graham kept copies of: a report in the Daily News (Sept.5th 1846) mentioning the outbreak of cholera in Kurrachee [sic]; the report on plague presented to the French Academy (report in The Athenaeum March 28th 1846); and a report of an outbreak of Yellow Fever in the Times Feb.13th 1849. He wrote an unpublished manuscript 'On contagion', which is undated and which shows that he supported the view that diseases could be transmitted by miasma. See Wellcome Unbound manuscripts of Graham, new no.2580 (old no.3390), Item (8) Remarks on contagion 411.

One possible reason for Graham's interest in the problem of air-borne disease may have been that he was asked to report on the proposed system for the ventilation of the House of Commons put forward by D. B. Reid in 1846.

46. Graham, Wellcome Volume of correspondence.

alone, between the electrodes and find whether coagulation is prevented? Casein may be more nearly fibrin than proper albumen is.

5...6. Distil at low temperatures an active solution of rennet. Does anything pass over in any circumstances? Study miasmata from rennet and the coagulating principle of the blood.

7. The power by which potash salts are separated in milk and urine from the blood, while soda salts left in the blood? By precipitation of potash salts in insoluble combination? By absorption of a fluid compound of potash salts and water, which separates in albuminous fluids? This would be an endosmose action of the secreting organ. Or by the surface attraction of fibre, and it being greater for potash salts than soda ones, so as to collect and accumulate the former. Has charcoal any elective action on different salts?

8...9. Any antagonistic ferment to rennet - neutralising its action? " ⁴⁴

These observations concluded his investigations on proteins as far as his surviving notebooks reveal them. It is interesting to note that in observation number 7, Graham considered that potash salts might be separated by osmosis from the albuminous fluids in the blood.

During 1846, Graham looked at the problems of the transmission of disease. He had read reports of outbreaks of cholera in India and Aden and the study of the Académie des Sciences on plague in Egypt, Syria and Turkey. ⁴⁵ He accepted the prevailing opinion that these diseases were probably caused by a "moist (vegetating) condition of the earth necessary to the production of the poison and also a subsequent dry and dusty state for its elevation into the atmosphere and its diffusion - any suitable method of producing downward ventilation to avoid surface currents? A frame supporting a veil of canvas 7' high surrounding each tent or 6 to 8 tents - drawn the moment the sun sets or when horizontal currents were to be apprehended." ⁴⁶ Reports of cholera outbreaks had shown that people who lived at ground level suffered more frequently from the disease than those who lived at greater heights. He speculated on the

47. Graham, 'On osmotic force', Phil.Trans. 144 (1854) pp 227-228.

possibility of measuring the quantity of dust in the atmosphere by catching dust on platinum foil or stucco and weighing it. Chemical reactions on the surface of the earth were thought to give rise to poisons, or miasma which were able to produce a given disease. Presumably, dust could also carry these poisons, and London was certainly a dusty city at this time. Graham does not seem to have followed up his plan of measuring the dust levels of the atmosphere but his notes show that he remained interested in contemporary medical problems.

Graham was careful to point out the applications of his researches on osmosis and colloids to physiology. Osmosis occurred in both plants and animals where there was an incessant change through decomposition and renewal. Animal and plant juices were dilute solutions, ideally-suited to the production of osmose. Graham accepted the concept of conservation of force in nature. Therefore, the force of chemical affinity could be transformed into the force of mechanical motion through the movement of muscles. Graham wrote: "in osmose there is, further, a remarkably direct substitution of one of the great forces of nature by its equivalent in another - force - the conversion as it may be said, of chemical affinity into mechanical power. Now, what is more wanted in the theory of animal functions than a mechanism for obtaining motive power from chemical decomposition as it occurs in the tissues? In minute microscopic cells the osmotic movements should attain the highest velocity, being entirely dependent upon extent of surface. May it not be hoped therefore to find in the osmotic injection of fluids the deficient link between chemical decomposition and muscular movement?"⁴⁷

The same conservation rule was observed in plants where the chemical affinity, evident in osmotic force, intervened in the ascent of sap in plants. Both Dutrochet and Liebig had previously attributed the ascent of sap in plants to osmosis and Graham went even further when he pointed out the analogy between the movement of sap in plants and the osmosis through his albuminated calico osmometer. The calico replaced the

48. Graham, 'Liquid diffusion applied to analysis', received May 8th 1861 and read June 13th 1861. Phil.Trans. 151 (1861) pp 183-224 and also in Researches. 552-600.

