From the great tendency of urea to form complexes with acids, bases and salts,[1] it is possible that an ammonium-urea complex, having an ionization constants less than that of ammonium hydroxide was formed.

WORCESTER, MASS.

STATISTICAL MECHANICS APPLIED TO CHEMICAL KINETICS.

BY RICHARD C. TOLMAN.
Received September 13, 1920.

I. Introduction.

The rate at which chemical reactions take place has long been one of the most important and most baffling of the problems of theoretical chemistry. The principles of thermodynamics provide a theoretical basis for predicting just which chemical reactions can take place, namely, those accompanied by an increase in entropy, and for predicting just how far they will proceed until equilibrium is attained. Thermodynamics, however, has been powerless to provide information as to the rate at which the thermodynamically possible reactions will actually proceed. Indeed chemical reactions which are accompanied by very large increases in entropy, such, for example, as the union of hydrogen and oxygen to form water, are often the ones which proceed with the slowest rates. The final solution of the problems of chemical velocity will be of extraordinary importance both for theoretical and for applied chemistry, since the chemist will then be able to predict not only the *possible* reactions in a given mixture of chemicals, but also the *actual* reactions which really do take place. The present article aims to make some contribution towards this final solution.

1. **Previous Work.**—Important contributions to the general theory of chemical velocity have been made by Guldberg and Waage,[2] Arrhenius,[3] Marcelin,[4] Trautz,[5] Perrin[6] and W. C. M. Lewis.[7]

Guldberg and Waage were the first to understand the effect of concentration on rate of reaction.

Considering the reaction

$$aA + bB + \ldots \longrightarrow cC + dD + \ldots \tag{1}$$

where a mols of the Substance A react with b mols of the Substance B, etc., to form the products C, D, etc., the equation of Guldberg and Waage,

---

[1] Meyer and Jacobson, "Lehrbuch der Organischen Chemie," 1, Pt. 2 (1913).

[2] Guldberg and Waage, Ostwald's "Klassiker" No. 104; *J. prakt. Chem.*, 19, 69 (1879).

[3] Arrhenius, *Z. physik. Chem.*, 4, 226 (1889).

[4] Marcelin, *Ann. phys.*, 3, 120 (1915).

[5] Trautz, see summary, *Z. anorg. Chem.*, 102, 81 (1918).

[6] Perrin, *Ann. phys.*, 11, 5 (1919).

[7] W. C. M. Lewis, *J. Chem. Soc.*, 113, 471 (1918); *Phil. Mag.*, 39, 26 (1920).

for the rate at which the concentration of the reactant A is decreasing may be written

$$-\frac{dC_A}{dt} = k_1\, C_A^a C_B^b\, \ldots \tag{2}$$

where C_A, C_B ..., etc., are the instantaneous concentrations of the reactive substances at the time t and k_1, the so-called specific reaction rate, is a constant, independent of the concentration, but dependent of course on temperature. Equation 2, which applies to single phase homogeneous systems, is a correct expression, provided the actual mechanism of the reaction is given by Equation 1 and provided the reacting substances are sufficiently dilute. The equation has a familiar and obvious derivation based on a consideration of the number of collisions between reacting molecules.

Arrhenius investigated the relation between temperature and rate of reaction, and showed that the variation of specific reaction rate with the temperature could be satisfactorily expressed by the equation

$$\frac{d\, ln\, k_1}{dT} = \frac{E_1}{RT^2} \tag{3}$$

where E_1 is a quantity, having the dimensions of energy, which is found experimentally to vary only slightly with the temperature.

Equation 3 has the same form as van't Hoff's well known thermodynamic equation for the relation between equilibrium constant and temperature, namely,

$$\frac{d\, ln\, K}{dT} = \frac{\Delta E}{RT^2} \tag{4}$$

where K is the (concentration) equilibrium constant and ΔE is the energy absorbed when the reaction takes place at constant volume and temperature.

The analogous forms of Equations 3 and 4 led Arrhenius to a partially satisfactory thermodynamic derivation of Equation 3. He postulated that chemical interaction does not take place between all molecules which collide in reacting proportions but only between molecules which are in a special activated state. These activated molecules are considered as a tautomeric form of the reacting substance existing at very small concentration in equilibrium with the unactivated form. Since the rate of the reaction will depend on the concentrations of the activated molecules, Equation 3 can then be derived by combining the individual van't Hoff equations which control the concentrations of the activated substances. k_1 is found to be proportional to the product of the equilibrium constants for the individual reactions by which the activated substances are formed, and E_1 the "energy of activation" is the sum of the heats of these reactions.

This treatment of Arrhenius is only partially satisfactory. Like any thermodynamic treatment it is powerless to give information as to the internal mechanism of the processes involved and hence cannot ultimately compete with a statistical mechanical treatment. It also seems questionable whether it is entirely justifiable to treat a portion of the molecules of a reactant namely, those having high energy content, as a "thermodynamically" distinct substance. Furthermore, the Arrhenius discussion takes no cognizances of the important rôle played by radiation in furnishing the energy of activation. It should also be noted that the idea of activated molecules which exist as a tautomeric form and react upon collision is apparently inapplicable to the important case of monomolecular reactions. Finally, modifications would have to be introduced to take care of the increased frequency and violence of collision with increased temperature, as well as the change in effective time of contact of the molecules which are to react.

Marcelin was the first to present any elaborate attempt to apply the methods of statistical mechanics to the problems of reaction velocity. His important contribution, however, is marred by a lack of appreciation of the rôle of radiant energy in the activation of molecules and by a confusion of Gibbs' expression for the canonical distribution of an ensemble of systems with Maxwell's distribution law.

Trautz, W. C. M. Lewis and Perrin, were the first to appreciate the importance of radiation as the source from which the energy of activation necessary for chemical reaction is to be obtained. The development of this idea has received its most complete expression in the very persuasive treatment of Perrin, "Matiére et Lumiére."[1] A brief account of Perrin's work will be necessary to indicate the point of departure for the present article.

In order to express the mechanism of a chemical reaction by which the substances A are changed into the substances A', Perrin writes the equation

$$H\nu + A = A' + H\nu' \qquad (5)$$

where ν is the frequency of the light which has to be absorbed in order to activate A, ν' is the frequency of the light which is g ven out by A' on formation, and H is Planck's constant h multiplied by Avogadro's number N.

$$H = Nh. \qquad (6)$$

It will be seen that Equation 5 takes cognizance of the quantum theory by making $H\nu$ the energy of activation per mol. of substance, and thus making the energy of activation per molecule exactly one quantum of energy $h\nu$.

[1] *Loc. cit.*

Equation 5 is regarded as reversible ν' being the frequency of light absorbed by A′ when the reaction proceeds in the reverse direction.

In accordance with Equation 5, Perrin writes for the total energy change accompanying the reaction

$$\Delta E = H(\nu - \nu'). \tag{7}$$

In order to investigate the rate of reaction and its dependence on temperature, Perrin assumes that the specific reaction rate k will be proportional to the intensity of radiant energy of the activating frequency ν. In the case of a purely thermal reaction this will obviously be the intensity of radiation in a hohlraum at the temperature in question. If u is the density of energy in a hohlraum at temperature T we may write in accordance with the Planck law for the distribution of radiant energy,

$$\frac{du}{d\nu} = \frac{8\pi h\nu^3}{c^3} \frac{1}{\epsilon^{h\nu/kT} - 1}. \tag{8}$$

On the basis of Planck's distribution law, Perrin then writes the following expression for specific reaction rate,

$$k_1 = \frac{s}{\epsilon^{h\nu/kT} - 1}, \tag{9}$$

s being a composite proportionality factor which in agreement with Perrin may be called the "*sensibility*" of the substances A to the action of radiation of frequency ν.

