

# I

## ABSORPTION SPECTRA AND CHEMICAL CONSTITUTION <sup>1</sup>

**T**HE first systematic observations of absorption spectra of organic compounds were made by Hartley and Huntington in 1879, and many substances were investigated by them.<sup>2</sup> The method of experiment consisted in photographing the spectrum of the light from the electric spark discharge between electrodes of an alloy of tin, lead, cadmium, and bismuth by means of a quartz spectrograph, a known thickness of a solution of the substance under investigation being placed in front of the slit. The spectrum of this alloy contains a considerable number of lines, and consequently it is an easy matter to detect absorption and measure its limits by comparing the photographs with one taken without the interposition of the absorption cell. The observations are necessarily restricted to the region of the spectrum which affects a photographic plate, and in Hartley and Huntington's investigations extended from the wave-length 5000 Angstroms to the wave-length 2200 Angstroms. The solvents used were water and methyl and ethyl alcohols, since it was found that these substances are diactinic to as far as 2200 Angstroms.

In an actual experiment a known thickness of a solution of a known concentration is used, and in this way a record

<sup>1</sup> A course of three lectures delivered by Professor E. C. C. Baly, C.B.E., M.Sc., F.R.S., of the University of Liverpool, in the Physics Amphitheatre of the Rice Institute, October 23, 24, and 25, 1924.

<sup>2</sup> Phil. Trans., 170, 257 (1879).

is obtained of the absorption exerted by a definite molecular concentration of the substance under investigation. The molecular concentration is then reduced by decreasing either the thickness or the concentration of the solution, and a second photograph is taken. This procedure is followed until no measurable evidence of absorption is obtained. The wave-lengths or frequencies of the limits of absorption are measured on each photograph and plotted against the molecular concentration of the substance under investigation, and the absorption curve is thus obtained.

This method is essentially similar to that used at the present time, but the qualitative measurements of the limits of absorption has given place to an accurate quantitative determination of the absorptive power. By common consent the absorptive power is expressed in terms of the Bunsen and Roscoe extinction coefficient,  $e = \log \frac{I_0}{I}$ , where  $I_0$  and  $I$  are the intensities of the light before and after passing through the absorbing layer. Moreover, by the use of the modern panchromatic plates the limits of absorption have been extended to about 8000 Angstroms, and, also, it has been found possible with specially sensitive plates to reach as far as 1850 Angstroms in the ultra-violet. The latter is the extreme limit possible with a quartz spectrograph working in air, and for work on the absorption of light of smaller wave-length it will be necessary to use a vacuum grating spectrograph; but, up to the present time, no investigations of the absorption spectra of organic compounds have been made with this instrument.

The original investigations of Hartley and Huntington were continued over a long period by Hartley who published many papers on this subject. Following the usual custom of considering that molecules are characterised by

definite frequencies of vibration he gave the name of molecular vibration curves to his absorption spectra curves, and he noted that these seemed to be of two types and

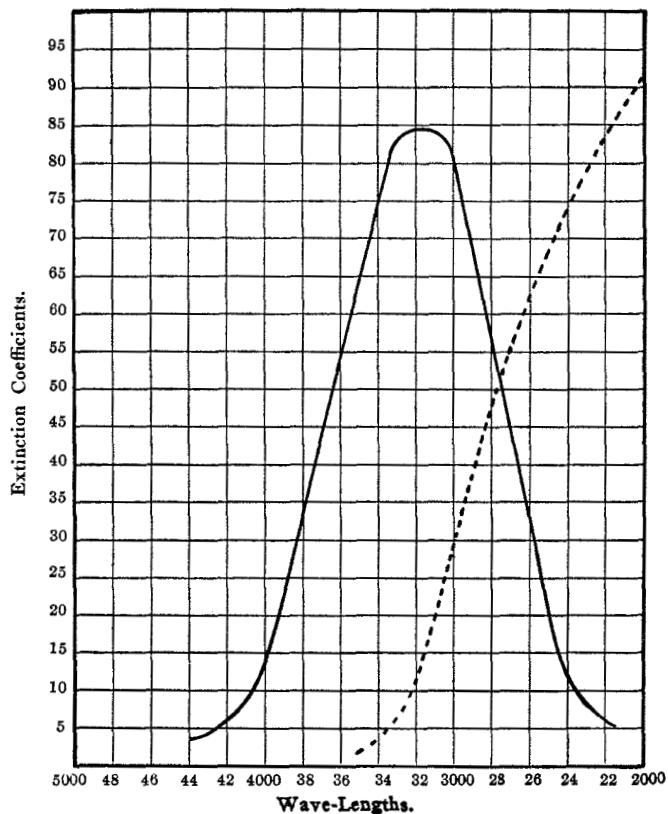


FIG. I.

that the absorption was either selective or general. In Fig. I the full curve A shows selective absorption with a well marked absorption band, as it is called, whilst the dotted curve B shows only general absorption; that is to

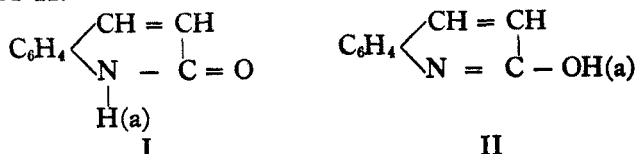
say, an absorptive power which steadily increases towards the shorter wave-lengths. Hartley considered that organic compounds could be broadly divided into two classes, according to whether they exhibit general or selective absorption; and, as far as his own experience went, the phenomenon of selective absorption was restricted to the aromatic series of organic compounds, even though some of these exhibited only general absorption.

After all his experience of this phenomenon characteristic of organic compounds, Hartley did not draw any far-reaching conclusions, nor did he formulate any definite theories as to the explanation of the phenomena. He noted certain analogies between the absorption spectra curves exhibited by various compounds; but he foresaw the danger of drawing too many conclusions from these analogies, since many compounds of entirely different character show very similar absorptive powers. He recorded, however, one or two conclusions of a simple character which he was able to draw from his observations. Of these one only need be mentioned here, namely, that in general the replacement of a hydrogen atom by the methyl or ethyl group makes very little difference in the absorption spectrum. For instance, he found that the absorption spectra of benzoic acid and methyl benzoate are identical, the replacement of the acid hydrogen atom of the acid by the methyl group having no effect on the absorptive power. He recognised that this was in the nature of a generalisation and that there are one or two exceptions, though these came to be better recognised as the experimental technique was improved.