49. ibid. Researches. 596.

ligneous matter found in plants and the film of albumen possessed the same active properties as the internal contents of a vegetable cell. The analogy was completed, when a solution of a vegetable salt, such as oxalate of potash was put in an albumen osmometer floating in pure water. An osmose was observed as water passed into the vegetable salt. This corresponded to the sap rising in a plant.

From his researches on osmosis, Graham was able to appreciate the division of solutions into two broad groups, colloids and crystalloids.⁴⁸ Colloidal molecules contained the ultimate source of force found in all vital phenomena. The high molecular weight colloid molecules included a lot of energy locked up inside them. Thus, colloid molecules were plastic and so they could easily change form and be adapted to produce the different organised structures by an aggregation process. Another important feature of colloids was their chemical indifference which made them stable to acidic and alkaline secretions. Water was easily transferred across colloidal membranes because water was itself only attached feebly in the colloidal hydrates composing the membranes. Thus, hydrates were themselves easy to hydrate further, or conversely, to dehydrate under the influence of different acidic, alkaline, or saline solutions. Also, the low diffusibility of colloids made them most suitable molecules for aggregation into organised structures. Crystalloids, on the contrary, were much more diffusible. As a result, they could pass through colloid membranes by dialysis, producing the secretions found in living organisms. Dialysis could be used to explain these secretions, for example Graham gave an essentially correct explanation of the secretion of hydrochloric acid in the stomach.⁴⁹ Perchloride of iron could be made colloidal by adding to it an excess quantity of peroxide of iron which produced a basic colloidal salt. This basic colloid was decomposed by dialysis. The crystalloid hydrochloric acid diffused into the stomach, leaving the much less diffusible colloid, hydrated peroxide of iron, in the mucous membrane.

These researches on dialysis, colloids and crystalloids provided

50. H. Spencer, The Principles of Biology, Vol. 1 (London, 1864)
pp 1-30 etc.
51. M. Traube's work is described in A. Findlay: Osmotic Pressure
(London, 1913) pp 2 and 66 and in 'Moritz Traube' J.Hist.Med. 10
(1955) 379-391.
52. C. W. von Nägeli, Theorie der Gärung, (Munich, 1879) p 121
See Partington, History of Chemistry 4 (London, 1964) 738-739.

physiologists with valuable evidence for the interpretation of cell formation, tissue formation, osmosis and the secretions in living organisms. The impact of Graham's discoveries can be seen both in the work of Herbert Spencer⁵⁰ and in Moritz Traube's development of artificial semi-permeable membranes.⁵¹ Traube used Graham's discoveries to explain how vegetable cells were formed and to explain how osmosis acted in this process. Nägeli also made use of Graham's distinction between colloids and crystalloids when he produced his cellular theory.⁵² Undoubtedly, Graham had supplied physiologists with valuable discoveries which could be used both in future experimental physiology and in the development of physiological theories.

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A preliminary survey

(1) Graham's printed papers

The main sources for pursuing a study of Graham's chemical work are his printed papers. They are listed in the:-

Royal Society's Catalogue of Scientific Papers (1800-1863) 2 977-9, 6 675 and (1864-73) 7 813-4. Sixty-three papers by Graham are listed here. It should be noted, however, that two of the papers listed are erroneous. Paper 40: 'Des différentes fonctions que l'eau peut remplir dans les composés à radical simple', Bruxelles Ann.Univ.Belg. 3 (1844) 95-231, was written by Maximilien Dugniolle as a prize-winning essay for the Universities of Belgium and so was not written by Graham. Likewise, paper 54: 'Remarks on the determination of nitrogen in organic analysis' [1842], Chem.Soc.Proc. 1 (1843) 44-45, was written by W. Francis and not by Graham. This latter reference should have been: Graham, 'On the division by three of the equivalents of the phosphorus family of elements', Chem.Soc.Proc. 1 (1843) 44. There is no separate account here of this lecture, which was given to the Chemical Society on Dec.20th 1842, but a short summary is found in Chemical Gazette 1 (1842-3) 158.

Some additions to the Royal Society's Catalogue of Scientific Papers of papers by Graham should include the following:-

'On the solution of gases in water' Quart.J.Sci. 22 (Oct.1826) 204.

'On the great weight of charcoal' [Charles] Chalmers' Journal of Useful Knowledge and Monthly Miscellany of Arts and Sciences 1 (March 1827) 25-26.

(Only one volume of this Journal was published between March and August 1827 and articles written by Graham are signed G.).

