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RADIATION AS A FACTOR IN CHEMICAL ACTION.

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Jean Perrin, in his book "Les Atomes" (1913), advanced the thesis that the action of light plays an essential part in all chemical reactions. In a more recent article[1] he shows that Arrhenius' equation for reaction velocity can be derived from the Planck or Wien radiation law upon the assumption that the chemical action depends on the absorption of a nearly monochromatic radiation. Thus the increase in the velocity of a reaction with rising temperature is supposed to be due to the increasing intensity of some particular part of the so-called black-body radiation. According to Wien's radiation law, the natural logarithm of the intensity of any monochromatic black-body radiation is a linear function of the reciprocal of the absolute temperature. The slope of the line representing this relation is $-h\nu/k$ where h is the quantum 6.6×10^{-27} erg seconds, ν is the frequency of the monochromatic radiation, and k is the gas constant per molecule, or 1.37×10^{-16} erg per degree. According to Arrhenius' equation, an exactly similar relation holds between the natural logarithm of the *reaction velocity* and the reciprocal of the temperature. Trautz, Marcelin, Wm. McC. Lewis and others, from analogy with van't Hoff's equation, have identified the slope of the line obtained from the Arrhenius equation with Q/R where R is the gas constant and Q is the energy (per gram molecule) required to *activate* the reacting substance. The quantity Q/R thus has the same relation to Arrhenius' equation that $h\nu/k$ has to the Wien equation. To correlate the two laws it is only necessary to equate these quantities

$$\frac{h\nu}{k} = \frac{Q}{R}. \qquad (1)$$

But $R = Nk$ where N is the Avogadro constant 6.1×10^{23} molecules per gram molecule. Therefore

$$Q = Nh\nu. \qquad (2)$$

In other words, the heat of activation per molecule is $h\nu$, a result in accord with the quantum theory.[2]

The radiation hypothesis, together with the quantum theory, thus furnishes a very simple explanation of the relation between the Arrhenius equation for reaction velocity and the Wien radiation law. According to this hypothesis, all chemical reactions are to be regarded as essentially

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[1] *Ann. phys.* [9] 11, 5–108 (1919).

[2] Haber, *Verh. deut. physik. Ges.*, 13, 1117 (1911), proposed a relation like that of Equation 2 for calculating the heats of chemical reactions from the natural frequencies of vibrations of the electrons in atoms and molecules.

photochemical reactions in which the energy of radiant heat or light is transformed into chemical energy or *vice versa*.[1]

Perrin has given one of the strongest arguments in favor of the hypothesis. In a unimolecular reaction the amount of substance reacting in a given time is proportional to the amount present. The chance that any molecule shall react during any small time interval is thus *independent of the pressure*. But the number of collisions which the molecule makes with others is proportional to the pressure. Therefore, as Perrin points out, the reaction of any molecule must be a phenomenon which is independent of collisions between molecules. If the reaction is not due to collisions, it seems almost necessary to conclude that it is caused by radiation.

There are two consequences of the radiation hypothesis which should serve as a test of its validity. In the first place, it is necessary that the reacting substance shall absorb the radiation which causes the reaction. Therefore, there must be an absorption band which includes the radiation in question. It is also to be expected that the frequency of this radiation should be the same as that obtained from the specific heat, the compressibility or the melting-point by the relations of Nernst, Einstein, or Lindemann.

In the second place, the total amount of energy absorbed from the radiation must be sufficient to activate the requisite number of molecules. Before any molecule can undergo reaction, it must become activated and this requires the absorption of the energy $h\nu$ or Q/N, an amount which can be determined experimentally for any given reaction from the temperature coefficient of the reaction velocity. As far as I have been able to find, no one has tested the radiation hypothesis from this point of view, although it would seem to constitute a decisive test. It is the principle object of this paper to compare the energy absorbed in a few thermal reactions with the total available radiant energy.

Trautz, Lewis and Perrin have attempted to correlate the frequencies calculated from Equation 2 with those of absorption bands or with the natural frequencies found from the specific heats, etc. The results taken as a whole do not seem to furnish satisfactory evidence for the radiation hypothesis. In a few cases the calculated frequencies do come within the range of absorption bands, but in most of these cases (for example, iodine)

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[1] The radiation hypothesis was proposed by Trautz in 1911, and has been developed in detail by him in a series of papers since then. A summary of Trautz' work with reference to the earlier papers, is given in the *Z. anorg. allgem. Chem.*, **102**, 81–129 (1918); and **106**, 149 (1919). During the last few years Wm. McC. Lewis has published numerous papers on this subject in the *J. Chem. Soc.* See particularly *J. Chem. Soc.*, **111**, 389, 457, 1086 (1917); *Phil. Mag.*, **39**, 26 (1920). In this last paper Lewis points out a serious difficulty in reconciling the radiation hypothesis with either Planck's or Einstein's views regarding the mechanism of radiation.