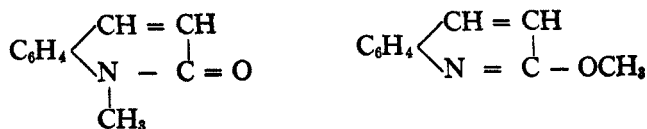
It was not long before Hartley saw the possibility of applying this generalisation to the determination of the constitution of a compound the methyl derivative of which possesses a known constitution. He foresaw the necessity

of caution in this new advance, and, indeed, the cases dealt with by him are very few in number.

The first instance of the application of this method was carbostyryl, which may have either of the two formulæ, I and II.

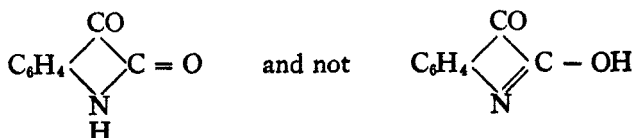


This substance gives in certain cases reactions which favour the first formula, and in other cases reactions which favour the second formula; one cannot decide from its chemical behaviour whether the hydrogen atom (a) is linked to the nitrogen atom or to the oxygen atom. The methyl derivatives of both substances are known and they can easily be proved to have the formulæ



Hartley and Dobbie examined the absorption spectra of the three substances and found that the absorption curve of carbostyryl agrees with that of methylpseudocarbostyryl and not with that of the methylcarbostyryl.<sup>1</sup> They concluded, therefore, that carbostyryl has the ketonic structure shown in formula I.

In exactly the same way they concluded that isatin has the structure

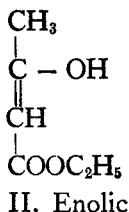
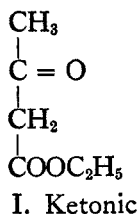


<sup>1</sup> Trans. Chem. Soc., 75, 640 (1899).

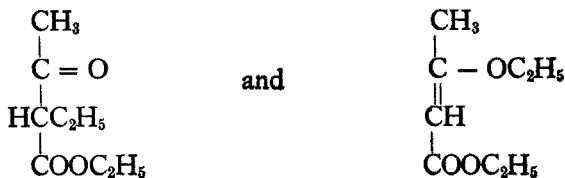
Hartley, Dobbie, and Paliatseas<sup>1</sup> examined the absorption spectra of *ortho*-oxycarbanil and by comparing it with the absorption spectra of the two alkyl derivatives concluded that it has the formula



A few years later attempts were made to apply this method to the settlement of the vexed question as to the constitution of ethyl acetoacetate by comparison of its absorption spectrum with those of its two ethyl derivatives, ethyl ethylacetoacetate, and ethyl  $\beta$ -ethoxycrotonate. It was then found that the problem is by no means as simple as had been previously supposed. Ethyl acetoacetate may exist in either of the forms I and II.



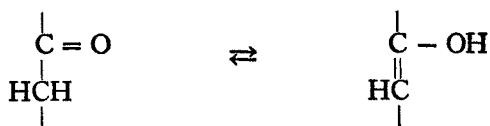
and it was not possible from the chemical evidence to decide in which of these two formulæ it exists. Since the two isomeric ethyl derivatives are known to have the formulæ



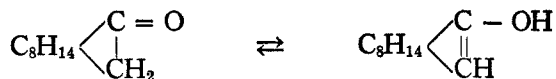
<sup>1</sup> Trans. Chem. Soc., 77, 839 (1900).

there seemed to be an admirable opportunity of applying Hartley's method of absorption spectra to decide the question of the constitution of the parent compound.

It was found, however, when the absorption spectra were examined, that the free ester and its metallic derivatives exhibit different absorptive powers from those of either of the two ethyl derivatives, the former showing selective absorption and the latter only general absorption.<sup>1</sup> This is a remarkable exception to Hartley's generalisation as to the substitution of a hydrogen atom by an alkyl group and justifies the conclusion that there is a marked difference in the free ester and its metallic derivatives compared with its two isomeric alkyl derivatives. The suggestion was put forward that the explanation of this difference might be found in the fact that the two alkyl derivatives possess fixed structures, whilst the free ester and its metallic derivatives might exist as equilibrium mixtures of the two desmotropic forms. On this view the selective absorption characteristic of the latter was attributed to the oscillating linkings involved in the equilibrium

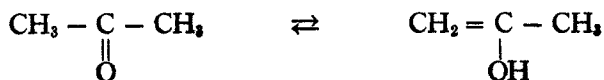


This explanation appeared also to satisfy the selective absorption exhibited by other compounds possessing a labile or potentially labile hydrogen atom, such for instance as camphor in which the equilibrium was postulated

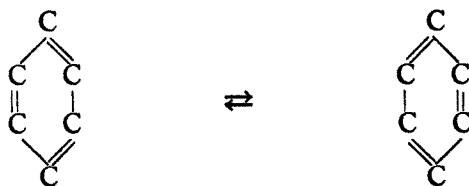


and acetone

<sup>1</sup> Baly and Desch, *Trans. Chem. Soc.*, 85, 1039 (1904).



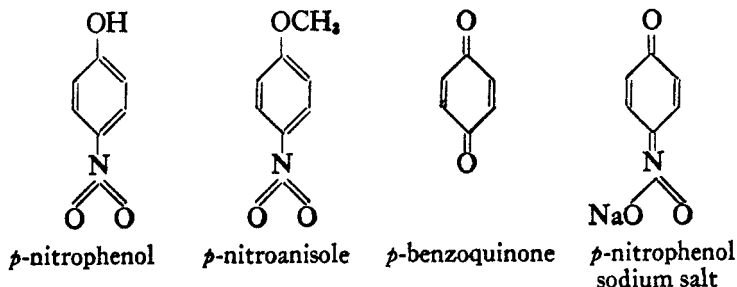
This theory had the further advantage in that it was able to explain the selective absorption exhibited by so many of the aromatic compounds, the oscillation being of the type expressed by the equilibrium between the two extremes of the Kekule formula



It may be noted in passing that this was the first attempt to find a physical explanation of the phenomenon of selective absorption.

