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THE RADIATION THEORY OF THERMAL REACTIONS.

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1. An Expression for the Velocity of a Unimolecular Process.

The main justification for regarding radiation as the origin and cause of physical and chemical change—photochemical, so-called, when the temperature of the radiation is greater than that of the material on which it acts, thermal, when the temperatures of the radiation and the matter are identical—lies in the fact that no other idea presents itself of sufficient generality to account for spontaneous or unimolecular processes, as well as multimolecular processes. Whatever criticisms therefore may be urged of attempts to apply the concept to thermal reactions must concern themselves with the mode of application, and not with the concept itself.

More than a year ago, one of the present writers pointed out¹ that the observed velocity constant of unimolecular or spontaneous dissociation of a gas was greatly at variance with the value calculated on the basis of Planck's expression for the rate of absorption of energy by an oscillator, (there identified with the electron), such absorption being regarded as continuous (*i. e.*, Planck's second formulation of the Quantum Hypothesis). An even greater discrepancy appeared to exist when an attempt was made to account for the observed velocity constant on the basis of discontinuous absorption of actual discrete quanta of energy (*i. e.* Einstein's view, which has much in common with Planck's first formulation of the Quantum Hypothesis). The discrepancy referred to is always in the sense that the observed velocity constant is many times, of the order 10^7 , greater than that calculated on the basis of continuous absorption. It appears to be of the same order of magnitude for different unimolecular reactions, and to be independent of temperature.

It would at first sight seem that such a discrepancy between theory and experiment would necessitate the discarding of the fundamental assumptions underlying the mechanism of chemical action as embodied in the radiation hypothesis. An attempt is here made, however, to demonstrate that such drastic action need not be resorted to, and that the disagreement between observation and theory may be eliminated by suitable modification of the formulas underlying the latter.

Considering the process of absorption to be continuous, Planck has shown that the rate of absorption of energy of frequency ν by an oscil-

¹ W. C. M. Lewis, *Phil. Mag.* [VI] 39, 26 (1920).

lator (electron) is given by

$$\frac{\pi \cdot e^2}{3m} \cdot u_\nu \quad (1)$$

where e and m are the charge and mass of an electron and

$$u_\nu = \frac{8\pi h n^3 \nu^3}{c^3} \cdot \epsilon \frac{1}{h\nu/kT} - 1 \quad (2)$$

where h is Planck's constant, n is the refractive index of the system, c is the velocity of light *in vacuo*, k is the gas constant per molecule, and T is the absolute temperature. Equation 2 becomes

$$u_\nu = \frac{8 \pi h n^3 \nu^3}{c^3} \cdot \epsilon^{-h\nu/kT}$$

since all frequencies responsible for chemical change are great enough to make $\epsilon^{-h\nu/kT}$ much larger than unity.

If we now consider a gaseous system, containing N molecules, and suppose that one valence electron per molecule is involved in the dissociation process, it is evident that the total amount of energy absorbed per second is

$$\frac{8 \pi^2 e^2 h n^3 \nu^3}{3 m c^3} \cdot \epsilon^{-h\nu/kT} N.$$

If one quantum of energy $h\nu$ is required by the valence electron for the decomposition of a molecule, it follows that the number decomposed per second is

$$\frac{8 \pi^2 e^2 n^3 \nu^2}{3 m c^3} \cdot \epsilon^{-h\nu/kT} N.$$

and hence the velocity constant of the unimolecular process is given by

$$k_{\text{uni}} = \frac{8 \pi^2 e^2 n^3 \nu^2}{3 m c^3} \cdot \epsilon^{-h\nu/kT}$$

$$i. e., \quad k_{\text{uni}} = 2.465 \times 10^{-22} \cdot n^3 \nu^2 \epsilon^{-h\nu/kT} \quad (3)$$

This is the theoretical expression which one of the present writers¹ has applied to various unimolecular reactions, n being taken as unity for gaseous systems, and ν being given by the critical increment of the unimolecular process concerned. In the case of phosphine, the observed velocity constant was shown to be 10^7 times the calculated value.² For other dissociations, such as those of hydrogen, chlorine, bromine, and

¹ Lewis, *loc. cit.*

² In the above treatment the critical increment required by the molecule for its decomposition has been identified with one quantum of frequency ν . It is possible that this should be replaced by more than one quantum of radiation of lower frequency. As a specific case let us consider a unimolecular chemical action produced by absorption of five quanta $h\nu_1$, per molecule, where $5h\nu_1 = h\nu$. For a stationary state the number of molecules containing four quanta is given by;

$$N_4 = N(1 - \epsilon^{-h\nu_1/kT}) \epsilon^{-4h\nu_1/kT} = N \cdot \epsilon^{-4h\nu_1/kT}.$$

without appreciable error, N being the total number of molecules present. The mech-

iodine, indirect results only are available since the velocity of the dissociations have not been directly observed for these gases. The velocity can however be indirectly obtained from the known equilibrium constant and the velocity of the reverse reaction, calculated according to the collision expression given by Lewis.¹ In all cases a similar discrepancy of the order 10^6 to 10^7 occurs. Recently, Daniels and Johnston's experimental results on the velocity of unimolecular decomposition for nitrogen pentoxide have become available.² These data are of interest in view of the great difference between the temperature range to which they refer and those temperatures associated with the reactions mentioned above. They have therefore been analyzed in order to determine whether the discrepancy between experiment and theory is of the same order of magnitude as before, the mean value of the critical increment $E = Nh\nu$ for the reaction is stated to be 24,700 cal. per gram molecule. On inspection of the five individual values of E quoted it is found that one is distinctly lower than the others. Omitting this one, the mean value of E is 25,130 cal. From this the characteristic frequency of the reaction is found to be 2.65×10^{14} , and therefore at the temperature of 25° the velocity constant calculated from Equation 3 is 2.85×10^{-12} sec.⁻¹ while the observed velocity constant at 25° is 3.4×10^{-5} sec.⁻¹. Comparing these figures we see that the discrepancy is again of the order 10^7 (strictly $10^7 \times 1.2$).