'On the advantage of copper bolts in soldering', Chalmers' J. 1 (March 1827) 26-27.

'A valuable appendage to kitchen fire-places', Chalmers' J. 1 (March 1827) 27-28.

'Application of the sandbath to domestic purposes', Chalmers' J. 1 (April 1827) 81-87.

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'On the division by three of the phosphorus family of elements', Chemical Gazette 1 (1842-3) 158.

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'On the supply of iodine from the kelp of Guernsey', (Chem.Soc.Nov.2 1846) Chemical Gazette 4 (1846) and Chem.Soc.Memoirs and Proc. 3 (1845-8) 252.

'On the principle of the endosmose of liquids', B.A.A.S. meeting Belfast 1852, The Literary Gazette (Sept.18th 1852) p 715 and The Athenaeum (1852) p 1013.

The majority of Graham's printed papers were collected and published together in:- T. Graham, Chemical and Physical Researches (Edinburgh, 1876), with a preface and analytical contents by Robert Angus Smith. For convenience I have referred to this collection as Researches throughout this thesis. Most of the important papers listed in the Royal Society Catalogue appear in Researches. The most significant omission is 'On osmotic force' the Bakerian lecture read to the Royal Society on June 15th 1854, Phil.Trans. 144 (1854) 177-228. Other omissions include Graham's discussion of the use of chemical symbols (Phil.Mag. 3 Ser.4 (1834) 106-107, 401-404); 'On the existence of charcoal in the lungs', Edin.Med. and Surg.J. 42 (Oct. 1834) 323-334 and Graham's papers read to the B.A.A.S. meetings of 1835, 1837, 1838, and 1852.

(2) Biographical material including discussion of some aspects of Graham's work

Biographical notices written during Graham's life time

E.Walford, 'Photographic portraits of living celebrities by Maull and Polybank with a memoir by E.Walford. No.8. Thomas Graham' (London, 1856).

John Timbs, 'Professor Graham, M.A., F.R.S., The New Master of Her Majesty's Mint', John Timbs's Yearbook of Facts in Science and Art (London, 1857) pp 3-4.

Charles Knight, 'Thomas Graham', English Cyclopaedia, third division Biography Vol.6 (1858) 996-997.

Lovell Reeve, 'Thomas Graham', Portraits of Men of Eminence in Science and Art with Biographical Memoirs, photographs by E. Edwards, Vol. 3 (London, 1865) biographical memoir of Graham by E. Walford pp 1-6.

E. Walford, The Men of the Time New edition. (London, 1865) p 363; also in 1857 edition p 767.

Obituary notices of Graham etc.

The Times Sept. 20th 1869 p 10; Illustrated London News Sept. 25th 1869 p 315.

The Lancet Sept. 25th 1869 Vol. 2 (1869) 456-457.

British Medical Journal Sept. 25th 1869 Vol. 2 (1869) 361.

Pharmaceutical Journal 2 Ser. 11 (1869-70) 245-246.

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(3) Nineteenth century accounts of Graham's life and work

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A Biographical Dictionary of Eminent Scotsmen (originally edited by Robert Chambers; continued by Rev. Thomas Thomson) Half Volume 6 (1875) 615-620. This is one of the most reliable accounts of Graham's life.

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Smith makes an interesting attempt to place Graham's view of atomism in its historical perspective. This essay is also included as an appendix to:-

Robert Angus Smith, The Life and Works of Thomas Graham (edited by J.J. Coleman) (Glasgow, 1884). Appendix pp 105-114. This is an incomplete and slight attempt to produce a life and works of Graham. It is still useful for the 64 letters of Graham which are included in its pages.

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W. Crookes, 'Review of Graham's chemical and physical researches' Chemical News 35 (Jan. 26th 1877) 40-43.

T. E. Thorpe, 'A lecture on Thomas Graham (with additions) delivered in the Yorkshire College, Leeds, Introductory to the evening class session, 1877-78'. Essays in Historical Chemistry 1st. edn. (London, 1894) 160-217.

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T.E.Thorpe, 'On certain modern developments of Graham's ideas concerning the constitution of matter'. The third Graham lecture, read on March 16th 1887, is found in Essays in Historical Chemistry 1st.edn. (London,1894) 217-235.