there is a very great number of bands and there is no way of predicting in advance which of the bands corresponds to the activation of the molecule. In many other cases there is not the slightest trace of an absorption band observed in the neighborhood of the calculated frequency. For example, according to Lewis' calculation, the critical frequency for the dissociation of hydrogen into atoms corresponds to a wave length of 325$\mu\mu$ which is in the ultra-violet region just slightly beyond the visible. There is, however, no measurable absorption of light of this frequency by hydrogen. The following data on the heats of activation of various dissociations will be given by Dr. Dushman in a forthcoming paper, PH_3 — 73,000; As_4 — 45,000; P_4 — 50,000; and $COCl_2$ — 61,000 g. cals. per mol. The heat of activation of nitric oxide in its decomposition into oxygen and nitrogen is 65,000 cal. The value for the decomposition of nitrous oxide is 60,000 cal. These values correspond to wave lengths of 390 $\mu\mu$ for PH_3, 630 for As_4, 570 for P_4, 474 for N_2O, 467 for $COCl_2$, and 437 for NO, which, according to the radiation hypothesis, should lie within absorption bands. It is evident that this conclusion cannot be correct, for the above wave lengths are in the visible spectrum, while the gases are all colorless and therefore do not absorb perceptible amounts of radiation in this range.

Is the Radiant Energy Absorbed by Gases Sufficient to Account for the Observed Reaction Velocities?

The only unimolecular gas reaction whose velocity has been directly measured, is the dissociation of phosphine.[1] At a temperature of 948° K. the velocity constant is 0.012 per second. This means that 1.2% of the phosphine present at any time decomposes within the next second. Under the conditions of the experiment the reaction was wholly irreversible. From the temperature coefficient of the reaction velocity Lewis has calculated that the heat of activation lies between 70,000 and 80,000 calories per molecule. Dushman will show that excellent agreement with the experimental data is obtained if we take 73,000 for the heat of activation. According to Equation 2, this corresponds to a frequency of 7.7×10^{14}, or to a wave length of 392 $\mu\mu$.

According to the radiation hypothesis, the energy required to activate the molecule before dissociation can occur, is supplied by the absorption of radiant energy having a wave length in the neighborhood of 392 $\mu\mu$. From the heat of activation and the reaction velocity we can calculate the rate at which energy must be supplied to bring about the reaction. From Wien's law we can also determine how much radiation there is at 948° within a given range of wave lengths, and in this way we can see if there is enough radiant energy to cause the observed reaction.

One cc. of phosphine at atmospheric pressure and 948° K. contains

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[1] Trautz and Bhandarkar, *Z. anorg. allgem. Chem.*, **106**, 95 (1919).

1.27×10^{-5} g. mols. The amount that dissociates in one second is 0.012 of this, or 1.52×10^{-7} g. mols. Taking 73,000 as the heat of activation, the energy which must be supplied per cc. per second is 0.0111 calorie, or 465,000 ergs.

According to the Stefan-Boltzmann law, the total radiation from a black body at 948° is 4.56×10^7 ergs per second per sq. cm. All but a minute fraction of this energy lies far in the infra red part of the spectrum. The Wien displacement law $\lambda_M T = 0.290$ cm., shows that the wave lengths corresponding to the maximum of the distribution curve is 3060 $\mu\mu$. Wien's radiation law gives for the energy radiated per sq. cm. per second between the frequencies ν and $\nu + d\nu$ the expression

$$E_\nu d\nu = \frac{2\pi h\nu^3}{c^2} e^{-h\nu/kT} d\nu. \qquad (3)$$

Here c is the velocity of light, 3.00×10^{10} cm. per second.

The radiation hypothesis gives no definite information regarding the width of the band $d\nu$ which should be absorbed except that the radiation must be reasonably nearly monochromatic in order to account for the similarity between the Wien and the Arrhenius equations. To calculate the total energy available in the radiation, let us assume that all energy of wave length shorter than 400 $\mu\mu$ can be used for activating molecules. This wave length corresponds to a frequency of 7.5×10^{14} per second. By integrating the expression in Equation 3 between this frequency and infinity, we find that the total energy radiated from a black body at 948° with a wave length less than 400 $\mu\mu$ is 1.3×10^{-5} erg per second per sq. cm. This is only $3. \times 10^{-13}$ of the total energy radiated (in all wave lengths) at this temperature, and is about 4×10^{10} times less than the amount of radiant energy needed to cause the reaction in one cubic cm. of phosphine (465,000 ergs. per sec.). In other words, a black body at 948° K. (675° C.) radiates so little energy in the neighborhood of 392 $\mu\mu$ that this energy would only be sufficient to activate molecules of phosphine in a layer having a thickness not greater than 3×10^{-11} cm., *even if all the radiation were absorbed within this layer.* The observed reaction velocity, therefore, cannot be due to the absorption of radiation of the wave length needed to account for the observed temperature coefficient.

