

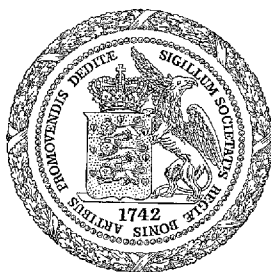
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ON THE VELOCITY OF  
UNIMOLECULAR REACTIONS

BY

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1. It is well known that the explanation of reactions which follow the unimolecular law (reactions of the first order) involves theoretical difficulties concerning the necessary rate of transfer of the activation energy. These difficulties seem to have been overcome mainly by O. K. RICE and H. C. RAMSPERGER<sup>1</sup>, R. H. FOWLER and E. K. RIDEAL<sup>2</sup>, and C. N. HINSHELWOOD<sup>3</sup>. Further contributions to the elucidation of these problems were made by G. N. LEWIS and D. F. SMITH<sup>4</sup>, and by the present author<sup>5</sup>. However, it should not be forgotten that already several years earlier M. POLANYI<sup>6</sup> applied a quite similar treatment of the problem. In the present paper, we shall not be concerned with these difficulties, as it will be assumed that the reacting molecules are dissolved in a sufficiently dense solvent, so that the necessary transfer of energy to the reacting molecules occurs by collisions with the solvent molecules. This way of avoiding the theoretical difficulties by means of realisable experimental conditions was proposed many years ago by F. A. LINDEMANN<sup>7</sup>. The necessary assumptions may be expressed as follows. All molecules of the same kind, the reacting ones included, have the same activity, i. e., the number of molecules in a given state of energy multiplied by the reciprocal Boltzmann-factor is independent of this state.

2. The problem investigated here is mainly that of the absolute values of the velocity constants but moreover, other sides of the velocity-problem will be treated.

<sup>1</sup> J. Am. Chem. Soc. **49** (1927) 1617.

<sup>2</sup> Proc. Roy. Soc. **113 A** (1926) 570.

<sup>3</sup> Proc. Roy. Soc. **113 A** (1926) 530.

<sup>4</sup> J. Am. Chem. Soc. **47** (1925) 1514.

<sup>5</sup> Proc. Cambridge Phil. Soc. **23** (1926) 438.

<sup>6</sup> Zs. f. Phys. **1** (1920) 341.

<sup>7</sup> Trans. Far. Soc. **17** (1922) 599.

As is well known, the constants may be expressed as a product of two factors, one of which is almost independent of the temperature and may conveniently be called the frequency factor ( $f$ ), and the other which has the exponential form  $e^{\frac{-Q}{RT}}$ . Both factors can be determined by experiments at different temperatures, the factor  $f$ , however, only with very moderate accuracy. This has always been a great difficulty for the theories, since, at least in many cases, any theory which gives only the right order of magnitude of  $f$  can be used to describe the experiments.

The experiments show that  $f$  is generally of the order of magnitude  $10^{+13} - 10^{+14}$  reciprocal seconds, a value which roughly corresponds to the frequencies of molecular oscillations. On the other hand, this value is not very different from  $\frac{RT}{h}$ , where  $R$  is the gas constant per molecule. With  $T = 300^\circ$ ,  $RN = 8.316 \cdot 10^7$  erg/ $^\circ\text{C}$ ,  $N = 6.06 \cdot 10^{23}$ ,  $h = 6.55 \cdot 10^{-27}$  we get  $\frac{RT}{h} = 6.28 \cdot 10^{12}$ . Incidentally, it is a rather old observation that  $f$  is of this order of magnitude (cf. for instance K. F. HERZFELD<sup>1</sup>, M. TRAUTZ<sup>2</sup>, and S. DUSHMANN<sup>3</sup>).

One further result of the experiments may be mentioned here. Investigations of groups of analogous reactions seem to indicate that a correlation between  $f$  and  $Q$  exists, viz.  $f$  is almost proportional to  $e^{\frac{+dQ}{r}}$ , where  $r$  is a positive constant of the order of magnitude  $RT$ , and  $dQ$  is the deviation of  $Q$  from some common value. However, it is doubtful in some cases whether this correlation is real, since an inaccuracy  $dQ$  in the determination of  $Q$  from a given series of experiments necessarily introduces an erroneous factor  $e^{\frac{+dQ}{RT_1}}$  into  $f$ .  $T_1$  is the mean temperature of the respective series of experiments. In view of the experimental evidence it seems difficult, however, completely to deny the existence of a correlation between  $Q$  and  $f$ . Finally,  $Q$  depends in some cases on  $T$ <sup>5</sup>. Obviously, such a dependency

<sup>1</sup> Ann. d. Phys. **59** (1919) 613.

