

XL.—*Studies in Catalysis. Part VII. Heat of Reaction, Equilibrium Constant, and Allied Quantities, from the Point of View of the Radiation Hypothesis.*

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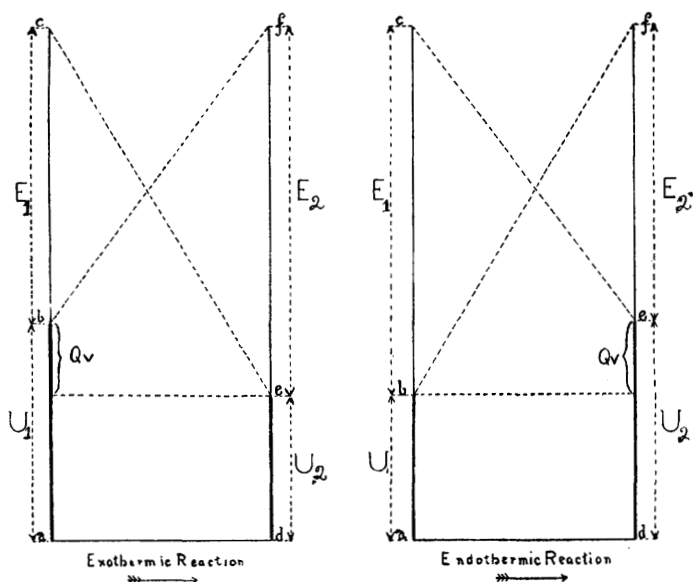
1. *Heat of Reaction and Critical Increment.*

It is well known that the absorption or evolution of heat which accompanies a reaction corresponds, if the reaction is carried out at constant volume, with the change in the average or mean internal energy, usually reckoned per gram-molecule of one of the reactants. In the previous papers of this series (see this vol., p. 389; also T., 1914, **105**, 2330; 1915, **107**, 233; 1916, **109**, 55, 67, 796) use was made of the concept of the critical increment, that is, the extra amount of energy which must be given to a molecule, in excess of its mean internal energy, in order to make the molecule reactive. This concept is due, in the first place, to Marcelin, and has been developed along more quantitative lines by Rice. The critical increment, E , represents in all cases an absorption of energy, such absorption preceding any reactivity which the molecule may exhibit. It is necessary to point out that the assumption of the critical increment having in all cases the same sign (energy absorbed) is, nevertheless, quite compatible with the reaction being as a whole either endothermic or exothermic.

The relation of the critical increment to the heat of the reaction

will be most clearly understood by the aid of the accompanying diagram.

Let us consider the simplest possible type of reaction, $1A \rightleftharpoons 1B$, taking place in the absence of all catalytic effects. The ordinates of the diagram denote internal energy, the length ab corresponding with the mean value U_1 of the internal energy possessed by the molecules of the substance A , and similarly the length de represents the mean energy U_2 of the substance B . Suppose that a given molecule of A possesses the mean value U_1 , then before it can become reactive its internal energy must rise to the point c , by the addition of the critical increment E_1 . At this stage the molecule



possesses internal energy $(U_1 + E_1)$. The molecule may now undergo chemical change into the substance B , with an evolution of energy denoted by the dotted line ce . The molecule now possesses the mean energy de or U_2 , characteristic of the substance B . In passing from c to e the energy emitted is $(U_1 + E_1) - U_2$. In passing from the mean state b to the mean state e , the total energy evolved is $(U_1 + E_1 - U_2) - E_1$, or $U_1 - U_2$. The molecule at e may now receive the critical increment ef or E_2 , and being in the reactive state may be re-transformed into A , possessing the mean energy U_1 . The total energy evolved in passing from e to b is $(U_2 + E_2 - U_1) - E_2$, or $U_2 - U_1$. This expresses the fact that if the reaction is exothermic

from left to right, it is necessarily endothermic on passing in the reverse direction.

When the molecule is in the critical state, it is impossible to say whether it belongs to the system *A* or to the system *B*. That is, the critical state is common to both *A* and *B*. If E_c denotes the critical energy, E_c will have the same value for the *A* and *B* molecules. This is indicated in the diagram by the lines *ac* and *df* being of equal length.