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(5) Graham's textbook

Two British editions of Graham's Elements of Chemistry Including the Applications of the Science in the Arts were published. The first complete edition was published as one volume in London in 1842 by H. Baillièrè. The second edition formed volume 8 of H. Baillièrè's Library of Illustrated Standard Scientific Works. It appeared in 2 volumes the first being published in 1850 and the second in 1858. The second volume was edited throughout by Henry Watts. This was because Graham was too preoccupied

with his work as Master of the Mint. Watts added a large amount of new matter including a supplement of over 300 pages.

However, it is important to recognise that both editions of Graham's textbook were issued in parts. These parts were designed to be bound together when the edition was complete. I have attempted to assign dates to these parts. They are as follows:

Thomas Graham, Elements of Chemistry Including the Applications of the Science in the Arts
Complete 1st.edition 1088 pages (London, 1842).

This volume was originally issued in six parts:

Part 1	pp 1-93	November 1837
Part 2	pp 94-197	August 1838
Part 3	pp 197-430	September 1839
Part 4	pp 431-526	March (?) 1840
Part 5	pp 527-696	January (?) 1841
Part 6	pp 697-1088	November 1841

The evidence for these dates is as follows:

Part 1. Graham wrote to his sister on Oct.21st 1837: "I have got 70 pages of my first number in type, it requires 93 or 96. It is likely to be ready in time so far as I myself am concerned, but there is a risk of the woodcuts, about 30 in number, not being all ready, as this is the busy season for annuals, and so forth. It is not a matter of much consequence, however, if it appears in the first week of November, as to the exact day." quoted in R.A.Smith, The Life and Works of Thomas Graham (Glasgow, 1884) p 41. On Nov.25th 1837, Graham wrote to Liebig: "I shall be exceedingly busy with my book probably till Autumn. The first no. was published a few weeks ago, and is meeting with a great sale, although exceedingly imperfect from the hasty manner in which it was got up. This publication from appearing in numbers will be well read." Unpublished MS. letter in the collection Liebigiana 58, Bayerische Staatsbibliothek, Munich.

Part 2. Graham wrote to Schönbein on August 10th 1838: "Permit me in return to offer for your acceptance the second part or no. of my Elements,

which contains a good deal of chemical disquisition on the topics of present interest." Unpublished MS. letter 4.81 Universitäts Bibliothek, Basel. Likewise Graham wrote to Liebig on August 10th 1838: "Altho' I have already forwarded a copy of this part of my book to you thro' Prof. Poggendorff, yet lest it maybe accidentally delayed, I now take the advantage of the journey of my friend and old pupil Dr. Lumsden to Frankfurt and possibly to Giessen to address another to you." Unpublished MS. letter, Liebigiana 58, Bayerische Staatsbibliothek, Munich.

Part 3. Graham wrote to Lyon Playfair on Sept. 30th 1839: "At present I shall take advantage of your kind offer to do me service in Germany only so far as to trouble you with a copy of the part of my book just published, for Liebig." Letter 313, Lyon Playfair Correspondence, Imperial College Archives, London.

Part 4. A copy of this separate part is in the Wellcome Library. I deduce the date from a balance sheet sent to Graham, and dated March 6th 1840, by the publisher H. Baillière in which there is an item:- '50 Chemistry part 4'. This is dated Feb. 27th 1840. Graham, Autograph Letters, Wellcome Library.

Part 5. Parts 1 to 5 were reviewed in January 1841 in the British and Foreign Medical Review 11 (1841) 129-151 and there is a note in The Athenaeum (March 13th 1841) p 210: "We may also notice the publication of the concluding part of the Inorganic Chemistry of Prof. Graham, which equally with the parts previously published sustains the high scientific character of the author."

Part 6. Graham wrote to J. B. Dumas on Nov. 30th 1841: "In soliciting here your acceptance of the concluding part of my book, I beg at the same time to call your attention to some speculations which it contains upon your law of substitutions. I refer particularly to the section pp 728-736 on a 'Molecular theory of organic compounds'. It contains also a method of notation which I think particularly applicable to the formulae of types in contradistinction to those of compound radicals." Unpublished MS. letter in

the Graham Dossier, Académie des Sciences, Paris. The publishing firm of H. Baillière have an advertisement for part 6, which stated that 'Subscribers have till February 1842 to buy separate parts, thereafter only complete editions would be sold.'

Thomas Graham, Elements of Chemistry Including the Applications of the Science in the Arts
Complete 2nd.edn. Volume 8 of the Library of Illustrated Standard Scientific Works:

Volume 1. 632 pages (London, 1850) and

Volume 2. 804 pages (London, 1858) the latter volume edited by Henry Watts.

