XLI.—*Studies in Catalysis. Part IX. The Calculation in Absolute Measure of Velocity Constants and Equilibrium Constants in Gaseous Systems.*

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IN previous papers of this series (compare T., 1916, **109**, 796; 1917, **111**, 457), expressions have been obtained, with the aid of the radiation hypothesis, for velocity constants and equilibrium constants as functions of temperature. In the expressions thus obtained, there occur certain proportionality factors which have to be determined by direct comparison with experiment. In the present paper an attempt is made to deal with the problem in a more complete manner by calculating velocity and equilibrium constants in terms of quantities, all of which have a definite physical meaning and may be determined, theoretically, without reference to the actual rate of the chemical reaction itself.

On the basis of statistical considerations, J. Rice (*Rep. Brit. Assoc.*, 1915, 397) has deduced an expression for the reaction velocity and velocity constant in the case of a unimolecular reaction, that is, the spontaneous decomposition of a single molecule. The assumption made by Rice is that the rate of such a reaction is determined by the rate at which the molecules become active in the physical sense. Active molecules, in unimolecular processes, have therefore no real existence. When, however, we deal with multimolecular reactions, it is conceivable that active molecules exist, the rate of the observed reaction depending on the number of collisions per second which take place between active molecules of the participating substances. The concept of active molecules

was first postulated by Arrhenius, but it is only within recent years that the differentiation between active and passive molecules has attained any degree of precision through the introduction of the concept of critical energy and critical increment. The most direct evidence of an experimental kind which we possess at the present time for the existence of active molecules is that afforded by the measurements of Baly and F. O. Rice (T., 1912, **101**, 1475) in the case of the sulphonation of certain aromatic compounds. In this case, the ultimate chemical reaction is multimolecular, probably bimolecular. We may adopt therefore with some confidence the view that active molecules have a real existence in the case of multimolecular reactions. These active molecules differ from the remainder in respect of their internal energy, which is considerably greater than that possessed by an average molecule of the substance at the temperature in question. The fact that the critical energy is high means that only a very small fraction of the total molecules will be active at any moment.

In the case of a bimolecular reaction, such as the decomposition of hydrogen iodide in the gaseous state, the fractional number of hydrogen iodide molecules which exist in the active state may be calculated by the aid of the expression

$$N_a/N = e^{-E/RT} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where N_a denotes the number of active molecules, N the number of passive molecules or the total number of molecules (since N_a is very small compared with N); E is the critical increment reckoned per gram-molecule, that is, the amount of energy which one gram-molecule of the substance must absorb in order to make it reactive, and R and T have their usual significance. This expression is the familiar one obtained on the basis of statistical mechanics for the distribution of molecules in a field of force. The justification for its application to the present case is furnished by the following calculation of the velocity constant of decomposition of gaseous hydrogen iodide.

In Bodenstein's experiments (*Zeitsch. physikal. Chem.*, 1899, **29**, 295), one gram-molecule was present in $22 \cdot 4$ litres. At $556°$ abs. the observed velocity constant was $9 \cdot 42 \times 10^{-7}$, the unit of time being the minute. On expressing the time in seconds and the concentration in gram-molecules per litre, the velocity constant becomes $3 \cdot 517 \times 10^{-7}$. This number represents the fraction decomposed per second at unit concentration.

We have now to calculate the velocity constant on the basis of the concept of active molecules, the equilibrium concentration of which is assumed to be given at all stages of the observed reaction

by equation (1). From the temperature-coefficient[*] of the reaction, it is calculated that the critical increment per gram-molecule is 22,000 cals. Hence, employing equation (1), it is found that the fraction of one gram-molecule which exists in the active state at $556°$ abs. is $2\cdot218 \times 10^{-9}$. If there is one gram-molecule of hydrogen iodide present in 1 litre, then this number represents the fractional number of active molecules. Since there are $6\cdot1 \times 10^{23}$ molecules in one gram-molecule, the actual number of active molecules per litre is $1\cdot35 \times 10^{15}$, or $1\cdot35 \times 10^{12}$ per c.c.

On the kinetic theory, the number of collisions per c.c. per second between like (active) molecules is given by the expression

$$\sqrt{2} \cdot \pi \cdot \sigma^2 \cdot u \cdot N_a^2$$

where N_a is the number of active molecules per c.c., u the mean velocity of translation per molecule, and σ the distance within which two molecules approach one another during a collision. Physical theory has not yet succeeded in defining σ with precision, beyond the fact that it is of the order of magnitude of the radius or diameter of the molecule. Such being the case, we shall take a mean value, 2×10^{-8} cm., and employ this in all cases examined. Naturally, this will introduce a certain error into the results, but its magnitude will not affect the general question of the verification of the method of treatment adopted.

In the case of hydrogen iodide at $556°$ abs., $u = 3\cdot3 \times 10^4$ cm. per second. The value of N_a we have already calculated to be $1\cdot35 \times 10^{12}$ per c.c. Hence the number of collisions per c.c. per second between the active molecules is $1\cdot065 \times 10^{14}$, or the number of collisions per litre is $1\cdot065 \times 10^{17}$. At each collision between active molecules, two such molecules react. Hence the number of molecules of hydrogen iodide which react per second per litre is $2\cdot13 \times 10^{17}$. Expressing this as a fraction of one gram-molecule, we obtain $2\cdot13 \times 10^{17}/6\cdot1 \times 10^{23} = 3\cdot5 \times 10^{-7}$. This should be the velocity constant of the reaction expressed in gram-molecules per litre per second. The observed value is $3\cdot517 \times 10^{-7}$. The agreement is very satisfactory, especially in view of the possible error in σ. This calculation serves to substantiate the concept of active molecules defined in the above sense.

The foregoing calculation may be carried out in a somewhat different manner which leads directly to the differential equation expressing the reaction velocity. Thus the number of molecules which react per c.c. per second is given by:

$$2\sqrt{2}\pi\sigma^2 u N_a^2.$$

[*] This is the most direct means of obtaining the critical increment. It may also be obtained from the position of the effective absorption band in the spectrum of the substance provided the data are available.

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Hence the number of molecules which react per litre per second is given by:

$$2000 \sqrt{2} \pi \sigma^2 u N_a^2.$$

N_a is the number of active molecules per c.c. Hence the number of active molecules per litre is $1000 \ N_a$. If N_0 be the number of molecules in one gram-molecule, the number of active gram-molecules per litre is $1000 \ N_a/N_0$. If we denote this by C_a, then $N_a = N_0 C_a/1000$, or $N_a^2 = N_0^2 C_a^2/10^6$. Hence the number of molecules which react per litre per second is:

$$2000 \sqrt{2} \pi \sigma^2 u N_0^2 C_a^2/10^{-6}.$$

The number of gram-molecules which react per litre per second is $1/N_0$ of the above quantity. That is, the number of gram-molecules which react per litre per second is

$$2000 \sqrt{2} \pi \sigma^2 u N_0 C_a^2/10^6.$$

From equation (1), it follows that $C_a = C e^{-E/RT}$, where C is the total concentration or number of gram-molecules of hydrogen iodide per litre. Hence the rate of the observed reaction is given by:

$$-dC/dt = 5 \cdot 40 \times 10^{21} . \sigma^2 . u . C^2 . e^{-2E/RT}.$$

But the rate, $-dC/dt = k_{\text{obs.}} . C^2$,

where $k_{\text{obs.}}$ is the velocity constant experimentally determined. Hence, $k_{\text{obs.}}$ (in gram-molecules per litre, per second)

$$= 5 \cdot 40 \times 10^{21} . \sigma^2 . u . e^{-2E/RT} \quad . \quad . \quad . \quad . \quad (2)$$

By making use of the concept of active molecules, we can calculate the velocity constants of decomposition of hydrogen iodide over the temperature range corresponding with Bodenstein's observations. The following table contains the calculated and observed velocity constants expressed in gram-molecules per litre per second.