On reviewing Equation 3, it will be observed that the numerical value attributed to the refractive index n in the neighborhood of the characteristic frequency of the valence electron is unity. It is well known of course that somewhat higher values for the refractive index at a band in the case of gases have been obtained, *e. g.*, Wood³ has found in the case of sodium vapor that n attains the value 1.386. An alteration in the valanism may be identified with absorption of one quantum $h\nu_1$ by the molecules which already contain four quanta. Hence as before the total energy absorbed per second is

$$\frac{8\pi^2 e^2 h n^3 \nu_1^3}{3mc^3} \cdot \epsilon^{-h\nu_1/kT} N \cdot \epsilon^{-4h\nu_1/kT}.$$

The number of molecules decomposed per second is given by,

$$\frac{8\pi^2 e^2 n^3 \nu_1^3}{3mc^3} \cdot \epsilon^{-5h\nu_1/kT} N$$

and therefore $k_{uni} = \frac{8\pi^2 e^2 n^3 \nu_1^3}{3mc^3} \cdot \epsilon^{-5h\nu_1/kT}$

i. e., the velocity constant is 25 times less than that calculated on the assumption that one quantum $h\nu$ (where $\nu = 5\nu_1$) brings about the required activation. It is obvious that the assumption of several quanta in place of a single quantum does not afford an explanation of the discrepancy referred to.

¹ W. C. M. Lewis, *J. Chem. Soc.*, **103**, 471 (1918).

² Daniels and Johnston, *THIS JOURNAL*, **43**, 53 (1921).

³ R. W. Wood, *Phil. Mag.* [VI] **8**, 293 (1904).

ue of n of this order of magnitude obviously could not explain the discrepancy. In fact if the discrepancy is to be explained on any such basis, it would be necessary to give to n a value of approximately 200, and further to assume that n maintains its value throughout the course of the reaction. From the experimental standpoint such a value is inadmissible though it cannot be definitely asserted that the maximum experimental values attributed to the n of a gas are necessarily the highest values attained inside an exceedingly narrow spectral region. Apart from this difficulty, however, the assumption that n should maintain its high value during the decomposition appears to be quite erroneous on the following grounds. As the original substance decomposes the number of molecules diminishes, and, since the value of the refractive index of the gaseous system depends on the number of molecules on any theory of dispersion, the refractive index should decrease progressively as the decomposition goes on. This difficulty might be overcome by assuming that the resultants of the reaction are equally "efficient" in contributing to the value of the refractive index. A more serious objection arises, however, if we consider the reacting system under different *initial* pressures. Since pressure is a determining factor in the value of the refractive index of the system, the velocity constant would depend on the pressure. This is, of course, contrary to all experience of unimolecular processes.

The only way out of the difficulty which presents itself is to regard n as referring to the individual molecules. This is equivalent to saying that the rate of decomposition is proportional to the radiation density *inside* the molecule, and not to the average radiation density throughout the mass of the gas. To distinguish the n of the system as a whole from the quantity which we regard as defining the rate of the reaction, we shall denote the latter by n_m . Although the value of the refractive index inside the molecule (*i. e.*, n_u) may be large compared with that in the space between molecules, the net refractive index of the system is not necessarily large. Obviously if n_m is characteristic of the individual molecules, its value will not depend upon the number of molecules present, *i. e.*, upon the pressure, and will also be independent of the stage of decomposition of the system as a whole.

To realize fully the implication of a high value of the refractive index term attributed to an individual molecule, it is necessary at this point to consider certain of the equations that Lorentz has put forward to explain the observed values of the refractive index of a gaseous system as a whole. According to Lorentz, the refractive index n of a gas may be derived from an equation of the form¹

¹ Compare Campbell. "Modern Electrical Theory," 2nd edition, p 51.

$$n^2 - 1 = \frac{4\pi m (\nu_0^2 - \nu^2) N \cdot e^2}{4\pi^2 m^2 (\nu_0^2 - \nu^2)^2 + g^2 \nu^2} \dots \dots \dots (4)$$

where e and m are the mass and charge of an electron, N is the number of gas molecules present per cc., and ν_0 and ν are the characteristic frequency of the gas and the frequency of the incident light, respectively. The term "g" is the viscous coefficient introduced to take account of the fact that n does not become infinite when $\nu = \nu_0$. Writing the above equation in the form

$$n^2 - 1 = \frac{4\pi m N e^2}{4\pi^2 m^2 (\nu_0^2 - \nu^2) + \frac{g^2 \nu^2}{(\nu_0^2 - \nu^2)}}$$

we see that since the denominator on the right hand side is the sum of two terms whose product is practically a constant at the band, the maximum value of $n^2 - 1$ is obtained when

$$4\pi^2 m^2 (\nu_0^2 - \nu^2) = g^2 \frac{\nu^2}{\nu_0^2 - \nu^2}$$

$$\text{or} \quad 2\pi m (\nu_0^2 - \nu^2) = g\nu \dots \dots \dots (5)$$

Hence the maximum value of n is given by the relation:

$$n^2 - 1 = \frac{N \cdot e^2}{g\nu} \dots \dots \dots (6)$$

No satisfactory basis has as yet been discovered for the viscosity coefficient "g." Thus Lorentz himself suggests that the viscosity effect is to be sought in molecular collisions, while Planck adopts the view that g has its origin within the molecule. The same conclusion has been arrived at by Ribaud,¹ in connection with his work on the absorption exhibited by bromine. Ribaud finds that his experimental data are entirely at variance with the collision idea, in that g is found to be independent of the pressure. The special assumption given by Planck is also shown to be inapplicable, and the position at the present time is best expressed in Ribaud's own words: "The mechanism of the viscous effect is exactly the same for a liquid or a solid as for a gas, and must be sought for in the interior of the individual molecule."