Another fact which should make the radiation hypothesis in its present form untenable is that the decomposition of phosphine is not brought about at measurable rate by ordinary daylight, although the intensity of blue and violet light in daylight is enormously greater than in the radiation from a body heated to 675° C.

The above objections to the radiation hypothesis apply not only in the case of the dissociation of phosphine, but to all unimolecular reactions.

It will be shown by Dr. Dushman[1] that the velocity of any unimolecular reaction is given by the expression

$$k_1 = \nu e^{-h\nu/kT}. \qquad (4)$$

The "frequency" ν can be determined experimentally from the temperature coefficient of the reaction velocity. The "heat of activation" is related to ν by Equation 2.

By means of the above equation we can now test the radiation hypothesis for the general case. Imagine a large vessel, bounded by plane walls, which contains a gas undergoing a unimolecular reaction. According to the radiation hypothesis, each molecule which reacts absorbs the energy $h\nu$ from the black body radiation having a frequency approximately equal to ν. Let us consider the reaction which takes place within a very short distance dx of one of the plane walls of the vessel. Since the number of molecules per cc. in a gas is p/kT we obtain the following expression for the energy required to activate the molecules which react within the distance dx of the wall (per second and per sq. cm. of wall)

$$\frac{ph\nu^2}{kT} e^{-h\nu/kT} dx. \qquad (5)$$

Let us now calculate how much energy will be absorbed by the gas within dx of the wall. If α is the absorption coefficient of the gas for light of the frequency ν the total energy absorbed by the gas in a slab of thickness dx is $2\alpha E_\nu d\nu dx$ where E_ν is given by Equation 3. The coefficient 2 comes into the expression because part of the radiant energy passes diagonally through the slab and is, therefore, more strongly absorbed than that passing normally. Let us assume that the gas can absorb energy from a band of finite width. We therefore, place $d\nu = \beta\nu$ where β expresses the width of the band as a fraction of the corresponding frequency. It does not seem reasonable that β should exceed say 0.1. The total energy absorbed in the slab (per second and per sq. cm.) is thus:

$$\frac{4\pi h\nu^4\alpha\beta}{c^2} e^{-h\nu/kT} dx. \qquad (6)$$

By equating Expressions 5 and 6, we obtain (in C.G.S. units)

$$\alpha\beta = \frac{pc^2}{4\pi\nu^2 kT} = 5.2 \times 10^{35} \frac{p}{\nu^2 T}. \qquad (7)$$

This expression gives the absorption coefficient which is required if radiation is to supply the energy for the activation of the molecules. Assuming a reaction in which the heat of activation is 100,000 calories (hence, $\nu = 1.05 \times 10^{15}$), and placing $p = 10^6$ (one atmosphere) and $T = 1000°$, we obtain $\alpha\beta = 4.8 \times 10^8$. If we take $\beta = 0.1$, this gives

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[1] A short abstract covering Dushman's theory has already been published in the *J. Franklin Inst.*, April, 1920.

an absorption coefficient of $5. \times 10^9$ per cm. In other words, the energy would be sufficient only for a gas layer of the order of 10^{-10} cm. in thickness. If we should choose reactions occurring at lower temperatures or having lower heats of activation, we see by Equation 7 that the absorption coefficient would be still larger.

Dissociation of Hydrogen.—The experiments on the dissociation of hydrogen into atoms which were carried out by Mr. G. M. J. Mackay and the writer[1] furnish strong evidence that this reaction is not caused by the absorption of radiation. When a tungsten filament is heated to high temperature in hydrogen, the heat carried away by the gas is many times greater than can be accounted for by ordinary heat conduction or convection.

TABLE I.

Heat Dissipation from Tungsten Filaments in Hydrogen in Watts per Centimeter

	Absolute temperature, ° K.		
	2500.	3000.	3400.
At 0.0 mm. pressure:			
W_r, heat radiated	1.92	4.46	9.41
At 50 mm. pressure:			
W_c, conduction and convection	6.5	9.1	11.0
W_d, dissociation	12.5	48.0	107.0
Ratio $W_d : W_r$	6.5	10.7	11.4
At 750 mm. pressure:			
W_c, conduction and convection	14.4	20.2	25.0
W_d, dissociation	6.3	29.0	69.0
Ratio $W_d : W_r$	3.3	6.5	7.3

A few typical results are summarized in Table I, which gives the heat losses from a tungsten filament of 0.0071 cm. diameter in hydrogen at 2 pressures. W_r represents the total energy radiated per second, W_c the energy carried by normal heat conduction and convection, while W_d gives the energy carried away as a result of the dissociation of the gas.