Since the quantity $\epsilon^{h\nu/kT}$ is in general very large compared with unity, Perrin rewrites Equation 9 in the form

$$k_1 = s\epsilon^{-h\nu/kT} \tag{10}$$

and indeed seems to feel that Equation 10 is presumably the exact form of the equation.

Taking the logarithm of Equation 10 and differentiating with respect to the temperature we obtain

$$\frac{d \ln k_1}{dT} = \frac{h\nu}{kT^2} \tag{11}$$

or since $Nk = R$ and $Nh = H$,

$$\frac{d \ln k_1}{dT} = \frac{H\nu}{RT^2}. \tag{11a}$$

We have thus derived Arrhenius' equation (3), $H\nu$ being the energy of activation previously called E_1.

2. **Criticism of Perrin's Treatment.**—Perrin's treatment is not entirely satisfactory for the following reasons.

(1) Equation 7 for the energy change accompanying a reaction would make the energy of reaction entirely independent of the temperature. This is known not to be the case.

(2) Perrin's treatment is based on the assumption that light of a single

frequency or rather of a very narrow range of frequencies will be the only light having activating properties. We have, however, very considerable evidence to show that photochemical reactions are produced by the action of light of a considerable range of frequencies. The simplest of all chemical reactions is the dissociation of a substance into positive ions and electrons, and it is well known that the photo-electric effect in metals is produced by a range of frequencies above the limiting threshhold frequency. This is not only true for solid metals, but I am informed by Dr. E. H. Williams that it was also found by Kunz and himself to be true for cesium vapor. The well known reactions of practical photography are also known to be produced by light of a great variety of wave lengths. Work carried on in this laboratory by Dr. Farrington Daniels[1] has also shown that the photo-chemical decomposition of gaseous nitrogen pentoxide is apparently produced by a range of frequencies. It is evident that a more general method of treatment involving integration over the whole range of frequencies is to be desired. Perrin's treatment, even if in other ways correct, would then be the limiting case of a more general theory, applicable when only a spectrum "line" is active. In this connection it should be pointed out that Perrin's s in Equation 9 must be thought of as containing a factor $\Delta\nu$, corresponding to the width of the supposed "line," since Equation 8 gives, not energy density, but change of energy density with frequency.

(3) Perrin's assumption that specific reaction rate is really exactly proportional to $\epsilon^{-h\nu/kT}$ instead of to $\dfrac{1}{\epsilon^{h\nu/kT} - 1}$ as would be expected from Planck's radiation formula, seems arbitrary.

(4) Perrin's treatment makes no allowance for the fact that the different molecules of a reacting substance are undoubtedly in many different internal states. Hence, the rate of reaction and its change with temperature must be thought of as depending on the condition of the molecules as well as on the condition of the surrounding "bath" of radiant energy.

(5) Perrin's treatment does not make what seems to be a necessary differentiation between monomolecular and polymolecular reactions. In the case of monomolecular reactions, we may think of the reaction as being completed as soon as the molecule has received its energy of activation In the case, however, of di- and polymolecular reactions, we shall find it advantageous to consider as 2 separate steps, (a) the process by which the proper quota of activated molecules is maintained, and (b) the actual chemical interaction. This latter viewpoint has as a matter of fact been appreciated both by Trautz and W. C. M. Lewis.[2]

[1] To be published in a later number of THIS JOURNAL.

[2] Since this article was written a further criticism of Perrin's development has been made by Langmuir, *ibid.*, 42, 2190 (1920). Langmuir points out (1) that many substances do not have absorption bands for radiant energy of the fre-

II. Method of Treatment Adopted in this Article.

The point of view adopted in the present article is essentially an extension of that of Perrin, the attempt being made to meet the 5 criticisms made above. The method of treatment, however, will differ from that of Perrin in being based as nearly as may be on the fundamental considerations of statistical mechanics.

Since many chemists are not familiar with the methods of statistical mechanics we shall first present a brief introduction to this important science.

All developments of statistical mechanics which have as yet reached any degree of elaboration have been based on the assumption that Hamilton's equation of motion are applicable to the different parts of the system under consideration, and this assumption will be made in the present treatment. In recent years many investigators have objected to such a use of Hamilton's equations of motion, since they have believed that a statistical mechanics founded on these equations necessarily led to the principle of the equipartition of energy which has been shown not to be true for the radiant energy in a hohlraum, and for other systems where "quantum" relations have been found important. The present writer, however, does not believe that the principle of the equipartition of energy is a necessary consequence of Hamilton's equations, but rather a consequence of an unnecessary and incorrect assumption that energy is necessarily a homogeneous quadratic function of the generalized coördinates and momenta. This point of view has already been presented by the author[1] in an article dealing with the general theory of energy partition, where it has been shown that a relation between energy and the generalized coördinates and momenta can be found which will even account for the distribution of energy in the hohlraum in accordance with the Planck radiation formula. For this reason we shall feel justified in using a statistical mechanics based on Hamilton's equations for the present investigation.

Before proceeding to our development, a word must be said about the rôle of radiant energy in the production of chemical reaction. In this connection, it is believed that Perrin's arguments that radiant energy is necessary for chemical reaction are unescapable. If we agree to the

quency which Perrin predicts as necessary for their activation, and (2) that the amount of radiant energy of such frequencies which is actually available in the hohlraum is too small to furnish the necessary energy of activation. The present writer agrees with both these criticisms of Perrin's treatment. He is not inclined at the present, however, to give up, as Langmuir suggests, the whole radiation theory of reaction velocity. As will be evident in the sequel, the present development, by assuming the possibility of a widely extended range of activating frequencies, meets the objections of Langmuir as well as the 5 objections noted above.

[1] Tolman, *Phys. Rev.*, **11**, 261 (1918).

general idea, as presented, indeed in the simple Arrhenius treatment, that reaction occurs only between activated molecules, we find experimentally from the temperature coefficient of rate of reaction (see Equation 3) that the energy necessary is usually very large, much larger than ordinary heats of reaction. In order to maintain a steady rate of reaction, the molecules of the reacting substances will have then to obtain in some continuous way this necessary energy of activation. It can come either from collision with other molecules or from the surrounding bath of radiant energy. If the only source of energy were collisional we should expect a decrease in specific reaction rate on increased dilution which is not found to be the case. We may conclude that radiant energy is an important source for the energy of activation and the only source for reactions in gases of high dilution.

III. Statistical Mechanics Applied to Chemistry.

1. The Equations of Motion.—Consider a chemical system such as a gaseous mixture of reacting molecules immersed in a bath of radiant energy of a character corresponding to the temperature. The configuration of the system at any instant will be determined by the specification of the position of the different molecules, the orientation of the atoms composing them, and the electromagnetic displacement in the different modes of vibration which are the seat of the radiant energy. If a statement of the values of n generalized coördinates, $\phi_1 \phi_2 \phi_3 \ldots \phi_n$ is just sufficient to specify the configuration, the system is said to have n degrees of freedom.