The second edition was originally issued in five parts:

Volume 1 Part 1 pp 1-160 November 1846

Part 2 pp 161-352 March (?) 1848

Part 3 pp 353-544 December 1848

Part 4 pp 545-632 September 1850

Volume 2 or Part 5 pp 1-804 January 1858

The evidence for these dates is as follows:

Part 1. Review of Dec. 1st 1846, in which it is stated that the work will be published in parts of unequal size and that it was expected to be completed in about six months. Pharm.J. 6 (1846-7) 286-287. Also John Herapath wrote of "the first part of his Graham's Elements of Chemistry, published last November 1846 ." J. Herapath, Mathematical Physics Vol. 2 (London, 1847) p 363.

Part 2. Review of part 2: "This long looked for 2nd part of Prof. Graham's work has at length appeared. It consists of 192 pages making with the previously published part 352 pages." Pharm.J. 7 (May 1st 1848) p 548.

Part 3. A letter dated June 17th 1848 in The Lancet part 1 (1848) p 674 reveals the delays which were being encountered with the second edition: "Sir, In addition to the works enumerated by your correspondent, 'A constant reader' as being delayed in publication, I would mention the 2nd.edn. of Graham's 'Chemistry'. The first no. appeared in Nov. 1846; the second a few months since, (I forget exactly when) and I have inquired

in vain for the third, although the whole work is promised in October next." A review of parts 1, 2, and 3, appeared in January 1849, in the British and Foreign Medical Review 3 (January 1849) p 219. The parts 1, 2, and 3 were dated (London, 1848). They contained 544 pages in all.

Part 4. A review of January 1851 noted that part IV (London, 1850) completes the first volume of Graham's textbook. British and Foreign Medical Review 7 (1851) p 240. Graham's preface to volume 1 is dated September 1850.

Part 5 or Volume 2. Graham's preface, or advertisement, is dated December 1857. Henry Roscoe wrote to W.S. Jevons on Feb. 1st 1858 "Have you seen the 2nd vol. of Graham's book - edited by Watts? - if not, get it - The appendix is particularly good and does Watts great credit - all the newest results in physical chemistry introduced most clearly and completely." The Papers and Correspondence of William Stanley Jevons edited by R.D. Collison Black Vol. 2 (London, 1973) p 316. See also the review in: Amer. J. Sci. 75 (March 1858) p 303: "Graham's Elements Volume 2 (1857) pp 804 edited by H. Watts. This long expected volume is at last published."

Manuscripts

The main collection of manuscript material written by Thomas Graham is that held in the library of the Wellcome Institute for the History of Medicine, 183 Euston Road, London. The collection was presented to the Wellcome library on September 26th 1929, by 'Mrs. Tweedie', of 8 Vicarage Gardens, Kensington, London. Almost certainly the collection belonged to Thomas Graham's niece, Mrs. Janet Clark Inglis (née Reid), 1843-1926. Janet Clark Inglis was the daughter of Thomas Graham's sole surviving sister Mrs. Mary Reid (née Graham), 1810-1878. It is probable that the Graham manuscripts were presented by Janet Clark Inglis's executrix, Miss Kathleen Alice Tweedie. Janet Clark Inglis lived at 8 Vicarage Gardens, with another widow, Louisa Bell (1832-Sept. 6th 1929), who was the

Aunt of Kathleen Alice Tweedie. Therefore, it can be understood why the Graham manuscripts were not presented until September 26th 1929. This was after the death of Louisa Bell.

The Graham manuscripts are described in S.A.J.Moorat, Catalogue of Western Manuscripts on Medicine and Science in the Wellcome Historical Medical Library, Volume 2, MSS.after 1650 A-M, (London, 1973) pp 462-464. The Graham MSS. are numbered 2551-2584, 3531, 4937.

In addition two other manuscripts should be included in the collection. They are:-

1717 Willibald G.Schmidt, Collectanea Anatomy and Physiology:- 'Experiments on the velocity of filtration of various liquids through animal membranes', (1856) 13 pp + 1 bl.1. A résumé in English of an article originally published in Pogg. Ann. 89 (1856), from Thomas Graham papers 67221^N.

5000 G.H.Wiedemann, 'On the motion of liquids in the current of the closed galvanic battery'. Anon. English translation 31 pp. [1852] From Pogg. Ann. 87, from Thomas Graham papers 67221^M.