It is not difficult to understand how it appeared possible to apply this theory of the origin of selective absorption to the determination of the constitution of certain aromatic compounds, such as the nitrophenols and their metallic derivatives. For some years previously the quinonoid theory of visible colour had been gaining ground, and on this theory the colour of the alkali metal salts of the nitrophenols was explained by their having the quinonoid structure. For instance *p*-nitrophenol and its ether, *p*-nitroanisole, are colourless substances, whereas the sodium salt is yellow and not very different in colour from *p*-benzoquinone. According to the quinonoid theory these substances possess the following formulæ





Similarly, a quinonoid structure was given to the nitroanilines since the colour of these is very similar to that of the corresponding nitrophenol sodium salts.

On the theory of the origin of selective absorption mentioned above, it seemed possible to settle the question of the constitution of the alkali metal salts of the nitrophenols, since it is to be expected that the oscillating linkings in the truly benzenoid nitrophenol would be different from those in the quinonoid structure. Absorption spectra observations showed that the nitrophenols exhibited absorption bands which differed materially from those given by their sodium salts, and, further, that the absorption spectra of the nitroanilines are very similar to those of the corresponding nitrophenol sodium salts.<sup>1</sup> This was accepted as evidence in favour of the quinonoid structure of the sodium salts of the nitrophenols and of the nitroanilines, and the argument was very materially strengthened when Hantzsch and Gorke described the preparation of unstable and highly coloured modifications of some nitroanisoles to which they gave the quinonoid structure.<sup>2</sup>

<sup>1</sup> Baly, Stewart, and Edwards, *Trans. Chem. Soc.*, 89, 514 (1906).

<sup>2</sup> *Ber.*, 39, 1073 (1906).

Further work was carried out on the three hydroxypyridines,<sup>1</sup> dimethylpyrone and some of its derivatives,<sup>2</sup> the hydroxyazo compounds,<sup>3</sup> the whole tending to confirm the view that there exists a definite correlation between chemical constitution and absorption spectra in the visible and ultra-violet regions, whatever might eventually prove to be the true physical explanation of selective absorption.

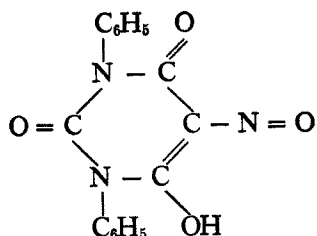
This theory was adopted by Hantzsch for reasons of a somewhat different kind, and a great wealth of material was added to the literature by him and his co-workers. Hantzsch developed the theory more rigidly by definitely connoting one absorption band and one structure. It is not possible to describe this work and the conclusions drawn, but one example may be quoted, namely, diphenylvioluric acid and its alkali metal salts.<sup>4</sup> The free acid dissolves in chloroform to form a colourless solution which exhibits an absorption band in the ultra-violet with central wave number of about 3740. The lithium salt, which is red, shows two bands with central wave numbers of about 1975 and 3210, whilst the blue caesium salt shows two bands with central wave numbers of about 1690 and 3210. Owing to the fact that the aliphatic nitroso compounds are blue in colour, and that there is a slight resemblance in shape between their absorption curves and that of the blue caesium salt, Hantzsch concludes that the constitution of the blue salts of diphenylvioluric acid is to be represented by the formula

<sup>1</sup> Baker and Baly, *Trans. Chem. Soc.*, *91*, 1122 (1907).

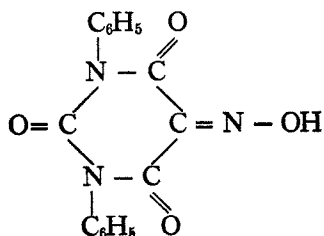
<sup>2</sup> Baly, Collie, and Watson, *ibid.*, *95*, 144 (1909).

<sup>3</sup> Tuck, *ibid.*, *91*, 449 (1907), *95*, 1809 (1909).

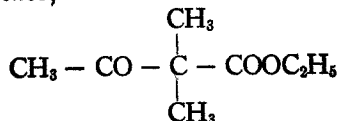
<sup>4</sup> Hantzsch and Robison, *Ber.*, *43*, 45 (1910).



that of the free acid being

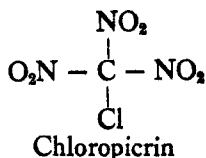
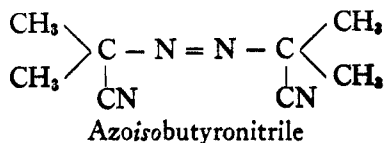
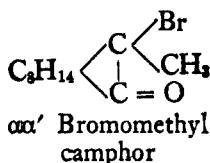


In the meantime results were being obtained in England which threw considerable doubt on the fundamental conceptions underlying the theory of correlation between chemical constitution and absorption spectra in the visible and ultra-violet regions. In the first place we have the theory, already mentioned, that an absorption band is due to an oscillation between two different linkings, a theory which is based on the observations made of the absorption spectra of ethyl acetoacetate and its derivatives. This theory received a severe blow when it was found that ethyl dimethylacetoacetate,



in which there is no labile hydrogen atom, exhibits a well marked absorption band in alcoholic solution in the presence of sodium ethoxide. Equally cogent criticism of this theory is found in the fact that many other compounds,

which contain no labile or potentially labile hydrogen atom, exhibit strong selective absorption. Amongst these compounds may be mentioned



It is obvious, therefore, that the oscillating linking theory must be abandoned.

Then again, the quinonoid explanation of the change in absorption when the nitrophenols are converted into their alkali metal salts, and the quinonoid explanation of the absorption spectra of the nitroanilines could not be made to agree with the following observations:—

1. The absorption spectra of the nitroanilines are very similar to those of the corresponding nitrodimethylanilines, which are known to be benzenoid and not quinonoid.

2. The nitrophenols and their ethers in concentrated sulphuric acid solution exhibit colours which are very similar to those of the corresponding alkali metal salts, but the absorption spectra of the acid and alkaline solutions are materially different.

The second observation is very antagonistic to Hantzsch's theory that each absorption band denotes the presence of one definite structure. *Ortho*-nitrophenol exhibits two absorption bands in each of the three solvents alcohol, alcoholic sodium ethoxide, and concentrated sulphuric acid, and each of the six bands is at a different wave-length. It

is not possible to conceive that there can exist six different structures for one simple nitrophenol. Indeed, Hantzsch in one of his later papers remarks that he has found in certain cases more absorption bands than can be accounted for, that is to say some compounds exhibit more bands than the number of different structures which can be devised.