<sup>2</sup> Zs. f. Physik **2** (1920) 113.

<sup>3</sup> J. Am. Chem. Soc. **43** (1921) 397.

<sup>4</sup> J. K. SYRKIN: Z. anorg. allg. Chem. **199** (1931) 28. G.-M. SCHWAB, Z. physik. Chem. **B 5** (1929) 406. Comp. the discussion by M. G. EVANS and M. POLANYI. Trans. Far. Soc. **32** (1936) 1334.

<sup>5</sup> Cf. f. inst. V. K. LA MER. J. chem. Phys. **1** (1933) 289. P. M. LEININGER and

is not at all surprising, since, in analogy with the equilibrium case, a heat capacity of the reacting molecules different from that of the normal molecules might very well be assumed. Many years ago, F. E. C. SCHEFFER<sup>1</sup> showed that the influence of this heat capacity effect, when it is only a few times  $R$ , on the velocity constants in dependence on temperature could not be detected, not even in experiments accurate to about 1 % and extending over the experimentally accessible temperature interval of 40 to 50 degrees. It is therefore astonishing that the existence of the effect has actually been proved beyond doubt in several cases; the corresponding "difference in heat capacity" was calculated from the experiments to as much as 40 to 50 times  $R$ ; regarding the relatively simple molecules investigated, these values are incredibly high.

In view of all these difficulties, a theory which is suited to meet the needs of the experimenter would be very useful. Numerous authors have treated this subject<sup>2</sup> and also the present author has made an attempt to give some contributions to this end<sup>3</sup>. These papers must to some extent be considered tentative and they are unsatisfactory in some respects, so that it was deemed necessary to review the whole question.

It is the trend of the present paper to look for solutions of the velocity problem on the basis of such knowledge which may be considered reasonably accurate. This should comprise:

- 1) The value of  $Q$  known from experiments with a reasonable degree of accuracy.
- 2) The force function for the atom displaced inside the molecule during the reaction in the field arising from the rest of the molecule. However, we shall only use the force function valid in the vicinity to the stable equilibrium points, and we shall endeavour to avoid a detailed formulation of the force function in the proximity of the unstable equilibrium point, cf.  $B$  in Fig. 1. The numerical value of the potential energy at this point is obviously given by  $Q$ .

M. KILPATRICK, J. Am. Chem. Soc. (1938) 2891. E. A. MOELWYN HUGHES, Proc. Roy. Soc. London **A 164** (1938) 295.

<sup>1</sup> Koninkl. Akad. Wetensch. Amsterdam **19** (1917) 636.

<sup>2</sup> H. EYRING, M. POLANYI, E. WIGNER: For references, cf. Trans. Far. Soc. **34** (1938), J. chem. Phys. **7** (1939).

<sup>3</sup> Z. physik. Chem. **B 33** (1936) 145, **37** (1937) 374, **40** (1938) 183.

- 3) The knowledge of the force function in the vicinity to the unstable equilibrium point will be replaced by an assumption concerning the definition of the surface in the space of configuration<sup>1</sup> (e. g. in ordinary space) which separates the two regions belonging to the two possible types of the molecule.

To make the essential features appear more clearly, the actual calculation will be restricted to unidimensional reactions, the mathematical difficulties thus being reduced to a minimum. In this case, the "surface" mentioned above is reduced to a point on a line which then represents the "space".

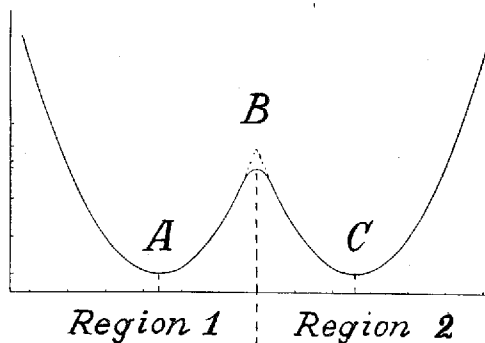


Fig. 1.

3. In recent years, it has become the general view that the "normal" value of  $f$  is  $\frac{RT}{h}$ ; this view has been shared by the present author. However, this assumption would be in contradiction to the classical theory, as then the equilibrium condition between two isomeric molecules would be  $K = e^{-\frac{\epsilon_1 - \epsilon_2}{RT}}$ , where  $\epsilon_1 - \epsilon_2$  is the energy difference between two isomeric molecules. According to classical statistical mechanics this does not hold, at least not in the simple case we are going to discuss.

