

Thomas Graham. II. Contributions to diffusion of gases and liquids, colloids, dialysis, and osmosis

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ABSTRACT

In this second part, the contributions of Thomas Graham in the areas of diffusion and transfer of gases and liquids through membranes are discussed.

KEYWORDS: colloids, dialysis, diffusion, effusion, occlusion of gases, osmosis, transpiration

Resumen (Thomas Graham. II. Contribuciones a la difusión de gases, líquidos, coloides, diálisis y ósmosis)

En esta segunda parte se describen las contribuciones de Thomas Graham en las áreas de difusión de gases, líquidos y soluciones, y transferencia de material a través de membranas.

Palabras clave: coloides, diálisis, difusión, efusión, oclusión de gases, ósmosis, transpiración

Introduction

In a previous publication (Wisniak, 2013) we described the life and career of Thomas Graham and his contributions in the areas of thermodynamics, chemistry, and occlusion of gases. Here we depict and analyze his contributions to diffusion, mass transfer of gases and liquids through membranes, and colloidal chemistry.

Diffusion of gases

The line of research which occupied most of the attention of Graham, and in which his results were perhaps the most important, was that of diffusion. In 1829 Graham published the first of his papers relating specifically to the subject of gaseous diffusion (Graham, 1829a). He allowed hydrogen (or oxygen) to escape through a small hole in a plate of platinum and found that hydrogen molecules moved out four times faster than those of oxygen. His experiments were so arranged as to enable him to measure the relative velocities of certain motions of the molecules. In addition, he found that heat increased the velocity of these molecular motions, while increasing the force with which a given weight of the gas resisted the atmospheric pressure. The experimental procedure was as follows: Each gas tested was allowed to diffuse from a horizontally placed bottle through a narrow tube directed either upward or downward, according as the

gas was heavier or lighter than air. so that the diffusion always was in a direction opposite to gravity. The results indicated that equal volumes of different gases escaped in very unequal times; the rate of escape had an inverse relation to the specific gravity of the gas. Thus hydrogen was found to escape four or five times quicker than the twenty-two times heavier CO₂. When using a binary mixture of gases, the lighter or most diffusible of the two left the bottle in the largest proportion, so that a sort of mechanical separation of gases could be conducted by means of their unequal diffusibility. Most of these last results were obtained by allowing the gaseous mixture to diffuse into a limited atmosphere of some other gas or vapor, capable of subsequent removal by absorption or condensation (Odling, 1871).

The numerical results of Graham's experiments indicated that the flow velocities were inversely proportional to the square root of the densities. According to Graham, his law proved that the specific gravity of gases could be determined with greater accuracy than by ordinary means (Williamson, 1870). Specific results indicated that as much hydrogen left a glass tube in two hours as CO₂ did in ten hours; so hydrogen was five times more diffusive than CO₂ and therefore the diffusiveness of a gas was inversely proportional to some function of the density (apparently the square root). Significantly, he also observed that in a given time, the more diffusive gas in a mixture escaped in a greater proportion than it did when it was on its own, a discovery that led Graham to suggest that the diffusion process must involve ultimate particles and not sensible masses (bulk) of a gas. After describing his experiments in detail he wrote: "It is evident that the diffusiveness of gases is inversely as some function of their density, apparently the square root of their density." He showed that that simple diffusion allowed the separation of gases: "imperceptible pores and orifices of excessive minuteness may be altogether impassable (by diffusion) by gases of a low diffusive power, that is, the dense gases, and passable only by gases of a certain diffusive energy" (Smith, 1884).

In a following publication (Graham, 1829b) Graham reported additional experiments done with a bladder. He first

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inflated the bladder partially with coal gas, closed it, and put it inside a bell jar filled with CO₂ standing over water. After twelve hours he found that the bladder had inflated almost to the point of bursting, while most of the CO₂ in the receiver had disappeared. Analysis of the internal gas indicated that it contained about 30% volume of CO₂ while the CO₂ remaining in the bell jar had acquired a very little amount of coal gas. His conclusion was unavoidable: the closed bladder was inflated by the penetration of CO₂ from the external atmosphere. The same results were obtained when the bladder was initially full with atmospheric air. It was clear then that the transfer of CO₂ was not dependent upon any peculiar property of coal gas.

Graham described his results as follows: "The jar of carbonic acid gas standing over water, the bladder was moist, and we know it to be porous. Between the air in the bladder and the carbonic acid gas without, there existed capillary canals through the substance of the bladder filled with water. The surface of water at the outer extremity of these canals being exposed to carbonic acid gas, a gas soluble in water would necessarily absorb it. But the gas in solution, when permeating through a canal, it arrived at the surface of the inner extremity would rise as necessarily into the air in the bladder and expand it. Nothing but the presence of carbonic acid within could prevent the disengagement of that gas. The force by which water is held in minute capillary tubes might retain that liquid in the pores of the bladder, and enable it to act in the transit of the gas even after the pressure within the bladder had become considerable" (Graham, 1829b).