In view of this conclusion regarding g it does not seem unreasonable to relate the quantity n_m (the refractive index inside the molecule) to the same viscous effect by means of an expression of the form derived above:

$$n_m^2 - 1 = n_m^2 = \frac{N' \cdot e^2}{g\nu} \dots \dots \dots (7)$$

in which the same numerical value is attributed to g as is required to account for the observed refractive index of the gas as a whole. N'

¹ Ribaud, *Ann. phys.* [IX] 12, 188 (1919).

represents the number of molecules which would be required to fill one cc. of space with closest possible packing. Obviously n_m is thus identified with the refractive index which the material as a whole would exhibit under the closest possible packing,¹ provided the mutual influence of molecules is neglected. Comparing Equations 6 and 7 we see at once that:

$$\frac{n_m^2}{n^2 - 1} = \frac{N'}{N} \dots\dots\dots (8)$$

On the basis of this equation an attempt may be made to calculate the order of magnitude of n_m . Taking by way of illustration the case of sodium vapor, Wood² has found that the maximum value of n in the neighborhood of the D line is 1.386 at 644°, but he has not given the density of the vapor corresponding to the temperature of the experiment. However, by extrapolation from the density data of Jewett,³ the density of the sodium vapor used is found to be 5×10^{-5} g. per cc. It follows that $N = 1.3 \times 10^{18}$. To obtain N' , the number of sodium atoms that would fill 1 cc., we must ascribe a value to the radius of the sodium atom. Let us assume this to be 10^{-8} cm. Then $N' = 1/\frac{4}{3}\pi r^3 = 2.39 \times 10^{23}$. Substitution in Equation 8 gives $n_m = 411$. Stress need not be laid on the absolute value of n_m which this rough calculation affords. It is evidently consonant, however, as far as order of magnitude obtains, with the large value of n_m which we assume to account for the discrepancy in the calculated velocity constant of reactions.

¹ Strictly speaking in place of $n^2 - 1$ we should write $[n^2(1 - \kappa^2) - 1]$, (compare Campbell, *loc. cit.*) in which κ is the absorption coefficient and is defined by the relation that the amplitude of the light is reduced in the ratio $e^{-2\pi\kappa}$ to 1 in traveling through one wave length. In the case of a gas even close to a band κ is necessarily very small compared with unity, and consequently can be neglected. We have likewise neglected it in the hypothetical case of close packing of the molecules. As justification for this it may be mentioned that the extinction coefficient in the case of a liquid (benzene) close to the centre of the band at 3μ approximately has been determined experimentally by Mr. H. A. Taylor in this laboratory, who finds that its value is of the order of unity. The extinction coefficient a is defined by the relation $I = I_0 \cdot e^{-ad}$ where d is in mms., and I_0 and I are the intensities of the incident and transmitted radiation. Since $I/I_0 = A^2/A_0^2$, where A_0 and A are the amplitudes of the radiation corresponding to these intensities, it follows that $a = \frac{4\pi\kappa}{\lambda}$, λ being measured in millimeters. Hence for benzene κ is in round numbers 2×10^{-4} and can be neglected compared with unity. In the liquid state the molecules although very close together compared with the gaseous, are still separated from one another by distances of the same order as their diameters. In the closely packed state, therefore, κ must still be greater than the above value, but even if increased one hundred fold, κ would still be small compared with unity.

² Wood, *loc cit.*

³ Jewett. *Phil. Mag.* [VI] 4, 551 (1902).

We have next to consider n_m in relation to temperature. This can be done by considering the variation of g with temperature. Ribaud¹ finds for bromine that the values of g at 620° and 20° are in the ratio of 1.14 to 1. This would mean that n_m varies relatively slowly with temperature, and consequently the discrepancy factor in the original comparison of calculated and observed velocity constants should remain very nearly the same for a given system over a wide range of temperature. This is in agreement with observation.

Further, Ribaud¹ has considered the continuous absorption bands of several substances, ozone, carbon dioxide, chlorine, bromine, iodine in solution, etc., and has shown as an experimental fact that the expression $\frac{\lambda_0}{\pi\delta}$ is approximately a constant number. λ_0 is the wavelength corresponding to the characteristic frequency of the substance, and δ is the width of the band as defined by Ribaud, which he regards as a measure of the value of g . The above is therefore equivalent to the statement that $g\nu$ is a constant for various substances. Now we have expressed n_m by the equation $n_m^2 = \frac{N' \cdot e^2}{g \nu}$ where N' is the number of resonators corresponding to the frequency ν , per cc. of condensed material. In the case of a monatomic vapor N' is identical with the number of atoms. In that of a diatomic gas, N' is presumably twice the number of molecules. Since the radii of different types of molecules do not differ greatly, N' will remain of the same order of magnitude for various substances, and therefore, $g\nu$ being constant, n_m is approximately the same for all substances. This is obviously in agreement with the fact that the discrepancy factor, assumed to be taken account of by n_m^3 , has been found to be the same for the various systems investigated.

The foregoing considerations serve to show that the magnitude which must be attributed to n_m , as well as its approximate constancy both in respect of temperature and in respect of change in the nature of the substance are not in disagreement with facts so far as they are known. It may be emphasized that in attributing a value of the order 200 to n_m , we are at the same time giving to the refractive index of the gas as a whole a value not greater than 1.4 close to the band.

It is of interest here to note that Lamb² has considered a mathematical development of the theory of selective absorption of light by a gas, in which the mechanism of the dissipation of energy, normally identified with the vague frictional coefficient g of Lorentz, is given an exact physical meaning by attributing a very large value to the dielectric constant of an individual molecule. For the purpose of the mathematical analysis, the molecule of course is considered as a sphere of homogeneous material.

¹ Ribaud, *loc cit.*

² Lamb, *Camb. Phil. Soc. Trans.*, 18, 348 (1899-1900).