One or two additional comments might be usefully added to the catalogue description of Graham's manuscripts. Firstly, MS.2551, contains an article 'Whether is the theory of electricity of Dr. Franklin or that of Dufay (not Dupuy) the more probable?'. This contains one page describing the production of electricity by friction and an admission that the nature of electricity was unknown. The remaining notes are copied, without alteration, from John Murray, System of Chemistry, 2nd.edn. Vol.1 (Edinburgh, 1809) pp 567-582, 'On Galvanism'. Secondly, MS.2578 'Remarks upon the modes of valuing Indigo, Gums and Bleaching powder' - read before the Manchester Literary and Philosophical Society upon December 1st 1838 (34 ll) is not written by Thomas Graham. It is written by his brother, John Graham (1812-1869), who was a chemist at Thomas Hoyle's calico-printing works in Manchester. There is a MS. 'History of calico-printing' by John Graham in Manchester Central Reference Library. Dalton had previously

written on the valuation of indigo; See Manchester Memoirs 9 (1824) 427-440.

I have found the following Graham manuscripts most useful

- MS.2577 'Notes taken at Faraday's lectures on electricity' 5 ll. (1838).
- MS.2579 'Notes and drafts for his lectures on Chemistry at University College' 154 ll. (1838-48). [Most of these notes seem to date from 1838. The 1848 notes are on the diffusion of liquids. They comprise a short inserted series of notes.]
- MS.2580 'Miscellaneous notes and oddments on chemistry', etc. 89 ll. (1840-68). The notes which have been particularly useful are:-
(1) Folder lettered 'Molecular theory etc. 1840'. 18 ll.
(5) Notes on gases 21/3/1868 5 ll.
(6) Of gelous hydration (9 pp), On liquid condition of matter (7 ff. + 6 ll).
- MS.2584 'On the molecular mobility ['diffusive movement' superscribed and crossed through] of gases'. Copy with holograph corrections and additions. 44 ff. (1863?)

Also in the Graham collection at the Wellcome Library there is a volume of letters and notes written by Graham, or received by him. This contains a number of useful items.

Other manuscript notebooks and essays by Graham:

The Andersonian Library, Strathclyde University, Glasgow:

Graham Laboratory notebook B (July 1832-August 1834) 450 pp.
Graham Laboratory notebook C (September 1834-July 1835) 252 pp.
These notebooks were purchased in 1973; notebooks A, D and E which are referred to in notebooks B and C seem to be missing at present.

Library of the Royal College of Physicians and Surgeons, Glasgow

Unpublished MS. Essays of the Glasgow Medical Society
Volume 19 (1831-1832). Author's holograph essay, by Thomas Graham, entitled 'Galvanism and organic action' 8 pp.

Manuscript letters

- (1) Bayerische Staatsbibliothek, Munich. Liebigiana 57: MS. letters from Liebig to Lyon Playfair; Liebigiana 58: MS. letters to Liebig from J.B.Dumas, Pelouze, and Graham. There are 24 Graham letters in this collection (including one from Mary Graham and another from William Graham). The Graham letters which I have used are:- Graham to Liebig, October 17th 1837, August 10th 1838, and August 16th 1842; Mary Graham to Liebig, September 17th 1869; Dumas to Liebig, November 29th 1837.