From the above considerations it follows that

$$E_c = U_1 + E_1 = U_2 + E_2.$$

Hence,

$$U_1 - U_2 = E_2 - E_1.$$

But the heat of the reaction, at constant volume, $+Q_v$, is defined thermodynamically as $U_1 - U_2$. Therefore,

$$+Q_v = E_2 - E_1 \quad \dots \quad (1).$$

This equation gives the relation between the heat of the reaction, at constant volume, and the respective critical increments of the reactants and resultants. If the reaction, $A \rightarrow B$, is exothermic, then U_1 is greater than U_2 , and hence E_2 is greater than E_1 . That is, a reaction is exothermic, if the critical increment of the resultants is greater than the critical increment of the reactants. A reaction is endothermic, if the reverse condition holds.

The above result also follows from Rice's equations for the variation with temperature of the velocity constants of the direct and reverse reactions which can be shown to lead to the ordinary van't Hoff isochore.

2. Heat of Reaction and the Critical Quantum.

It has been pointed out in Part V. (*loc. cit.*), on the basis of the radiation hypothesis, in which the active mass of a substance is written as proportional to the product of its concentration into the radiation density of the frequency which the substance is capable of absorbing, that the critical increment, E , is expressed in general by:

$$E = N h \nu,$$

the unit of mass being the gram-molecule, N the number of molecules in one gram-molecule, and h is Planck's constant. The frequency ν , which gives rise to the quantum $h\nu$, which, in turn, supplies the critical increment E , may be conveniently termed the critical frequency. The critical frequency is, in general, considerably higher than the characteristic frequency used in the sense of Einstein to account for atomic or molecular heat. For many reactions, the critical frequency lies in the short infra-red region. This point is referred to later.

If we consider the above simple reversible reaction, $A \rightleftharpoons B$, it is evident that

$$E_1 - E_2 = Nh(v_1 - v_2),$$

where v_1 is the critical frequency of the substance A , and v_2 the critical frequency of B . It follows, therefore, that the heat of the reaction is given by:

$$-Q_v = Nh(v_1 - v_2) \quad . \quad . \quad . \quad (2),$$

and that the van't Hoff isochore may be written:

$$d \log K / dT = Nh(v_1 - v_2) / RT^2 \quad . \quad . \quad (3).$$

Equations (2) and (3) show the relation between the critical frequencies of the reacting substances and the heat of reaction, and consequently the variation of the equilibrium constant with temperature.

If the critical frequency of the reactant is identical with that of the resultant, the heat of the reaction is zero, and the equilibrium constant is independent of temperature. We are here dealing with the ordinary mass action equilibrium constant. If the critical frequency of the reactant is greater than that of the resultant, heat will be absorbed on passing from reactant to resultant, and K as defined above will increase with the temperature. If the critical frequencies of substances are known, it can be stated whether the reaction will be exothermic or endothermic, and the magnitude of the heat effect can be calculated.

Equation (2) was obtained by the author as a logical consequence from the considerations already given in Part V. The relation is not new, however. It has already been deduced by Haber, for a rather special case (*Ber. Deut. physikal. Ges.*, 1911, **13**, 1117), involving the transfer of valency electrons from the reacting substances, calculation being made with the help of data obtained from the selective photoelectric effect. The above method of treatment is of a more general nature, although we have restricted ourselves to the simplest type of chemical equilibrium. In a later section the expression will be given in a more general form.

Equation (2) also gives us information regarding the effect of temperature on the critical frequencies, v_1 and v_2 . On differentiating (2) with respect to temperature, we obtain:

$$-dQ_v/dT = Nh(dv_1/dT - dv_2/dT).$$

Further, from Kirchhoff's equation we have:

$$dQ_v/dT = C_1 - C_2,$$

where C_1 and C_2 are the molecular heats at constant volume of the reactants and resultants. Hence, $C_1 - C_2 = Nh(dv_2/dT - dv_1/dT)$.