We consider a model of a pair of isomeric molecules consisting of a unidimensional field of force in which a particle of a mass  $m$  is moving. The field of force is supposed to have the form of two parabolas as indicated in Figure 1. The two parabolas may not have the same parameter, i. e. we assume that

<sup>1</sup> Cf. J. chem. Physics 7 (1939) 23, and p. 12 of this paper.

the force acting on the particle is  $-\alpha_1 x_1$  in the region 1 and  $-\alpha_2 x_2$  in the region 2, where  $\alpha_1$  and  $\alpha_2$  are the force constants and  $x_1$  and  $x_2$  the distances from the respective equilibrium points  $A$  and  $C$ . In order to describe the state of the particle in the classical way we need two coordinates, hence in the present case simply one coordinate in ordinary space and one which specifies the momentum of the particle. If these coordinates are denoted as  $q$  and  $p$ , respectively, we get for the energy in the region 1

$$\epsilon = \frac{1}{2} \alpha_1 q^2 + \frac{1}{2m} p^2 + \text{const.} \quad (1)$$

According to GIBB's statistical mechanics, the phase density of the probability  $P$  in our two-dimensional space is a function of the energy alone and has the form  $A \cdot e^{\frac{-\epsilon}{RT}}$ . Of course, we may put the potential energy at the boundary between the two regions equal to zero and, consequently, the phase density of particles in rest at this boundary equal to  $A$ , which constant thus is common to both regions.

The density in phase becomes accordingly

$$P = A \cdot e^{\frac{\epsilon_1}{RT}} \cdot e^{\frac{-\frac{1}{2}(\alpha_1 q^2 + \frac{1}{m} p^2)}{RT}}, \quad (2)$$

where  $\epsilon_1$  is the height from the vertex of parabola 1 to the maximum point, as we have  $\epsilon = -\epsilon_1 + \frac{1}{2} \alpha q^2 + \frac{p^2}{2m}$  (1 a).

The total number of particles in region 1 is thus

$$N_1 = A \cdot e^{\frac{\epsilon_1}{RT}} \iint e^{\frac{-\frac{1}{2}(\alpha_1 q^2 + \frac{1}{m} p^2)}{RT}} dq dp. \quad (3)$$

The integration with respect to  $p$  has to be performed from  $p = -\infty$  to  $p = +\infty$ , and thus we get

$$N_1 = A \cdot e^{\frac{\epsilon_1}{RT}} \sqrt{2mRT\pi} \int e^{-\frac{1}{2} \alpha_1 q^2} dq. \quad (4)$$

Here, the integration must be performed from  $q = -\infty$  to a positive value of  $q$  given by the equation  $\epsilon_1 = \frac{1}{2} \alpha_1 q^2$ . If, however,  $\epsilon_1$  is

some times (f. inst. 10 times) greater than  $RT$ , it is admissible to choose the upper limit positively infinite; in this way we obtain

$$N_1 = A \cdot e^{\frac{\epsilon_1}{RT}} \sqrt{2mRT\pi} \sqrt{\frac{2}{\alpha_1} RT\pi}. \quad (5)$$

However,  $\frac{m}{\alpha_1} = \frac{1}{4\pi^2\nu_1^2}$  (6), where  $\nu_1$  is the frequency of the oscillator in the region 1 (which is independent of the energy) which leads to

$$N_1 = A \cdot e^{\frac{\epsilon_1}{RT}} \frac{RT}{\nu_1}. \quad (5_1)$$

In exactly the same way we get  $N_2$ .

$$N_2 = A \cdot e^{\frac{\epsilon_2}{RT}} \frac{RT}{\nu_2} \quad (5_2)$$

(where  $A$  is the same constant as above while  $\nu_2$  and  $\epsilon_2$  may be different from  $\nu_1$  and  $\epsilon_1$ ), and the equilibrium constant becomes

$$\frac{N_1}{N_2} = \frac{\nu_2}{\nu_1} e^{\frac{\epsilon_1 - \epsilon_2}{RT}}. \quad (6)$$

If  $k_1$  is the velocity constant of the reaction  $1 \rightarrow 2$ , and  $k_{-1}$  is the constant of the reverse reaction  $2 \rightarrow 1$ , we have, as usual,

$$\frac{k_1}{k_{-1}} = \frac{N_2}{N_1} \quad \text{or} \quad \frac{k_1}{k_{-1}} = \frac{\nu_1 e^{\frac{-\epsilon_1}{RT}}}{\nu_2 e^{\frac{-\epsilon_2}{RT}}}. \quad (7)$$

Hence, the classical expression for the velocity of a reaction in the harmonic case must contain the factor  $\nu$ , the frequency of the oscillation in question.