The effect of the dissociation is to cause a transfer of heat from the hot filament to the walls of the surrounding vessel, amounting in some cases to more than 10 times the total heat radiated from the filament.

According to the radiation hypothesis, the dissociation of the hydrogen is produced by the absorption of a radiation of a wave length of approximately 325 $\mu\mu$. It is clear, however, that the absorption of the radiation from the filament by the gas cannot be made to account for an increase in the heat carried from the filament. In fact, such absorption must decrease the heat loss, for whatever heat is absorbed by the gas in causing dissociation, will be reradiated when the atoms recombine, and some of this heat will thus be returned to the filament, while if there is no absorption, the radiated heat travels away with the velocity of light.

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[1] THIS JOURNAL, 36, 1708 (1914); and 37, 417 (1915).

The evidence that radiation does not play an appreciable part in the reaction is even more striking when we consider the small proportion of radiation present in the shorter wave lengths. Calculation by means of Wien's equation indicates that of the total energy radiated by the filament, only the following fractions are of wave lengths less than 325 $\mu\mu$: at 2500° K. — 0.00006; at 3000° K. — 0.0006; at 3400° K. — 0.002. The observed rate of dissociation is thus thousands of times greater than could be accounted for by the absorption of radiation even if the hydrogen absorbed the radiation in question completely.

It may be objected that the dissociation of hydrogen takes place in contact with the tungsten filament and that the radiation hypothesis has not usually been applied to reactions involving solid bodies. It would seem, however, that the radiation hypothesis is of such a fundamental nature that if true for gases it should also be applicable for liquids and solids. Moreover, the difficulty is not removed even in this way, for although the dissociation occurs in contact with the solid, the recombination certainly takes place in the gas phase, and this, on the basis of the radiation hypothesis, would produce a radiation of an intensity greater than that of a black body at the same temperature. This result for an endothermic reaction, is in conflict with the principles of thermodynamics.

Dissociation of Iodine.—Isnardi[1] has studied the heat conductivity of iodine vapor in contact with a heated platinum wire having an effective surface of 0.25 sq. cm. With the wire at 1080° K., the total energy carried by normal conduction corresponded to 0.70 watt, while that caused by dissociation (W_d) amounted to 3.49 watts. These results were obtained by subtracting the radiated energy from the total energy loss, but Isnardi does not give the amount of this correction. The radiation from a black-body surface of 0.25 sq. cm. at 1080° K. is 1.95 watts. Since platinum at this temperature radiates about 11% as much as a black body, the radiation in Isnardi's experiments must have been about 0.2 watt. The heat carried from the wire by the dissociation was thus about 17 times greater than the total heat radiated from the wire.

Dissociation of Nitrogen Peroxide.—Nernst[2] developed a quantitative theory of heat conduction in dissociating gases and applied it to experimental data obtained by Magnanini for the heat conductivity of nitrogen peroxide at various temperatures. At 190° C. the nitrogen peroxide is practically completely dissociated into nitrogen dioxide, and the heat conductivity is about the same as that of carbon dioxide, but at 40°, where the degree of dissociation is only about 30%, the heat conductivity is greater than that of hydrogen and is about 6.7 times as great as at the higher temperature. The experimental results furnish

[1] Isnardi, *Z. Elektrochem.*, **21**, 405 (1915).

[2] "Boltzmann-Festschrift," p. 904, Leipzig, 1904.

quantitative confirmation of Nernst's theory, which treats the problem as involving dissociation of the gas in a hot region and diffusion of the dissociation products to a cold region, where recombination takes place. The following analysis will make it clear that the observed facts are in radical disagreement with the radiation hypothesis.

According to the data given by Nernst, the heat conductivity κ of nitrogen peroxide at 40° is 0.00041 calorie per cm. sec. degree. Of this, the conductivity 0.00037 is due to the dissociation, while 0.00004 is ordinary heat conduction. Let us consider 2 parallel plane surfaces one cm. apart, differing in temperature by one degree and having an average temperature of 40°. If the space between the planes is filled with nitrogen peroxide, 0.00037 calorie per sq. cm. per sec. will pass across the space because of the dissociation. This corresponds to 0.00155 watt per sq. cm. According to the Stefan-Boltzmann law, the total heat transferred by radiation should be 0.00070 watt per sq. cm., which is less than half of that caused by the dissociation.

If the medium between the 2 plane surfaces does not absorb radiation, the heat transferred by radiation is independent of the distance between the surfaces, although the heat conducted is inversely proportional to this distance. When the medium absorbs the radiation, as it must, according to the radiation hypothesis, if a chemical reaction takes place, the transfer by radiation also varies inversely as the distance between the planes. Let us calculate how much heat can flow in this way. The problem involves the multiple scattering of heat rays.