For the simple case which we have been considering, it may be inferred on general grounds that C_1 and C_2 are almost identical.

Since, in general, C_1 and C_2 differ, it follows that the critical frequencies vary with temperature. The variation required by the above relation is not to be attributed to a true change in a given frequency, for Planck's equation, which forms the basis of the above deduction, assumes that ν is independent of temperature. The variation is due to the fact that at a higher temperature a different frequency contributes the energy necessary for the reaction.

Referring to Rice's equation (Part V., *loc. cit.*), it is evident that the critical increment E , which stands for the difference $E_c - U_m$, must diminish as temperature rises, for the average energy increases with temperature and E_c is presumably a fixed quantity.

The variation of the critical increment E is given by:

$$dE/dT = d(E_c - U_m)/dT = -dU_m/dT = -C,$$

where C is the molecular heat of the substance decomposing. For reactions in the gaseous state, the value of C per gram-molecule at the ordinary temperature lies between 5 and 10 calories. Hence an increase in temperature of 100° causes U_m to increase or $(E_c - U_m)$ to decrease by 500—1000 calories. From measurements of the temperature-coefficients of various reactions it is known that $(E_c - U_m)$ is of the order of 20,000 cal., so that an increase of 100° will cause E , and therefore ν , to diminish by about 5 per cent. Its exact change can be determined from the values of the molecular heats. It is evident that, for not too great temperature intervals, the effect is negligible as a first approximation.

3. The Magnitude of the Heat Effect accompanying a Reaction.

Determinations of heats of reaction have shown that in many cases such quantities are of great magnitude, for example, the heat of union of hydrogen and oxygen. Since the heat of reaction, at constant volume, is the difference of the mean internal energies of reactants and resultants, it follows that at least one of the systems must possess on the average a correspondingly high internal energy content. An examination of the order of magnitude involved indicates that the mean internal energy in many cases is a great deal higher than can be accounted for by the temperature. If C_v is the molecular heat at constant volume the average internal energy which one gram-molecule of a substance will possess in virtue of its temperature T is represented by $\int_0^T C_v dT$. The average energy of the system $2\text{H}_2 + \text{O}_2$ at the ordinary temperature must be greater than 116,000 calories, since this is the amount of heat evolved by the union of the two substances. This number is, therefore, the lowest conceivable limit of the internal energy of the two gases, and it is evident that, to account for it on the basis of temperature

alone, we should have to ascribe impossibly great values to the molecular heats of the gases. It follows, therefore, that substances in general possess a very large amount of energy at absolute zero, and this energy, which is independent of temperature, manifests itself in chemical reactions. This is evidence, of a chemical nature, in favour of Planck's later assumption, that at absolute zero each resonator contains energy which on the average is $\hbar\nu/2$, where ν is the characteristic frequency.

4. *Temperature and Velocity of Reaction.*

When a reaction proceeds with measurable velocity, this indicates, on the radiation hypothesis, that the temperature radiation existing is capable of giving rise to a sufficient number of quanta of the absorbable frequency, which are required to raise the internal energy of a sensible number of the molecules of the decomposing substance from the mean to the critical state. An examination of a number of the reactions which proceed at the ordinary temperature shows that the effective or critical frequency, one quantum of which is capable of activating a molecule, belongs to the short infra-red region. It has been pointed out in earlier papers that the greater the critical increment the slower is the reaction, a result in good agreement with the radiation hypothesis, for a large critical increment means a correspondingly large critical frequency, and at the ordinary temperature, it is well known, the density of radiation of this type is small. As the temperature is raised, however, there is an increase in the radiation density at all frequencies, and, at the same time, the position of maximum density is moved towards the shorter wave-lengths. We may infer, therefore, that, if a reaction mixture requires to be raised to a high temperature before the reaction becomes measurable, the critical increment, and therefore the critical frequency, is correspondingly high. Reactions which occur with measurable velocity at the ordinary temperature require, as already stated, a quantum of the short infra-red type. Those which become measurable at a temperature, of the order of 1000° , may be expected to require a quantum corresponding with the visible spectrum, whilst those which only take place at still higher temperatures require a quantum belonging to the ultra-violet region. We are considering true thermal reactions, not photochemical reactions as ordinarily carried out.