The mechanism of selective absorption is ascribed to scattering of the incident waves by the molecule, and Lamb has shown that when the period of the incident waves is coincident, or nearly coincident, with that of a free vibration of the molecule, the scattered waves attain an abnormal intensity and the incident wave system is correspondingly weakened. Lamb himself says: "In order to comply with current numerical estimates of molecular magnitudes, it is necessary to assume that for the substance of the molecule, K [the dielectric constant] has some such value as 10^7 . This assumption may be somewhat startling; but it is not necessarily inconsistent with a very moderate value of the specific inductive capacity of a dense medium composed of such molecules, arranged in fairly close order, and it may conceivably represent in a general way the properties of a molecule, regarded as containing a cluster of positive and negative 'electrons'." Obviously, Lamb's treatment involves a very large value for n_m , even greater than that which has to be attributed to a molecule to account for chemical change.

From the point of view of the theory of dielectrics, one would expect the dielectric capacity of the molecule to be included in the factor f , where fx is the restoring force on the displaced electron. As a matter of fact, Sir J. J. Thomson has suggested that f may take the form e^2/r^3 where e is the charge on the electron and r the radius of the uniform positive sphere the existence of which was assumed in the early theory of atomic structure. In view of the fact that f is a measure of the tendency of the electron to revert to its position of equilibrium, it would seem more reasonable to identify r with the maximum amplitude of vibration of which the electron is capable in the intact molecule or atom. A value for this is obtained from the application of Hertz's expression to Wiedemann's observation¹ on the intensity of the light emitted from incandescent sodium vapor from which $r = 8 \times 10^{-10}$ cm. Further f is given by the expression $\nu^2 = f/4\pi^2m$ where m is the mass of the electron and ν the characteristic frequency. For the case of a wave length of the order $600 \mu\mu$ the frequency is 5×10^{14} and consequently $f = 9 \times 10^3$. If the dielectric capacity inside the molecule is D in place of unity, it follows on the above basis that $f = e^2/Dr^3$, whence $D = 4.6 \times 10^4$, so that n_m is approximately 214, of the order required. Incidentally if n_m is a constant, then $\nu^2 r^3$ is a constant; *i. e.*, the higher the frequency the smaller the amplitude of the vibration.

In the deduction of his expression for the radiation density, Planck undoubtedly attributes to n the average value throughout the volume of the system. It must be remembered, however, that Planck envisages a somewhat artificial case, *viz.*, a space uniformly occupied with reson-

¹ Cf. Lewis: "System of Physical Chemistry," Vol. II, 3rd Ed., p. 400

ators, acting independently of one another. No concept analogous to that of molecules as distinct from inter-molecular space is considered; *i. e.*, no molecular surfaces of abrupt discontinuity are taken into account. We believe therefore that the treatment of the problem based on close packing of the molecules so as to give a space uniform in properties reproduces Planck's conditions more or less accurately. This view at the same time meets the difficulty which naturally presents itself in attributing a physical meaning to the refractive index of a single molecule on the grounds that the diameter of a molecule is small compared with the wave length of radiation usually employed. Of course, if light passes through a medium of refractive index 200, the wave length is reduced in this proportion, and thus for light in the visible region, λ would become of the order 10^{-7} cm. (instead of 10^{-5} cm.), a quantity which is still definitely greater than molecular dimensions. The view adopted may virtually be expressed by saying that the velocity constant of a unimolecular reaction is regarded as independent of the degree of condensation of the material, and would be the same for highly compressed matter as for the gaseous state. This is not quite the same thing as saying that the velocity constant is independent of the physical state of the system, for the passage from such actual states involves latent heat terms which would necessarily affect the velocity constant. These latent heat terms, however, have their origin in intermolecular effects, which by hypothesis are absent in the condensed state envisaged above. The physical state most closely approximating to that considered here would be that exhibited by a gas under extremely great pressure above its critical temperature.

It will be observed that in the expression for the velocity of a unimolecular reaction, the effect of the radiation field is expressed by the quantity u , and not by $u_\nu d\nu$ which might perhaps have been anticipated at first sight, more especially as all continuous bands exhibit spectral width, amounting in some cases to as much as $100 \mu\mu$.¹ It is evident that the term u refers to an average effect within the band at the frequency which may be identified with the band head, or central optical frequency. From the point of view of the concept of critical energy and critical increment, the idea naturally suggests itself that the observed width of the band round the central frequency which corresponds to decomposition of the compound is a measure of the departure of the molecules from the mean or normal value of their average internal energy content. A molecule the internal energy of which is slightly below the normal value will require an amount of energy greater than $h\nu_0$, where ν_0 is the central frequency, while a molecule with internal energy somewhat

¹ Ribaud (*loc. cit.*) defines the width of a band as the difference of the wave lengths corresponding to a decrease in the absorption to half the maximum value.

greater than the average will require a correspondingly smaller amount of energy than $h\nu_0$ in order to attain the total energy content required for decomposition. Owing to the fact that the majority of the molecules possess internal energy not far removed from the normal value, the band although theoretically infinite in width will actually possess a limited finite width insofar as this can be exhibited by experiment, since observation of absorption necessarily depends on the magnitude of the effect, and this in turn on the number of molecules involved. The above view of the width of the band obviously means that the molecules composing a given material differ somewhat from one another in that the valence electrons do not possess exactly the same absolute frequency, but that the values lie more or less closely around a mean value ν_0 . Hence radiation of any frequency within the band should be capable of bringing about chemical change, a conclusion which is borne out by observation of photochemical reactions. It must be remarked, however, that although a small range of frequencies is chemically efficient, it is assumed that a given molecule will at any instant respond to one frequency alone; so that in considering the decomposition of a single molecule we are limited to the quantity u_ν , and not to the product of this into the frequency difference corresponding to the width of the band. Actually, the molecules as a whole are decomposed by a small range of frequencies, but precisely the same rate of decomposition would be brought about if every molecule were capable of responding to the mean frequency ν_0 .