Decomposition of Hydrogen Iodide.

$T.$	$u \times 10^{-4}$	Fraction of one gram-molecule in the active state $= e^{-E/RT}$.	$e^{-2E/RT}$.	k calculated [equation (2)].	k observed.
$556°$	$3 \cdot 30$	$2 \cdot 218 \times 10^{-9}$	$4 \cdot 898 \times 10^{-18}$	$3 \cdot 5 \ \times 10^{-7}$	$3 \cdot 517 \times 10^{-7}$
575	$3 \cdot 356$	$2 \cdot 704 \times 10^{-9}$	$1 \cdot 820 \times 10^{-17}$	$1 \cdot 319 \times 10^{-6}$	$1 \cdot 217 \times 10^{-6}$
629	$3 \cdot 510$	$2 \cdot 244 \times 10^{-8}$	$5 \cdot 012 \times 10^{-16}$	$3 \cdot 800 \times 10^{-5}$	$3 \cdot 02 \ \times 10^{-5}$
647	$3 \cdot 559$	$3 \cdot 656 \times 10^{-8}$	$1 \cdot 318 \times 10^{-15}$	$10 \cdot 23 \ \times 10^{-5}$	$8 \cdot 587 \times 10^{-5}$
666	$3 \cdot 612$	$5 \cdot 970 \times 10^{-8}$	$3 \cdot 548 \times 10^{-15}$	$2 \cdot 768 \times 10^{-4}$	$2 \cdot 195 \times 10^{-4}$
683	$3 \cdot 657$	$8 \cdot 995 \times 10^{-8}$	$8 \cdot 128 \times 10^{-15}$	$6 \cdot 421 \times 10^{-4}$	$5 \cdot 115 \times 10^{-4}$
700	$3 \cdot 702$	$1 \cdot 337 \times 10^{-7}$	$1 \cdot 778 \times 10^{-14}$	$1 \cdot 422 \times 10^{-3}$	$1 \cdot 157 \times 10^{-3}$
716	$3 \cdot 744$	$1 \cdot 905 \times 10^{-7}$	$3 \cdot 548 \times 10^{-14}$	$2 \cdot 87 \ \times 10^{-3}$	$2 \cdot 501 \times 10^{-3}$
781	$3 \cdot 912$	$6 \cdot 918 \times 10^{-7}$	$4 \cdot 786 \times 10^{-13}$	$4 \cdot 04 \ \times 10^{-2}$	$3 \cdot 954 \times 10^{-1}$
1000	$4 \cdot 42$	$1 \cdot 545 \times 10^{-5}$	$2 \cdot 371 \times 10^{-10}$	$22 \cdot 63$	—

The agreement between the observed and calculated values is satisfactory. The number of active molecules per c.c. rises from 1.35×10^{12} at 556° abs. to 4.22×10^{14} at 781° abs. Further, it is seen that at 556° abs., when the total concentration is one gram-molecule per litre, the ratio

$$\frac{\text{number of effective collisions per c.c. per second}}{\text{total number of collisions per c.c. per second}} = \frac{1.065 \times 10^{14}}{2.18 \ \times 10^{31}}$$
$$= 4.9 \times 10^{-18}.$$

By the term effective collision is meant, of course, the number of collisions between active molecules. This ratio is seen to be an exceedingly small quantity. This quantity may be called conveniently the 'chemical efficiency' of the reaction, since it denotes the number of chemically effective collisions expressed as a fraction of the total number of collisions in the same time. This quantity, as we would expect, increases rapidly with the temperature. Thus, at 781° abs., the chemical efficiency of the reaction considered is 4.8×10^{-13}. At a very high temperature, the upper limit of the efficiency, namely, unity, should be attained theoretically. This temperature must be such that the quantity $e^{-E/RT}$ shall be unity. At 2000° abs., the value of $e^{-E/RT}$ would be 3.9×10^{-3}, and therefore the number of active molecules per c.c., when one gram-molecule is present in one litre, is 2.38×10^{18}. The chemical efficiency is therefore 1.5×10^{-5}. We conclude, therefore, that over any temperature range amenable to experiment in the above reaction the chemical efficiency will be a small quantity.

Bodenstein (*loc. cit.*) has also measured the velocity of union of hydrogen and iodine, and has shown it to be a bimolecular reaction. From the temperature-coefficient, it is easily calculated that the sum of the critical increments per gram-molecule of hydrogen and of iodine is 40,000 cals. This quantity is the analogue of the term $2E$ in the case of the bimolecular decomposition of hydrogen iodide. The quantity 40,000 cals. is made up of two terms, namely, the respective increments of hydrogen and iodine, but at the present stage we do not know each of these terms separately. This is unnecessary, however, for the immediate object in view. It may be noted that the critical increment here referred to is not the critical increment of complete dissociation of hydrogen and of iodine into the atomic state. It will be shown later that the total energy necessary to effect complete dissociation of one gram-molecule of hydrogen and the same mass of iodine is $(87,000 + 41,000)$, or 128,000 cals. The quantity, 40,000 cals., corresponds with a partial activation or polarisation of the hydrogen and iodine molecules sufficient to allow them to react on collision. The partly

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activated molecules have a real existence, the system being quite analogous to the partly activated molecules of hydrogen iodide.

On the kinetic theory, the number of collisions per second per c.c. between two unlike molecules is given by the expression :

$$\pi \cdot \sigma^2 \cdot N_1 \cdot N_2 \cdot \sqrt{u_1^2 + u_2^2},$$

where σ is the average distance to which the molecules approach during a collision, u_1 and u_2 are the mean velocities of translation of the two kinds of molecules, and N_1 and N_2 are the number of active molecules of each kind present in unit volume.   The value 2×10^{-8} is assigned to σ.   Following the same line of argument as that employed in the deduction of equation (2), we find that the bimolecular velocity, expressed in gram-molecules per litre per second, is given by :

$$-dC/dt = 3 \cdot 8 \times 10^{21} \times \sigma^2 \times \sqrt{u_1^2 + u_2^2} \times C_{H_2} \cdot C_{I_2} \cdot e^{-40,000/RT}$$

or,

$$k_{obs.} = 3 \cdot 8 \times 10^{21} \times \sigma^2 \times \sqrt{u_1^2 + u_2^2} \cdot e^{-40,000/RT} \quad . \quad . \quad (2a)$$

The following table contains the values of the velocity constants calculated by means of equation $(2a)$ and those observed by Bodenstein.

Union of Hydrogen and Iodine.