The future behavior of the system will be determined by the instantaneous values of these n generalized coördinates and by the instantaneous values of the corresponding n generalized velocities $\dot{\phi}_1 \dot{\phi}_2 \dot{\phi}_3 \ldots \dot{\phi}_n$, the dot being used in general to indicate differentiation with respect to time. If the system is a conservative one, the equations of motion can be written in the remarkably symmetrical Hamiltonian form

$$\frac{\partial H}{\partial \psi_1} = \dot{\phi}_1 \quad \frac{\partial H}{\partial \psi_2} = \dot{\phi}_2 \quad \frac{\partial H}{\partial \psi_3} = \dot{\phi}_3 \ldots$$

$$\frac{\partial H}{\partial \phi_1} = -\dot{\psi}_1 \quad \frac{\partial H}{\partial \phi_2} = -\dot{\psi}_2 \quad \frac{\partial H}{\partial \phi_3} = -\dot{\psi}_3 \ldots \tag{13}$$

where the new quantities, $\psi_1 \psi_2 \psi_3 \ldots \psi_n$, are known as the generalized momenta for the system and are themselves functions of the ϕ's and $\dot{\phi}$'s, and H, the so-called Hamiltonian function, is the energy of the system E expressed as a function of the generalized coördinates and momenta.

$$H = E\,(\phi_1 \phi_2 \ldots \phi_n \psi_1 \psi_2 \ldots \psi_n). \tag{14}$$

2. Geometrical Representation.—The state of our system at any instant will be completely determined by the specification of the $2n$ variables, $\phi_1 \phi_2 \ldots \phi_n \psi_1 \psi_2 \ldots \psi_n$. We shall find it convenient to think of

the state of the system as represented by the position of a point in a $2n$ dimensional space.

Suppose now we have a great many systems of the same structure but differing in state. Then for each system we shall have a point in our $2n$ dimensional space, and if the systems are left to themselves these points will describe stream lines in accordance with the equations of motion (13).

3. **The Maintenance of Uniform Density.**—Suppose now that the points representing the states of the different systems are originally distributed with the uniform density ρ throughout the $2n$ dimensional space. Then it is a necessary consequence of the equations of motion that the density will remain uniform. For the rate at which the density would increase at any point we can obviously write

$$\frac{d\rho}{dt} = \rho \left(\frac{\partial \dot{\phi}_1}{\partial \phi_1} + \frac{\partial \dot{\phi}_2}{\partial \phi_2} + \ldots + \frac{\partial \dot{\psi}_1}{\partial \psi_1} + \frac{\partial \dot{\psi}_2}{\partial \psi_2} + \ldots \right)$$

and since the equations of motion (13) evidently necessitate the relations

$$\frac{\partial \dot{\phi}_1}{\partial \phi_1} + \frac{\partial \dot{\psi}_1}{\partial \psi_1} = 0, \quad \frac{\partial \dot{\phi}_2}{\partial \phi_2} + \frac{\partial \dot{\psi}_2}{\partial \psi_2} = 0, \quad \text{etc.,}$$

we conclude that the original uniform density will not change.

This maintenance of uniform density is a very important result. It means that there is no tendency for the representative points to crowd into any particular portion of the $2n$ dimensional space. For this reason if we start some one isolated system going and plot its state in our $2n$ dimensional space, we shall assume that after an indefinite lapse of time its representative point is equally liable to be in any one of the infinitesimal elements of equal volume $(d\phi_1 \, d\phi_2 \ldots d\phi_n \, d\psi_1 \, d\psi_2 \ldots d\psi_n)$ into which we can divide our space, provided this elementary region corresponds to the energy content of the system.

4. **Probability of a Given Microscopic State.**—As a convenient nomenclature, we shall say that the *microscopic state* of a system is specified by a statement of the particular element of volume $(d\phi_1 \, d\phi_2 \ldots d\phi_n \, d\psi_1 \, d\psi_2 \ldots d\psi_n)$ in which the representative point for the system falls. On the basis of the conclusion reached in the last paragraph we shall state the important principle that *all the different microscopic states of a system have the same probability*.

5. **Probability of a Given Statistical State.**—Let us suppose that our system is a chemical one composed of a large number of identical elements such as atoms, molecules, modes of electromagnetic vibration, etc. Let A, B, C, etc., be the number of elements of each of the various kinds which go to make up the complete system, and let us consider that our $2n$ generalized coördinates and momenta can be assigned to the individual elements of the system.

For a chemical system of this kind, we shall be particularly interested in the number of elements of any particular kind A which have coördinates and momenta falling in any given infinitesimal range,

$$d\sigma_A = d\phi_{A_1} d\phi_{A_2} \ldots d\psi_{A_1} d\psi_{A_2} \ldots \tag{15}$$

where $\phi_{A_1}, \phi_{A_2} \ldots \psi_{A_1} \psi_{A_2} \ldots$ are generalized coördinates and momenta of the kind that are assigned to one of the elements of the kind A. We shall specify the *statistical state* of our system by stating the number of elements of the various kinds A, B, C, etc., which fall in the different possible infinitesimal ranges $d\sigma$.

A specification of the *microscopic state* of the system determines the coördinates and momenta for each individual element of which the system is composed. The *statistical state* merely determines the number of elements of each of the different kinds which have coördinates and momenta of a particular magnitude, without attempting to make any distinction as to which particular elements are taken to supply the quota. We thus see that corresponding to a given statistical state there will be a large number of different microscopic states which can be obtained by the inter-transposition of elements of a given kind from one region $d\sigma$ to another without disturbing the total number in each region. Since we have already concluded that all microscopic states are equally probable, we may now conclude that *the probability of any given statistical state is propor-tional to the number of microscopic states to which it corresponds.*

Let us specify a given statistical state by stating that $A_1 A_2 A_3 \ldots B_1 B_2 B_3 \ldots C_1 C_2 C_3 \ldots$, etc., are the number of elements of each of the kinds which have coördinates and momenta falling in the particular infinitesimal ranges Nos. 1A, 2A, 3A..., 1B, 2B, 3B, ... etc.

Then it is evident from the principles of permutation that the num-ber of microscopic states corresponding to this statistical state will be

$$W = \frac{\lfloor A \rfloor \lfloor B \rfloor \lfloor C}{\lfloor A_1 \rfloor \lfloor A_2 \rfloor \lfloor A_3 \ldots \lfloor B_1 \rfloor \lfloor B_2 \rfloor \lfloor B_3 \ldots \lfloor C_1 \rfloor \lfloor C_2 \rfloor \lfloor C_3 \ldots} \tag{16}$$

where A, B, C, etc., are the total number of elements of each of the kinds. We shall call W the probability of the given statistical state, without in-troducing any proportionality factor.

Let us now assume that each of the numbers A A_1 $A_2 \ldots B$ B_1 $B_2 \ldots$, etc., is large enough so that we may apply Stirling formula for factorial N,

$$\lfloor N = \sqrt{2\pi N}(N/e)^N. \tag{17}$$

Substituting in Equation 16, taking the logarithm of W for greater con-venience and omitting negligible terms, we obtain

$$\begin{aligned}
\log W = {}& A \log A + B \log B + C \log C + \ldots \\
& - A_1 \log A_1 - A_2 \log A_2 - A_3 \log A_3 - \ldots \\
& - B_1 \log B_1 - B_2 \log B_2 - B_3 \log B_3 - \ldots \\
& - C_1 \log C_1, - \text{etc.}
\end{aligned} \tag{18}$$

which can be rewritten in the form

$$\log W = A \log A + B \log B + C \log C + \ldots$$
$$- \Sigma A_i \log A_i - \Sigma B_j \log B_j - \Sigma C_k \log C_k - \ldots \quad (18a)$$

where the summation Σ is to be taken over all the infinitesimal regions, $i = 1, 2, 3, \ldots j = 1, 2, 3 \ldots k = 1, 2, 3 \ldots$ etc.