Finally, it may be of interest to compare our equation for the velocity constant of a uni-molecular process, *viz.*,

$$k_{\text{uni}} = \frac{8\pi^2 \cdot e^2 \cdot n_m^3 \nu^2}{3 mc^3} \epsilon^{-h\nu/kT} \quad (9)$$

with the equation suggested by Dushman,¹ *viz.*,

$$k_{\text{uni}} = \nu \cdot \epsilon^{-h\nu/kT} \quad (10)$$

If these expressions are really equivalent, it follows that

$$8\pi^2 \cdot e^2 \cdot \nu \cdot n_m^3 = 3 mc^3$$

that is $\nu \cdot n_m^3 =$ a universal constant. The frequency term however varies with the nature of the material, and at the same time we have found it necessary to regard n_m^3 as a universal constant. It is evident, therefore, that the two expressions cannot be reconciled.

2. The Mass-action Equilibrium Constant.

In the case of a diatomic gas such as iodine, we have seen that the velocity constant of the unimolecular reaction is given by

$$k_{\text{uni}} = \frac{8\pi^2 \cdot e^2 \cdot n_m^3 \nu^2}{3mc^3} \epsilon^{-h\nu/kT} \quad (9)$$

¹ S. Dushman, *J. Franklin Inst.*, **189**, 515, (1920).

where the symbols retain the significance ascribed to them above. The velocity constant of the reverse reaction, expressed in gram molecules per liter per second is given¹ by

$$k_{bi} = 1.21 \times 10^{21} \cdot \pi \cdot \sigma_1^2 \cdot \sqrt{2u^2}$$

where σ_1 is the radius of the iodine atom, and u is the r. m. s. velocity of the atom at the temperature of the reaction. Expressing u in terms of this temperature and the atomic weight M of iodine, we obtain

$$k_{bi} = 1.21 \times 10^{21} \cdot \pi \cdot \sigma_1^2 \sqrt{\frac{6RT}{M}} \quad (11)$$

Hence the equilibrium constant is given by

$$K = \frac{k_{uni}}{k_{bi}} = \frac{8\pi \cdot e^2 n_m^3 \nu^2}{3.63 \times 10^{21} \cdot mc^3 \cdot \sigma_1^2} \cdot \sqrt{\frac{M}{6RT}} e^{-h\nu/kT}$$

or

$$\log_e K = -\frac{N_0 h \nu}{RT} - \frac{1}{2} \log_e T + \log_e \frac{8\pi e^2 n_m^3 \nu^2}{3.63 \times 10^{21} \cdot mc^3 \cdot \sigma_1^2} \sqrt{\frac{M}{6R}}$$

Assuming n_m, ν , and σ_1 independent of temperature, we may write

$$\frac{d(\log_e K)}{dT} = \frac{N_0 h \nu - \frac{1}{2} RT}{R \cdot T^2}$$

i. e. the heat effect of the reaction is $N_0 h \nu - \frac{1}{2} RT$.

For the more general type of dissociation, $A \rightarrow B + C$, where B and C are molecules requiring activation in order to produce the reverse reaction we have the analogous equation

$$\frac{d(\log_e K)}{dT} = \frac{N_0 h (\nu_A - \nu_B + \nu_C) - \frac{1}{2} RT}{R \cdot T^2}$$

the heat effect of the reaction being $N_0 h (\nu_A - \nu_B + \nu_C) - \frac{1}{2} RT$.

Reverting to the case of the dissociation of iodine, since it is more usual to express the equilibrium constant in terms of the partial pressures of reactants and resultants, we may write

$$\log_{10} K_p = -\frac{N_0 h \nu}{2.3 RT} + \frac{1}{2} \log_{10} T + \log_{10} \frac{8\pi e^2 n_m^3 \nu^2 \sqrt{RM/6}}{3.63 \times 10^{21} \cdot mc^3 \sigma_1^2} \quad (12)$$

absolute units being used.²

It may be noted that the last term in this equation is the logarithm of a pressure, so that dimensional conditions are satisfied. Moreover, this term can be split up into two expressions, the one containing the terms which vary with the nature of the system, the other being the logarithm of a universal constant. This last is analogous to, but of course differs in

¹ W. C. M. Lewis, *J. Chem. Soc.*, 113, 471 (1918).

² The factor 1.21×10^{21} has therefore been replaced by 1.21×10^{24} .

dimensions from the corresponding term (involving $k^{3/2}/h^3$) in the Sackur-Tetrode analysis¹ of the chemical constant which appears in the expression for $\log K_p$ on the basis of the Nernst heat theorem.

Bodenstein and Starck² have carried out measurements of the equilibrium constant for the dissociation of iodine, by means of which we may test the numerical accuracy of Equation 12. At a temperature of 1273° A., K_p was found to be 0.165, the pressure being expressed in atmospheres, that is K_p is 0.165×10^6 in absolute units. $N_0 h \nu$ is given equal to 35,480 cal. Considering n_m to be a constant, its most probable value has been found above, from the experimental results of Daniels and Johnston to be 1.2×10^7 . Employing these data in Equation 12, and solving for the unknown σ_1 (radius of the iodine atom), we obtain $\sigma_1 = 2.85 \times 10^{-8}$ cm. The fact that this calculated value is a reasonable estimate of the radius of an iodine atom supports the view that n_m ³ is practically a constant for all substances. Further, we may employ this value of σ_1 in Equation 12 to compute the values of K_p at different temperatures, and compare these with Bodenstein and Starck's experimental data. Thus at 1473° A., we calculate K_p to be 1.2×10^6 as compared with the experimental value 1.23×10^6 . At 1073° A., the values are respectively 1.11×10^4 and 1.14×10^4 . It is evident that the agreement is very satisfactory, and this in itself lends experimental support to the conclusion that n_m is independent of temperature.