T abs.	$\sqrt{u_1^2 + u_2^2} \times 10^{-4}$	$e^{-40,000/RT}$.	k calculated by equation $(2a)$.	k observed.
556°	26·5	$1 \cdot 862 \times 10^{-16}$	$7 \cdot 39 \times 10^{-5}$	$4 \cdot 44 \times 10^{-5}$
629	28·2	$1 \cdot 23 \times 10^{-14}$	$5 \cdot 19 \times 10^{-3}$	$2 \cdot 25 \times 10^{-3}$
666	29·0	$7 \cdot 24 \times 10^{-14}$	$3 \cdot 14 \times 10^{-2}$	$1 \cdot 415 \times 10^{-2}$
700	29·7	$3 \cdot 16 \times 10^{-13}$	$14 \cdot 0 \times 10^{-2}$	$6 \cdot 42 \times 10^{-2}$
781	31·4	$6 \cdot 31 \times 10^{-12}$	2·97	1·336

The agreement between observed and calculated values is moderate.   The concordance is evidently limited mainly by the degree of approximation in the value taken for σ.   In general, the theoretical basis upon which the calculations are founded may be regarded as justified.*

Stegmüller (*Zeitsch. Elektrochem.*, 1910, **16**, 85) has measured, by an electromotive force method, the equilibrium constant of the hydrogen iodide reaction at much lower temperatures than those with which Bodenstein's measurements correspond.   By employing equations (2) and $(2a)$, it should be possible to calculate the equilibrium constant at any temperature provided the gases do not deviate seriously from the perfect gas.   The following table con-

* From the above data it is found that by setting $\sigma = 1 \cdot 34 \times 10^{-8}$ cm. the calculated and observed values of the velocity constants become nearly identical.   This value has been employed in the table dealing with Stegmüller's results.

tains the values so calculated and those obtained by Stegmüller. Stegmüller's values have been recalculated to give the equilibrium constant in the form $C_{H_2} \times C_{I_2}/C^2_{HI}$. The velocity constants are expressed in gram-molecules per litre per second.

Equilibrium Constant of the Hydrogen Iodide Reaction at Low Temperatures.

T abs.	Bimolecular velocity constant of decomposition (equation 2).	Bimolecular velocity constant of union (equa tion $2a$) ($\sigma = 1 \cdot 34 \times 10^{-8}$)	Equilibrium constant calculated.	Equilibrium constant, Stegmüller.
$304 \cdot 6°$	$1 \cdot 356 \times 10^{-21}$	$2 \cdot 51 \times 10^{-18}$	$5 \cdot 4 \times 10^{-4}$	$11 \cdot 9 \times 10^{-4}$
$328 \cdot 2$	$2 \cdot 62 \ \times 10^{-19}$	$3 \cdot 0 \ \times 10^{-16}$	$8 \cdot 7 \times 10^{-4}$	$20 \cdot 3 \times 10^{-4}$
$354 \cdot 6$	$4 \cdot 123 \times 10^{-17}$	$2 \cdot 98 \times 10^{-14}$	$14 \ \ \times 10^{-4}$	$38 \cdot 3 \times 10^{-4}$

The calculated equilibrium constants are between one-half and one-third of the observed values. Closer agreement is obtained in other reactions, considered later. As illustrated in the above table, we are able to calculate with a moderate degree of accuracy the velocity constants of the opposing reactions, quantities which, owing to their exceedingly small magnitude over the range of temperature considered, could not be determined experimentally.

So far, we have dealt with reaction velocity in gaseous systems from the point of view of molecular statistics. We have now to consider it from the point of view of the radiation hypothesis.

We have seen already that the critical increment of the bimolecular decomposition of hydrogen iodide is 22,000 cals. per gram-molecule. On the radiation hypothesis, this energy is supplied by $N_0 h\nu$ quanta, where N_0 is the number of molecules in one gram-molecule, h is Planck's constant, and ν the frequency of the effective radiation. It is easily calculated that the required frequency is $2 \cdot 33 \times 10^{14}$, or $\lambda = 1 \cdot 3 \, \mu$, in round numbers. If the above reasoning is correct, gaseous hydrogen iodide should exhibit an absorption band at this wave-length, especially if the gas be heated. The author is unaware of any experimental data bearing on this point.

On the basis of the quantum theory, Planck has considered the problem of the relation of emission to non-emission by an oscillator (compare Planck, "Theory of Heat Radiation," English trans., p. 164). According to Planck, the ratio of the probability that no emission takes place to the probability that emission does take place is proportional to the radiation density u_ν of the frequency ν. The ratio is given by the expression $p \cdot u_\nu$. The factor p is shown to be identical with the expression $c^3/8\pi h n^3 \nu^3$, where c is

the velocity of light in a vacuum and n the refractive index of the system for the frequency v. For gaseous systems, n is practically unity. It will be observed that the probability that no emission takes place is inversely as the cube of the frequency. So long as no emission takes place, the energy of the oscillator, and therefore of the whole atom or molecule containing one or more oscillators, remains high. Such a molecule will correspond with an active one in the chemical sense. It is reasonable, therefore, to apply Planck's principle to a case such as the decomposition of hydrogen iodide and write,

$$\frac{\text{the number of chemically active molecules in existence}}{\text{the number of passive molecules}} = p \cdot u_v$$

Since the number of active molecules is exceedingly small, the number of passive molecules is practically identical with the total number present, or, employing the symbols used previously,

$$Na/N = p \cdot u_v.$$

This relation expresses the fact that the higher the radiation density the greater is the number of molecules in the active state. We may also write this expression in the form:

Fraction of one gram-molecule in the active state $= pu_v$.

Further, for the short infra-red, visible and ultra-violet regions,

$$u_v = \frac{8\pi h n^3 v^3}{c^6} e^{-N_0 hv/RT},$$

Hence,

$$p \cdot u_v = e^{-N_0 hv/RT}$$

or the fraction of one gram-molecule in the active state is $e^{-Nh_0 v/RT}$ But $N_0 hv = E$, the critical increment per gram-molecule. Hence the fraction of one gram-molecule in the active state $= e^{-E/RT}$, which is the expression already obtained on the statistical mechanical basis, and verified by the experimental data. We are justified, therefore, in making the assumption that the chemically active fraction of each gram-molecule of hydrogen iodide is given by the expression $p \cdot u_v$. This should hold good for any substance which reacts in the bimolecular, or in general the multimolecular manner. It is only in such cases that active molecules have any real existence. In the case of unimolecular reactions, active molecules do not exist as such.