4. It is now the question whether these considerations may also be extended to the case where an equilibrium between the two forms is lacking. This means that we must try to evaluate the flow of particles at the boundary which separates the two forms of molecules from each other. We consider again the case of quasi-elastic oscillations around one of two centers.



Statistical mechanics then offers an expression for the flow across a boundary  $q_1$ , given by  $\frac{1}{2} \alpha_1 q_1^2 = \varepsilon_1$ . In the equilibrium case, the flow will be

$$s = \int P \dot{q} dp, \text{ where } \dot{q} \equiv \frac{dq}{dt}$$

and

$$P = A \cdot e^{\frac{\varepsilon_1}{RT}} \cdot e^{-\frac{1}{2} \alpha_1 q_1^2} \cdot e^{-\frac{1}{2m} \frac{p^2}{RT}}.$$

According to the canonical equation,  $\dot{q} = \frac{\partial \varepsilon}{\partial p} = \frac{\partial \varepsilon_p}{\partial p}$ , and we thus get the total flow for positive values of  $p$

$$s_+ = A \int_0^{\infty} e^{-\frac{1}{2m} \frac{p^2}{RT}} d\varepsilon_p = ART \quad \text{or} \quad s_+ = N_1 e^{\frac{-\varepsilon_1}{RT}} \cdot \nu_1. \quad (8)$$

The flow in the opposite direction will be of exactly the same value but of a negative sign, and the resultant flow thus becomes zero. If it was permissible to suppose that the reaction in the direction from left to right occurs with the velocity  $s_+$  and that in the opposite direction with the same velocity, the above expression would be the solution of the problem. Unfortunately, however, this is not the case, as we have to assume that the motion of the particle is disturbed by collisions with the solvent molecules. In this case we must treat the problem as a diffusion problem, and our expression for the flow must contain a diffusion coefficient which is difficult to evaluate.

5. We shall, however, attack the problem just from this point of view. Recently, the author showed that a natural extension of the Arrhenius picture concerning the mechanism of a chemical reaction would lead to a process in which particles diffuse inside the molecule (or complex of molecules) in the intramolecular field of force<sup>1</sup>. When applied to actual problems, this picture of the mechanism is not very different, if at all, from that known as the transition state method developed by H. EYRING, M. POLANYI, E. WIGNER and others<sup>2</sup>. However, I consider it an advantage to state explicitly that the problem will be treated as a diffusion problem.

<sup>1</sup> Cf. ref. 3) p. 5, and H. A. KRAMERS, *Physica* 7 (1940) 284.

<sup>2</sup> Cf. ref. 2) p. 5.

6. It can easily be shown that EINSTEIN's expression for the intensity of flow  $s$  in a unidimensional field of force may be written

$$s = -D\varphi^{-1} \frac{d}{dx} c\varphi, \quad (9)$$

where  $D$  is the diffusion coefficient which we assume to be constant in time and space.  $c$  is the linear density of the points representing the position of the particle on the  $x$ -axis and  $\varphi$  is defined by  $\ln \varphi = V$ , where  $V$  is the potential energy  $U(x)$  divided by  $RT$ . This leads to

$$s = -D \frac{dc}{dx} + c \frac{D}{RT} K_x$$

which is the well known EINSTEIN expression for the diffusion in a force-field.

From the equation expressing the conservation of the number of particles

$$-s' = \dot{c} \quad (10)$$

and (9) we get by substitution of  $c\varphi = y$

$$D(y'' - V'y') = \dot{y}, \quad (10 a)$$

as  $\varphi$  is independent of time.

7. In reaction kinetics we are only interested in reactions which are so slow that  $y$  with a very high approximation can be considered stationary in time. This can easily be seen in the special case  $V = \frac{x^2}{4a} = \frac{\alpha x^2}{2RT}$ , i. e. the harmonic oscillator. In this case, our equation becomes

$$2ay'' - xy' = \frac{2a\dot{y}}{D}, \quad (11)$$

and may be solved as follows: We look for a solution which obeys the differential equation  $\dot{y} = -ky$ , indicating that the linear point density decreases with time everywhere in the same proportion.  $k$  is the ordinary unimolecular velocity constant. Thus, the partial differential equation (11) becomes an ordinary differential equation

$$2ay'' - xy' = -y \frac{2ak}{D}, \quad (12)$$

where the pure number  $\frac{2ak}{D}$  is exceedingly small as compared to 1. The estimation is as follows: Per definitionem  $2a = \frac{RT}{\alpha}$ ; at room temperatures and the usual values of  $\alpha$  this is of the order of magnitude  $10^{-18}$  cm<sup>2</sup>. We know almost nothing about  $D$ , but as a reasonable assumption we might choose the values found for ordinary diffusion coefficients in liquids; in the case of water, this value happens to be of the same order of magnitude as  $\frac{h}{4\pi m}$ , where  $h$  is PLANCK'S constant and  $m$  the mass of the molecule. Hence, we consider  $D$  to be of the order of magnitude  $10^{-4}$  cm<sup>2</sup>/sec. For reactions with measurable velocities,  $k$  must be less than  $1$  sec<sup>-1</sup>, and the order of magnitude of  $\frac{2ak}{D}$  thus becomes  $10^{-14}$  or less.