3. Criticisms of the Radiation Hypothesis.

With the foregoing considerations in mind, it may not be out of place to deal here with certain criticisms of the radiation theory of thermal processes which have recently been put forward by I. Langmuir.³

His first principal criticism concerns the question as to whether the available energy absorbable by a gas is sufficient, on the radiation hypothesis to account for the observed reaction velocity. Langmuir approaches this from the point of view that the amount of radiation available for the reaction in 1 cc. of gas is that fraction (in the neighborhood of the characteristic frequency of the reaction) contained in the total radiation from one square centimeter of a black body at the temperature of the reaction. Applying Wien's radiation law, he shows for the specific case of phosphine gas at 948° A., that a black body at that temperature radiates so little energy in the vicinity of $392 \mu\mu$ (the wave length characteristic of the decomposition of phosphine), that the energy would only be sufficient to activate molecules of phosphine in a layer having a thickness not

¹ Sackur, *Ann. Physik.*, **40**, 67 (1913); Tetrode, *ibid.*, **38**, 434 (1912); and **39**, 255 (1912).

² Bodenstein and Starck, *Z. Elektrochem.*, **16**, 961 (1910).

³ I. Langmuir, *This Journal*, **42**, 2190 (1920).

greater than 3×10^{-11} cm., even if all the radiation were absorbed within this layer.

It seems to us that Langmuir is tacitly assuming photochemical conditions throughout. Even although he makes the temperature of the gas equal to that of the external radiation causing the reaction, he is implicitly dealing with an effect perfectly analogous to the action of radiation at a high temperature on a cold system, because he assumes that no modification is introduced as a consequence of the temperature of the gas itself. The concept of matter and radiation being at one and the same temperature means that as a result of absorption and emission among the molecules, the system as a whole maintains a certain distribution of energy among all the frequencies. If by some means a set of frequencies were removed, the system would tend to make good the deficiency at the expense of all the other frequencies. The occurrence of a chemical process in the system is equivalent to the removal of a certain small range of frequencies, the removal being made good completely, provided it is physically possible to maintain the system (*e. g.*, by means of a thermostat) at a constant temperature, *i. e.*, provided the reaction is not too rapid. The reactions considered here belong to this class, as otherwise to speak of a velocity constant would be meaningless. Langmuir regards the velocity of a chemical process as being defined by the rate of emission of radiation from the surface of a black body, given by the expression $E_\nu d\nu$. This would certainly be all the energy that one would draw upon under strictly photochemical conditions. Under thermal conditions, however, the removal of a certain type of energy tends immediately to be made good by the system as a whole, and consequently it would seem more correct to regard the integral of $E_\nu d\nu$ between the limits zero and infinity as the greatest attainable rate at which the deficiency can be made good. Numerically, for the case of phosphine cited, this is a large quantity, of the order 10^7 ergs per second. That the actual rate of the chemical reaction is not governed by the rate of emission from a given surface, but is governed by the radiation density in the system, is shown on the basis of the following considerations. Langmuir postulates that the reaction in a one centimeter cube of gas is to be attributed to the radiation emitted by one centimeter square of black body. If the centimeter cube of gas be distorted in such a way as to have thickness $1/x$ and face-area x square centimeters, the above postulate necessarily means that now the black body surface is x square centimeters, and hence the available energy for the cubic centimeter has been increased x times by adjustment of the linear dimensions of the volume. Such a conclusion that the amount of thermal reaction in a given volume should depend on the special configuration of the volume is evidently fallacious.

The most direct evidence that the conditions envisaged by Langmuir are essentially photochemical as opposed to thermal is the introduction of an ordinary optical absorption coefficient α . In the thermal case, a coefficient of the same nature does not enter because there is no directed effect, *i. e.*, there is no source as distinct from the system itself. We therefore fail to see that Langmuir's Equation 6 involving α , and consequently his later criticism in connection with thermal conductivity (which depends on the numerical value of α), applies. Under photochemical conditions, in which α is involved, the amount of decomposition is not comparable with that under thermal conditions, as is borne out by Langmuir's statement regarding the absence of photochemical sensitivity on the part of phosphine, and therefore his expression 5 is an erroneous estimate of the amount of energy required photochemically in a layer dx . It follows that his estimate of α , the absorption coefficient necessary on the radiation hypothesis, is enormously too great. Thus it will readily be admitted that phosphine which has no marked band (in the region $392 \mu\mu$) must possess an optical absorption coefficient which is very much less than that possessed say by bromine vapor at $421 \mu\mu$, the center of the broad continuous absorption band. Ribaud,¹ however, has measured the quantity χ for the latter case, and α as defined by Langmuir is related to χ according to the expression $\alpha = 4 \frac{\pi n^2}{\lambda}$ whence the maximum value of α in the case of bromine at atmospheric pressure is 15 in round numbers. For the band with maximum at $510 \mu\mu$ obtained by Ribaud, which presumably is the band responsible for the dissociation of the gas, the maximum value of α at one atmosphere is 1.5 approximately. The absorption coefficients of chlorine and iodine at their chemical bands are presumably of the same order of magnitude, while that of phosphine at $392 \mu\mu$ is certainly much less than unity. There is an enormous difference between these actual values and Langmuir's estimate of the absorption coefficient of a gas, *viz.*, 10^9 . Now Langmuir has shown that the coefficient of heat conductivity of an absorbing dissociating gas is given by $\frac{4}{3\alpha} \frac{dW_1}{dT}$ where $\frac{dW_1}{dT}$ represents the heat flow per cm^2 . per second between two surfaces differing in temperature by one degree, when there is no absorbing medium between. If this formula were applicable, the experimental fact that the presence of an absorbing medium increases the heat flow would necessitate values of α much smaller than unity. The applicability of the formula for such absorption coefficients is uncertain. While it might hold for a very large α , it evidently could not apply for small absorption coefficients, for this would mean enormous increase of heat flow for those spectral regions which are not specially absorbed. It therefore remains unsettled

¹ *Loc. cit.*

whether the experimental facts of thermal conductivity in a dissociating medium are really in contradiction to the radiation theory of the dissociation process.