In a bimolecular reaction of the type considered, if C denotes the total number of gram-molecules in a given volume, say 1 litre, then the number of active gram-molecules in the same volume may be expressed by

$$C \cdot p \cdot u_v \text{ or } C \cdot e^{-N_0 hv/RT} \text{ or } C \cdot e^{-E/RT}$$

On the purely kinetic basis, we have seen that the rate of reaction between like molecules in a bimolecular reaction per litre per second is :

$$-dC/dt = 5\cdot4 \times 10^{21} \cdot \sigma^2 \cdot u \cdot C^2 e^{-2E/RT}.$$

The term $C^2 \cdot e^{-2E/RT}$ is evidently identical with $C^2 \cdot p^2 \cdot u_\nu{}^2$, so that the rate of reaction may be written,

$$-dC/dt = 5\cdot4 \times 10^{21} \cdot \sigma^2 \cdot u \cdot p^2 \cdot C^2 \cdot u_\nu{}^2.$$

That is, the rate of the observed bimolecular reaction depends on the square of the radiation density, a conclusion which is in agreement with the assumption made in earlier papers in connexion with bimolecular reactions. The advantage of the present mode of treatment is, however, that all the factors which go to make up the observed velocity constant are calculable quantities. It is evident that the observed velocity constant, expressed in gram-molecules per litre per second, for a bimolecular reaction involving like molecules is given by :

$$k_{\text{obs.}} = 5\cdot4 \times 10^{21} \cdot \sigma^2 \cdot u \cdot p^2 \cdot u_\nu{}^2,$$

or

$$k_{\text{obs.}} = 5\cdot4 \times 10^{21} \cdot \sigma^2 \cdot u \cdot e^{-2N_0 h\nu/RT}.$$

It is obvious that differentiation of this expression with respect to temperature yields the well-known Arrhenius equation as a first approximation.

In a bimolecular reaction such as that considered, the function of the radiation of the absorbable type is to maintain a certain number of molecules in the chemically active state, a state which means high energy content. The number of active molecules at any moment is the difference between their rate of production and their rate of disappearance. Their rate of disappearance is due to retransformation of some into the passive state, and at the same time the transformation of others in the ordinary chemical sense into the resultants. It is simply the number of active gram-molecules *in existence* at any moment which has been written as $C \cdot p \cdot u_\nu$. The actual rate of production of active molecules per second is a quantity necessarily much greater than this. An attempt will now be made to estimate this rate.

In the case of hydrogen iodide at a concentration of one gram-molecule per litre at 556° abs., we have seen that the number of active molecules maintained by the radiation in the active state per litre is $1\cdot35 \times 10^{15}$. The number of active molecules which react per second per litre is $2\cdot13 \times 10^{17}$. If we denote by R_1 the rate of production of active molecules per second per litre, by R_2 the rate of chemical reaction $(2\cdot13 \times 10^{17})$, and by R_3 the rate at

which active molecules are retransformed into passive molecules per litre per second, we have the relation :

$$R_1 - (R_2 + R_3) = 1 \cdot 35 \times 10^{15}.$$

In order to maintain the active molecules and allow for the rate of the observed reaction, the minimum rate of production of active from passive molecules is $> 2 \cdot 13 \times 10^{17}$. The true rate may, however, be much greater than this lower limit. It is evident that the rate of production of active molecules must depend on the radiation density u_ν, but it is evident the rate is not given by the expression $N_0 \cdot p \cdot u_\nu$, for this would only account for a production of $1 \cdot 35 \times 10^{15}$ active molecules per second from one gram-molecule. A quantity having a higher numerical value than $N_0 \cdot p \cdot u_\nu$ is required. The terms N_0 and u_ν would be expected to remain unaltered, and we are limited to some function of p. It will be shown later, in connexion with the dissociation of iodine, bromine, and chlorine, that the experimental values can be accounted for if we assume provisionally that the required function is $10^3 p^2$.* With this assumption, the rate of production of active molecules from one gram-molecule is $N_0 \cdot 10^3 \cdot p^2 \cdot u_\nu$. Since u_ν itself can be written as $\dfrac{1}{p} e^{-N_0 h\nu/RT}$, our assumption means that the rate of production of active molecules is given by $10^3 \cdot N_0 \cdot p e^{-N_0 h\nu/RT}$, or $10^3 \cdot N_0 \cdot p \cdot e^{-E/RT}$. This expression should be the correct one for any spontaneous unimolecular reaction, for in such a case the process of activation is identical with the chemical reaction. That is, the velocity constant of a unimolecular reaction should be given by :

$$k_{\text{obs.}} = 10^3 \cdot p \cdot e^{-E/RT}$$

We shall now apply this expression to the calculation of the rate of production of active molecules of hydrogen iodide. The term p is given by $c^3/8\pi h n^3 \nu^3$, and since, for the process considered, $E = N_0 h\nu = 22{,}000$ cals. per gram-molecule, the frequency ν must be $2 \cdot 33 \times 10^{14}$. Further, the system is gaseous, and therefore the refractive index is practically unity. Hence $p = 1 \cdot 307 \times 10^{13}$. Hence the number of active molecules produced per second from one gram-molecule of hydrogen iodide at $556°$ abs. $= 6 \cdot 1 \times 10^{23} \times 1 \cdot 307 \times 10^{13} \times 2 \cdot 218 \times 10^{-9} = 1 \cdot 768 \times 10^{28}$. If we divide this number by $6 \cdot 1 \times 10^{23}$, we obtain the fraction of one gram-molecule activated per second. A rate of this magnitude is quite possible in the sense that it is sufficient to account for the observed rate of the

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* This function will be dealt with in a later paper, in which an alternative expression, having a similar numerical value, but possessing a more precise physical significance, will be given.

bimolecular reaction, and likewise for the maintenance of the free active molecules. Since the rate of production of active molecules is considerably greater than the sum of the two effects just mentioned, it follows that the rate at which active molecules are re-transformed into passive is likewise of the order 10^{28}. ·If these extremely high opposing velocities exist, we are led to the conclusion that the equilibrium between active and passive molecules is attained practically instantaneously. This is in agreement with experience, but, of course, such evidence is very inconclusive. Quantitative evidence is furnished by the calculation of the equilibrium constant in the case of the dissociation of iodine, bromine, and chlorine. This will be considered later.

Whilst the ordinary thermal decomposition of hydrogen iodide is a bimolecular process, Bodenstein has shown (*Zeitsch. physikal. Chem.*, 1907, **61**, 447) that the photochemical decomposition is unimolecular. In this case, the process is the decomposition of hydrogen iodide molecules into atoms of hydrogen and iodine. This is effected by short waves. That is, the process of completely decomposing the hydrogen iodide molecule is a much more difficult one to carry out and requires a greater size of quantum than is required simply to displace the atoms somewhat with respect to one another inside the hydrogen iodide molecule, thereby permitting the bimolecular process to take place. In Bodenstein's experiments on the photochemical decomposition, the hydrogen iodide was exposed to bright sunlight in glass vessels. Berthelot and Gaudechon (*Compt. rend.*, 1913, **156**, 889) find that hydrogen iodide is decomposed by blue or violet light. More precise knowledge is wanting, but it is evident that the active wave-length is of the order $450 \mu\mu$, or $\nu = 6\cdot66 \times 10^{14}$. That is, the critical increment E' per gram-molecule of hydrogen iodide for the unimolecular decomposition is 63,000 cals. in round numbers. It will be shown later that a more exact value for this quantity is 66,000 cals. This is just three times the increment for the bimolecular reaction. The bimolecular reaction takes place, therefore, more readily, since a molecule will oftener possess the energy corresponding with E than the energy corresponding with E'. This unimolecular process must take place, however, as a thermal effect along with the bimolecular process, for, at any temperature, the radiation density, even at $\nu = 7\cdot0 \times 10^{14}$, cannot be entirely wanting. Since, however, the radiation density diminishes rapidly as the frequency increases from the short infra-red into the ultra-violet, the unimolecular reaction, compared with the bimolecular, will remain negligible until very high temperatures are reached. On the basis of the considerations already developed, it is quite possible to calculate what this uni-