Further, the fact that certain reactions occur with immeasurably slow velocity at the ordinary temperature, is evidence that one quantum of the critical frequency is required in general to activate a single molecule, and not a large number of smaller quanta, for these smaller quanta are undoubtedly present at the ordinary tem-

perature. One would expect this result on Planck's theory. Thus, if we consider the energy of a molecule as being gradually built up in a field of quanta of relatively small size, it is evident that the energy possessed by the molecule becomes an even multiple of one of these quanta, the oftener, the smaller the quantum. When, however, the internal energy is an even multiple of a quantum, there is, according to Planck, a favourable opportunity for emission. If, therefore, a molecule requires a number, not necessarily a large number, of quanta to bring it into the reactive condition, the probability that it will reach the critical condition is vanishingly small, owing to the opportunities of emission which occur in the building up process. As a simplification of the theory, a simplification which is reasonable in view of the above considerations, we may neglect any contribution made to the rate of decomposition by quanta smaller than the critical quantum. As already pointed out in Part V., the effect of a positive catalyst is to reduce the magnitude of the critical increment, and therefore of the critical frequency, and hence bring about a chemical change at a measurable speed at a lower temperature. It is essential, therefore, when different reactions are compared, that the catalytic effects themselves should be comparable.

5. *Uncatalysed Bimolecular Reactions.*

In Part V. the radiation hypothesis was restricted to a consideration of unimolecular reactions. It is now necessary to extend it to the bimolecular type, as this type is more frequently met with in practice than any other, and, further, from the expressions obtained in this case the necessary modifications for any bimolecular reaction may be easily written down. The fundamental idea is that the active mass of a given species is proportional to the product of its concentration into the radiation density of the absorbable type. That is, active mass \propto concentration $\times u_\nu$, where u_ν is the radiation density of the frequency ν . It was shown that this assumption led to certain conclusions, in the case of unimolecular reactions, which were in agreement with experiment.

If two substances, *A* and *B*, react together in a dilute system the principle of active mass states that the rate of the reaction is proportional to the product of the active masses. We are considering the reaction in one direction only in the first instance. Expressing active mass in terms of the radiation hypothesis, the above statement becomes:

$$\text{rate of reaction} \propto C_A \times C_B \times u_{\nu A} \times u_{\nu B}.$$

If the temperature is maintained constant and the system is dilute, the radiation density terms are constant, and the new formu-

lation reduces to the ordinary expression for the rate of a bimolecular reaction.

The next step consists in substituting Planck's expression for each of the radiation density terms. For the short infra-red region, it has been shown (Part V) that a simplified form may be employed, namely,

$$u_{\nu_A} = \frac{8\pi h \nu_A^3 n_A^3}{c^3} \cdot e^{-h\nu_A/kT};$$

where ν_A is the critical frequency absorbed by the substance A ; n_A the refractive index of the system for the frequency ν_A ; h Planck's constant; c , the velocity of light in a vacuum; k , the gas constant per molecule. $Nk=R$, where R is the gas constant per gram-molecule, and N is the Avogadro number. T , the absolute temperature.

For u_{ν_B} an analogous expression can be written down. Hence,

$$u_{\nu_A} \times u_{\nu_B} = \frac{64\pi^2 h^2 \nu_A^3 \nu_B^3 n_A^3 n_B^3}{c^6} \cdot e^{-h(\nu_A + \nu_B)/kT}.$$

Let us suppose that the initial concentrations of A and B are a and b mols. per litre respectively. If x mols. have reacted after a certain time, t , the rate of the reaction is

$$dx/dt \propto (a-x)(b-x) \times \frac{64\pi^2 h^2 \nu_A^3 \nu_B^3 n_A^3 n_B^3}{c^6} \cdot e^{-h(\nu_A + \nu_B)/kT}.$$