6. **Statistical State of Maximum Probability.**—We shall be specially interested in the statistical state of maximum probability with a system having a given energy content. The condition for maximum probability will evidently be

$$\delta \log W = -\Sigma(\log A_i + 1)\delta A_i - \Sigma(\log B_j + 1)\delta B_j - \ldots = 0 \quad (19)$$

The variation δ however cannot be carried out entirely arbitrarily since the total number of elements of any kind A, B, C, etc., will not be taken as subject to variation, and the total energy of the system will be taken as constant.

For the total number of elements of each kind we may write

$$A = \Sigma A_i \quad B = \Sigma B_j \quad C = \Sigma C_k, \text{ etc.},$$

and since these totals are not to vary we obtain

$$\Sigma \delta A_i = 0, \quad \Sigma \delta B_j = 0, \quad \Sigma \delta C_k = 0, \text{ etc.} \quad (20)$$

For the total energy of the system we may write,[1]

$$E = \Sigma A_i E_i + \Sigma B_j E_j + \Sigma C_k E_k + \ldots$$

where E_i is the energy of an element of kind A in the i'th region, etc. Since the total energy is to remain constant during the variation, we obtain

$$\delta E = \Sigma E_i \delta A_i + \Sigma E_j \delta B_j + \Sigma E_k \delta C_k + \ldots = 0. \quad (21)$$

The simultaneous Equations 19, 20 and 21 may be combined by the method of undetermined multipliers giving us

$$\Sigma(\log A_i + 1 + \lambda_A + \mu E_i)\delta A_i$$
$$+ \Sigma(\log B_j + 1 + \lambda_B + \mu E_j)\delta B_j \quad (22)$$
$$+ \Sigma(\log C_k + \ldots \text{ etc.} \quad = 0$$

where the quantities $\lambda_A \lambda_B \ldots$ and μ are undetermined multipliers. The introduction of these undetermined multipliers now makes the variations δA_i, etc., entirely arbitrary, so that Equation 22 may be solved in the form

$$\log A_i + 1 + \lambda_A + \mu E_i = 0$$
$$\log B_j + 1 + \lambda_B + \mu E_j = 0 \quad (23)$$
$$\log C_k +, \text{ etc.}$$

These relations may be rewritten in the form

---

[1] We introduce at this point the tacit assumption that no error will be introduced into the discussion, if we take the energy of an element as independent of the state of other elements of the sytsem.

$$A_i = \alpha_A \epsilon^{-\mu E_i}$$
$$B_j = \alpha_B \epsilon^{-\mu E_j} \qquad\qquad (23a)$$
$$\text{etc.}$$

where α_A, α_B, etc., correspond to the original undetermined multipliers, λ_A, λ_B, etc., and ϵ is the base of the natural system of logarithms. It should be specially noticed that α_A, α_B, etc., are dependent on the kind of element in question, but that the quantity μ occurring in Equations 23 and 23a is the same for elements of any kind.

7. **Introduction of a Continuous Variable.**—Let us now express the information contained in Equations 23a in a slightly different form. The quantity A_i occurring in Equations 23a is the number of elements of the kind A in the i'th region $d\sigma_i = (d\phi_{A_1}d\phi_{A_2} \ldots d\psi_{A_1}d\psi_{A_2} \ldots)$ when we have the distribution of maximum probability, and this quantity A_i is as we see determined solely by the kind of element involved and the energy of an element in the i'th region. Now A_i/A will be the chance that an element of kind A will be in the i'th infinitesimal region when we have the distribution of greatest probability, let us write A_i/A proportional to the volume of the infinitesimal region, we have

$$\frac{A_i}{A} = w_i d\sigma_i$$

where w_i is the chance per unit generalized volume that an element of kind A will have coördinates and momenta of the specified magnitude. w_i will evidently depend as does A_i solely on the kind of element involved and on the energy of an element in the particular region $d\sigma$ involved. It is evident from Equation 23a that we can then write as an expression for the chance that the coördinates and momenta of an element will fall in a particular infinitesimal region $d\sigma$,

$$w_A d\sigma_A = a_A \epsilon^{-\mu E_A} d\sigma_A,$$
$$w_B d\sigma_B = a_B \epsilon^{-\mu E_B} d\sigma_B,$$
$$\text{etc.}$$

where the quantities a_A, a_B, etc., correspond to the original undetermined multipliers, λ_A, λ_B, etc., and hence depend on the kind of element involved and where μ is the same for all kinds of elements.

Now it is well known that for a perfect monatomic gas μ has the value $1/kT$ where T is the absolute temperature and k is the gas constant R divided by Avogadro's number N, for the number of molecules in a gram molecule. Since part of our system could always be a dilute indifferent monatomic gas without influencing any phenomena, we may write in general as our final expressions for the chance that an element of a given kind will have coördinates and momenta falling in a given infinitesimal region,

$$w_A d\sigma_A = a_A \epsilon^{-E_A/kT} \, d\sigma_A = a_A \epsilon^{-E_A/kT} \, d\phi_{A_1} d\phi_{A_2} \ldots d\psi_{A_1} d\psi_{A_2} \ldots$$
$$w_B d\sigma_B = a_B \epsilon^{-E_B/kT} \, d\sigma_B = a_B \epsilon^{-E_B/kT} \, d\phi_{B_1} d\phi_{B_2} \ldots d\psi_{B_1} d\psi_{B_2} \ldots$$
$$w_C d\sigma_C = \text{etc.} \tag{24}$$

Or, in general,

$$w d\sigma = a \epsilon^{-E/kT} \, d\sigma = a \epsilon^{-E/kT} \, d\phi_1 d\phi_2 \ldots d\psi_1 d\psi_2 \ldots$$

This may be called the generalized Maxwell's distribution law.

8. Three Fundamental Equations of Statistical Mechanics.—Since the probability that a given element has some value for its generalized coördinates is unity we may write

$$\oint a\epsilon^{-E/kT} d\sigma = \oint \ldots \oint a\epsilon^{-E/kT} d\phi_1 d\phi_2 \ldots d\psi_1 d\psi_2 \ldots = 1 \quad (25)$$

where the symbol $\oint$ indicates that the integration is to be carried out over the whole region of the generalized space involved. This equation may be regarded as determining the quantity a, which is seen to be a function of the temperature.

Since $a\epsilon^{-E/kT} d\sigma$ is the chance that an element will be found in the region $d\sigma$ it is evident that the average value of any property P of the elements will be given by the equation

$$\overline{P} = \int a\epsilon^{-E/kT} \, P d\sigma = \int \ldots \int a\epsilon^{-E/kT} \, P d\phi_1 d\phi_2 \ldots d\psi_1 d\psi_2 \ldots \quad (26)$$

where P is to be regarded as a function of the coördinates and momenta and where the integration is to be taken over the whole or a part of the generalized space, according as the average of P is desired for all or a part of the elements.