molecular decomposition velocity amounts to at any temperature. Thus, the rate of unimolecular decomposition of hydrogen iodide per gram-molecule is given by $10^3 . N_0 . p . e^{-66,000/RT}$, where $p = 4.66 \times 10^{11}$. At 556° abs., this rate should be 3.12×10^{12} molecules per second when one gram-molecule is present initially. Hence the unimolecular velocity constant $= 10^3 . p . e^{-66,000/RT}$ is 5.1×10^{-12}. It will be observed that this is a small quantity compared with the bimolecular velocity constant (3.5×10^{-7}) under the same conditions. At 781° abs., the unimolecular velocity constant is 1.54×10^{-4}, whilst the bimolecular constant is 4.0×10^{-2}. The conclusion that the unimolecular decomposition is small compared with the bimolecular over the range examined by Bodenstein (556—781° abs.) is in agreement with the fact that the bimolecular formula holds good. We can easily calculate the bimolecular constant at 1000° abs. by the methods already employed at lower temperatures, the value obtained being 22·63. At the same temperature, the unimolecular velocity constant is calculated to be 1·73. At 1200° abs., the unimolecular constant is 435, whilst the bimolecular is 998. It is evident, therefore, that at a temperature somewhat above 1200° abs., the two types of decomposition will occur at the same rate. At this temperature, therefore, the bimolecular formula would be expected to break down.

We now turn to the consideration of unimolecular dissociation, such as that of iodine in the gaseous state into atoms. From the known behaviour of nascent atoms, it may be inferred that their normal state in respect of energy content is sensibly identical with the critical state, so that the exponential term in equation (2) containing the critical increment reduces to unity. Let C_u denote the equilibrium concentration of undissociated molecules of iodine expressed in gram-molecules per litre, and C_i the equilibrium concentration of the iodine atoms in the same units. The rate at which the molecular species dissociates is then given by $C_u . 10^3 . p . e^{-N_0 h\nu/RT}$ or $C_u . 10^3 . p . e^{-E/RT}$. In an earlier paper (T., 1917, **111**, 1086), the value 41,000 cals., per gram-molecule, has been assigned to the critical increment of iodine. The corresponding frequency ν is 4.3×10^{14}, or $\lambda = 700 \ \mu\mu$. Hence $p = c^3/8\pi h\nu^3 = 2.08 \times 10^{12}$. At $T = 1073$ ($t° = 800°$), the term $e^{-E/RT} = 4.385 \times 10^{-9}$. Hence the rate of dissociation, expressed in gram-molecules per litre per second, is $C_u \times 10^3 \times 2.08 \times 10^{12} \times 4.385 \times 10^{-9} = 9.16 \times 10^6 C_u$. The number 9.16×10^6 is the unimolecular velocity constant of dissociation. The rate at which the atoms combine is given by the total collision frequency, for in the case considered, the atoms are all active and every collision is effective. Since there are C_i gram-atoms per litre, the actual number of atoms per c.c. is

$C_i \times 6 \cdot 1 \times 10^{20}$.   The collision frequency per c.c. per second is $\sqrt{2} \cdot \pi \cdot u \cdot \sigma^2 \cdot C_i^2 \times 37 \cdot 2 \times 10^{40}$.   The average velocity of translation u of one iodine atom at $1073°$ abs. is $4 \cdot 6 \times 10^4$ cm. per second. Taking σ as 2×10^{-8} cm., the number of collisions per c.c. per second is $3 \cdot 031 \times 10^{31} \cdot C_i^2$.   The number of atoms which combine is just twice this quantity, namely, $6 \cdot 062 \times 10^{31} \cdot C_i^2$.   Hence the number of *gram*-atoms which combine per second per litre is $9 \cdot 94 \times 10^{10} \cdot C_i^2$.   Alternatively, using equation (2) and writing the exponential term as unity, we arrive at the same result.   It follows that $C_i^2/C_u = 9 \cdot 16 \times 10^6 / 9 \cdot 94 \times 10^{10} = 9 \cdot 2 \times 10^{-5}$.   Bodenstein and Starck (*Zeitsch. Elektrochem.*, 1910, **16**, 961) have measured the equilibrium constant, C_i^2/C_u, at $1073°$ abs., with the concentration expressed in gram-molecules per litre, the value obtained being $1 \cdot 29 \times 10^{-4}$.   The calculated equilibrium constant agrees well with the observed value.   Again, consider the dissociation at $1473°$ abs.   The value of $e^{-E/RT}$ is $8 \cdot 166 \times 10^{-7}$.   Hence the rate of dissociation in gram-molecules per second is

$$2 \cdot 08 \times 10^{15} \times 8 \cdot 166 \times 10^{-7} \, C_u.$$

From equation (2), taking σ as 2×10^{-8} and $u = 5 \cdot 38 \times 10^4$, we get for the rate of union of the atoms, expressed in gram-atoms per litre per second, the value $1 \cdot 14 \times 10^{11} \times C_i^2$.   Hence

$$C_i^2/C_u = 1 \cdot 699 \times 10^9 / 1 \cdot 14 \times 10^{11} = 1 \cdot 49 \times 10^{-2}.$$

The observed equilibrium constant is $1 \cdot 02 \times 10^{-2}$.

The foregoing considerations, which are based partly on molecular statistics and partly on the quantum theory of radiation, allow us to calculate with a moderate degree of precision not only the equilibrium constant of a dissociation of a molecule into atoms (a quantity which is amenable in general to experimental determination), but likewise the separate velocity constants which, owing to their great magnitude, cannot be measured directly.   The table on p. 484 contains the values of the equilibrium constants and the velocity constants in the above units for the dissociation of iodine over the range of temperature investigated by Bodenstein and Starck.

The agreement between the calculated and observed equilibrium constants is satisfactory.   This affords considerable support for the assumptions made as regards the velocity constants.   It may be pointed out that the term $e^{-E/RT}$ in this case does *not* represent the number of the active molecules of molecular iodine.   No active molecules exist apart from the atoms.   The conditions obtaining are quite distinct from those met with in the case of the bimolecular decomposition of hydrogen iodide.

Bodenstein (*Zeitsch. Elektrochem.*, 1916, **22**, 327) has measured

Dissociation of Iodine.