Perhaps the most damaging criticism of the Hantzsch theory is to be found in the fact that several compounds, for instance pyridine, piperidine, benzaldehyde, exhibit different absorption bands in the vapour and liquid phases. This is one of the most remarkable facts yet recorded, and it obviously is in strong opposition to the Hantzsch view, since it is not possible to believe that a substance, monomolecular in the liquid state, changes its structure when vapourised. Indeed, it is not too much to say that it is in direct opposition to any theory which connotes the primary structure of a compound with its absorption in the ultra-violet or visible regions.

A very important observation was made by Coblenz during his measurements of the absorption spectra of organic compounds in the infra-red region of the spectrum.<sup>1</sup> He noted that certain atomic groups such as  $\text{CH}_3$ ,  $\text{C}_6\text{H}_5$ ,  $\text{NH}_2$ ,  $\text{OH}$ ,  $\text{CNS}$ , give rise to definite absorption bands in the short-wave infra-red, and that these bands are quite independent of the rest of the molecule containing the group. The importance of this fact will be discussed in the next lecture, but it may be pointed out that this observation establishes a connection between groups of atoms independently of any question of structure. Thus, aniline and ammonia both show the characteristic absorption bands of the  $\text{NH}_2$  group, and water, the aliphatic alcohols, and phenol all show the bands characteristic of the  $\text{OH}$  group.

<sup>1</sup> Pub. Carnegie Inst. Washington, No. 35 (1905).

It is not out of place here to draw attention to the remarkable arbitrariness of the structure-absorption correlation theory in that it attempts to establish such correlation from observations made in the visible and ultra-violet regions, which are such a minute fraction of the whole spectrum. It is now known that the frequencies characteristic of material substances extend over a very great range which in wave-lengths reaches from 30,000,000 Angstroms to 1 Angstrom, whereas the visible and ultra-violet regions extend from 8000 Angstroms to 2000 Angstroms, which is 1/5000th of the whole. It is inconceivable that any physical theory can be sound which is based on observations made in so minute a fraction of the whole range of frequencies known to be characteristic of all substances.

Sufficient has been said to indicate that many substances can exhibit different absorption bands under different conditions of temperature and solvent. To this it may be added that many substances exhibit two and even three absorption bands under the same conditions. In order to obtain as much information as possible about the various frequencies characteristic of compounds, numerous observations were made of the absorption spectra of a few substances, and attempts were made to correlate the various frequencies in each case. As will be seen from the full curve in Fig. I on page 3, the absorption band has a measurable breadth, but there is one frequency, known as the central frequency, for which the absorptive power is a maximum. It was found that, if the central frequencies characteristic of a given compound are considered, there exist constant differences between them. It seems necessary to conclude from this relationship between the characteristic frequencies that the different absorption bands must have their origin in different physical states of one and the

same molecule and not in different structural modifications. Indeed, we were driven to the conclusion that the accumulated evidence is definitely opposed to the structure-absorption correlation theory as far as the visible and ultra-violet regions are concerned, and so the theory was finally abandoned in spite of its attractiveness.

At this stage in the development of the subject there was no theory to take the place of the discarded theory, nor was there any explanation to hand of the origin of the absorption bands themselves. The first evidence which appeared to lead to a possible solution of the problem was obtained by a study of the absorption spectra of certain aminoaldehydes and aminoketones of the aromatic series and their hydrochlorides.<sup>1</sup> These compounds in alcoholic solution exhibit a well-marked absorption band in the ultra-violet, whilst the hydrochlorides obtained by the addition of excess of hydrochloric acid exhibit an absorption band with its centre shifted towards the shorter wave-lengths. If, however, an alcoholic solution of hydrogen chloride be slowly added to the alcoholic solution of the base, a visible colour is developed which reaches a maximum when from 0.1 to 0.2 equivalent of the acid has been added. This colour disappears when one equivalent of acid is present. The visible colour is due to the presence of a new absorption band situated on the red side of the band characteristic of the free base.

It is obvious from these results that the free base is not converted directly into the salt on the addition of the acid, but that it is first changed into an intermediate phase which is stable in the presence of small quantities of acid and is converted into the salt when the amount of acid present is increased. In the case of these particular compounds it

<sup>1</sup> Baly and Marsden, *Trans. Chem. Soc.*, 93, 2108 (1908).

was not found possible to obtain the whole of the base in the intermediate phase, since the absorption spectrum revealed the presence either of the free base or the hydrochloride along with the intermediate phase. In the case of the sulphonation of certain phenotic compounds the same phenomenon was observed, and here it was found possible to convert the whole of the parent phenol into the intermediate phase by solution in concentrated sulphuric acid.<sup>1</sup> In the cold this solution of the intermediate phase is quite stable, but on gently warming the intermediate phase passes into the sulphonic acid.

The question at once arises as to the nature of the intermediate phase, for we must determine whether it is a new substance, structurally different from, but isomeric with, the parent compound, or whether it is the same molecule in a different physical state. Of these two alternatives there is no doubt that the latter statement is nearer the truth, as indeed the previous evidence has tended to establish. Fortunately the question was answered when the fluorescence of the parent compounds was examined. Many of the parent compounds dealt with in the last two communications cited, exhibit this phenomenon, that is to say, when they are illuminated with those light rays which they absorb, they emit rays of a longer wave-length. It is perfectly possible to observe the fluorescence spectrum of these parent compounds, and the striking fact was noted that in every case the fluorescence spectrum of the parent substance is the same as the absorption spectrum of the intermediate phase. Obviously, therefore, the same frequencies are characteristic of the two, parent compound and intermediate phase, since the former emits and the latter absorbs the same rays. There can be no doubt, therefore,

<sup>1</sup> Baly and Rice, *Trans. Chem. Soc.*, 101, 1475 (1912).



that we must be dealing with the same molecule in the structural sense, the physical properties of which differ in the two states.

The establishment of the intimate connection between two phases of a given molecule, a connection which has been confirmed in a great number of instances, together with the constant difference between the central frequencies which are characteristic of all the phases of a given molecule, gives almost overwhelming support to the view provisionally put forward above, namely, that under different conditions of temperature and solvent a molecule can exist in different phases, the difference between them being of a physical nature and not chemical in the structural sense. To this may be added that each phase is characterised by its specific set of vibration frequencies which, in absorption spectra observations, are recognised as an absorption band.