It seems that Graham was attracted to the subject of the transmission of gases through porous diaphragms by the findings reported by Johann Wolfgang Döbereiner (1780-1849) who found that directing a stream of hydrogen on black platinum powder at room temperature resulted in the instant combustion of the gas (Döbereiner, 1823; Odling, 1871). In Graham's words: "While collecting for storage some quantities of hydrogen over water, Döbereiner accidentally made use of a fissured jar, and was surprised to find that the water of the pneumatic trough rose in this jar by almost 7.5 cm in twenty-four hours. In other experiments, Döbereiner substituted glass vessels of very different forms, all of which had fissures. In every one of these vessels, filled with hydrogen, the water rose... to a certain height. On covering one of these vessels, containing hydrogen, by a receiver — or on filling the vessel with atmospheric air, oxygen or nitrogen, instead of hydrogen; he never observed a change in the original volume of the gas." Döbereiner attributed the phenomenon to the capillary action of the cracks, which were able only to attract hydrogen, the gas being capable to escape through the fissure due to the small size of its atoms. According to Graham, Döbereiner's explanation was not plausible because it was known that other porous materials, such as charcoal, hardly absorbed hydrogen and "there was no reason to suppose that the particles of hydrogen are

smaller than those of other gases" (Graham, 1833, 1849, 1850b, 1863ab).

Graham repeated Döbereiner's experiments and made the important observation that the escape of hydrogen outward was always accompanied by a penetration of air in an amount to about one-fourth of the volume of hydrogen escaping; that is, the fissure was permeable to the grosser air as well as to the finer hydrogen. In order to quantify his results, he constructed what he called a *diffusion tube*, in which Döbereiner's bell jar was replaced by a piece of glass tube about 1.2 cm in diameter and 20 to 36 cm long, and the fissure in the jar by a plug of stucco closing one end of the tube (Odling, 1871). He then measured the escape of different gases from his diffusion tube into air. In order to quantify his results, he defined the *equivalent diffusion volume* of a gas, as the ratio between the volume of the gas diffused and the volume of air eventually found in the tube. He expressed the numerical value of this parameter by considering the replacing volume of air as unity: "If the two gases are separated at the outset by a screen having apertures of insensible magnitude, the interchange of equivalent volumes of diffusion takes place through these apertures, being effected by a force of the highest intensity; and if the gases are of unequal density, there is a consequent accumulation on the side of the heavy gas, and loss on the side of the light gas. In the case of air... on the one side of the screen, and hydrogen on the other, a process of exchanging one measure of air for 3.7947 measures of hydrogen, through the apertures, is commenced, and continues till the gases on both sides of the screen are in a state of uniform mixture." He performed diffusion experiments with different gases and obtained the following values for the equivalent diffusion volumes: hydrogen, 3.83; methane, 1.344; ethylene, 1.0191; carbon monoxide, 1.0149; nitrogen, 1.0143; oxygen, 0.9487; hydrogen sulfide, 0.95; nitrogen monoxide, 0.82; carbon dioxide, 0.812, and sulfur dioxide, 0.68. The results indicated that each gas had a particular diffusion volume, which was inversely as the square of its specific gravity: "The diffusion or spontaneous intermixture of two gases in contact, is effected by an interchange in position of indefinitely minute volumes of the gases... not necessarily of equal magnitude, being, in the case of each gas, inversely proportional to the square root of the density of that gas" (Graham, 1829b, 1833).

According to Graham, "the superior aptitude of stucco for exhibiting the unequal diffusion of gases of different densities, seems to depend upon its pores being excessively numerous, but exceedingly minute, making in the aggregate a considerable channel. In the bladder, the pores I suppose to be few in number but wide, making, however, when added together, but a *small channel*. Air passes through them but little impeded by friction. Dry and sound cork answers exceedingly well as a substitute for the stucco-plug. The diffusion takes place slowly, but is not apt to be deranged by a slight mechanical pressure. So do thin laminæ of many granular minerals, such as the flexible magnesian limestone,

etc.; charcoal also, and woods, if not too porous, may be applied to the purpose... The diffusion, or spontaneous intermixture of two gases in contact, is effected by an interchange in position of indefinitely minute volumes of the gases. My experiments... on the diffusion of mixed gases, afford the first demonstration of the fact, that diffusion takes place between the ultimate particles of gases, and not between sensible masses, and therefore that diffusion cannot be the result of accident" (Graham, 1829b).

Graham extended his thoughts to the explanation of two other important physical phenomena: "Evaporation, or the elevation of a vapor from a liquid into air, or any other gas, may 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 vapor from the surface of the liquid, as a vacuum would do. Once elevated, the vapor 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 a property of vapor, namely, that the particles of any vapor condense when they approximate within a certain distance... I... mention an application of the law of diffusion, in explanation of the mechanism of respiration. It is in the respiration of insects that the operation of this law will be most distinctly perceived. The minute air tubes accompanying the blood vessels to every organ, and like them ramifying till they cease to be visible under the most powerful microscope, are kept distended during the most lively movements of the little animals, and the necessary gaseous circulation maintained, wholly, we may presume, by the agency of diffusion" (Graham, 1850b, 1863ab).

In 1846 and 1849 Graham published two memoirs "On the Motion of Gases" (Graham, 1846, 1849) reporting a phenomenon which he named *effusion* of gases into a vacuum through a thin plate, "leaving no doubt of the truth of the general law, that 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," and that "the effusion-time of air of different temperatures is proportional to the square root of its density at each temperature."

The experimental procedure was as follows: A jar standing on the plate of an air pump was kept continuously under vacuum while a measured quantity of gas was introduced into the jar through a minuscule gap in a thin metallic plate. The admission of 0.983 liters of dry air into the jar, within about 1,000 seconds, showed that the times of passage of the same volume of air did not vary by more than two or three seconds, in successive experiments. Experiments with different gases showed that the relative times of passage or of effusion were approximately identical with the square roots of the specific gravities. The rate of effusion of a mixed gas corresponded in most cases with the calculated mean of

the constituents, but the rates of effusion of the light gases, methane and hydrogen, were disproportionately retarded by the admixture with them, even to a small extent, of the heavier gases oxygen and nitrogen (Graham, 1846, 1849).