$t°$.	T abs.	$e^{-E/RT}$.	Mean velocity of translation of an iodine atom in cm. per sec. $\times 10^{-4}$.	Unimolecular velocity constant of dissociation.	Bimolecular velocity constant of recombination.	Equilibrium constant (calculated).	Equilibrium constant (observed).
800	1,073°	$4 \cdot 385 \times 10^{-9}$	4·6	$9 \cdot 16 \times 10^{6}$	$9 \cdot 94 \times 10^{10}$	$9 \cdot 2 \ \times 10^{-5}$	$1 \cdot 29 \times 10^{-4}$
900	1,173	$2 \cdot 265 \times 10^{-8}$	4·83	$4 \cdot 71 \times 10^{7}$	$1 \cdot 04 \times 10^{11}$	$4 \cdot 5 \ \times 10^{-4}$	$4 \cdot 92 \times 10^{-4}$
1,000	1,273·	$8 \cdot 995 \times 10^{-8}$	5·058	$1 \cdot 87 \times 10^{8}$	$1 \cdot 08 \times 10^{11}$	$1 \cdot 7 \ \times 10^{-3}$	$1 \cdot 58 \times 10^{-3}$
1,100	1,373	$2 \cdot 944 \times 10^{-7}$	5·24	$6 \cdot 12 \times 10^{8}$	$1 \cdot 13 \times 10^{11}$	$5 \cdot 4 \ \times 10^{-3}$	$4 \cdot 37 \times 10^{-3}$
1,200	1,473	$8 \cdot 166 \times 10^{-7}$	5·38	$1 \cdot 69 \times 10^{9}$	$1 \cdot 14 \times 10^{11}$	$1 \cdot 49 \times 10^{-2}$	$1 \cdot 02 \times 10^{-2}$

the dissociation constant of gaseous bromine between 800° and 1200°. He finds that the equilibrium constant, expressed in partial pressure terms, is given by the expression:

$$\log K_p = -10100/T + 1\cdot75 \log T - 0\cdot000409T + 4\cdot726 \times 10^{-8}T^2 + 0\cdot548.$$

Further details are not given in the abstract, which alone is available. At 1000° abs., this expression gives $\log K_p = \bar{5}\cdot336$, whence the equilibrium constant K_c, expressed in gram-molecules per litre, is $2\cdot64 \times 10^{-7}$.

An attempt will now be made to calculate this equilibrium constant. The critical increment E per gram-molecule of bromine is not known with accuracy (compare T., 1917, **111**, 1086). It may be taken to be of the order 50,000 cals. The corresponding frequency $\nu = 5\cdot3 \times 10^{14}$. Hence $p = 1\cdot1 \times 10^{12}$ and

$$e^{-E/RT} = 1\cdot175 \times 10^{-11}.$$

At the equilibrium point, the rate of dissociation of the bromine molecules is $10^3 \cdot p \cdot C_u \ e^{-E/RT} = 10^3 \times 1\cdot1 \times 10^{12} \times 1\cdot175 \times 10^{-11} \times C_u = 1\cdot29 \times 10^4 C_u$, where $1\cdot29 \times 10^4$ is the calculated unimolecular velocity constant of decomposition and C_u is the number of gram-molecules per litre. In dealing with the union of the atoms, we shall again make the assumption that the atoms are all active. At 1000° abs., the average speed u of a bromine atom is $5\cdot6 \times 10^4$ cm. per second. Setting $\sigma = 2\cdot0 \times 10^{-8}$ cm., and employing equation (2), we obtain for the rate of union of the atoms per second per litre the value $1\cdot21 \times 10^{11}C_i^2$, where the numerical coefficient is the bimolecular velocity constant. The equilibrium constant is therefore given by $C_i^2/C_u = 1\cdot29 \times 10^4/1\cdot21 \times 10^{11} = 1\cdot0 \times 10^{-7}$. This agrees satisfactorily with the observed value when we consider the possible error in σ and in E.*

The dissociation of chlorine has been measured by Pier (*Zeitsch. physikal. Chem.*, 1908, **62**, 417), but the values appear to be much less accurate than those of Bodenstein in the case of bromine and iodine. Thus, the heat of the reaction when calculated from successive values of the equilibrium constant varies in quite an unexpected manner with the temperature. As the possibility of error seems to be less in the higher temperature range, we shall restrict ourselves to this region. Thus, at 1940° abs., the observed degree of dissociation of chlorine is $0\cdot0157$, the pressure being $0\cdot5$ atmosphere. Hence $K_c = x^2/(1-x)V = 7\cdot8 \times 10^{-7}$. The critical increment of chlorine is taken to be 86,000 cals. per gram-molecule

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[1] In the paper referred to, E for bromine was taken to be 57,000 cals. per gram molecule. Employing the value 50,000 cals., the calculated heat of formation of potassium bromide is in rather better agreement, and the heat of formation of silver bromide in rather worse agreement with the corresponding observed value than are the numbers given in the former paper.

(compare T., 1917, **111**, 1086). Hence at 1940° abs., $e^{-E/RT} = 2 \cdot 014 \times 10^{-10}$. The frequency $\nu = 9 \cdot 1 \times 10^{14}$. Hence $p = 2 \cdot 2 \times 10^{11}$. At the equilibrium point, the rate of dissociation of chlorine is consequently $4 \cdot 43 \times 10^4 C_u$, where $4 \cdot 43 \times 10^4$ is the unimolecular velocity constant expressed in gram-molecules per second. The average speed u of a chlorine atom at 1940° abs. is $8 \cdot 3 \times 10^4$ cm. per second. Taking σ as $2 \cdot 0 \times 10^{-8}$ cm., and using equation (2), we obtain, for the rate of union of the atoms, $1 \cdot 793 \times 10^{11} C_i^2$, the velocity constant being expressed in gram-molecules per litre per second. Hence the equilibrium constant, C_i^2/C_u should be $4 \cdot 43 \times 10^4/1 \cdot 793 \times 10^{11}$, or $2 \cdot 47 \times 10^{-7}$. It will be seen that the calculated and observed values of the equilibrium constant are of the same order of magnitude. The results obtained in the case of the three halogens, iodine, bromine, and chlorine, afford a considerable amount of evidence in favour of the theoretical treatment employed.

In the type of reaction just considered, namely, the dissociation of a molecule into atoms in the gaseous state, the position of equilibrium is given by the relation:

$$10^3 \cdot p \cdot e^{-E/RT} \cdot C_u = 5 \cdot 40 \times 10^{21} \cdot \sigma^2 \cdot u \cdot C_i^2 \quad . \quad . \quad (3)$$

or

$$K = C_i^2/C_u = \frac{10^3 p \cdot e^{-E/RT}}{5 \cdot 40 \times 10^{21} \cdot \sigma^2 \cdot u}$$

where the concentration is expressed in gram-molecules per litre. In a gaseous system p may be written as $1 \cdot 6 \times 10^{56}/\nu^3$, where ν is the frequency of the radiation responsible for the dissociation process. For a given substance, ν is a constant independent of temperature so long as the mechanism of the process remains the same. We can write the above expression in the form:

$$\log K = -E/RT - \log u + \log 10^3 \cdot p/5.40 \times 10^{21} \times \sigma^2.$$