Equations 25 and 26 will permit us to obtain important information as to the multiplier a. If we differentiate Equation 25 with respect to the temperature T we obtain

$$\oint da/dT \, \epsilon^{-E/kT} \, d\sigma + \oint a\epsilon^{-E/kT} \, E/kT^2 \, d\sigma = 0.$$

Dividing the first term of this equation by $\oint a\epsilon^{-E/kT} \, d\sigma = 1$, and noting that the second term in accordance with Equation 26 is the average value of E/kT^2 for all the elements of the kind in question we obtain

$$\frac{\oint da/dT \, \epsilon^{-E/kT} \, d\sigma}{\oint a\epsilon^{-E/kT} \, d\sigma} = -\frac{\overline{E}}{kT^2} \tag{27}$$

or

$$\frac{d \ln a}{dT} = -\frac{\overline{E}}{kT^2}$$

where we have used the symbol $\overline{E}$ to indicate the average value of E. We shall find later use for this important equation.

IV. Application of Statistical Mechanics to Rate of Chemical Reaction.

It is evident that statistical mechanics is a much more powerful, although more complicated, tool for the treatment of chemical problems than is thermodynamics. It is more powerful because it is based on a

consideration of the behavior of the ultimate elements of which the system is composed.

1. **Nature of Systems to be Considered.**—In the present article we shall apply statistical mechanics to a consideration of the rate of chemical reaction in gaseous systems, and shall make a number of restrictions as to the nature of these systems.

(a) In the first place, we shall assume that the reactions which we consider do not proceed with explosive violence, but at a slow and measurable rate. We shall assume this rate slow enough, so that we can assume that the elements of our system at any instant of time are in the statistical state of maximum probability. The instantaneous rate of chemical reaction will then be determined by the characteristics of this particular statistical state concerning which we have already obtained important information.

(b) We shall further assume for the sake of simplicity that the reactions which we are considering consist of a single molecular change of the general type

$$a\mathrm{A} + b\mathrm{B} \longrightarrow \text{Products.}$$
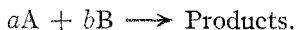
In practice, there are of course many reactions which take place in steps, with the formation of intermediate compounds which later react again, or with the formation of temporary compounds with some substance which acts as a catalyst. Since, however, the total process can be thought of as analyzed into a series of simple steps of the above type we shall confine our immediate theoretical treatment to a consideration of single molecular changes.

(c) We shall assume our gaseous mixtures dilute enough so that the gas laws hold for each of the reactants and each of the products of the reaction, and dilute enough so that the specific reaction rate for the forward reaction k_1 and for the reverse reaction k_2 are independent of concentration. This assumption that the gases are dilute entails several important consequencies.

Since the gases are dilute enough to obey the perfect gas laws, van't Hoff's equation for the equilibrium constant will be exactly true, namely,

$$\frac{\mathrm{d}\, ln\, K}{\mathrm{d}T} = \frac{\Delta E}{RT^2}, \tag{28}$$

where K is the (concentration) equilibrium constant, ΔE, is the energy change accompanying the reaction at constant temperature and volume and R and T have their customary significance.

As a further consequence of the dilution we shall have as an exact relation,

$$K = k_1/k_2, \tag{29}$$

and hence our theory of rate of reaction must lead exactly to the relation,

$$\frac{\mathrm{d}\ ln\ k_1}{\mathrm{d}T} - \frac{\mathrm{d}\ ln\ k_2}{\mathrm{d}T} = \frac{\Delta E}{RT^2}. \qquad (30)$$

As a final consequence of the dilution assumed, we are led to the conclusion that radiant energy takes a *necessary* part in the mechanism of the chemical change. If reactions take place only between "activated" molecules which have considerably more energy than the average, it is evident that in order to maintain a steady rate of chemical change, there must be some source from which molecules may receive the necessary "energy of activation." The source of the "energy of activation" must either be molecular collision or the bath of radiant energy in which the molecules are immersed. If our gases are assumed dilute enough so that further dilution leads to no change in the specific reaction rate, we must conclude, since dilution decreases the number of molecular collisions, that radiant energy is the source of the energy of activation and hence takes an essential part in the chemical change.

2. **Thermal Rate of a Monomolecular Reaction.**—Let us first· consider monomolecular reactions, which might consist either in a decomposition of the molecules or in the formation of an isomer. The decomposition of nitrogen pentoxide, which has been studied in this laboratory by Daniels, is the most satisfactory example of a gaseous monomolecular reaction.

In the case of monomolecular reactions, we may conceive of the reaction taking place as soon as the molecule has received its energy of activation. This differs from the case of di-, and poly-molecular reactions, where we shall expect cases in which the molecules exist for an appreciable length of time in the activated state and then react upon collision.

The chance that a molecule will react, *i. e.*, will pick up the necessary energy of activation from its bath of radiant energy, will be determined in the first place by the state of the molecule itself, and this means of course by the values of the generalized coördinates and momenta which describe the condition of the molecule. If C_A is the number of molecules in unit volume of the reacting gas, then by Equation 24,

$$A_i = C_A a_A \epsilon^{-E_i/kT} \mathrm{d}\sigma_i, \qquad (31)$$

is the number of molecules whose coördinates and momenta fall in the small region $\mathrm{d}\sigma_i$, provided we assume that the molecules are distributed in the statistical state of maximum probability. This latter assumption cannot of course, be exactly true, since some of the regions $\mathrm{d}\sigma_A$ correspond to an activated condition of the molecule and hence one which immediately leads to a destructon of the molecule. Since, however, we shall find that the energy E_i is very large for activated molecules, the number of such molecules, even without reaction, would be negligibly small. As to the re-establishment of the statistical state of maximum probability, as mole-

cules are removed by reaction, we have already assumed the reaction slow enough to permit of this adjustment.

The chance that a molecule will take up the necessary energy of activation will depend not only on the condition of the molecule but also on the condition of the surrounding bath of radiant energy. If the electromagnetic disturbances in a hohlraum be analyzed into periodic disturbances by the methods of Fourier's series, it can be shown that the number of modes of vibration per unit volume having a frequency between ν and $\nu + d\nu$ is equal to

$$N = \frac{8\pi\nu^2}{c^3} \, d\nu \tag{32}$$

where c is the velocity of light. The complicated derivation of Equation 32 need not detain us here. It is sufficient to note that except for the magnitude of the factor 8π, Equation 32 is a necessary consequence of the theory of dimensional homogeneity, since N must have the dimensions of a number per unit volume.

The electromagnetic condition in which a given mode of vibration finds itself will be determined by a specification that certain generalized coordinates and momenta fall in a particular infinitesimal region $d\sigma_k$. If we have the statistical state of maximum probability the number of modes of vibration per unit volume having frequencies in the range $d\nu_j$ and coordinates and momenta in the region $d\sigma_r$ will be in accordance with Equations 24 and 32,

$$\nu_{jk} = \frac{8\pi\nu^2}{c_3} \, d\nu_j a_\nu \epsilon^{-E_k/kT} \, d\sigma_k. \tag{33}$$

Let s_{ijk} be the chance per unit time that a molecule in state $d\sigma_i$ will undergo its monomolecular chemical change when it is surrounded by unit density of modes of electromagnetic vibration in state $d\sigma_k$. Then for the total number of molecules which react in unit time, we may write in accordance with Equations 31 and 33,

$$-\frac{dC_A}{dt} = \Sigma s_{ijk} C_A a_A \, \epsilon^{-E_i/kT} \, d\sigma_i \frac{8\pi\nu^2}{C^3} \, d\nu_j a_\nu \, \epsilon^{-E_k/kT} \, d\sigma_k, \tag{34}$$

where the summation Σ is to be carried out for all frequencies and for all possible regions i and k. Dividing through by C_A and replacing the summation by the integration form, we obtain

$$-\frac{1}{C_A} \frac{dC_A}{dt} = k_1 = \oint \oint \oint sa_A \, \epsilon^{-E_A/kT} \frac{8\pi\nu^2}{c^3} a_\nu \, \epsilon^{-E_\nu/kT} \, d\sigma_A d\nu d\sigma_\nu \tag{35}$$

as an expression for the specific rate k_1 of our reaction.