Some evidence has also been adduced that the chemical reactivity of two phases is different since it has already been shown in the case of the amino-aldehydes that the free aldehyde does not give a salt with acid whilst the intermediate phase does. This difference in reactivity between the different phases of a given molecule is evidenced still more strongly by the phenols in the sulphonation reaction already mentioned. Let us consider, for example, the case of quinol dimethyl ether which reacts with sulphuric acid to give the sulphonic acid according to the equation



The ether in alcoholic solution exhibits one absorption band with a central frequency of  $1.035 \times 10^{15}$  and if sulphuric acid be added to this solution no sulphonation will take place even though the molecular concentration of the acid be five times that of the ether. If, however, the ether be

dissolved in concentrated sulphuric acid, the solution exhibits two absorption bands with central frequencies of  $6.69 \times 10^{14}$  and  $1.0875 \times 10^{15}$  respectively. The ether, therefore, must now exist in a condition different from that obtaining in alcoholic solution, and in this condition sulphonation readily takes place since the reaction commences immediately the solution is warmed. Clearly, therefore, the reactivity of quinol dimethyl ether in the two solvents is different.

Another example of the difference in reactivity shown when the absorption spectra are different may be quoted, namely, benzaldehyde. This compound in alcoholic solution and concentrated sulphuric acid solution shows different absorption spectra. In alcoholic solution it is readily oxidised by atmospheric oxygen and is not sulphonated even when five times the molecular concentration of sulphuric acid is added. In concentrated sulphuric acid solution the aldehyde is not oxidised by atmospheric oxygen, but it readily undergoes sulphonation.

Instances of the change in reactivity associated with change in absorption spectra might be multiplied, but two examples are sufficient to establish the truth of this fact. We are justified, therefore, in concluding that under different conditions of temperature and solvent any given molecule may exist in one of a number of phases, each phase being characterised by its own characteristic frequency in the visible or ultra-violet region of the spectrum, and by its own reactivity. Further, the differences between the various frequencies characteristic of a molecule can be expressed as integral multiples of a constant difference.

Up to the present we have not discussed the question of the energy relations which must have a fundamental bearing on the problem, since the very fact that a substance

exhibits an absorption band at a definite frequency shows that it is capable of absorbing radiant energy of that frequency. The enunciation by Planck of the energy quantum theory enables us to consider the energy problems of absorption spectra and the relations between the various molecular phases in a quantitative way. There can be no doubt that when molecules are absorbing light their energy content is increased, at any rate temporarily, and, further, that if no chemical or physical change is permanently established thereby, the whole of the absorbed energy is again radiated to the surroundings. According to the energy quantum theory the absorption or emission of energy by a molecule is not a continuous process, but consists in the taking up or giving out of definite and fixed amounts of energy, these definite quantities being called energy quanta. If a molecule possesses a characteristic frequency  $\nu$ , then, when it absorbs or emits energy at that frequency, the process consists in the absorption or radiation of a single quantum at a time, this quantum being  $h\nu$  erg where  $h$  is a constant and has the value of  $6.56 \times 10^{-27}$ .

This conception can be applied in a very simple manner to the absorption of energy by a molecule under conditions when no permanent physical or chemical change is established and when its energy content is not permanently altered. Under these conditions it is obvious that the whole of the energy absorbed must be radiated to the surroundings. It is possible of course that the energy could be radiated at the same frequency as the absorbing frequency, a phenomenon known as optical resonance, but this is very uncommon. By far the more usual case is the radiation of the energy in the infra-red region, and it was commonly believed that the energy was frittered away, as it were, in the form of heat. It would seem, however, on the

energy quantum theory that this very unsatisfactory notion is untenable and that the radiation must take place in quanta at infra-red frequencies characteristic of the molecule. In order to guard against any possible misconception, it may be stated that every single substance possesses characteristic frequencies in the infra-red to as far as the limit of the spectrum previously stated to lie at about the wave-length of  $3000\mu$  or  $30,000,000$  Angstroms.

Let us consider the case of a single molecule with a characteristic frequency  $\nu_1$  in the ultra-violet and let this molecule absorb one quantum  $h\nu_1$  erg. Under the prescribed conditions of no permanent physical or chemical change in the molecule this increment of energy will be radiated to the surroundings at smaller frequency in the infra-red characteristic of the molecule. The process will consist of the radiation of quanta at that infra-red frequency, and, since no energy can be destroyed, the total energy increment will be radiated as a whole number of these quanta. If the radiating frequency be  $\nu_x$  then obviously we equate  $xh\nu_x = h\nu_1$ , where  $x$  is a positive integer. Dividing both sides by  $h$  we have  $x\nu_x = \nu_1$  and, therefore, the absorbing frequency must be an integral multiple of the radiating frequency.

As has already been demonstrated, a substance may exhibit several absorption bands, depending on the phase in which the molecules exist. The above relation must hold for every such absorption band, the central frequencies being integral multiples of an infra-red frequency characteristic of the molecules. The simplest possible condition would be that all the frequencies characteristic of the molecule in the visible and ultra-violet are integral multiples of the same infra-red frequency characteristic of the molecule. If that were so, we should have  $\nu_1 = a\nu_x$ ,  $\nu_2 = b\nu_x$ ,  $\nu_3 = c\nu_x$ ,

$\nu_4 = d\nu_x$ , etc., where  $\nu_1, \nu_2, \nu_3, \nu_4$ , etc., are the visible and ultra-violet frequencies,  $\nu_x$  is the fundamental infra-red frequency, and  $a, b, c, d$ , etc., are positive integers. It further follows that the frequency differences between the various visible and ultra-violet bands can be expressed in terms of a constant difference  $\nu_x$ .

Now, it has already been shown that this relation does actually exist between the central frequencies of the various phases of a given molecule, and the question arises as to whether the central frequencies themselves are integral multiples of the constant difference. That this is actually the case has been conclusively proved in a great number of instances. As an instance of this the two absorption bands of pyridine may be quoted,<sup>1</sup> the true central frequencies of which are  $1.0761 \times 10^{15}$  and  $1.1739 \times 10^{15}$  respectively. The difference between these two values is  $978 \times 10^{13}$ , and  $11 \times 9.78 \times 10^{13} = 1.0758 \times 10^{15}$  and  $12 \times 9.78 \times 10^{13} = 1.1736 \times 10^{15}$ , the differences between the calculated and observed frequencies being too small to be observed. If this relation has a sound physical basis the fundamental frequency in the infra-red will be capable of measurement by absorption spectra methods. The infra-red absorption spectra of pyridine vapour has not been observed, but liquid pyridine exhibits an absorption band at the frequency  $4.8 \times 10^{13}$ , which is very nearly half of  $9.78 \times 10^{13}$ .<sup>2</sup> This shows that the two absorbing frequencies in the ultra-violet should be expressed as  $22 \times 4.89 \times 10^{13}$  and  $24 \times 4.89 \times 10^{13}$ , respectively. The case of pyridine is quoted, since, although only two absorption bands are known, the complete relation is proved by the independent observation of the fundamental band

<sup>1</sup> Baly and Tryhorn, *Trans. Chem. Soc.*, 107, 1121 (1915).