In a paper published in France (Graham, 1850b), Graham repeated his findings that the velocity at which different gases flow through a tube was highly dependent on their law of effusion when the tube was short and its aperture similar to that of an orifice in a thin wall. A progressive increase of the length of the tube resulted in an increase of the resistance and a reduction of the velocity of flow until it deviated substantially from the velocity of effusion. Hence, it seemed that the velocity of flow of different gases was in a certain ratio with the length of the tube and the resistance to flow; a ratio that remained constant for quite different lengths and resistances. Once this ratio was attained, the flow of all gases diminished proportionally to the increase in the tube length, that is, to the flow resistance.

Graham repeated again his feeling that the flow rate of the gases seemed to depend on a new particular property, which he named *transpirability*, which was independent of the material of construction of the tube. Some of the most remarkable results obtained were that the velocity of transpiration of hydrogen was exactly double that of nitrogen, in spite of the large ratio, 1:14, of their densities. Nevertheless, carbon monoxide, and nitrogen had the same transpirability and specific gravity. For nitrogen and oxygen, the transpirability was found to vary inversely to their densities, that is, for equal times, the individual volumes flowing were different although their weights were the same. Graham reported the value of the transpirability for a large number of gases, among them, hydrogen, methane, carbon dioxide, air, hydrogen cyanide, hydrogen sulfide, sulfur dioxide and sulfur trioxide, carbon disulfide, methyl chloride and ethyl chloride, bromine and chlorine. Some additional consequences were: (1) the velocity of hydrogen was exactly double that of nitrogen and carbon monoxide, (2) the velocities of nitrogen and oxygen were inversely proportional to their densities, (3) the velocity of methyl derivatives was smaller than those of the corresponding ethyl derivatives, (4) the resistance offered by a capillary tube to the flow of a gas was directly proportional to the length of the tube, (5) the rate of flow of equal volumes of air at the same temperature but at different pressures was directly proportional to the density, and (6) heat acted by decreasing the flow velocity, in the same manner as the decrease in the pressure (Graham, 1850b).

Graham reported additional findings of the diffusion of gases on two papers published in 1863 (Graham, 1863ab). The concept of mobility of gases was explained in reference to their passage under pressure through a thin porous plate or septum. He now reported that he had obtained an improved version of his diffusimeter by replacing the stucco plug by a disk (wafer) made of the artificially compressed graphite manufactured by William Brockedon (1787-1854)

for making writing pencils. According to Graham, "The pores of artificial graphite appear to be really so minute that a gas in mass (bulk flow) cannot penetrate the plate at all. 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 graphite must be tunnels in magnitude to the ultimate atoms of a gaseous body. The sole motive agency appears to be that intestine movement (kinetic energy) of molecules,...an essential property of the gaseous condition of matter. According to the physical hypothesis...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. If the containing vessel were porous, like a diffusometer, then gas is projected through the open channels by the atomic motion described, and escapes. Simultaneously, the external air is carried inward in the same manner and takes the place of the gas, which leaves the vessel... The molecular movement is accelerated by heat and retarded by cold; the tension of the gas being increased in the first instance and diminished in the second. Even when the same gas is present both within and without the vessel, or is in contact with both sides of our porous plate, the movement is sustained without abatement, molecules continuing to enter and leave the vessel in equal number, although nothing of the kind is indicated by a change of volume or otherwise. If the gases in communication were different, but possess sensibly the same specific gravity and molecular velocity, as nitrogen and carbonic oxide do, an interchange of molecules also takes place without any change in volume. With gases opposed of unequal density and molecular velocity, the permeation ceases of course to be equal in both directions" (Graham, 1863ab).

According to Graham, a gas may pass into a vacuum in three different modes: "(a) by passing through a minute aperture in a thin plate, such as a puncture in platinum foil, made by a fine steel point... The rate of passage of different gases is regulated by their specific gravities; the gas rushes into vacuum with the velocity which a heavy body would acquire on a free fall through an atmosphere of the gas in question... Since this velocity is proportional to the square root of the height, the rate of flow into a vacuum will be proportional to the square root of the density... The phenomena of effusion and diffusion are distinct and essentially different in their nature. The effusion movement affects masses of gas (a bulk phenomenon); the diffusion movement affects molecules... a gas is carried by the former kind of impulse with a velocity many thousand times greater than by the latter. The effusion velocity of air is the same as the velocity of sound, (b) if the aperture of efflux is in a plate of increased thickness, it becomes a tube and the effusion

rates are disturbed. The rates of flow of different gases... assume a constant ratio when the capillary tube is considerably elongated (when the length is at least 4000 times the diameter). These new proportions of flux are the rates of capillary transpirability of gases... and appear to be independent of the material of the capillary. A film of gas no doubt adheres to the inner surface of the tube (boundary layer) and is consequently unaffected by the construction material. The rates of transpiration are not governed by specific gravity... The transpiration ratios of gases appear to be in constant relation with no other property of the same gases ..., (c) a plate of artificial graphite, although it appears to be practically impenetrable by either of the two modes of passage previously described, is readily penetrated by... molecular or diffusive movement of the gases" (Graham, 1863ab).