- (2) University College, London.
 Graham's MS. letter of application for the Chair of Chemistry addressed to the Council of University College, London, February 25th 1837, Letter 3937.
 William Sharpey Correspondence, MS. Add.227. MS.letter No.148, from G.G.Stokes to W.Sharpey, August 10th 1863.
- (3) King's College, London.
 Graham's MS. letter of application for the Chair of Chemistry addressed to: the Secretary of the Council, King's College, London, dated July 30th 1830 - kept in the London Collection, King's College, London.
- (4) University Library, Cambridge.
 MS. letter from J.C.Maxwell to Graham, dated May 1st 1865.
 Add. MSS.7655 Box II item 23.
G.G.Stokes Correspondence, Add. MSS.7656
 MS. letter from Graham to Stokes, July 6th 1861 (G.394). This letter is reprinted, with some errors, in J.Larmor, Memoir and Scientific Correspondence of the Late Sir George Gabriel Stokes 2 (Cambridge, 1907) pp 73-74.
 MS. letter from Edward Sabine to Stokes, August 1st 1863 (RS 409)
 MS. letter from Graham to Stokes, August 11th 1863 (RS 410)
 MS. letter from Graham to Mr. White, Assistant Secretary of the Royal Society, May 7th 1863 (RS 377)
- (5) Imperial College Archives, London.
 Lyon Playfair correspondence:
 MS. letter from Graham to Playfair, May 11th 1841 (316)
 MS. letter from Liebig to Playfair, July 22nd 1841 (425)
 MS. letter from Liebig to Playfair, August 14th 1841 (426)
 MS. letter from Graham to Playfair, May 10th 1860 (329)
- (6) Queen's University, Belfast
 Thomas Andrews' collection:
 Letter from Graham to Thomas Andrews, November 25th 1856.
 This is a copy made by one of Andrews' daughters.
- (7) University Library, University of St.Andrews
 J.D.Forbes collection,
 MS. letter from J.D.Forbes to Graham, April 6th 1837.
- (8) Edinburgh City Council Archives
 A copy of the letter from Dr.S.M.Brown to Councillor Logan, as the representative of the Lord Provost and magistrates of the City Council, withdrawing his candidature for the Chemistry Chair of the University of Edinburgh.
 This letter is copied down in the Council Minutes. It is dated February 27th 1844. Council Minutes (February 27th 1844) pp 192-197.
- (9) Académie des Sciences, Paris.
 Graham dossier: MS. letter from Graham to Dumas, November 30th 1841
 Dumas letters: MS. letters from Liebig to Dumas, November 29th 1837, December 19th 1837.
 Pelouze letters: MS. letters from Liebig to Pelouze, November 20th 1837, December 9th 1837, and April 18th 1838.
- (10) Gesellschaft, Liebig Museum, Giessen.
 MS. letter from Liebig to Graham, August 8th 1838.

- (11) Universitäts Bibliothek, Basel.
 MS. letters 482-484 from Graham to Schönbein, June 23rd 1838, and May 28th 1839.
 Draft of a letter from Schönbein to Graham [August?] 1840.
 MS. letter 483 from Graham to Schönbein, January 9th 1862 published in G.W.A.Kahlbaum and F.V.Darbishire, The Letters of Faraday and Schönbein (1836-1862), (Basel and London, 1899) p 209.
- (12) Royal Swedish Academy of Sciences, Stockholm.
 Copy of MS. letter from Graham to J.F.W.Johnston (or in his absence for Berzelius), September 8th 1832; the original letter is in Leningrad.
 MS. letter from Liebig to Berzelius, January 5th 1838. This letter has been published but it has been incorrectly dated January 5th 1837. The MS. letter shows that the year should have been 1838, as do the contents of the letter. The published letter (incorrectly dated) is in J.Carrière (editor), Berzelius und Liebig, Ihre Briefe von 1831-1845, 1st.edn. (Munich and Leipzig, 1893) pp 121-123. This error is repeated in the 2nd.edn. of 1898.
- (13) Translation of a letter from Liebig to A.W.Hofmann, October 2nd 1850, kindly supplied by Dr.W.H.Brock from his draft for the forthcoming edition of the Liebig-Hofmann correspondence.
- (14) Institution of Electrical Engineers, London.
 MS. letter from Graham to Faraday, May 15th 1837.

Royal Society Manuscripts

MS. papers submitted by Graham:-

'On liquid diffusion' (1849) R.S. MS. 37.1

'On the molecular mobility of gases' (1863) R.S. MS. 69.2

Referees reports:-

R.R. 180, Report by Graham on F.Penny's paper: 'On the application of the conversion of chlorates and nitrates, into chlorides and of chlorides into nitrates, to the determination of several equivalent numbers'. Phil.Trans. 129 (1839) 13-33. Report dated February 21st 1839.

R.R. 184, Report by Graham on R.Phillips' paper: 'Researches on the chemical equivalents of certain bodies' Phil.Trans. 129 (1839) 35-38, Report dated February 21st 1839.

R.R. 5.83, Report by W.Allen Miller on Graham's paper 'On the molecular mobility of gases', Report dated July 10th 1863.

R.R. 5.84, Report by A.W.Williamson on the above paper, July 29th 1863.

R.R. 5.85, Report by G.G.Stokes to the Officers of the R.S. on the above paper, July 29th 1863.

R.R. 5.137, Report by W.Allen Miller on Graham's paper 'On the absorption and dialytic separation of gases by colloid septa' Report dated July 4th 1866.

R.R. 5.138, Report by J.C.Maxwell on the above paper. Report dated July 17th 1866.

R.R. 6.15, Report by Graham on Thomas Andrews' paper 'On the continuity of the gaseous and liquid states of matter', Phil. Trans. 159 (1869) 575-590. Report dated July 19th 1867.