<sup>2</sup> Coblenz, *loc. cit.*

in the infra-red. Many cases are known in which the central frequencies of the several absorption bands shown by one substance are integral multiples of the constant frequency difference between them, no direct measurement of the infra-red absorption having been made. One such instance may be given, namely, isatin, the three absorption bands of which have central frequencies as follows

$\lambda$	Frequency	Difference	Factors
2490	$1234.57 \times 10^{12}$	$217.62 \times 10^{12}$ which divided by 3 = $72.54 \times 10^{12}$ .	$1234.57 \times 10^{12} = 17 \times 72.62 \times 10^{12}$
2950	$1016.95 \times 10^{12}$	$290.56 \times 10^{12}$ which divided by 4 = $72.64 \times 10^{12}$ .	$1016.95 \times 10^{12} = 14 \times 72.64 \times 10^{12}$
4130	$726.39 \times 10^{12}$		$726.39 \times 10^{12} = 10 \times 72.64 \times 10^{12}$

It may be stated with some confidence that the existence of the above integral relationships and their direct connection with a single fundamental frequency in the infra-red establishes the reality of the various phases of a molecule which differ in physical properties and in reactivity. The question may well be asked as to what is the essential difference between the various phases. There seems little doubt that this difference is one of energy content, since it is possible to change a molecule from one phase into another, and indeed into a phase with smaller characteristic frequency by the supply of energy. This is shown clearly enough by the fact that when many substances are converted into vapour they undergo a change of phase which can be observed with the spectroscope, the new phase invariably being one with a smaller frequency. Then again substances are converted into phases with smaller frequency on exposure to light, but the new phase generally exists for too short a time for it to be recognised with the spectroscope. It is possible in some cases to introduce a second substance which increases the stability of the new phase and this phase can then be detected by its absorption spectrum. A typical case of this is trinitrobenzene which forms

a colourless solution in alcohol containing a trace of piperidine. On exposure to ultra-violet light the solution turns red owing to the development of a new absorption band in the blue region of the spectrum, and if this coloured solution is allowed to remain in the dark the colour vanishes and the trinitrobenzene reverts to its original phase.

An interesting extension of the integral relations discussed above may be deduced from the fact that the various phases of a given molecule differ in energy content and that the smaller the characteristic frequency of a phase, the larger is its energy content. The general case was dealt with of the absorption of a single quantum of energy by a molecule at a frequency in the visible or ultra-violet, and the radiation of this increment of energy as a whole number of quanta at the fundamental infra-red frequency of the molecule. This does not always take place, for at times the phenomenon of fluorescence is observed when some of the energy is radiated, not in the infra-red, but at a frequency characteristic of a phase of higher energy content and with smaller frequency than the initial phase of the molecule. Let a molecule absorb one quantum  $h\nu_1$  and emit as fluorescence light at a smaller frequency  $\nu_2$  which is characteristic of another phase. The emitted light will consist of one quantum  $h\nu_2$  and the difference  $h\nu_1 - h\nu_2$  will obviously be emitted as quanta at the fundamental infra-red frequency  $\nu_x$ . Since we know that  $h\nu_1 = xh\nu_x$  and  $h\nu_2 = yh\nu_x$ , where  $x$  and  $y$  are positive integers, it follows that the difference in energy content of the two phases will be  $h\nu_1 - h\nu_2 = (x - y)h\nu_x$ . We thus arrive at the very interesting result that the difference in energy content of any two phases is equal to a whole number of quanta at the fundamental infra-red frequency of the molecule and that the difference between any two consecutive phases is one

fundamental infra-red quantum. This deduction is of considerable importance since we now have for the first time a quantitative definition of the various phases of a molecule. Every molecule exists in one of a number of possible energy levels or phases, the difference in energy content of any two consecutive phases being one energy quantum measured at the fundamental frequency of the molecule in the infra-red.

It can be understood from the foregoing that the phenomenon of fluorescence and the kindred phenomenon of phosphorescence are intimately connected with absorption spectra, but their physical significance does not seem to be generally understood. In the first place it is often stated that the two phenomena are identical in nature, the only difference being that phosphorescence persists for a measurable time after the source of exciting energy is removed, whilst fluorescence ceases instantly. This statement, however, does not seem to be true if the two terms are restricted, as they usually are, to radiation in the visible or ultra-violet regions of the spectrum. When molecules absorb energy at the frequency characteristic of the phase in which they exist, they may be converted into another phase of higher energy content. The increment of energy thereby gained is 1, 2, 3, or 4, etc., quanta at the molecular frequency, depending on which phase the molecule passes into. The difference between the quantum of energy absorbed and the increment of energy retained is radiated during the process. It is obvious that this difference is exactly equal to one quantum of energy at the frequency of the new phase, and this excess energy can be radiated either as one quantum at the frequency of the new phase, or as a whole number of quanta at the fundamental infra-red frequency. In the former case we have the phenomenon of fluorescence,



wherein the excess of the energy quantum absorbed, over and above the increment of energy retained by the molecule in its phase change, is radiated at the frequency of the new phase. The reverse process, during which the newly formed phase returns to the original phase, is accompanied by the evolution of the difference in energy content between the two phases as a few quanta at the fundamental frequency.