In order to have a complete understanding of the significance of Equation 35 we may note that σ_A, ν, σ_ν and T are to be regarded as independent variables. The other quantities on the right hand side of Equation 35 are functionally dependent on these variables as follows:

$$s = s(\sigma_A, \nu, \sigma_\nu)^1$$
$$a_A = a_A(T)$$
$$E_A = E_A(\sigma_A) \tag{36}$$
$$a_\nu = a_\nu(\nu, T)$$
$$E_\nu = E_\nu(\sigma_\nu)$$

A complete knowledge of these functional relations would permit an exact prediction of the specific reaction rate, and this must be regarded as an ultimate problem of chemical kinetics.

In the meantime, we can get important further information from Equation 35 without any knowledge of these functional relations.

3. **Temperature Coefficient for Monomolecular Reaction Rate.**—If we differentiate Equation 35 with the temperature, we shall obtain a derivation of the Arrhenius expression for the temperature coefficient of specific reaction rate, which will give a real insight into the meaning of that equation. Differentiating Equation 35, dividing by k_1, and noting in accordance with Equation 27 that

$$\frac{da_A}{dT} = a_A \frac{d \ln a_A}{dT} = - a_A \frac{\overline{\overline{E}}_A}{kT^2}$$

$$\frac{da_\nu}{dT} = a_\nu \frac{d \ln a_\nu}{dT} = - a_\nu \frac{\overline{\overline{E}}_\nu}{kT^2}$$

we obtain

$$\frac{1}{k_1} \frac{dk_1}{dT} = \frac{d \ln k_1}{dT} = \frac{1}{k_1} \oint \oint \oint - \frac{\overline{\overline{E}}_A}{kT^2} s a_A \epsilon^{-E_A/kT} \frac{8\pi\nu^2}{c^3} a_\nu \epsilon^{-E_\nu/kT} d\sigma_A d\nu d\sigma_\nu$$

$$+ \frac{1}{k_1} \oint \oint \oint \frac{E_A}{kT^2} s a_A \epsilon^{-E_A/kT} \frac{8\pi\nu^2}{c^3} a_\nu \epsilon^{-E_\nu/kT} d\sigma_A d\nu d\sigma_\nu$$

$$+ \frac{1}{k_1} \oint \oint \oint - \frac{\overline{\overline{E}}_\nu}{kT^2} s a_A \epsilon^{-E_A/kT} \frac{8\pi\nu^2}{c^3} a_\nu \epsilon^{-E_\nu/kT} d\sigma_A d\nu d\sigma_\nu \tag{37}$$

$$+ \frac{1}{k_1} \oint \oint \oint \frac{E_\nu}{kT^2} s a_A \epsilon^{-E_A/kT} \frac{8\pi\nu^2}{c^3} a_\nu \epsilon^{-E_\nu/kT} d\sigma_A d\nu d\sigma_\nu,$$

Examining this equation in the light of Equation 35 itself, it will be found that each of the terms on the right hand side is the average value of some property of the molecules or of the modes of vibration that enter into the reaction, we obtain

$$\frac{d \ln k_1}{dT} = \frac{\overline{\overline{E}}_A - \overline{E}_A + \overline{E}_R - E_R}{kT^2} \tag{38}$$

where $\overline{\overline{E}}_A$ is the average energy of the molecules which actually enter into the reaction, $\overline{E}_A$ is the average energy of all the molecules of this kind in the system, $\overline{E}_R$ is the average radiant energy of the modes of vibration

---

[1] Since σ_i must vary when ν varies, the introduction of ν into this equation is not essential, although informing.

upon participation in the reaction, and $\overline{E}_R$ is the average radiant energy of such modes of vibration whether or not they are in a reactive condition.

Equation 38 may be written in the form

$$\frac{d \ln k_1}{dT} = \frac{E_{\text{activated}} - E_{\text{average}}}{RT^2} = \frac{E_c}{RT^2} \qquad (39)$$

where $E_{\text{activated}}$ is the energy entering into the decomposition of one mol of molecules through their interaction with one "mol" of modes of vibration. E_{average} is the average energy of these elements, and their difference is E_c, which may be called the critical increment.

In obtaining Equation 39 we have completed our derivation of the Arrhenius expression for the temperature coefficient of reaction velocity, for the special case of monomolecular reactions. It should be noted that the quantity E_c, is one which will not vary much with the temperature, since neither the energy of the activated molecules and modes of vibration, nor their average energy will change rapidly with the temperature. This approximate constancy of E_c agrees with the experimental facts, as determined for example, by Daniels, for the monomolecular decomposition of nitrogen pentoxide.

4. Photochemical Rate of a Monomolecular Reaction.—In the foregoing development we have regarded a thermal monomolecular reaction essentially as a photochemical reaction, in which the activating light has its energy distributed among the different frequencies in accordance with the normal distribution in a hohlraum which has come to thermal equilibrium. By a photochemical reaction in the narrower sense we mean one in which we have monochromatic illumination. Our method of treatment will permit us to obtain important information as to the effect of monochromatic light.

Returning to Equation 35, we have as an expression for the thermal specific reaction rate,

$$k_1 = \oint \oint \oint s a_A \, \epsilon^{-E_A/kT} \, \frac{8\pi\nu^2}{c^3} \, a_\nu \, \epsilon^{-E_\nu/kT} \, d\sigma_A d\nu d\sigma_\nu. \qquad (35)$$

It is evident that for the part of the reaction which is due to frequencies between ν and $\nu + d\nu$ we may write the reaction rate

$$k' = \frac{8\pi\nu^2}{c^3} \, d\nu \oint \oint s a_A \, \epsilon^{-E_A/kT} \, a_\nu \, \epsilon^{-E_\nu/kT} \, d\sigma_A d\sigma_\nu. \qquad (40)$$

Furthermore, in accordance with measurements which have been made on black body radiation, we may write for the density of radiant energy having frequencies between ν and $\nu + d\nu$,

$$du = \frac{8\pi\nu^2}{c^3} \, \frac{h\nu}{\epsilon^{h\nu/kT} - 1} \, d\nu. \qquad (41)$$

If then we assume, in accordance with the available experimental data,

that the rate of a photochemical reaction is proportional to the intensity of illumination, we may divide Equation 40 by Equation 41 and write as an expression for *photochemical specific reaction rate*

$$k_\nu = \frac{\epsilon^{h\nu/kT} - 1}{h\nu} \oint \oint s a_A\, \epsilon^{-E_A/kT}\, a_\nu \epsilon^{-E_\nu/kT}\, d\sigma_A d\sigma_\nu. \qquad (42)$$

This expression is important, since k_ν is a quantity which can be determined experimentally by measuring the rate of reaction under a known intensity of illumination with monochromatic light of frequency ν. Having determined the value of k_ν over the complete range of active frequencies we may then predict the thermal reaction rate by a process of integration. This will afford a valuable check of the soundness of the theory.

We have from Equations 42 and 35

$$\oint \frac{8\pi\nu^2}{c^3} \frac{h\nu}{\epsilon^{h\nu/kT} - 1} k_\nu d\nu = k_1. \qquad (43)$$

Hence the value of k_1 can be predicted from a complete knowledge of k_ν. It is hoped that quantitative photochemical experiments will be made on the decomposition of N_2O_5 suitable for testing Equation 43.