Of all the gases tested, oxygen was found to have the longest transpiration time, or slowest transpiration velocity. Graham provided a table comparing the times of effusion of different gases (oxygen = 1): Hydrogen 0.437, methane 0.551, nitrogen 0.877, oxygen 1.000, and carbon dioxide 0.730. As a rule, the observed transpiration rate of a mixture of gases corresponded with the calculated mean rate of its constituents; but the transpiration rates of the light gases, hydrogen, and methane, were found to be disproportionately retarded to a greater extent even than their effusion rates by the admixture with them of heavier gases (Graham, 1863ab).

Referring to the approximately equally rapid passage of hydrogen into a vacuum and aerial space, Graham referred as follows to the subject of inter diffusion: "In summary, there can be little doubt left on the mind that the permeation through the graphite plate into a vacuum, and the diffusion into a gaseous atmosphere through the same plate, are due to the same inherent mobility of the gaseous molecule. They are the exhibition of this movement in different circumstances. In inter diffusion, we have two gases moved simultaneously through the passages in opposite directions, each gas under the influence of its own inherent force; while with gas on one side of the plate and a vacuum on the other side, we have a single gas moving in one direction only. The latter case may be assimilated to the former if the vacuum be supposed to represent an infinitely light gas. It will not involve any error, therefore, to speak, of both movements as gaseous diffusion, the diffusion of gas into gas (double diffusion) in the one case, and the diffusion of gas into a vacuum (single diffusion) in the other. The inherent molecular mobility may also be justly spoken of as the diffusibility or diffusive force of gases. The diffusive mobility of the gaseous molecule is a property of matter, fundamental in its nature, and the source of many others. The rate of diffusibility of any gas has been said to be regulated by its specific gravity, the velocity of diffusion having been observed to vary inversely as the square root of the density of the gas. This is true, but not in the sense of the diffusibility being determined or caused by specific gravity. The physical basis

is the molecular mobility. The degree of motion... 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 be molecular motion of 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 equivalent combining volumes" (Graham, 1863ab).

Graham's results indicated that the penetration of the graphite plate by gases appeared to be completely due to their own molecular motion, without that of transpiration. The graphite became "a *molecular sieve*, allowing only molecules to pass through." It was possible to obtain a partial separation of vapors and gases of different diffusibility by allowing the mixture to permeate through a graphite plate. Graham believed that this finding had considerable potential uses and suggested naming the phenomenon *atmolysis* and the apparatus for performing it, *tube atmolyzer*, which he described in this second paper (Graham, 1863b). The instrument was built of one or more lengths of ordinary tobacco pipe (for conveying the current of mixed gas), surrounded by an evacuated glass tube exhausted by an air pump. The most diffusible constituent of the mixed gas passed away in largest proportion through the porous material of the tobacco pipe, and the least diffusible constituent became concentrated in the residue of gas passing along; and finally delivered by the pipe. In this simple manner, the proportion of oxygen in ordinary air transmitted by the tobacco pipe, was increased from below 21% to 24.5%, as a result of the small superior diffusibility of nitrogen 1.01 over that of oxygen 0.95 (Odling, 1871).

Graham realized that the degree of separation of a gaseous mixture that could be achieved by atmolysis would be adequate only for gases that differ considerably in diffusivity and specific gravity. Hence, the process was very limited for separating oxygen and nitrogen of atmospheric air; gases which differed so little in density from each other. Other means had to be looked upon for achieving the goal, and for this purpose he decided to test the findings of John K. Mitchell (1793-1858) (Graham, 1866). It was known that animal membranes were micro porous and hydrophilic, and rubbery membranes were homogeneous and hydrophobic. Mitchell tested both of them and found that gases were able to penetrate natural rubber built as a thin sheet or in the form of little transparent balloons. He remarked that such balloons promptly collapsed when inflated with hydrogen than with atmospheric air, and even faster when filled with CO₂. Mitchell connected the last fact with the observation that a solid piece of natural rubber was capable of absorbing its own volume of carbon dioxide when left long enough in the pure gas. He also found that various gases passed spontaneously through the rubber membrane when there was air on the other side, with different degrees of velocity. The amount of ammonia transmitted in one minute was equivalent

to that of carbon dioxide transmitted in five minutes; that as much of ammonia gas was transmitted in one minute as of carbon dioxide in 5.5 minutes, of hydrogen in 37.5 minutes, and as of oxygen in 113 minutes. The ratio of permeation was found to be independent of the membrane used, in opposition with liquid permeation being dependent upon both the nature of the liquid and the membrane (Mitchell, 1831). These results led him to think about the possibility of selective withdrawal of oxygen from air through a gum elastic membrane (the opposite process performed by an artificial gill). Mitchell explained his results by drawing on the similarity of absorption affinity and ease of condensation of certain gases on charcoal. Sorption of carbon dioxide was envisioned as interstitial infiltration and not by conducting capillaries as suggested by Graham. Mitchell's paper was commented and extended by John William Draper (1811-1882) (Draper, 1844), who also added many new observations on the passage of both gases and liquids through membranous septa (Graham, 1866).