Further, Langmuir points out the great similarity between the laws governing the photo-electric effect and chemical action. From what has been said, it will be evident that the analog of the photo-electric effect should be found in *photochemical* action, and that the true analogue of chemical action under *thermal* conditions should be sought in the phenomenon of thermionic emission of electrons. It is an experimental fact¹ that the number of electrons emitted thermionically from a body at temperature T is of the order of a million times greater than the number that can be produced by the photo-electric effect of black body radiation of temperature T acting on the cold body. Similarly, the amount of thermal chemical action in a system at a given temperature is in general many million times greater than the photochemical action which could be produced by black-body radiation of the same temperature falling on the cold system.

Assuming the photo-electric effect and the thermionic emission of electrons to be due to the same cause, *viz.*, absorption of radiation, we may carry out a simplified calculation to find the order of the ratio of the effects. Considering the photo-electric effect due to the radiation from one square centimeter of black body at temperature T , the amount of effective radiation emitted per second is given by $\int_{\nu}^{\infty} E_{\nu} d\nu$, where ν is the threshold frequency. Assuming this radiation to be absorbed within a layer of molecular thickness, we may denote the magnitude of the photo-electric effect per second by

$$\int_{\nu}^{\infty} \frac{2 \pi h \nu^3}{c^2} \cdot \epsilon^{-h\nu/kT} \cdot d\nu = \frac{2 \pi k T \nu^3}{c^2} \cdot \epsilon^{-h\nu/kT} \text{ (approximately) } \quad (13)$$

For the thermionic effect, we may write the amount of energy absorbed

per second by one electron as $\frac{\pi e^2}{3 m} \cdot u_{\nu}$, where

$$u_{\nu} = \frac{8 \pi h n_m^3 \nu^3}{c^3} \cdot \epsilon^{-h\nu/kT}.$$

Hence the total energy absorbed per second in a layer of molecular thickness which we may take as a measure of the thermionic emission is given by

$$\frac{8 \pi^2 e^2 h n_m^3 \nu^3}{3 m c^3} \cdot N \cdot \epsilon^{-h\nu/kT} \dots \dots \dots (14)$$

where N is the number of molecules per square centimeter of the surface layer. The ratio of the photo-electric to the thermionic effect is given by

¹ Langmuir, *loc. cit.*

(13) divided by (14). This ratio is

$$\frac{3kT \cdot m \cdot c}{4 \pi \cdot e^2 \cdot h \cdot n_m^3 N}$$

Putting T as 2000°A. , n_{3m} as 10^7 , and N as 10^{15} , the ratio becomes $1/8.6 \times 10^6$; *i. e.*, the thermionic effect is of the order of ten million times greater than the photoelectric effect of radiation at the same temperature.

It should be noted that in the above thermionic emission is regarded as being due to absorption of radiation by the electrons in the metal. The older view of a distribution of velocities among the electrons was based on the concept of freely moving electrons inside the metal. This concept has now been replaced¹ by that of a lattice structure, a metal being considered to comprise a lattice of electrons interpenetrating a similar lattice of ions. Such a structure makes impossible the view of Maxwellian distribution of velocities among freely moving electrons.

The second principal criticism of Langmuir is the statement that decomposition of phosphine is not brought about by ordinary daylight at a measurable rate, although here the intensities of the blue and violet frequencies are enormously greater than in the radiation from a black body heated to 675° . We are unaware of direct experiment in this connection but accepting it as a fact, we believe that it does not constitute an adverse criticism for the reasons given below. Lindemann² in a recent paper has put forward a similar criticism for the case of reactions such as the inversion of sucrose.

Chemical action in a low-temperature system brought about by sunlight or other high-temperature radiation is essentially photochemical, and the absolute amount of chemical action in any layer depends entirely on the radiation falling on it and on the absorption coefficient α of the matter. In general the absorption coefficient involves two different terms, which we may call physical absorption and chemical absorption respectively. Physical absorption means degradation of light of relatively high frequency into radiation of longer wave length, with the result that the temperature of the system rises. This is the more usual type of absorption encountered. In certain photochemical cases, such as those referred to by Langmuir and Lindemann, there is the possibility of a certain fraction of the absorbed radiation being converted into chemical work. This fraction we may call the "chemical absorption coefficient γ ." The distinction between physical and chemical absorption has long been recognized, and is explicitly introduced for example, in the well known work of Luther and Weigert³ and Byk⁴ on the photopolymerization of anthracene, in which the energy

¹ Lindemann, *Phil. Mag.*, 29, 127 (1915).

² F. A. Lindemann, *Phil. Mag.*, [VI] 40, 671 (1920).

³ Luther and Weigert, *Z. physik. Chem.*, 63, 408 (1908).

⁴ Byk, *ibid.*, 62, 454 (1908); *Z. Elektrochem.*, 14, 460 (1908).

absorbed by the anthracene is written E_A , of which only the fraction γE_A brings about the polymerization process. The value of γ found by Weigert¹ is about 0.045.

As a possible explanation of the mechanism which underlies the appearance of the γ term, we might suggest that the system, monochromatic radiation + matter, does not represent a physical equilibrium, and hence a large part of the monochromatic radiation is taken up in a physical sense by the matter and transformed in an attempt to produce radiation black with respect to the matter. This view is analogous to that already suggested in the case of a system in which matter and radiation are maintained in equilibrium, even when a chemical (*i. e.*, thermal) reaction is occurring. There is this distinction, however, that in the thermal case the more or less monochromatic radiation which is being removed by the chemical change is made good at the expense of all the other frequencies, while in the photochemical case the approximately monochromatic radiation impinging on the system tends to be converted into radiation of all frequencies, the temperature of which is much lower than that of the initial beam. Both phenomena represent a trend towards the stabilizing of an unstable condition.