Retaining the refractive index terms n_A^3 and n_B^3 , and collecting together the factor of proportionality and the quantity,

$$\frac{64\pi^2 h^2 \nu_A^3 \nu_B^3}{c^6}$$

under the symbol P , we obtain

$$dx/dt = P(a-x)(b-x)n_A^3 n_B^3 \cdot e^{-h(\nu_A + \nu_B)/kT} \quad . \quad . \quad (4)$$

On integrating this expression, the temperature being maintained constant, we obtain

$$\frac{1}{(a-b)t} \log \frac{a(b-x)}{b(a-x)} = P n_A^3 n_B^3 e^{-h(\nu_A + \nu_B)/kT}.$$

But the expression on the left-hand side is simply the observed velocity constant of the reaction. Hence,

$$k_{\text{obs.}} = P n_A^3 n_B^3 \cdot e^{-h(\nu_A + \nu_B)/kT} \quad . \quad . \quad . \quad (5)$$

Now, if we regard P , and the refractive index terms, as sensibly independent of temperature—for gaseous systems the indices are practically unity (compare Part V)—we can easily obtain the expression for the effect of temperature on the observed velocity constant. The expression is:

$$\frac{d \log k_{\text{obs.}}}{dT} = \frac{h(\nu_A + \nu_B)}{kT^2} = \frac{Nh(\nu_A + \nu_B)}{RT^2} \quad . \quad . \quad . \quad (6)$$

The term P has been regarded as independent of temperature. P , however, includes a proportionality factor, which appears to involve the probability of a molecule of A meeting a molecule of B . This factor depends on the average speed of the molecules, which in turn is known to vary as the square root of the absolute temperature. For a rise of 10° at the ordinary temperature, this variation amounts to 2 per cent. of the velocity constant, a quantity which is small compared with the actual effect of temperature observed. We can allow for the variation of P by writing $P = P_0 \sqrt{T}$, where P_0 is independent of temperature, in so far as the refractive index terms are independent of temperature. Equation (3) then becomes:

$$k_{\text{obs.}} = P_0 \sqrt{T} \cdot n_A^3 n_B^3 e^{-h(\nu_A + \nu_B)/kT}. \quad (7)$$

The final expression for the variation of the velocity constant with temperature may be put in the form:

$$\frac{d \log k_{\text{obs.}}}{dT} = \frac{Nh(\nu_A + \nu_B)\frac{1}{2} + RT}{RT^2} \quad (8)$$

At the ordinary temperature, $\frac{1}{2}RT$ is of the order 300 calories, whilst $Nh(\nu_A + \nu_B)$ is of the order 20,000 calories, so that the correction term is small. It will be observed that this small quantity occurs in the complete Marcellin-Rice equation. It is evident from the above that as a first approximation we can regard P as independent of T .

If the reaction is a multimolecular one, we can obtain a general form for equation (6), namely,

$$\frac{d \log k_{\text{obs.}}}{dT} = Nh \Sigma \nu_{\text{reactant}} / RT^2 \quad (9)$$

Experimental illustrations of equations (6), (8), and (9) will be given in a subsequent paper.

6. The Order of a Reaction and the Magnitude of the Temperature-coefficient.

The problem of finding a connexion between the order of a reaction and the temperature-coefficient has already received some attention. The conclusions arrived at, however, are wholly discordant. Thus, von Halban (*Zeitsch. physikal. Chem.*, 1909, **67**, 129) concludes that a true unimolecular reaction possesses a higher temperature-coefficient than a multimolecular reaction, and claims that this is borne out by experiment. On the other hand, Skrabal (*Chem. Zeit.*, 1913, **37**, 1169; *Monatsh.*, 1914, **35**, 1157) concludes that the higher the order of the reaction, the greater the tempera-

ture-coefficient. That experimental evidence can be adduced in favour of both views is simply due to the fact that velocity constants, measured at various temperatures, are not comparable quantities, owing to the existence of catalytic effects, which vary from case to case.

It will be observed, at the same time, that the radiation hypothesis points to the general correctness of Skrabal's contention. This arises from the fact that in a multimolecular reaction (equation 9), in its simplest form, the Arrhenius quantity A is the sum of the quanta involved, each of which refers to one of the reacting species, and therefore the higher the order of the reaction the greater the number of quanta required, and hence the greater the value of the temperature-coefficient. This conclusion is based on the assumption that the critical frequencies concerned are of comparable magnitude. This restriction is important in view of the considerations advanced in section 4 of this paper.