The phenomenon of phosphorescence is different in that the new phase has a measurable life period, very often lasting for protracted periods of time; and, further, the evolution of the phosphorescence is associated with the return of the new phase to the original phase, which is in fact the exact converse of fluorescence. In phosphorescence, just as in fluorescence, the energy is radiated at the characteristic frequency of the new phase, and a little consideration will show that there is a limit to the phase changes in which the phenomenon can be observed. Once again, let a molecule absorb one quantum  $h\nu_1$  at its phase frequency, and let it thereby be converted into a new phase with frequency  $\nu_2$ , the increment of energy retained by the molecule being as before  $h\nu_1 - h\nu_2$ . When the new phase reverts at a later date to the original phase, this energy increment is radiated as one or more quanta at the frequency characteristic of the new phase. We have, therefore,  $h\nu_1 - h\nu_2 = xh\nu_2$  and  $h\nu_2 = \frac{h\nu_1}{x+1}$ , where  $x = 1, 2, 3, 4$ , etc.

It follows, from this, that the phenomenon of phosphorescence can only be observed when the frequency of the new phase is a sub-multiple of the frequency of the original phase.

The phenomena of phosphorescence and fluorescence have been discussed because it is possible by their means

to obtain valuable information as to the phase frequencies of molecules.

We may now sum up the information we have gained of the molecular phases.

1. A molecule exists in one of a number of possible phases.
2. Each phase is characterised by its own chemical reactivity and by its power of absorbing or radiating energy of definite frequency in the visible or ultra-violet region of the spectrum, this frequency being an integral multiple of a fundamental frequency characteristic of the molecule in the infra-red.
3. Each phase is characterised by its energy content, the difference in energy content between any two consecutive phases being one energy quantum measured at the fundamental infra-red frequency.

When a large number of molecules of a given compound are considered, it by no means can be assumed that they all must exist in one phase, and, indeed, the most usual condition is an equilibrium mixture between two or more phases. Many substances exhibit two, or even three, absorption bands in the visible or ultra-violet regions, and, in general, when only one band is shown in these regions there is definite proof that one or more bands exist in the extreme ultra-violet region, lying beyond the limit of the quartz spectrograph working in air. The proof of the existence of these bands with large frequencies is found in the well-known dispersion formulæ, which are based on the characteristic frequencies of the molecules.<sup>1</sup> This cannot be discussed now, but attention may be drawn in passing to the misleading nature of the statement that a substance only

<sup>1</sup> Baly, *Astrophys. Journ.*, *47*, 28 (1915); Baly and Morton, *J. Phys. Chem.* *28*, 659 (1924).

exhibits general absorption. All this statement means is that the characteristic frequencies of the phases in which the molecules exist do not happen to lie in the visible or ultra-violet, but are in the extreme ultra-violet region.

The application of this theory to the problem of the interpretation of absorption spectra observations is quite straightforward. It is very obvious, in the first place, that the accumulated evidence may be accepted as having entirely disposed of the theory that there is any correlation between absorption bands and chemical constitution; and, in the second place, that the theory of the bands being due to oscillating linkings is also disproved. This evidence supports the view that a compound in the free state exists as an equilibrium mixture of two or more molecular phases, this equilibrium being dependent on the temperature of the system. This equilibrium is modified by the presence of a second substance, the amount of change depending mainly on the nature of that substance. Absorption spectra measurements give us a means of determining the phases which are present in the equilibrium in so far as the frequencies of the phases lie in the region of the spectrum observed, for it must not be forgotten that, very possibly, there are present phases, the frequencies of which lie in the extreme ultra-violet. It is not improbable that the relative intensities or absorptive powers measured at the characteristic frequencies are proportional to the relative number of molecules existing in those phases, although there is at present no absolute proof that this is true. It is possible that the dye-stuffs, which exhibit unusually high absorptive powers at their characteristic frequencies, exist very largely in that one phase. If so, this would give an explanation of their great colouring powers.

Of the instances already mentioned as having been used

in support of the structure-absorption correlation theory, two may be discussed in the light of the phase hypothesis—namely, the nitrophenols, and diphenylvioluric acid and its salts. In neutral alcoholic solution the nitrophenols exist as an equilibrium of two or more phases, and in alkaline solution a new equilibrium is established containing different phases; and, since one of these has a characteristic frequency in the visible region, the solution is visibly coloured. A third equilibrium exists when the nitrophenols are dissolved in concentrated sulphuric acid; and, again, one of the component phases has its frequency in the visible region, with the result that the solution is visibly coloured.

We may digress for a moment in order to discuss the application of the phase hypothesis to the existence of two modifications of the same compound. Many instances of this phenomenon are known in organic chemistry, and generally one modification is more stable than the other and has a higher melting point. According to the phase hypothesis, a pure compound, under a given condition of temperature, will exist as a definite equilibrium mixture of certain phases. There is no reason, however, why another equilibrium mixture might not exist in a metastable condition when solid compounds are considered. This metastable equilibrium mixture must be one of higher energy content, and would easily pass into the normal state with evolution of the excess energy. Since less energy will be required to convert the metastable solid equilibrium into the equilibrium characteristic of the liquid compound, the melting point of the unstable modification will be lower than that of the stable compound.

The existence of these metastable phase equilibria among inorganic compounds is well recognised, although, perhaps, the close connection between the phenomena in the two

fields of chemistry has not previously been emphasised. Many inorganic compounds on exposure to radiant energy, such as ultra-violet light or X-rays, exhibit the phenomenon of phosphorescence, that is to say, they acquire the power of emitting radiant energy which persists for a long time after the exciting cause has been removed. In some cases the energy increment is retained by the substance for an indefinitely long period, the phosphorescence not being developed until the substance is heated (thermoluminescence) or crushed (triboluminescence). This phenomenon finds a ready explanation in the phase theory, since the absorption of the energy establishes a metastable equilibrium between the phases present, which reverts to the normal equilibrium with the evolution of the excess energy, sometimes spontaneously whilst at other times an external stimulus must be applied to initiate the escape of this energy.

In general it may be stated, if it be desired to prepare an unstable phase equilibrium and if the method of supplying radiant energy to the system is not possible, that the best method will be to prepare the substance under conditions which favour a phase equilibrium of higher energy content than the normal. For example, absorption spectra show that in its salts a nitrophenol exists in a phase equilibrium of higher energy content than the normal. When the ethers are prepared from these salts they must, at the moment of formation, exist in the equilibrium of higher energy content. If every precaution is taken to guard against change in this equilibrium, the nitrophenol ether will be obtained in an unstable form with an absorption spectra and colour similar to those of the original salt. It would seem highly probable, therefore, that the so-called *aci*-nitrophenols ethers of Hantzsch and Gorke<sup>1</sup> are not

<sup>1</sup> Loc. cit.

structural isomers of the normal ethers, but the normal ethers existing in a metastable phase equilibrium. The experimental conditions of their preparation are such as to favour the stability of the equilibrium with higher energy content, namely, the action of the alkyl halide at low temperatures on the carefully dried silver salt suspended in a non-aqueous solvent. Hantzsch and Gorke were unable to prove the quinonoid structure for these compounds, but based the formulæ on their colour, instability, and on the fact that they are monomolecular "isomers" of the normal ethers.