Consider the radiation of heat between 2 parallel plane surfaces having a gas between them which absorbs heat in accordance with the radiation hypothesis. For example, consider a dissociating gas in which the reaction velocity is so high that chemical equilibrium prevails at every point in the gas. The absorption of the radiation causes the dissociation, while the recombination must produce an equal emission of radiation of the same wave length. Under these conditions the radiation of heat from molecule to molecule becomes strictly analogous to the energy carried between molecules in heat conduction in gases. We are thus justified in saying that the average distance that the heat rays travel before being absorbed is $1/\alpha$ where α is the absorption coefficient. The distance $1/\alpha$ corresponds to the mean free path of the molecules. Similarly, the radiation which arrives at any point may be considered as having come from a point at the average distance $1/\alpha$.

Let us choose a coördinate system in which the flow of heat takes place parallel to the X axis, so that the planes YZ are isothermal surfaces. Let T be the temperature at a plane having the coördinate x. Consider the radiation passing through a unit area of this plane in a direction making an angle θ with the X axis. Since $1/\alpha$ is the effective distance from which this radiation comes, we may take the temperature of its source as being

$$T - \frac{dT}{dx} \cdot \frac{\cos\theta}{\alpha}.$$

Let R be proportional to the heat radiated by a unit area of a black body at the temperature T. Then the energy in the radiation considered is

$$R - \frac{dR}{dT} \cdot \frac{dT}{dx}\, \frac{\cos\theta}{\alpha}.$$

The spherical angle from which this radiation falls on the unit area is proportional to $\sin\theta . d\theta$ and the energy that can pass through this unit area is proportional to $\cos\theta$. Hence the total flux of radiation through the unit area is

$$dw = \left(R - \frac{dR}{dT} \cdot \frac{dT}{dx} \cdot \frac{\cos\theta}{\alpha}\right) \sin\theta \cos\theta \, d\theta. \qquad (8)$$

The total flux obtained by integrating this expression from $\theta = 0$ to $\theta = \pi/2$ and placing $dT/dx = 0$ must equal the energy radiated per unit area per second from a black body at the temperature T. If we call this quantity W_1 we find $W_1 = 2R$. By integrating from 0 to π we obtain

$$W = \frac{2}{3\alpha} \frac{dR}{dT} \cdot \frac{dT}{dx} = \frac{4}{3\alpha} \frac{dW_1}{dT} \frac{dT}{dx}. \qquad (9)$$

This represents the rate at which heat flows between the 2 parallel surfaces. Since it depends on the temperature gradient between the planes rather than the temperature difference, the flow of heat follows the laws of heat conduction. The coefficient of heat conductivity due to this scattered radiation is

$$\kappa_r = \frac{W}{dT/dx} = \frac{4}{3\alpha} \frac{dW_1}{dT}. \qquad (10)$$

In this equation dW_1/dT represents the heat flow per sq. cm. per second between 2 surfaces differing by one degree in temperature when there is no absorbing medium between the plates. With surfaces separated by the distance x and with the absorbing gas between them, the rate of heat flow will be $\kappa_r \div x$ or $\frac{4}{3\alpha x}\, dW_1/dT$. Thus with surfaces one cm. apart and with an absorption coefficient of 1000, the effect of the gas would be to decrease the flow of radiant energy in the ratio 3000:4. Of course the above equation must be applied only to that part of the radiation which is strongly absorbed.

We have already seen that to account for chemical reactions on the basis of the radiation hypothesis it is necessary to assume very large values for the absorption coefficient and the existence of relatively broad absorption bands. From the foregoing reasoning it is apparent that this must lead to a marked decrease in the heat that can be transferred through the gas. It is evident, then, that if chemical reactions take place in accordance with the radiation hypothesis, dissociation of a gas should decrease rather than increase the total heat flow. Even if it be admitted that part of the heat may be carried by the diffusion and subsequent recombination of the dissociation products, there will still be less heat flow than if the energy had been radiated through the gas instead of having been absorbed. It would seem that the only increase of heat conductivity in a dissociating gas which would be consistent with the radiation hypothesis is that due to the increased heat conductivity of the dissociation products resulting from their lower molecular weight. This should never cause an increase of more than about 40%, whereas experimental values show several-fold increase.

Discussion.

The evidence of the preceding pages seems to prove beyond question that the energy involved in chemical reactions is not in general derived from the absorption of radiant heat or light. Must we then consider that the similarity between the Wien relation law and the Arrhenius equation is a mere coincidence, and how are we to explain the fact that in a unimolecular reaction the velocity is independent of the collision frequency?

Among any large number of molecules in thermal equilibrium at the temperature T the probability P that a given molecule shall have the energy E or an energy lying between E and $E + dE$ is qiven by

$$P = ce^{-E/kt}, \tag{11}$$

where c is either independent of the temperature or varies with the temperature at a rate which is negligible, compared with the variation of the exponential factor. Maxwell's distribution law of molecular velocities is a special case of the above statistical law applying to kinetic energy. The equation also holds for potential energy of position and for internal energy of molecules, even under conditions where the equipartition law is not applicable. Einstein[1] has shown, for example, that the Planck radiation equation may be derived by a very simple method from a fundamental statistical law of the above type.