For his experiments, Graham employed a tube considerably much larger than the barometric column, opened at one end and closed at the other by a thin film of natural rubber stretched over a plate of highly porous stucco. Filling the tube with mercury and inverting it into a cup of mercury created vacuum, which caused the external gas to permeate through the rubber film and depress the mercury column. Experiments performed with nitrogen, methane, oxygen, hydrogen, and carbon dioxide proved that each gas penetrated the rubber with a characteristic velocity, was clearly different from the velocities of diffusion and transpiration of the same gas. This suggested immediately the possibility of using a rubber septum to separate the gases present in a mixture. For example, the transmission velocities of oxygen and nitrogen were 2.55 and 1.0 respectively, so that atmospheric air transmitted through India rubber into a vacuum should consist of 40% oxygen and 60% nitrogen [oxygen (20.8)(2.55) = 53.04]; nitrogen [(70.2)(1.0) = 79.20]. Unfortunately for the practical application of the process, the entire volume of air sucked through proved to be very small, about 2.25 cm³/min·m² at 20°C. At 60°C, however, the passage of air through the rubber was almost exactly three times as rapid as at 20°C (Graham, 1866).

Graham concluded that the entire phenomenon was very complex and consisted of many stages: dissolution of the gas in the soft India rubber (and hence becoming liquefied) (Wisniak, 2013), diffusion of the liquefied gas through the thickness of the India rubber, evaporation of the liquefied gas from the internal surface of the India rubber, and finally, diffusion of the evaporated gas into the internal space. Thus, in reference to the remarks of Mitchell and Draper, he wrote: "These early speculations lose much of their fitness from not taking into account the two considerations already alluded to, which appear to be essential to the full comprehension of the phenomenon, namely, that gases undergo liquefaction when absorbed by liquids and such colloid

substances as India rubber, and that their transmission through liquid and colloid septa is then effected by the agency of liquid and not gaseous diffusion. Indeed, the complete suspension of the gaseous function during the transit through colloid membrane cannot be kept too much in view" (Graham, 1866).

The penetration of rubber was strongly influenced by temperature, and apparently in two different ways at the same time. An increase in temperature rendered all gases less easily liquefied by pressure, and, consequently, less considerably absorbable by any liquid or colloid. Such an influence of heat appeared to be counteracted in rubber by the tendency of that colloid to become softer when heated, and to acquire more of liquid and less of solid properties. With the softening of rubber by heat, its retentive power for gases appeared to be modified. Soft rubber, charged with carbon dioxide at 20°C and then made rigid by cold, appeared to lose its carbon dioxide when it was afterwards freely exposed to air, less rapidly than the same rubber equally charged but exposed from the first in its soft condition (Graham, 1866).

Diffusion of liquids

Graham's early study of the spontaneous movement of gases, so as to mix with one another, led him to investigate the similar phenomenon in liquids. His results appeared in two papers communicated to the Royal Society in 1850 and 1861 (Graham, 1850a, 1861a). In the opening statements of his first paper he wrote: "Any substance in solution is diffused uniformly through the mass of the solvent by a spontaneous process. It has often been asked whether this process is of the nature of the diffusion of gases...there is no satisfactory answer to the question owing to the subject having been studied in the operation of endosmosis where...diffusion is complicated by the imbibing power of the membrane, which is peculiar for each soluble substance, but...not connected with the diffusibility of the substance in water...Hence...it was not the diffusion of the salt but rather the diffusion of the solution, which was generally regarded. A diffusibility like that of gases, if it exists in liquids, should afford means of separation and decomposition even of unequally diffusible substances..." (Graham, 1850a, 1861a).

Graham's first explorative experiments were conducted on the liquid diffusion of carbon dioxide, for which there was ample experimental data on his diffusion as a gas. For this purpose two glass bottles were carefully connected through their necks; the lower bottle contained an aqueous solution of CO₂ and the upper one pure distilled water. It was expected that after some time both bottles would have the same concentration of carbon dioxide. The results were different: after two days the upper bottle was found to contain only one eleventh of amount present in the lower one (1:11). After five days, the ratio was still 1:5, proving that liquid diffusion was a slow process compared with gaseous diffusion (Graham, 1850a, 1861a).

Other series of experiments were conducted to determine how far the diffusion of various salts was governed or modified by the density of their solutions. For this purpose Graham prepared solutions of many hydrated acids and salts (e.g. NaCl, HNO₃, H₂SO₄, KCl, KHSO₄, NaNO₃, MgSO₄, CuSO₄, sugar, glucose, Arabic gum, and albumen), and put them in an open, wide-mouthed vial placed in a jar of pure distilled water. In course of time part of the dissolved substance (the *diffusate*) passed gradually from the vial into the external water (these experiments he called vial-diffusion experiments). Additional experiments looked into the influence of the concentration of the salt on the amount of diffusion and the influence of temperature. The results indicated that the amounts of diffusate yielded by different substances varied greatly. For example, under the same conditions of concentration and temperature, NaCl yielded twice as large a diffusate as MgSO₄ and the latter twice as large a diffusate as Arabic gum. Every substance examined in this way was found to have its own rate of diffusibility in the same liquid medium, the rate varying with the nature of the medium whether water or alcohol, for instance. Temperature resulted in a clear increase in the diffusion. Graham believed that liquid diffusion was analogous with evaporation; and as the squares of the times of equal diffusion of gases are in the ratio of their densities, so by analogy could be inferred that the molecules of the several salts, as they existed in solution, possessed densities which were to one another as the squares of the times of equal diffusion (Graham, 1850a, 1861a).

The most remarkable results were that the diffusion of albumen was extremely low; out of proportion when compared with saline bodies, and that its presence did not impair the diffusion of salts dissolved together in the same solution although the liquid retained its viscosity.