The final term on the right-hand side is analogous to the integration constant which occurs in the thermodynamic treatment of mass-action equilibrium. In the present case, however, the final term is calculable quite apart from the reaction itself. On differentiating the above expression with respect to temperature, we obtain:

$$d \log K/dT = E/RT^2 - d \log u/dT.$$

The mean velocity of translation of an atom (which has been taken as practically identical with the root-mean-square-velocity) is proportional to the square root of the absolute temperature, u being given by the expression $\sqrt{3RT/M}$, where M is the gram-molecular weight of the atom. Hence

$$d \log K/dT = (E - 1/2 \cdot RT)/RT^2.$$

The term $(1/2)RT$ is, in general, small compared with E, and therefore the critical increment in the case of reactions of the above type is practically identical with the heat of dissociation at constant volume. This is the assumption which has been made in the foregoing treatment. If $-Q_v$ denotes the heat absorbed at constant volume per gram-molecule dissociated, we obtain the van't Hoff isochore from the above expression. For the type of reaction considered, the exact relation between the critical increment and the heat of the reaction is given by:

$$-Q_v = E - 1/2 \cdot RT \quad . \quad . \quad . \quad . \quad . \quad (4)$$

We are now in a position to deal with the dissociation of hydrogen. Langmuir (*J. Amer. Chem. Soc.*, 1915, **37**, 417) finds that the heat of dissociation at constant volume at $3000°$ abs. is 84,000 cals. per gram-molecule. Hence, from equation (4), we obtain 87,000 cals. as the critical increment per gram-molecule of hydrogen. The corresponding frequency is $9\cdot21 \times 10^{14}$, or $\lambda = 325 \ \mu\mu$. Hence $p = 2\cdot04 \times 10^{11}$. At $2000°$ abs., $e^{-E/RT} = 3\cdot055 \times 10^{-10}$. Hence the rate of dissociation $= 10^3 \cdot p \cdot e^{-E/RT} \cdot C_u = 6\cdot23 \times 10^4 C_u$. At $2000°$ abs., u for one hydrogen atom is $7\cdot1 \times 10^5$ cm. per second. Taking $\sigma = 2 \times 10^{-8}$ cm., and using equation (2), the rate of union of hydrogen atoms, assuming all the atoms active, is $1\cdot53 \times 10^{12} C_i^2$, the velocity constant being expressed in gram-atoms per litre per second. Hence the equilibrium constant is $4\cdot07 \times 10^{-8}$. The degree of dissociation of hydrogen as determined by Langmuir is $0\cdot0033$ at $2000°$ abs. and under one atmosphere's pressure. Hence Langmuir's equilibrium constant, expressed in concentration terms, is $6\cdot6 \times 10^{-8}$. This agrees fairly well with the calculated value. The main cause of the discrepancy is probably the fact that in the case of the hydrogen atom, σ is less than 2×10^{-8} cm. If we set $\sigma = 1\cdot57 \times 10^{-7}$ cm., the two values of the equilibrium constant become identical. This value of is used in the following table, which contains the values of K obtained by Langmuir and those obtained by the above method of calculation.

Dissociation of Hydrogen.

T abs.	u in cm. per sec. $\times 10^{-5}$	Unimolecular velocity constant of dissociation.	Bimolecular velocity constant of union.	Equilibrium constant, calculated.	Equilibrium constant, Langmuir.
$1,500°$	$6\cdot15$	$41\cdot66$	$8\cdot2 \ \times 10^{11}$	$5\cdot1 \times 10^{-11}$	$4\cdot6 \times 10^{-11}$
$2,000$	$7\cdot1$	$6\cdot23 \times 10^4$	$9\cdot4 \ \times 10^{11}$	$[6\cdot6 \times 10^{-8}]$	$6\cdot6 \times 10^{-8}$
$2,500$	$7\cdot95$	$4\cdot98 \times 10^6$	$1\cdot1 \ \times 10^{12}$	$4\cdot7 \times 10^{-6}$	$5\cdot1 \times 10^{-6}$
$3,000$	$8\cdot66$	$9\cdot26 \times 10^7$	$1\cdot2 \ \times 10^{12}$	$8\cdot0 \times 10^{-5}$	$7\cdot0 \times 10^{-5}$
$3,500$	$9\cdot37$	$7\cdot46 \times 10^8$	$1\cdot3 \ \times 10^{12}$	$6\cdot0 \times 10^{-4}$	$6\cdot1 \times 10^{-4}$
$4,000$	$10\cdot0$	$3\cdot58 \times 10^9$	$1\cdot33 \times 10^{12}$	$2\cdot7 \times 10^{-3}$	$2\cdot9 \times 10^{-3}$

The agreement throughout is satisfactory.   It should be observed, however, that both series of K values are dependent on the numerical value for the heat effect, namely, 84,000 cals. at constant volume.   This quantity has been verified approximately by Isnardi (*Zeitsch. Elektrochem.*, 1915, **21**, 405).

The following considerations also afford some support in favour of Langmuir's value for Q_v.   We have seen that when hydrogen iodide decomposes in the *uni*molecular manner, the critical increment E' is approximately 63,000 cals. per gram-molecule.   Let us suppose that two gram-molecules decompose in this manner, not in the ordinary bimolecular manner.   That is, we have the reactions :

$$2HI \longrightarrow 2H + 2I \longrightarrow H_2 + I_2.$$
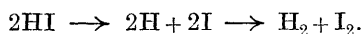
This will be referred to as the ' atomic ' process.   Although this is formally the same as the ordinary bimolecular process, the actual mechanism, involving as it does the formation of free atoms, is different, for in the bimolecular process we deal only with a polarisation or partial activation of each of the molecules H_2, I_2, and HI, a process which requires much less energy to reach the respective critical states than is required for the actual dissociation of each molecular species into atoms.   Every chemical process, occurring spontaneously, follows the path of least resistance, that is, the path involving minimal critical increments.   Hence the atomic process referred to is not the naturally occurring one. Since, however, the chemical change as a whole is the same in the two cases, the total heat effect must be the same.   The heat absorbed when two gram-molecules of hydrogen iodide decompose is 4000 cals. approximately.   Applying the expression developed and tested in former papers, namely,

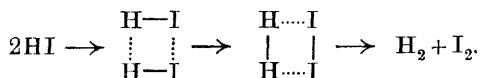$$\text{heat evolved} = (E_{\text{resultants}} - E_{\text{reactants}}),$$

to the above atomic process, we obtain :

$$4000 = E_{H_2} + E_{I_2} - 2E'_{HI}.$$

The symbol E_{I_2}, which is the critical increment of dissociation of iodine into its atoms, has the value 41,000 cals. per gram-molecule. $2 \times E'_{HI} = 2 \times 63,000$ cals.   Hence the quantity E_{H_2}, which denotes the critical increment of dissociation of one gram-molecule of hydrogen into its atoms, has the value 81,000 cals.   This should be sensibly identical with the heat absorbed in the dissociation of hydrogen.   It is seen to be in fair agreement with Langmuir's value.   The source of the discrepancy is due mainly to error in the value of E'_{HI}, which we have taken to be 63,000 cals. per gram-molecule on the basis of the rather qualitative statement

made by Berthelot and Gaudechon that hydrogen iodide is decomposed by blue or violet light. If we take the critical increment of hydrogen, in respect of dissociation into atoms, to be 87,000 cals. per gram-molecule (the value which has been employed in the compilation of the above table), it follows from a consideration of the atomic process of the decomposition of hydrogen iodide that E'_{HI} should be 66,000 cals., this being the quantity required to dissociate one gram-molecule of the substance into free atoms of hydrogen and iodine. From what has been said, this may be regarded as a more exact value of the critical increment of unimolecular decomposition than the value 63,000 cals. Certain conclusions have been drawn from this as regards the relative speeds of the unimolecular and bimolecular decompositions of hydrogen iodide in an earlier part of this paper. A further conclusion is that gaseous hydrogen iodide, when heated, should exhibit an absorption band in the region of $\nu = 7 \times 10^{14}$, or $\lambda = 429\,\mu\mu$. The author is unaware of any measurements in this connexion.