It would seem, therefore, that the similarity in form between the Arrhenius and the Wien equations may very probably be due to the dependence of both of these relations upon the statistical laws. In fact, the Arrhenius equation follows directly from Equation 11 if we assume that the chance that a given molecule will undergo a chemical reaction is proportional to the probability that it contains a specified amount of energy. The exponential factor $e^{-E/kt}$ gives the fraction of the molecules which have an energy in excess of E and which may thus be called "active" molecules. This factor, however, is a pure number and does not involve

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[1] A. Einstein, *Physik. Z.*, **18**, 121 (1917).

time. The velocity of a unimolecular reaction is measured by $(1/n)\,dn/dt$ where dn is the number of molecules which react in the time dt and n is the total number of molecules of the reacting substance. This quantity has the dimensions of a frequency. The velocity of a reaction may thus be expressed by

$$k_1 = \frac{1}{n}\frac{dn}{dt} = \nu_0 e^{-E/kt}, \tag{12}$$

where ν_0 is a frequency (dimensions t^{-1}) characteristic of a particular reaction, but which is at least approximately independent of the temperature.

In interpreting this equation we must keep in mind that Equation 11, upon which it is based, depends upon the assumption of thermal equilibrium. In order that Equation 12 may hold, it is, therefore, necessary that the number of molecules which dissociate per second shall be very small compared to the number that become active. The active molecules must thus remain active for only very short periods of time. Let τ be the average duration of these periods.

There are 2 types of mechanism which may underlie Equation 12.

I. We may assume that ν_0 represents the rate of dissociation of the active molecules. Thus $\nu_0 dt$ is the chance that a given active molecule will dissociate in the time dt. As we have seen, however, the chance that any molecule will dissociate during any single period of activity must be very small. Therefore, $\nu_0\tau$ must be small compared to unity or

$$\tau << 1/\nu_0. \tag{13}$$

II. We may assume that a regular periodic phenomenon of frequency ν_0 is taking place in all molecules, so that there are ν_0 "crises" in each molecule per second. Whenever a crisis occurs in an *active molecule* dissociation results. The chance that a crisis shall occur during any single period of activity of a molecule is, in this case also, equal to $\nu_0\tau$ so that the condition of Equation 13 must be fulfilled.

To obtain a more concrete conception of the mechanism of a unimolecular reaction, let us consider again the dissociation of phosphine at 948° K., at which temperature the velocity of the reaction is 0.012 per second. Taking the heat of activation as 73,000 calories per g. molecule, we find that the exponential factor of Equation 12 is equal to 1.6×10^{-17}, and therefore, since $k_1 = 0.012$, the value of ν_0 is 7.5×10^{14}. It follows, then, from (13), that τ, the average period of activity, must be *very small* compared to 1.3×10^{-15} seconds. At atmospheric pressure each molecule of phosphine makes only 4.2×10^{9} collisions per second with other molecules. The average time between collisions is thus 2.4×10^{-10} seconds. In other words, the duration of a free path is many millions of times greater than the period during which the molecules remain active.

It is natural, then that the rate of reaction should not be dependent upon the number of collisions. This result may also be reached in the following manner.

Suppose we should assume that the activation of molecules is brought about only by collisions. Since the proportion of active molecules is given by the exponential factor whose value is 1.6×10^{-17}, it follows that the only one collision out of 6.2×10^{16} could result in the formation of an active molecule. But each molecule makes only 4.2×10^{9} collisions per second, so that it would become active only once every 1.5×10^{7} seconds (170 days). The average life of a molecule of phosphine is, however, only 83 seconds (the reciprocal of the reaction velocity). The equilibrium between active and inactive molecules must therefore be brought about enormously more rapidly than is possible by the direct action of collisions.

This brings us face to face with a fundamental difficulty. It is generally assumed that the activation of a molecule depends on the acquisition of an amount of energy corresponding to the heat of activation. In the case of the dissociation of an elementary gas into atoms, the heat of activation has been found to be equal to the heat of dissociation. The question arises, How does the molecule acquire this energy? We have just seen that by means of collisions at 948° K. the molecule of phosphine can receive enough energy for activation only once every 170 days. Since the actual life of the molecule is very short compared to this, it is evident that the molecules which do dissociate must have acquired the energy for activation subsequently to their last collisions. We have already proved that the radiant energy (assuming full black-body radiation) is millions of times too small to supply the energy needed for the dissociation. This discrepancy is further magnified when we consider that the number of molecules which become active per second must be much greater than the number which dissociate. The radiation hypothesis, therefore, does not help us out of the difficulty.