Additional experiments were conducted with aqueous solutions of mixed salts, which did not combine. As expected, the salts diffused separately and independently of each other, a result that suggested the possibility of their partial separation, analogous to the process of separating unequally volatile substances by distillation. The experimental results allowed Graham to provide a possible explanation of the discordance in the analysis of the waters of the Dead Sea, made by several prominent chemists (Wisniak, 2002). It was known that evaporation caused the lake level to fall 3.0 to 3.6 meters every year. In the rainy season this loss was replenished by rainwater, which flowed over a fluid of nearly 1.2 in density, without greatly disturbing it. The two-layer system resulted in salts rising from the below into the superior stratum by diffusion, bringing up the alkaline salts faster than the earth ones and the chlorides more rapidly than the sulfates. The process caused a change in the composition of the water near the surface as the process advanced.

Experiments done with potassium bisulfate and potash alum (a double sulfate) proved that these salts decomposed when diffusing, the first one yielding potassium sulfate and the second, alumina and potassium sulfate. The same

decomposition phenomenon was observed during the diffusion of double salts, such as the double sulfate of magnesium and potassium.

According to Graham his results showed that that the rate of diffusion was approximately proportional to the concentration of the original solution; it increased with rise in temperature, and was almost constant for groups of chemically similar salts at equal absolute (not molecular) concentrations and different with different groups. He believed that liquid diffusion was similar to gaseous diffusion and vaporization with dilute solutions, but with concentrated solutions he noted a departure from the ideal relationship, similar to that in gases approaching liquefaction under pressure. Diffusion was a property of fundamental character, upon which other properties depended, like the volatility of substances. The fact that the relations in diffusion of different substances involved equal weights of those substances and not their molecular weights or equivalents, was one that reached to the very basis of molecular chemistry. In liquid diffusion we did not deal with chemical equivalents, but with masses even more simply related to each other in weight (Graham, 1850a, 1861a).

According to Graham, a simple and easily applicable mode of carrying on a diffusive separation was to place the mixed substances under a column of water, contained in a cylindrical glass jar 13 or 15 cm deep. The spontaneous diffusion, which immediately commenced, was allowed to go on for several days, after which it was interrupted by siphoning off the water from the surface in successive strata, from the top to the bottom of the column. The unequal diffusion of the substances was equivalent to a distillation process; the most rapidly diffusive substance becoming more and more concentrated as it ascended. The degree of separation was improved by using a higher water column and enough time given to enable the most diffusive substance to appear at the top. A marked effect was obtained even when the difference in diffusibility was not considerable, for example, the method allowed the separation of KCl from NaCl, for which the relative diffusibility are as 1 to 0.841 (Graham, 1861a).

The range in the degree of diffusive mobility exhibited by different substances appeared to be as wide as the scale of vapor pressures. Thus the diffusive velocity of potassium hydroxide was double that of potassium sulfate, and potassium sulfate diffused at double the velocity of sugar, alcohol, and magnesium sulfate. Graham indicated "that the above-mentioned substances belong, as regards diffusion, to the more volatile class". The comparatively "fixed" class, as regards to diffusion, was represented by a different order of chemical substances, marked out by the absence of the power to crystallize, which diffused very slowly. Among the latter were hydrated silicic acid, hydrated alumina, and other metallic peroxides of the aluminum class, when they exist in the soluble form; together with starch, dextrin and the gums, caramel, tannin, albumen, gelatin, vegetable and

animal extractive matter. The latter group of substances not only possessed a very low diffusivity; they could also be distinguished by the gelatinous character of their hydrates. Although often largely soluble in water, they were held in solution by a most feeble force. They appeared singularly inert in the capacity of acids and bases and in all the ordinary chemical relations. But on the other hand, their peculiar physical aggregation with the chemical indifference referred to, appeared to be required in substances that can intervene in the organic processes of life. The plastic elements of the animal body were found in this class. As gelatin appeared to be its type, Graham proposed to name substances of this class *colloids* and to speak of their peculiar form of aggregation as the *colloidal condition of matter*. Opposed to the colloidal was the crystalline condition; Substances affecting the latter form were classed as *crystalloids* (Graham, 1861a).

Graham continued as follows: "Although chemically inert in the ordinary sense, colloids possess compensating activity of their own arising out of their physical properties. While the rigidity of the crystalline structure shuts out external impressions, the softness of the gelatinous colloid partakes of fluidity and enables the colloid to become a medium for liquid diffusion, like water itself. The same penetrability appears to take the form of cementation in such colloids as can exist at a high temperature. Hence the wide sensitivity of colloids to external agents. Another and eminently characteristic quality of colloids is their mutability. Their existence is a continued metastasis. A colloid may be compared in this respect to water while existing liquid at a temperature under its usual freezing point, or to a supersaturated saline solution. Fluid colloids appear to have always a *pectous* (curdled) modification, and they often pass under the slightest influences from the first into the second condition. The solution of hydrated silicic acid, for instance, is easily obtained in a state of purity, but it cannot be preserved. It may remain fluid for days or weeks in a sealed tube, but is sure to gelatinize and become insoluble at last. Nor does the change of this colloid appear to stop at that point. For the mineral forms of silicic acid, deposited from water, such as flint, are often found to have passed during the geological ages of their existence, from the vitreous or colloidal into the crystalline condition. This colloidal is, in fact, a dynamical state of matter, the crystalloidal being the statical condition. The colloid possesses ENERGIA (Graham uses capital letters to emphasize this critical property). It may be looked upon as the probable primary source of the force appearing in the phenomenon of vitality. To the gradual manner in which colloidal changes take place (for they always demand time as an element) may the characteristic protraction of chemical-organic changes also be referred to" (Graham, 1861a).