The decomposition of hydrogen iodide is particularly interesting, because it is one that is capable of occurring in two distinct ways, namely, the unimolecular and the bimolecular, and, if the previous considerations be accepted, we have fairly complete information regarding the mechanism of both. In the case of the ordinary bimolecular decomposition of hydrogen iodide, the critical increment E per gram-molecule is 22,000 cals. This is just one-third of the critical increment E', 66,000 cals., which is required for the complete dissociation of the molecule into free atoms. The ordinary bimolecular process occurs, therefore, with much greater ease, that is, at lower temperatures, than does the unimolecular process. The bimolecular process involves, therefore, a certain separation or polarisation of the atoms in the molecule, but not their complete separation. The bimolecular process may be represented in the following manner, in which an additive compound is formed :

$$2HI \longrightarrow \begin{array}{c} H\!-\!I \\ \vdots \quad \vdots \\ H\!-\!I \end{array} \longrightarrow \begin{array}{c} H\cdots I \\ |\quad | \\ H\cdots I \end{array} \longrightarrow H_2 + I_2.$$

The total amount of energy required to activate two gram-molecules of hydrogen iodide in this manner is 44,000 cals.

In conclusion, we may collect together the various numerical values for the critical increments of the substances dealt with in the present paper.

Substance (gaseous).	Critical increment in cals. per gram-molecule.	Reaction involving the critical increment of the previous column.
Hydrogen iodide	22,000	$2HI \rightarrow H_2 + I_2$ ordinary bimolecular reaction.
Hydrogen iodide	66,000	$HI \rightarrow H + I$ unimolecular reaction, identical with the photochemical decomposition.
Hydrogen	87,000	$H_2 \rightarrow 2H$.
Iodine	41,000	$I_2 \rightarrow 2I$.
Bromine	50 000	$Br_2 \rightarrow 2Br$.
Chlorine	86,000	$Cl_2 \rightarrow 2Cl$.

Summary.

(1) The observed rate of a unimolecular reaction is identical with the rate at which the molecules pass from the passive to the active state per second. The active state differs from the passive in respect of internal energy. The activation is ascribed to the radiation density of the absorbable radiation. In unimolecular reactions, active molecules have no real existence. They are, in fact, the resultants of the reaction. The critical increment E, that is, the quantity of energy which must be added to an average gram-molecule to raise its energy content to the critical state, is given by the expression $N_0 h\nu$, where h is Planck's constant, ν the frequency of the absorbable radiation, and N_0 the number of molecules in one gram-molecule. This statement is simply Einstein's law of the photochemical equivalent.

If the concentration of the decomposing substance is C, the provisional expression for the rate of decomposition in a unimolecular process is :
$$-dC/dt = 10^3 \cdot p \cdot C \cdot e^{-E/RT},$$

where $p = c^3/8\pi h n^3 \nu^3$, c being the velocity of light in a vacuum and n the refractive index of the system for the frequency ν. In the case of gaseous systems, $n = 1$ very nearly, and $p = 1 \cdot 6 \times 10^{56}/\nu^3$. It follows that the observed velocity constant of a unimolecular process is given by :
$$k_{obs.} = 10^3 p \cdot e^{-E/RT}.$$

Alternatively, the rate of unimolecular decomposition is given by :
$$-dC/dt = 10^3 \cdot p^2 \cdot Cu_\nu,$$
where u is the radiation density of the effective frequency ν, the radiation density being determined by the temperature of the system.

(2) The rate of a bimolecular reaction is identical with the

number of collisions which occur per second between the active molecules. As already pointed out in the case of *uni*molecular reactions, active molecules have no real existence. In bimolecular and multimolecular reactions generally, active molecules exist, their rate of formation being very much greater than their rate of collision, which latter term defines the observed rate of reaction. The number of active molecules in existence at any moment is proportional to the radiation density. In multimolecular reactions, the fraction of one gram-molecule existing in the active state is given on the basis of molecular statistics by the expression $e^{-E/RT}$, where E is the critical increment per gram-molecule. The fraction of one gram-molecule existing in the active state is given on the radiation basis by pu_ν, which is identical with $e^{-N_0 h\nu/RT}$ and therefore with $e^{-E/RT}$. If C is the total concentration in gram-molecules per litre, the number of active gram-molecules per litre is $C \cdot e^{-E/RT}$. The number of "effective" collisions which occur in a gaseous system between like molecules (such as molecules of hydrogen iodide) per c.c. per second is given on the molecular kinetic theory by the expression,

$$\sqrt{2} \cdot \pi \cdot u \cdot \sigma^2 \cdot (\text{number of active molecules per c.c.})^2,$$

where u is the average velocity of translation of a molecule at the temperature considered and σ is the range of approach of two molecules during a collision. At each collision between active molecules, two molecules react. Hence the rate of reaction in a bimolecular process between like molecules occurring in the gaseous state is given by:

$$- dC/dt = 5 \cdot 40 \times 10^{21} \cdot u \cdot \sigma^2 \cdot C^2 \cdot e^{-E/RT}.$$

Alternatively, since $e^{-2E/RT} = p^2 \cdot u_\nu{}^2$, the rate of reaction may be written:

$$- dC/dt = 5 \cdot 10 \times 10^{21} \times u \times \sigma^2 \times p^2 \times u_\nu{}^2 \times C^2.$$

The observed bimolecular velocity constant, for a reaction between molecules of the same kind (expressed in gram-molecules per litre per second), is given by:

$$k_{\text{obs.}} = 5 \cdot 40 \times 10^{21} \cdot u \cdot \sigma^2 \cdot e^{-2E/RT}$$

or

$$k_{\text{obs.}} = 5 \cdot 40 \times 10^{21} \cdot u \cdot \sigma^2 \cdot p^2 \cdot u_\nu{}^2.$$

If the reaction occurs between molecules of different kinds, for example, the union of hydrogen and iodine, the velocity constant is given by:

$$k_{\text{obs.}} = 3 \cdot 8 \times 10^{21} \cdot \sigma^2 \cdot \sqrt{u_1{}^2 + u^2{}_2} \cdot e^{-(E_1 + E_2)/RT}.$$

where u_1 and u_2 are the average velocities of translation of the two kinds of molecules, E_1 is the critical increment of the one kind (per gram-molecule), and E_2 is the corresponding quantity for the other kind. When the bimolecular reaction occurs between nascent atoms, all the reactants are normally in the reactive state, and therefore the exponential term reduces to unity. In such a case, for example, the combination of atoms to form the undissociated molecule of a gas, the bimolecular velocity constant is given by the expression:

$$k = 5{\cdot}40 \times 10^{21} . u . \sigma^2.$$

(3) The various statements made in (1) and (2) are borne out quantitatively in the cases examined, namely, the decomposition of hydrogen iodide (bimolecular reaction), the union of hydrogen and iodine molecules, and the dissociation of iodine, bromine, chlorine, and hydrogen gases. It is shown that the opposing velocity constants, as well as the equilibrium constants, can be calculated in regions in which, owing to the rate being either extremely great or extremely small, the chemical change cannot be determined experimentally.

(4) The velocity constant of *uni*molecular decomposition of gaseous hydrogen iodide has been calculated at various temperatures, and is shown to be negligible compared with the bimolecular constant over the range of temperature examined by Bodenstein. In the neighbourhood of $1200°$ abs., it is calculated that the two velocity constants should be of the same order of magnitude, and therefore the ordinary bimolecular expression should fail to apply quantitatively.

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