Unless we are to assume some new and unknown agency by which energy may be transmitted to isolated molecules, or are willing to renounce the conservation of energy, it seems necessary to conclude that each molecule must contain within itself the energy required for its own dissociation. This must be true no matter what the temperature may be. We are thus forced to assume a "Nullpunktsenergie" or zero temperature energy. The difference between the active and inactive molecules is thus not one of total energy content, but lies rather in the availability of the internal energy for the purposes of chemical action. The exponential factor of Equations 11 and 12 must then represent the probability that the energy is in a form that renders the molecule active.

We must thus conceive of a thermal equilibrium between the electrons or other parts of a molecule, brought about by the collisions between molecules. This thermal agitation inside the molecule will presumably be governed by statistical laws and by quantum relations and will not even approximately be in accord with the equipartition law, and, therefore, the energy will be relatively small in amount. The distribution of this energy among the different parts of the molecule determines, however, the availability of the comparatively large store of zero temperature or latent energy within the molecule. According to this view it is not surprising that τ, the period during which molecules remain active, should be small even when compared to 10^{-15} seconds.

As far as I am aware, the above reasoning has not previously been applied to chemical reactions, although it resembles in many points some of the physical theories of radiation, photoelectric effect, etc. For example, in the theory of heat radiation it has been necessary to conceive of temperature as applying to the oscillations of single electrons in atoms. The velocity of electrons emitted in the photoelectric effect is independent of the intensity of the light, so that it has seemed necessary to assume, at least, for low intensities, that the energy must have resided in the atom, and that the effect of the light is to render the energy available to the electron by some sort of trigger action. In this case, radiation plays a part analogous to that of the collisions in chemical reactions. Thus in the photoelectric effect, the energy of the electron emitted by any atom may be very great compared to the radiant energy absorbed by *that atom*, although the total energy of the electrons emitted by any large surface is always less than the toal radiant energy absorbed. Similarly, in a chemical reaction, the energy required to activate a molecule may be very great compared to the energy that is transferred to *that molecule* by a collision, although the total energy required for the chemical reaction in a mass of gas is always less than the total energy that is transferred by collisions, but is usually enormously greater than the total energy transferred by radiation. Both in the photoelectric effect and in chemical reactions, it is necessary to assume a kind of trigger action by which an energy of low intensity is able to control the disposition of an energy of high intensity.

The difficulties of explaining the photoelectric effect have seemed nearly insuperable. Planck and later, Nernst,[1] have assumed a "Nullpunktsenergie" in order to help explain this and other phenomena. The conception of Nernst bears many resemblances to that which has been developed in the present paper. Nernst assumes, however, that the zero temperature energy owes its origin to a zero temperature radiation of great intensity which passes through all bodies without absorption, except insofar as it can be rendered available by a trigger action depending upon certain

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[1] *Verh. deut. Physik. Ges.*, 18, 83 (1916).

thermal changes in bodies. It hardly seems necessary to assume this zero temperature radiation to explain chemical reactions. But by doing so, we would have a new radiation hypothesis for chemical action which would be free from the objections that we have raised against the old one.

As an illustration of the difficulties that have arisen in connection with the photoelectric effect, I may refer to a recent paper by D. L. Webster,[1] in which it is proposed to abandon the conservation of energy except as a statistical result, in order to explain some of these difficulties. Webster's reasoning can be applied with nearly equal force to the case of chemical reactions, but it seems that the assumption of a zero temperature energy which we have made above is preferable to an abandonment of the conservation of energy. The problem, however, is by no means solved, but it seems probable that the final solution will clear up both the chemical and the photoelectric problem.

The similarity between the Wien radiation law and the Arrhenius reaction velocity law is in many respects analogous to the relation between the laws of photoelectric and thermionic electron emission. It has been found by Richardson that the thermionic emission from a heated body increases with the temperature according to an equation similar to the Wien or Arrhenius equation. Also he found that the distribution of velocities among the electrons is given by Maxwell's distribution law. On the other hand, the number of photoelectrons emitted is proportional to the intensity of the light and the energy of the electrons is proportional to the frequency of the light. But if we let the total radiation from a heated black body fall on a metal, the number of photoelectrons emitted should increase with the temperature of the black body in accord with Wien's equation, and the energy of the electrons should increase in proportion to the temperature, and thus in accord with Maxwell's law, because the average frequency of the light from a black body increases in proportion to the temperature. As a matter of fact, A. Becker[2] has recently shown that the distribution of velocities, as well as the most probable velocity, among the photoelectrons emitted from any substance as a result of illumination by black-body radiation (temperature T) is the *same* as that found among the electrons emitted by thermionic emission when the emitting body has the temperature T. It is thus natural to assume that the thermionic emission from a heated body is caused by the photoelectric effect of the radiation emitted by the body. Experiments show, however, that the number of electrons emitted thermionically is of the order of a million times greater the number that can be produced by the photoelectric effect from black-body radiation of corresponding

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[1] *Phys. Rev.*, **26**, 31 (1920).