Graham now described how colloids could be used to effect separations: "A certain property of colloid substances comes into play most opportunely in assisting diffusive

separations. The starch jelly, that of animal mucus, of pectin...and other solid colloidal hydrates, all of which are strictly speaking, insoluble in cold water, are themselves *permeable* when in mass, as water is, by the more highly diffusive class of substances. But such jellies greatly resist the passage of the less diffusive substances and cut off entirely other colloid substances like themselves that may be in solution. They resemble animal membrane in this respect. The most suitable of all substances for the dialytic septum appears to be the commercial paper known as vegetable parchment or parchment paper...having no power to act as a filter. It is mechanically impenetrable and denies a passage to the mixed fluid as a whole (bulk flow). Molecules only permeate this medium and not masses...The hydrated compound itself is solid and also insoluble. Sugar, however, with all other crystalloids, can separate water, molecule after molecule, from an hydrated colloid such as starch. The sugar thus obtains the liquid medium required for diffusion and makes its way through the gelatinous medium. Gum, on the other hand, possessing as a colloid an affinity for water of the most feeble description, is unable to separate the liquid from the gelatinous starch, and so fails to open the door for its own passage outwards by diffusion...It may perhaps be allowed to me to apply the convenient term *dialysis* to the method of separation by diffusion through a septum of gelatinous matter” (Graham, 1861a).

This part of the paper ends with a description of the equipment Graham designed (which he called a hoop dialyzer) to separate substances with the aid of parchment paper.

The following section described the so-called jar-diffusion experiments (in opposition to the vial-diffusion experiments described above): The salt was allowed to rise from below into a cylindrical column of water and after some time, layers at different heights were analyzed in order to determine the proportion of salt that had diffused. The water was contained in a cylindrical glass jar, 152 mm high and 87 mm diameter. Initially, $7/10^{\text{th}}$ of the water were first placed in the jar and then $1/10^{\text{th}}$ of a liter of the liquid to be diffused was introduced very carefully at the bottom. After a prescribed time, the top liquid was drained and analyzed.

A particular advantage of the new method was that it allowed determining the absolute rate or velocity of diffusion, as cm/s. According to Graham the value thus determined must enter into all the chronic phenomena of physiology and held a place in vital science not unlike the time of the falling stones in the physics of gravitation. A table gave the velocity of diffusion, at temperatures between 10° to 13.5°C , in 10% wt. aqueous solutions of magnesium sulfate, albumen, caramel, sodium chloride, gum, and tannin, as well as the times required for equal diffusion of the same substances. Experiments were also performed using ethanol instead of water as the solvent, and on the simultaneous diffusion of two substances in the same fluid. The latter confirmed the general observations reported previously (Graham, 1861a).

In other experiments, the medium was changed from water to a gelatinous or colloid mass (dialysis). Graham found that diffusion of a crystalloid appeared to proceed through a firm jelly with little or not abatement of velocity. Numerous experiments were made on the diffusion of crystalloids through various dialytic septa such as gelatinous starch, coagulated albumen, gum tragacanth, animal mucus, and parchment paper; all of them proved how little the diffusive process was affected by the intervention of colloid matter. Salts appeared to preserve their usual relative diffusibility unchanged. The same partial separation was observed as in the water jar (Graham, 1861a).

A following section was devoted to the preparation of colloid substances by dialysis. In Graham's words: “The purification of many colloid substances may be effected with great advantage with...[a]...dialyzer. Accompanying crystalloids are eliminated and the colloid is left behind in a state of purity. The purification of soluble colloids can rarely be effected by any other known means, and dialysis is evidently the appropriate mode of preparing such substances”. He went on to describe in great detail the preparation and properties of numerous inorganic colloids such as soluble silicic acid, soluble alumina (a mordant), soluble ferric oxide, cupric ferrocyanide, Prussian blue, the sucrares of ferric oxide, calcium; stannic acid, ferric oxide, copper tartrate, etc.; and organic colloids such as tannin, gum Arabic, dextrin, caramel, and egg albumen. The dialyzer could be used very effectively to purify many colored substances. Accompanying crystalloids were eliminated and the colloid left behind in a state of purity. The purification of soluble colloids, rarely possible by other known means, was shown to feasible by means of dialysis (Graham, 1861a).

Graham also described the use of dialysis for separating arsenious acid and strychnine from organic liquids and biological media such as milk and blood. Before ending his paper he discussed the radical differences, which exists between colloids and crystalloids in their intimate molecular constitution. He believed that the distinction between these kinds of matter was the one subsisting between the material of a mineral and the material of an organized mass.

The paper ended with a discussion of osmosis, a subject closely connected with colloidal septa (Graham, 1861a).

Graham concluded his paper with the following statements: “It now appears...that the water movement in osmosis is an affair of hydration and of dehydration in the substance of the membrane, or other colloidal 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 as it affects the state of hydration of the septum...Placed in pure water, such colloids (as animal membrane) are hydrated to a higher degree than they are in neutral saline solutions. Hence the equilibrium of hydration is different on the two sides of the membrane of an osmometer. The outer surface of the membrane being in contact with pure water, tends to hydrate itself in a higher degree than

the inner surface does, the latter surface being supposed to be in contact with a saline solution. When the full hydration of the outer surface extends through the thickness of the membrane and reaches the inner surface, it there receives a check. The degree of hydration is lowered, and the water must be given up by the inner layer of the membrane, and it forms the osmoses...Far from promoting this separation this water, the diffusion of the salt throughout the substance of the membrane appears to impede osmoses by equalizing the condition as to saline matter of the membrane through its whole thickness. The advantage which colloidal solutions have in inducing osmoses, appears to depend in part upon the low diffusibility of such solutions, and their want of power to penetrate the colloidal septum" (Graham, 1861a).