Bearing the above consideration in mind let us now enquire into the amount of chemical action to be anticipated under photochemical conditions. For a volume of gaseous material of thickness dx and cross section one square centimeter at a temperature T_1 , the number of molecules present is given by $p \cdot dx / kT_1$, where p denotes the pressure of the gas in absolute units. Considering the action due to the emission from one square centimeter of black body at the temperature T_2 the total energy of frequency ν absorbed per second is $2\alpha E_\nu \cdot d\nu \cdot dx$, as Langmuir shows, and the chemically effective energy absorbed per second is $2\alpha \cdot \gamma \cdot E_\nu \cdot d\nu \cdot dx$ which is equal to

$$\frac{4\pi \cdot \alpha \cdot \gamma \cdot h \nu^3}{c^2} \cdot \epsilon^{-h\nu/kT_2} \cdot d\nu \cdot dx$$

This energy divided by $h\nu$ gives the number of molecules decomposed per second as $\frac{4\pi \cdot \alpha \cdot \gamma \nu^2}{c^2} \cdot \epsilon^{-h\nu/kT_2} \cdot d\nu \cdot dx$. Since the total number of molecules is $p \cdot dx / kT_1$, it follows that the fractional number of molecules decomposed in the layer per second is

$$\frac{4\pi \cdot \alpha \cdot \gamma \cdot \nu^2 \cdot kT_1}{c^2 \cdot p} \cdot \epsilon^{-h\nu/kT_2} \cdot d\nu$$

On giving $d\nu$ the probable value 10^{13} , and considering the specific case of phosphine at atmospheric pressure and 300°A. , acted on by black body radiation of temperature 6000°A. , the fraction of molecules decomposed per

¹ Weigert, *Ahrens Sammlung*, 17, 178 (1912).

second is $5.48\alpha.\gamma$. For the case of the action of sunlight, this value must be multiplied by $1/4 \theta^2$ where θ is the apparent angular semi-diameter of the sun, = 4.65×10^{-3} radians. The value of this factor is therefore 5.42×10^{-6} . Hence the fractional decomposition per second in a layer of phosphine due to the action of sunlight is $2.97 \times 10^{-5}.\alpha.\gamma$. Now a unimolecular reaction which is characterized by a velocity constant of the order 10^{-5} per second would be regarded as a very slow one *i. e.*, one which was approximating to the limit of detection. Incidentally such a value would be exceedingly great compared with the velocity constant of decomposition which phosphine would possess thermally under ordinary temperatures. It is reasonable to assume that the absence of observed photochemical action in the case of phosphine means that the fraction of molecules decomposed per second does not exceed 10^{-5} , and may of course be very much less. On this basis it would follow that $\alpha.\gamma$ is less than 0.34, which would be in agreement with the fact that no appreciable absorption has as yet been observed.¹

In the case of sucrose inversion mentioned by Lindemann, the above line of reasoning applies to an equal degree. The temperature of the system is 303°A. , and the effective frequency for the decomposition is given by Lindemann as 2.86×10^{14} . Taking the osmotic pressure p of the sucrose in solution to be one atmosphere, and introducing the above mentioned correction for the apparent area of the sun, we see that the fraction of molecules decomposed per second by sunlight is $2.4 \times 10^{-4} \alpha.\gamma$. approximately. Now in the infra-red region where the characteristic frequency of the inversion process lies, the purely physical absorption of the solvent water is known to be very great. This point has already been emphasized by H. S. Taylor² in connection with the experiments of Rideal and Hawkins³ on the acceleration produced in the velocity of hydrolysis of methyl acetate by short infra-red radiation. It follows that the proportion of the radiation of frequency 2.86×10^{14} in sunlight absorbed by the sucrose itself is small, and since of this only the fraction γ is chemically efficient, it follows that the numerical estimate of the fraction of molecules decomposed per second, *viz.*, $2.4 \times 10^{-4} \alpha.\gamma$. is very small. The reaction of inversion will therefore proceed at appreciably the same rate whether it is exposed to sunlight or not.

Summary.

1. An expression has been obtained for the velocity of a unimolecular reaction in a gaseous system, on the basis of the radiation hypothesis of thermal reactions, making use of the concept of continuous absorption of

¹ Work in this connection is at present being carried out in this laboratory.

² H. S. Taylor, *J. Ind. Eng. Chem.*, **13**, 75 (1921).

³ Rideal and Hawkins, *J. Chem. Soc.*, **117**, 1288 (1920).

radiation by an oscillator. The expression is

$$k_{\text{uni.}} = \frac{8 \pi^2 e^2 n_m^3 \nu^2}{3 m c^3} \cdot e^{-h \nu / k T}.$$

where $k_{\text{uni.}}$ is the unimolecular velocity constant, e and m are the charge and mass of the electron, ν is the frequency of the radiation characteristic of the reaction, h and k are the constants of Planck and Boltzmann respectively, T is the absolute temperature, and n_m is the refractive index of the substance in an ideal state corresponding to the closest possible packing of the molecules. This term n_m is shown to have a value of approximately 200, practically independent of the system considered and of the temperature. The expression for the velocity constant is seen to agree with experimental data of unimolecular reactions, so far as they are known.

2. By considering reversible reactions of the dissociation type, an expression for the equilibrium constant is obtained. This is shown to be in good agreement with the experimental data on iodine given by Bodenstein and Starck.

3. Recent criticisms of the radiation hypothesis have been considered, and it is believed that these criticisms have been met. In view of the nature of the criticisms referred to, it is essential to emphasize the distinction rather than the resemblance between thermal and photochemical processes. That both kinds of process are attributed to radiation constitutes, of course, the resemblance. The distinction enters in the manner and extent to which the transformation of radiant energy occurs. Thus Langmuir attributes the mechanism of a *thermal* process to rate of emission from a surface, which mechanism however characterizes *photochemical* action only. On the other hand, Lindemann considers *photochemical* action, but regards it from the point of view of radiation density, which we have shown defines *thermal* velocity not photochemical velocity, when the radiation has the same temperature as the matter.

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