If there were only one narrow range of activating frequencies as assumed by Perrin, then it would be possible to carry out the inverse process of predicting k_ν from k_1, but in general this does not seem to be true. In the case of the decomposition of nitrogen pentoxide, Daniels predicts, on the basis of Perrin's theory, that light of wave length $1150\mu\mu$ should be photochemically active, but finds experimentally that this is not the case.

5. **Temperature Coefficient for Monomolecular Photochemical Reaction Rate.**—By the temperature coefficient of a photochemical reaction, we shall understand the change in rate produced when the temperature of the gas is raised but the nature of the monochromatic illumination is kept constant. Referring again to Equation 42, we have for the reaction rate under the influence of monochromatic illumination of frequency ν and unit energy density

$$k_\nu = \frac{\epsilon^{h\nu/kT} - 1}{h\nu} \oint \oint s a_A \epsilon^{-E_A/kT}\, a_\nu \epsilon^{-E_\nu/kT}\, d\sigma_A d\sigma_\nu. \qquad (42)$$

If we raise the temperature of the gas, but hold our artificially produced illumination constant, we shall vary the quantity $a_A \epsilon^{-E_A/kT} d\sigma_A$, which determines the distribution of the molecules in the different regions $d\sigma_A$, but shall leave the other quantities unaffected. We may thus obtain

$$\frac{1}{k_\nu} \frac{dk_\nu}{dT} = \frac{1}{k_\nu} \frac{\epsilon^{h\nu/kT} - 1}{h\nu} \oint \oint \frac{d \ln a_A}{dT} s a_A \epsilon^{-E_A/kT}\, a_\nu \epsilon^{-E_\nu/kT}\, d\sigma_A d\sigma_\nu$$

$$+ \frac{1}{k_\nu} \frac{\epsilon^{h\nu/kT} - 1}{h\nu} \oint \oint \frac{E_A}{kT^2} s a_A \epsilon^{-E_A/RT}\, a_\nu \epsilon^{-E_\nu/RT}\, d\sigma_A d\sigma_\nu.$$

Applying the same considerations and symbols used in connection with Equation 38, we obtain as an expression for the temperature coefficient of a monomolecular photochemical reaction,

$$\frac{\mathrm{d}\,ln\,k_\nu}{\mathrm{d}T} = \frac{\overline{\overline{E}}_A - \overline{E}_A}{kT^2}. \tag{44}$$

In other words, the temperature coefficient of the photochemical reaction rate is proportional to the difference between the energy of the molecules which actually react and the average energy of all the molecules of that kind. It will be remembered that the temperature coefficient of the thermal reaction rate was proportional to the energy of the molecules *and* modes of vibration that entered into the reaction minus the average energy of these molecules and modes of vibration. Hence it does not surprise us to learn experimentally that photochemical reactions actually have in general a small temperature coefficient compared with thermal reactions. We conclude that the ability of the molecules of a substance to take up radiant energy is *on the average* but slightly affected by rise in temperature.

As far as the author knows, this is the first theoretical treatment of the temperature coefficient of photochemical reactions.

6. Di- and Poly-molecular Reactions.—Our considerations up to this point have concerned themselves strictly with the monomolecular reactions of dilute gases, although the extension to more complicated reactions and even to non-gaseous systems will in many cases be obvious.

The case of polymolecular reactions in dilute gases is somewhat different from that of monomolecular reactions. We may distinguish two steps in the process; first, the actual interaction of the molecules, which will at least in many reactions occur only between specially "activated" molecules containing more than the average amount of internal energy, and second, the continuous re-establishment of the statistical state of maximum probability for the remaining molecules as those of high internal energy are removed by the progress of the reaction.

In the case of dilute enough gases, since the number of molecular collisions can be made as small as desired by increasing dilution, it is evident that the maintenance of statistical equilibrium for the molecules of the reactants will be mainly the business of the bath of radiant energy in which they are immersed. The interaction between molecules which come into contact may conceivably take place either with or without the intervention of radiant energy.

Consider our expression for the mechanism of a chemical reaction,

$$a\mathrm{A} + b\mathrm{B} \ldots \longrightarrow c\mathrm{C} + d\mathrm{D} + \ldots \tag{1}$$
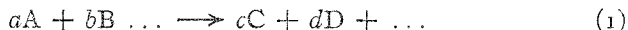
To make our considerations as general as possible let us assume that this reaction may take place with the interaction of radiant energy simul-

taneously from any number of modes of vibration of any frequency. Employing the same considerations that led to Equation 34, it will be found that we may write for the rate of reaction

$$\frac{-dC_A}{dT} = \Sigma \{ s_{ijklmn} \ldots \times C_A a_A \, \epsilon^{-E_i/kT} \, d\sigma_i \times C_A a_A \, \epsilon^{-E_j/kT} \, d\sigma_j \ldots$$

$$\times C_B a_B \, \epsilon^{-E_k/kT} \, d\sigma_k \times C_B a_B \, \epsilon^{-E_l/kT} \, d\sigma_l \ldots \times \ldots \qquad (45)$$

$$\times \frac{8\pi\nu^2}{c^3} \, d\nu_m a_\nu \, \epsilon^{-E_n/kT} \, d\sigma_n \times \frac{8\pi\nu^2}{c^3} \, d\nu_o a_\nu \epsilon^{-E_p/kT} \, d\sigma_p \ldots \}.$$

C_A, C_B, etc., are the instantaneous concentrations of the reacting substances. The product of the factors of the type $C_A a_A \epsilon^{-E/kT} d\sigma$ is continued a times where a is the number of molecules of kind A that enter into the reaction; similarly there are b factors for molecules of Type B, etc. There are as many factors of the type $\frac{8\pi\nu^2}{c^3} \, da_\nu \epsilon^{-E_\nu/kT} \, d\sigma_\nu$ as are necessary to take care of the fact that quantities of radiant energy of more than one frequency might be drawn simultaneously into the reaction. $s_{ijklmn} \ldots$ is the chance per unit time that the indicated chemical change will occur when there is one molecule of the Type A in region $d\sigma_i$, one of Type A in region $d\sigma_j$, etc., similar considerations applying to molecules of Type B, etc., and to the modes of vibration of different frequencies. The summation is to be considered as taken for all possible regions $i\,j\,k\,l\,m\,n \ldots$, for which $s_{ijklmn} \ldots$ has an appreciable value. Cases in which no radiant energy enters into the reaction will, of course, be included if they exist. Their existence is improbable in the case of monomolecular reactions. In the case of many polymolecular reactions the interaction of radiant energy may be entirely unnecessary for the actual chemical change, although the interplay of radiant energy is necessary as we have already shown for the maintenance of the statistical state of maximum probability.

Equation 45 may be rewritten in the integral form

$$-\frac{1}{C_A^a C_B^b} \cdots \frac{dC_A}{dT} = k_1 = \mathscr{S} \ldots \mathscr{S} s (a_A \epsilon^{-E_A/kT} \, d\sigma_A)^a$$

$$(a_B \epsilon^{-E_B/kT} \, d\sigma_B)^b \ldots \left(\frac{8\pi\nu^2}{c^3} \, d\nu a_\nu \epsilon^{-E_\nu/kT} \, d\sigma_\nu \right)^n \quad (46)$$

where the meaning of the symbolism is evident. It should be noticed that our earlier Equation 35 for specific reaction rate is merely a special example of Equation 46 for the particular case of a monomolecular reaction taking place with the inter-action of radiant energy from a single mode of vibration.