As previously pointed out, these compounds have been adduced as strong evidence in favour of the structure-absorption theory, but the phase hypothesis offers a different explanation and correlates them with similar metastable phase equilibria amongst both inorganic and organic compounds.

The various absorption bands exhibited by the alkali metal salts of diphenylvioluric acid, and interpreted by Hantzsch as evidence of different structural isomers, are very simply explained by the phase theory. The phase equilibria characteristic of this acid in its salts depend on the electropositivity of the metal. The greater the electropositivity, the higher the energy content of the equilibrium which is present, and the absorption bands exhibited by the various salts indicate the phases in which the acid exists in those salts.

In discussing the difference between the melting points of the stable and unstable modifications of a compound, I referred to the phase equilibrium characteristic of the compound in the liquid state. In view of the numerous cases known in which a vapour exhibits a different absorption band from the liquid, it is quite obvious that, at any rate

in these cases, there is a marked difference between the phase equilibria characteristic of the vapour and liquid states of the same compound. The latent heat of evaporation at the boiling point must, therefore, be a measure of the difference in energy content of the phase equilibria characteristic of the vapour and liquid at the boiling point. It has already been proved that the difference in energy content of any two consecutive phases of one molecule is exactly one quantum measured at the fundamental molecular frequency of that molecule, a quantum which may be called a molecular quantum. It follows, therefore, that the latent heat of evaporation must be a whole number of these molecular quanta. It might even be possible that, in some cases, the change from liquid to vapour at the boiling point be associated with the absorption of a whole number of molecular quanta by every molecule.

Now the size of the molecular quantum may be calculated from the frequency of the principal absorption band in the infra-red, and it is remarkable how accurately the molecular latent heat of vaporisation can be calculated in the case of some substances, the infra-red spectra of which have been measured. Whilst it cannot be claimed that in every case the molecular latent heat of vapourisation is the same whole number of quanta for every molecule, the agreement shown in the table on the following page is too close to be entirely fortuitous.<sup>1</sup>

In the cases of carbon tetrachloride and sulphur it may be noted that the infra-red measurements are not so trustworthy as those of the other compounds.<sup>2</sup>

Before concluding this discussion of absorption spectra and their interpretation, I must refer to Hartley's work

<sup>1</sup> Baly, *Phil. Mag.*, 40, 30 (1920).

<sup>2</sup> Coblenz, *Pub. Carnegie Inst., Washington*, No. 35 (1905).

## HEAT OF VAPORISATION

	Observed molecular latent heat	Latent heat in ergs per molecule	Principal band in infra-red	Infra-red frequency	Quantum at infra-red frequency in ergs per molecule	Number of quanta	Calculated molecular latent heat
Carbon disulphide . . . .	6384	$4.332 \times 10^{13}$	4.6 $\mu$	$6.522 \times 10^{13}$	$4.278 \times 10^{13}$	1	6305
Water . . . . .	9650	$6.548 \times 10^{13}$	6.115 $\mu$	$4.906 \times 10^{13}$	$3.218 \times 10^{13}$	2	9485
Ammonia . . . . .	4950	$3.359 \times 10^{13}$	12.04 $\mu$	$2.500 \times 10^{13}$	$1.64 \times 10^{13}$	2	4834
Acetic acid . . . . .	5094	$3.458 \times 10^{13}$	11.5 $\mu$	$2.609 \times 10^{13}$	$1.711 \times 10^{13}$	2	5044
Methyl acetate . . . . .	8166	$5.541 \times 10^{13}$	7.1 $\mu$	$4.225 \times 10^{13}$	$2.772 \times 10^{13}$	2	8170
Ether . . . . .	6660	$4.519 \times 10^{13}$	8.75 $\mu$	$3.429 \times 10^{13}$	$2.249 \times 10^{13}$	2	6629
Chloroform . . . . .	6984	$4.739 \times 10^{13}$	8.3 $\mu$	$3.614 \times 10^{13}$	$2.371 \times 10^{13}$	2	6988
Carbon tetrachloride . .	7190	$4.879 \times 10^{13}$	12.9 $\mu$	$2.326 \times 10^{13}$	$1.526 \times 10^{13}$	3	6744
Sulphur . . . . .	23160	$1.572 \times 10^{13}$	11.8 $\mu$	$2.547 \times 10^{13}$	$1.671 \times 10^{13}$	9	22158



on the determination of the constitution of isatin, carbostyryl, and *o*-oxycarbanil by comparison of their absorption spectra with those of their methyl ethers, for it might be considered that the theory now brought forward negatives the value of Hartley's evidence. This conclusion, however, by no means follows as a matter of course. If the two standards of reference show differences in absorption, a similarity between the absorption exerted by the parent compound and the absorption of one of the standards may be assumed to prove that the constitution of the two is similar. On the other hand, the availability of this method is very restricted, because observations made since Hartley's time have shown that phase changes sometimes take place on alkylation, which render the simple comparison of absorption spectra useless as a means of comparing two structures. A typical case, in which absorption spectra comparisons are useless, has already been mentioned, namely, ethyl acetoacetate and its alkyl derivatives. It is obvious that the parent ester must be ketonic, enolic, or a mixture of the two, yet its absorption spectrum differs from those of both of its alkyl derivatives and any mixture of the two. The reason for this difference is that the phase equilibria present in the free ester and its metallic derivatives are different from those characteristic of the alkyl derivatives, with the result that the simple comparison of their absorption spectra gives no immediate assistance to the chemist.

In conclusion I must emphasise the fact that, although the phase hypothesis offers an interpretation of absorption spectra and rests on a quantitative energy basis, there still remain to be filled many lacunæ in this theory. We do not know why a molecular phase is characterised by a frequency and by a specific reactivity. We do not know the origin

of the phases themselves, nor why the phases present so often vary with the solvent. The answers to these questions cannot be found from a study of absorption spectra alone. I believe, however, that they have been found from a consideration of the phenomena of chemical reaction and reactivity, but all discussion of this must be deferred until my next lecture.