Minutes of the Committee of Papers, Royal Society, Volume III

Annotated copies of Graham's textbook: Elements of Chemistry. 1st.edn. (1842)

Graham possessed an interleaved edition of his textbook which he partly annotated. Only two parts survive and these are now in the library of University College, London. It is possible that Graham made these annotations either for his lectures or for a second edition of his textbook. The latter alternative seems more likely, from the comparison I have made, between his annotations and the first volume of the second edition of Elements of Chemistry.

The two annotated volumes are:

Volume 1 (1842) pp 431-696

Volume 2 (1842) pp 697-1088

These volumes were part of Graham's library which was presented to University College library, London on July 11th 1879. The library was donated by John Cameron Graham (1847-1929), who was the nephew of Thomas Graham. The first part of Graham's textbook pp 1-430 is not recorded in the original gift. See:- Catalogue of Thomas Graham's Library (Printed by John Graham of Glasgow, 1869) in University College library, (History of Science Stores 901530).

Some other parts of Graham's Elements of Chemistry, which belonged to the author, are also to be found in the Wellcome Library:-

Elements of Chemistry 1st.edn. part 4 (1840) pp 431-526 - not annotated

1st.edn. part 6 (1841) pp 697-1088.

Part 6 contains a few unimportant annotations.

Elements of Chemistry 2nd.edn. part 2 (1848) pp 161-352

This part is annotated by Graham. From the dates accompanying these notes it seems that Graham used this volume in his University College lectures from 1848 to 1854. The text also contains some inserted notes

written by Graham. They are:- found between pp 244-245: two double sheets on 'chemical polarity' - experimental memo. and between pp 330-331: a sheet marked Dr.R.D.Thomson 'Weight of atmospheric air' and a double sheet marked 'Climate-Arctic and Torrid Zone'.

Notes taken at Graham's lectures on Chemistry

James Young, Book of notes probably taken at Graham's lectures (at the Andersonian University, Glasgow dated March 1831) 14 pp. Andersonian Library, Strathclyde University. These brief notes include the end of arsenic chemistry; chromium; a brief mention of molybdenum, tungsten and columbium; antimony - Graham said that he preferred the Berzelian view of the oxides of antimony; tartar emetic. No symbols are used in these notes.

Frederick J.Furnivall, MS. notebooks of Thos. Graham's lectures on Chemistry at University College, London. Two of Furnivall's notebooks survive. The first notebook contains lectures 1 to 23 given between October 4th 1841 and November 3rd 1841. These lectures are mainly concerned with heat and light. The second notebook contains lectures, 108 to 135, given between March 7th 1842 and April 14th 1842. These lectures include the end of inorganic chemistry, for example lead and bismuth, and organic chemistry. These notebooks are kept in the London Collection, King's College, London.

William J.Russell, 'MS. notes of lectures given by Thomas Graham in the session 1848-9 at University College, London'. Two volumes MS. nos. 8920-8921, kept in the National Library of Scotland, Edinburgh. These notes follow quite closely the contents of volume 1 of the second edition of Graham's Elements of Chemistry. Of interest, are the sections on chemical polarity and organic chemistry.

Other manuscripts which have been used:-

James Young MSS., The Andersonian Library, University of Strathclyde:-

Book of notes 1834-1840, which includes Young's 1836 experiments on galvanism and his new design of battery. Also there is a draft of a

letter, which Young sent to Faraday, concerning his battery, dated March 1836.

Diary, August 1835 (mainly). Here, Young gives short notes of his visit to Dublin with Graham. This includes brief notes on the meeting of the British Association for the Advancement of Science.

William Stanley Jevons MSS. The John Rylands Library, Manchester.

MS. note on the 'Theory of heat', dated March 24th-28th 1853, 6 pp.

Thomas Charles Hope

MS. notes taken by a student who attended Hope's Chemistry lectures in the session 1797-8, Chemical Society, London.

MS. lecture notes written by T.C.Hope, 5 boxes containing his own lecture notes written between 1790 and 1842. These are kept at Edinburgh University Library, MSS. General 268-272.

Thomas Thomson

MS. notes taken by Robert Dundas Thomson of his uncle Thomas Thomson's Chemistry lectures at Glasgow University. This volume is dated from November 1828 to May 1829. These notes are interesting because Graham may have attended the same lectures during this session. This volume is kept in the library of the Chemical Society, London.

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