7. Mass Action Equilibrium in an Uncatalysed Multimolecular Reversible Reaction.

Let us consider the following reaction occurring in a dilute gaseous system: $A + B = C + D$.

For the reaction from left to right, we have from equation (5) the following expression for the velocity constant:

$$k_{\text{obs.}} = P n_A^3 n_B^3 \cdot e^{-h(\nu_A + \nu_B)/kT}.$$

For the reverse reaction we have

$$k'_{\text{obs.}} = P' n_C^3 n_D^3 \cdot e^{-h(\nu_C + \nu_D)/kT}.$$

If we write $k_0 = P n_A^3 n_B^3$, and $k'_0 = P' n_C^3 n_D^3$, in which k_0 and k'_0 are constants, practically independent of temperature, we obtain the relation

$$K = k_{\text{obs.}}/k'_{\text{obs.}} = \frac{k_0}{k'_0} \cdot e^{+h(\nu_C + \nu_D - \nu_A - \nu_B)/kT}.$$

where K is the ordinary mass-action equilibrium constant, and varies with temperature. k_0 and k'_0 may be termed the "ideal" velocity constants, and their ratio, K_0 , the "ideal" equilibrium constant, for K_0 is independent of temperature as a first approximation.

It follows, therefore, that

$$d \log K/dT = -Nh(\nu_C + \nu_D - \nu_A - \nu_B)/RT^2,$$

which may be written in the general form

$$d \log K/dT = \frac{Nh(\sum \nu_{\text{reactants}} - \sum \nu_{\text{products}})}{RT^2} \quad \dots \quad (10)$$

Hence the general form of equation (2) is:

$$-Q_p = Nh(\sum \nu_{\text{reactants}} - \sum \nu_{\text{products}}) \quad \dots \quad (11)$$

Experimental illustration of this expression will be given in a subsequent paper.

8. *Intermediate Compound Formation in Bimolecular Reactions.*

In section 5 of this paper, bimolecular reactions were considered on the assumption that the observed rate was due to the direct interaction of the two components. In many cases there is evidence that an additive compound is formed, such addition preceding the substitution reaction. Such additive compounds occur especially in the case of reactions in solution, for example, the inversion of sucrose and the hydrolysis of esters. The existence of such compounds has to be considered to complete the treatment of bimolecular reactions. The important case is that in which a single stable intermediate compound, AB , is formed practically instantaneously from its components, A and B , and exists in mass-action equilibrium with these components.

The condition for equilibrium is given by

active mass of $A \times$ active mass of $B =$ active mass of AB ,
or

$$K_0 C_A u_{\nu_A} \times C_B u_{\nu_B} = C_{AB} u_{\nu_{AB}} \quad . \quad . \quad . \quad (12)$$

where K_0 is the ideal equilibrium constant independent of temperature as a first approximation.

The observed rate of the reaction, dx/dt , is proportional to the active mass of AB , that is, proportional to the product of the active masses of A and B . Hence

$$dx/dt \propto K_0 C_A C_B u_{\nu_A} u_{\nu_B} = K_0 P \cdot (a-x)(b-x) n_A^3 n_B^3 \cdot e^{-h(\nu_A + \nu_B)/kT}$$

Hence

$$k_{\text{obs.}} = K_0 P \cdot n_A^3 n_B^3 \cdot e^{-h(\nu_A + \nu_B)/kT} \quad . \quad . \quad . \quad (13)$$

This expression differs from that previously obtained (equation 5) in containing the constant K_0 .

It follows, from equation (13), that

$$d \log k_{\text{obs.}}/dT = Nh(\nu_A + \nu_B)/RT^2 \quad . \quad . \quad . \quad (14)$$

which is identical with equation (6).

The above result may be obtained in a somewhat different way.