[2] *Ann. Physik.*, **60**, 30 (1919).

temperature.[1] This result is probably closely related to the fact that chemical action follows laws similar to those of radiation, but the amount of chemical action is millions of times greater than can be explained by radiation.

Summary.

In order to account for the close similarity between the Arrhenius equation for the velocity of chemical reactions and the Wien radiation law, and also to explain the fact that the velocities of unimolecular reactions cannot be dependent upon the number of collisions between molecules, it has been proposed by Trautz, Wm. McC. Lewis, Perrin, and others, that molecules can take part in chemical reactions only after they have become activated, and that this activation is brought about by the absorption of a nearly monochromatic radiation. There seems to be ample evidence in support of the activation of molecules, but the *radiation hypothesis*, by which this activation depends upon the absorption of radiation, does not rest upon such a firm foundation.

There are two decisive tests of the validity of the radiation hypothesis: (1) the reacting substance must absorb radiation of the frequency required to produce activation, and there must, therefore, be an absorption band which includes this frequency; (2) the total amount of radiant energy absorbed must be sufficient to supply the known heat of activation to the molecules which react.

Examination of the available data indicates that there is little evidence that absorption bands occur which include the frequency corresponding to the activation. Thus in the dissociations of the following substances, phosphine, nitrous oxide, nitric oxide, phosgene, and the vapors of phosphorus and arsenic, the activation frequencies lie within the range of the visible spectrum, but the fact that the gases are all colorless proves that there are no absorption bands in this region.

An analysis of the experimental data on the velocity of dissociation of phosphine proves that the energy actually required for activation in one cc. at 948° K. is 4×10^{10} times greater than the amount that can be supplied by radiation from one sq. cm. of surface at 948° K. Further-

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[1] Richardson, Becker and others have given evidence of this kind. In 1912 I made some very careful experiments (unpublished) to see whether photoelectric emission from tungsten could explain the thermionic emission. Tungsten filaments were heated nearly to their melting-point in highly evacuated bulbs immersed in liquid air. The vaporized tungsten produced an exceptionally high vacuum as a result of the clean-up effect, and formed an opaque conducting film on the glass which was made to serve as a gas-free electrode for collecting electrons emitted thermionically or for emitting photoelectrons. The photoelectric effect of the light from the filament on the clean film of distilled tungsten was easily detected, and increased with the temperature in the manner expected, but the magnitude of the photoelectric currents was of the order of one-millionth of the corresponding thermionic currents.

more, when the intensity of the radiation in question is increased enormously (as by using daylight), the reaction velocity does not show a corresponding increase.

Experiments with nitrogen peroxide, hydrogen, and iodine vapor have proved that the heat conductivity of dissociating gases is many times greater than that of similar gases which do not dissociate. The increase in heat loss from small wires, due to the dissociation of a surrounding gas, is often more than 10 times the total energy radiated from the wire. On the basis of the radiation hypothesis, however, the dissociation entails an absorption of radiation and thus could produce only a decrease in the heat lost from the filament. These experiments furnish conclusive evidence against the radiation hypothesis.

The similarity between the Arrhenius and the Wien equation thus results from the fact that both reaction velocity and radiation are fundamentally dependent upon phenomena involving probability. Both equations can be derived from the same statistical law. It is shown that the energy for the activation of molecules must be derived from *internal* energy of the molecules. This conclusion involves certain very fundamental difficulties, but it is shown that these are of the same nature as those that are encountered in the theory of the photoelectric effect, thermionic emission, and other phenomena involving quantum relations.

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THE INDEPENDENT ORIGIN OF ACTINIUM.

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Actinium has been shown[1] to be derived from Antonoff's "uranium Y,"—isotopic with uranium X_1 (and thorium)—through a long-lived intermediate variously known as uranium Z, eka-tantalum and protactinium. This element, as the second name indicates, is homologous to tantalum and is isotopic only with brevium (uranium X_2). The production of uranium Y from chemically pure uranium shows that it must be derived by an α-ray transformation from uranium or an isotope of uranium. Hahn and Meitner[2] believe that Hönigschmid's value (206.05) for the atomic weight of uranium-lead proves uranium Y to be derived from uranium II, since 3% of actinum-lead of atomic weight 210 (if uranium Y were derived from uranium I) would raise the mean to 206.12. The suggestion

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[1] Frederick Soddy and John A. Cranston, *Proc. Roy. Soc.* **94A**, 384–404 (1918); Otto Hahn and Lise Meitner, *Ber.*, **52B**, 1812–28 (1919); *Physik. Z.*, **20**, 529–33 (1919).

[2] *Loc. cit.*