Closely associated with the passage of different liquids through membranes was the action known as *endosmosis*, discovered by René Joachim Henri Dutrochet (1776-1847) (Durochet, 1827). Graham's principal results on this subject were recorded in a very detailed paper (Graham, 1854).

As summarized by Odling (Odling, 1871), in the course of his experiments Graham examined the osmotic movement produced with liquids of most diverse character, employing osmometers of animal membrane, albuminated calico, and baked earthenware. In one of his experiments he found that with 1% solutions in a membrane *osmometer*, the liquid rose in the stem 2 mm in the case of common salt, 20 mm with calcium chloride, 88 mm with nickel chloride, 121 mm with mercury chloride, 289 mm with tin protochloride, 351 mm with copper chloride, and 540 mm with aluminum chloride. Graham results disproved Dutrochet's claims that the velocity of the osmotic flow was proportional to the quantity of salt or other substance originally contained in the solution; and that the flow depended on capillarity. Eventually he was led to the conclusion that osmosis was essentially dependent on a chemical action, which took place between one or the other of the separated liquids and the material of the septum (Odling, 1871).

An additional work of Graham on the diffusion of liquids was the extension of the concept of transpiration to the flow of liquids under pressure in a capillary tube (Graham, 1861b). The starting point of this research was Poiseuille's finding that diluted ethanol had a point of maximum retardation, which coincided with the degree of dilution at which the greatest condensation of the mixed liquids took place (lower boiling point azeotrope). At this point, the composition was one equivalent of alcohol and six equivalents of water (Graham, 1861b). The rate of transpiration appeared to depend upon chemical composition and to afford an indication of it. A new physical property may thus become available for the determination of the chemical constitution of substances. After finding that that methanol exhibited the same remarkable feature in its transpiration, Graham extended his experiments to other liquids such as nitric acid, sulfuric acid, acetic acid, hydrogen chloride, methanol, ethanol, amyl alcohol, ethyl formiate, acetate, butyrate, and

valerate, acetone, and glycerin. He used an apparatus very similar to the one employed by Poiseuille to measure the transpiration of equal volumes of aqueous solutions of increasing dilution (Poiseuille, 1840), and found that the property would decrease until when the composition corresponded to particular hydrates, for which the transpiration time would rise to a maximum value. For example, at 20°C, for highly concentrated nitric acid the time of passage through a capillary 28 mm long and 0.0942 mm bore was found to be 344.5 seconds, slightly less than that of water (348 seconds). Addition of water resulted in a decrease of the transpiration of an equal volumes of liquid; the transpiration time reached a maximum (732 seconds) when the composition corresponded to the well-known hydrate $\text{NHO}_6 + 3\text{HO}$, having a specific gravity of 1.4. Further dilution caused the acid to flow more freely until the transpiration time approached again that of water. Hence, it appeared that a certain hydrate of nitric acid is marked out by its low transpirability so distinctly that nitric acid could be identified by that physical property (Graham, 1861b).

It was clear then that there was a relation between the transpirability of liquid and their composition. Judging from the limited number of observations he performed, Graham hypothesized that the order or succession in any homologous series would be indicated by their degree of transpirability, the same as it was by their comparative volatility. For hydrated substances transpiration also afforded a manifestation of definite composition (Graham, 1861b). In this paper Graham reported the change in the transpiration rates of water in the range 0° to 70°C. The transpiration velocity of water was found to increase uniformly from 0.559 at 0° to 1.000 at 20° and thence to 2.350 at 70°C, while the transpiration times decreased in the same proportion.

In a supplementary paper (Graham, 1864), Graham analyzed in detail the properties of silicic acid and other analogous colloidal substances. Hydrated silicic acid, when in the soluble state, is a liquid body miscible with water in all proportions. The liquidity of the acid is only influenced by a permanent change (coagulation or pectization) by which the acid is converted into a gelatinous form and loses its miscibility with water. According to Graham, dilution weakened the colloidal character of substances and probably increased their crystallizing tendency. The ultimate pectization of silicic acid was preceded by a gradual thickening of the liquid, which manifested itself in a slow flow through a capillary tube so that a liquid transpiration tube could be employed as a colloidoscope. A liquid compound of alcohol and silicic acid is obtainable by adding ethanol to aqueous silicic acid and then using an appropriate procedure for removing the water, for example a dialyzing bag of parchment paper. Graham named the alcoholic solution and the jelly of silicic acid *alcosol* and *alcogel*, respectively. The alcosol of silicic acid, containing 1% of the acid, was found to be a colorless liquid, not precipitated by salts and water. It could be boiled or evaporated without change but became gelatinous

by a slight concentration. The alcogel was a slightly opalescent solid substance, which decomposed gradually when placed in water. Graham also described the preparation and properties of the glycerin and sulfuric acid compounds of silicic acid, and of the liquid stannic, metastannic, titanic, tungstic and molybdic acids (Graham, 1864).

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