The equilibrium condition of the reaction $A + B \rightleftharpoons AB$ is represented on the ordinary mode of formulation by the expression

$$K \cdot C_A C_B = C_{AB},$$

where K is the ordinary mass-action equilibrium constant, and varies with temperature according to the relation

$$d \log K/dT = -Q_0/RT^2.$$

The disappearance of A and B is due to the decomposition of the compound AB . Hence the rate of the reaction dx/dt is pro-

portional to C_{AB} on the usual mass-action formulation. Introducing the radiation hypothesis, the rate is given by

$$\begin{aligned} dx/dt &= P \cdot C_{AB} \cdot n_{AB}^3 e^{-h\nu_{AB}/kT} \\ &= P \cdot K \cdot C_A C_B n_{AB}^3 e^{-h\nu_{AB}/kT}, \end{aligned}$$

and hence

$$k_{\text{obs.}} = P \cdot K \cdot n_{AB}^3 e^{-h\nu_{AB}/kT}.$$

Writing $P \cdot n_{AB}^3$ as k_0 , we obtain the relation

$$\log k_{\text{obs.}} = \log k_0 + \log K - Nh\nu_{AB}/RT.$$

But from equation (11)

$$-Q_v = Nh(\nu_A + \nu_B - \nu_{AB}).$$

Therefore

$$\log k_{\text{obs.}} = \log k_0 + \log K - \frac{Q_v + Nh(\nu_A + \nu_B)}{RT}.$$

Hence

$$d \log k_{\text{obs.}}/dT = d \log K/dT + Q_v/RT^2 + Nh(\nu_A + \nu_B)/RT^2.$$

But

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

Therefore

$$d \log k_{\text{obs.}}/dT = Nh(\nu_A + \nu_B)/RT^2,$$

which is identical with equation (14).

We conclude from equations (13) and (14) that the existence of an intermediate additive compound, which takes part in the reaction, introduces a numerical change into the velocity constant at any given temperature, but introduces no change in the value of the temperature-coefficient of the reaction.

In the above consideration of equilibrium conditions we have assumed that catalytic effects, such as those due to the solvent in the case of reactions in solution, are absent. In a subsequent paper, reactions in solution will be considered, as it can be shown that the anti-catalytic effect which many solvents exhibit involves certain changes, not only in the magnitude of the temperature-coefficient of the velocity constant, but also in the expression for the equilibrium concentration of intermediate compounds. These modifications indicate that, for reactions in solution, the ordinary van't Hoff isochore is not strictly accurate, although the deviation, which is a calculable quantity, is small. The integration of the isochore, in terms of the radiation hypothesis, will also be considered. This problem is of special interest, as the quantity K_0 , which has been called the ideal equilibrium constant, appears to include the integration constant, which is usually taken account of by means of Nernst's heat theorem. Finally, the thermodynamic affinity of a chemical process is intimately bound up with the same quantity.

9. Summary.

(1) The heat of reaction has been considered from the point of view of the statistical expression of Marcelin and Rice, as well as from the point of view of the radiation hypothesis. It is shown that the concept of the critical increment, as energy absorbed, is quite compatible with the existence of exothermic and endothermic changes.

(2) The heat of reaction is shown to depend on the difference between the critical frequencies of reactants and resultants, a relation previously obtained, on a less general basis, by Haber.

(3) It is pointed out that the magnitude of the heat effect accompanying certain reactions leads to the conclusion that molecules contain large amounts of energy even at absolute zero.

(4) A consideration of the temperature region at which an uncatalysed reaction first proceeds with measurable velocity yields some qualitative information respecting the order of magnitude of the quantum required to activate a molecule of the substance.

(5) Bimolecular reactions have been treated from the point of view of the radiation hypothesis, and quantitative expressions found for the velocity constant and for the temperature-coefficient. It is inferred that, *ceteris paribus*, the higher the order of the reaction the greater is its temperature-coefficient likely to be.

(6) The question of the formation of intermediate compounds in multimolecular reactions is considered, and it is shown that the existence of such a compound will modify the value of the velocity constant, but will not affect the temperature-coefficient provided catalytic effects are excluded.

The work is being extended in various directions.

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