By differentiating Equation 46 with respect to the temperature, we may obtain in the same way that we derived Equation 39, a general expression for the temperature coefficient of specific reaction rate,
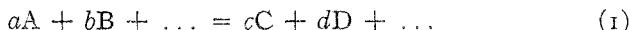
$$\frac{\mathrm{d}\ln k_1}{\mathrm{d}T} = \frac{E_{\text{activated}} - E_{\text{average}}}{RT^2} = \frac{E_c}{RT^2} \qquad (47)$$

where $E_{\text{activated}}$ is the actual energy of the molecules and modes of vibration which enter into the reaction of a mols of A with b mols of B, etc., and E_{average} is the average energy of these elements.

We have thus obtained equations for thermal reaction rate and for the temperature coefficient of thermal reaction rate entirely analogous to those for monomolecular reactions.

As to the photochemical reaction rate for a polymolecular reaction, we cannot make such definite statements as in the case of monomolecular reactions. Since we have come to the conclusion that the state of maximum statistical probability is maintained by the interaction of radiant energy, we are of course forced to the conclusion that all reactions are photochemical. If we illuminate a reacting gas with radiation other than that corresponding to the temperature of the enclosure, there will certainly be some frequencies which will increase the proportion of "activated" molecules over the normal and hence increase the reaction rate. More specific statements on this point, however, do not now seem possible.

7. **Conditions at Equilibrium.**—If we consider again our expression for the mechanism of a chemical change,

$$a\mathrm{A} + b\mathrm{B} + \ldots = c\mathrm{C} + d\mathrm{D} + \ldots \qquad (1)$$

we may write in accordance with Equation 40, for the temperature coefficient of the specific reaction rate in the forward direction

$$\frac{\mathrm{d}\ln k_1}{\mathrm{d}T} = \frac{E_{1\,\text{activated}} - E_{1\,\text{average}}}{RT^2} \qquad (48)$$

and for the temperature coefficient of the specific reaction rate in the reverse reaction

$$\frac{\mathrm{d}\ln k_2}{\mathrm{d}T} = \frac{E_{2\,\text{activated}} - E_{2\,\text{average}}}{RT^2}. \qquad (49)$$

$E_{1\,\text{activated}}$ is the energy that enters into the reaction when a mols of A combine with b mols of B, etc., and $E_{2\,\text{activated}}$ is the energy that enters into the reaction when c mols of C combine with d mols of D, etc. Now it is evident that when the concentrations are such that equilibrium is maintained, a mols of A will combine with b mols of B, etc., in exactly the same time interval that it takes for c mols of C to combine with d mols of D, etc., to reform A, B, etc. Since there will be no transfer of energy to or from the system at equilibrium, it is then evident that the following equation must be true,

$$E_{1\,\text{activated}} = E_{2\,\text{activated}}. \qquad (50)$$

It is also to be noted that at equilibrium we may write

$$K = k_1/k_2 \qquad (51)$$

where K is the equilibrium constant. Combining Equations 48, 49, 50 and 51, we obtain

$$\frac{\mathrm{d}\,ln\,k_1}{\mathrm{d}T} - \frac{\mathrm{d}\,ln\,k_2}{\mathrm{d}T} = \frac{\mathrm{d}\,ln\,K}{\mathrm{d}T} = \frac{E_{2\,average} - E_{1\,average}}{RT^2}$$

It is evident, however, that we may write

$$\Delta E = E_{2\,average} - E_{1\,average}$$

where ΔE is the internal energy change accompanying the reaction. We obtain

$$\frac{\mathrm{d}\,ln\,K}{\mathrm{d}T} = \frac{\Delta E}{RT^2} \tag{53}$$

and have thus deduced the well known van't Hoff equation from the principles of statistical mechanics. This is an important test of the correctness of our development.

V. Further Developments.

The foregoing development has been valuable in providing a derivation of the Arrhenius equation for the temperature coefficient of reaction rate, in providing information as to the relation between thermal reaction rate and photochemical reaction rate, in providing an expression for the temperature coefficient of photochemical reactions and generally in leading to more specific ideas as to the mechanism of chemical reactions. The work, however, has provided no method of predicting the actual magnitude of any individual reaction rate, and this must be regarded as the most important task which chemical kinetics must yet solve.

Some progress towards the solution of the problem is possible in the case of polymolecular reactions. Let us consider for example, the dimolecular reaction

$$A + B \longrightarrow Products. \tag{54}$$
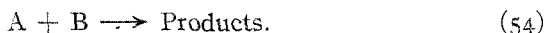
Let us now assume that radiant energy, although necessary for the maintenance of the statistical state of maximum probability, does not enter into the actual chemical change involved in the reaction. Then, in accordance with our general Equation 46, we can write for the specific reaction rate of the above chemical change

$$k_1 = \int\!\!\int s a_A \epsilon^{-E_A/kT} a_B \epsilon^{-E_B/kT} \,\mathrm{d}\sigma_A \mathrm{d}\sigma_B. \tag{55}$$

If now we had sufficient knowledge of the quantities involved in Equation 55, it is evident that we could predict the reaction rate. The dependent and independent variables in Equation 55 are functionally related, as follows:

$$s = s(\sigma_A, \sigma_B)$$
$$a_A = a_A(T)$$
$$E_A = E_A(\sigma_A)$$
$$a_B = a_B(T)$$
$$E_B = E_B(\sigma_B)$$

As to s, it is obvious that s is zero when σ_A and σ_B have such values that the molecules involved are far apart. We might further assume that s has the value unity (i. e., reaction is sure to occur) when the values of σ_A and σ_B are such that the molecules have certain minimum energy contents and such that they have come into contact in the sense of the kinetic theory. Hypotheses of this type have led to useful considerations in the hands of Trautz and W. C. M. Lewis.[1] Any really satisfying solution of the problem, however, would necessitate much more information than we now have as to the nature of the functional relationships of the type

$$E_A = E_A(\sigma_A)$$

connecting the energy of a molecule with its coördinates and momenta. Such information will become available as our knowledge of atomic structure increases, and this is a field where great advances may be expected in the near future. As to the functional relationships of the type $a_A = a_A(T)$, these can be obtained with the help of Equation 25 as soon as the nature of the relationships $E_A = E_A(\sigma_A)$ is known.

In conclusion, although the considerations of this paper have dealt solely with reactions in dilute gases, the general nature of their extension to concentrated gases, non-gaseous systems, and even non-homogeneous systems, will be evident even if exact mathematical treatments are not now possible.

WASHINGTON, D. C.

THE STANDARDIZATION OF WEIGHTS.

BY A. J. HOPKINS, J. B. ZINN AND HARRIET ROGERS.

In order that the student beginning quantitative analysis should acquire, at the very first, a thorough manipulative knowledge of the balance, it has been our custom to provide, as a first exercise, the standardization of his box of weights. This has proved in the past an excellent method of accomplishing the result indicated and in addition he has obtained a knowledge of the relative values of his weights.

During the progress of such a standardization, from the fractional denominations to the 50 g. weight, any error, however slight, is multiplied until at the end a not inconsiderable but factitious correction is accumulated. Richards, in his excellent and well known contribution,[2] has given us a method of redistributing this error according to the relative values of the weights. This method of calculation is now in general use.

[1] *Loc. cit.*
[2] THIS JOURNAL, 22, 144 (1900).