The exact solution of the equation

$$2ay'' - xy' + \nu y = 0,$$

where  $\nu$  is a fraction, was given by N. NIELSEN<sup>1</sup>; for practical purposes, however, this solution seems too laborious. It is easier and sufficiently accurate to use an approximation which we obtain in the following way:

In accordance with the foregoing remarks, the solutions of (11) must differ but slightly from the solutions of

$$2ay'' - xy' = 0 \tag{13}$$

which are  $y = A = \text{const.}$  (in space) and  $y = \int_0^x \varphi dx$ , where  $\ln \varphi = \frac{x^2}{4a}$ . However, when no reaction occurs, the distribution must evidently be given by  $y = A$  which expresses the "barometric formula"  $c = A\varphi^{-1}$ . The solution of (11) must therefore be  $y = A + \eta$  which, by multiplication with  $\varphi^{-1}$  and integration, gives the total number of particles  $N = A \int_{-\infty}^l \varphi^{-1} dx$ , since the integral  $\int_{-\infty}^l \eta \varphi^{-1} dx$  must be small as compared to  $N$ .

Correspondingly, we may assume  $y = B + \eta$  and  $N = B \int_{-\infty}^l \varphi^{-1} dx$ , since the integral  $\int \eta \varphi^{-1} dx$  must be small as compared to  $N$ . Disregarding  $\eta$  as compared to  $B$  we therefore get from (11)

<sup>1</sup> D. Kgl. Danske Vidensk. Selsk. Math.-fys. Medd. I, 6 p. 61 (1918).

$$2a\eta'' - x\eta' = B\frac{2a}{D} \quad (14)$$

from which by "variation of the constants"

$$\eta = -\frac{B}{D} \left[ \int^x J\varphi^{-1} dx - J \int^x \varphi^{-1} dx \right]. \quad (15)$$

Here,  $y_1 = 1$ ,  $y_2 = J = \int_0^x \varphi dx$  and  $y_1 y_2' - y_1' y_2 = \varphi$ , respectively, are the two particular solutions of (13) and their differential-determinant.

In order to employ these expressions for the determination of  $\frac{\dot{N}}{N} = -k$ , we introduce a definition of the point  $x = l$ , which separates the regions (on the  $x$ -axis) corresponding to the two forms of the molecule (the transition point): In one region  $c$  (or  $y$ ) decreases everywhere with time, and in the other one  $c$  increases everywhere with time. Consequently, at  $x = l$ ,  $c$  must remain constant; on account of the time-dependent constants  $A$  and  $B$ , this is only possible if  $c$ , and thus  $y$ , are zero at that point. At  $x = l$  we get therefore

$$0 = y = A - \frac{B}{D} \left[ \int_{-\infty}^l J\varphi^{-1} dx - J \int_{-\infty}^l \varphi^{-1} dx \right], \quad (16)$$

where the lower limit of integration is now determined by the condition that the flow  $s$  defined by  $-D\varphi^{-1}y'$  must be zero in the negative infinite; at  $x = l$  it becomes  $-B \int_{-\infty}^l \varphi^{-1} dx$ .

Since  $J$  is an odd function of  $x$  and  $J\varphi^{-1} \rightarrow \frac{2a}{x}$  for great values of  $x$ <sup>1</sup>, the second term on the right side must cancel as compared to the third one, and we get with good approximation

$$k = -\frac{B}{A} = -\frac{\dot{N}}{N} = \frac{D}{J\sqrt{4\pi a}}, \quad (17)$$

as  $\int_{-\infty}^l \varphi^{-1} dx \rightarrow \sqrt{4\pi a}$  when  $\ln \varphi = \frac{l^2}{4a}$  is only moderately high.

<sup>1</sup> T. J. STIELTJES: Acta mathematica 9 (1887), 157.

As said above  $J$  approximates  $\frac{2a}{l} \cdot \frac{l^2}{e^{4a}}$  for high values of  $\frac{l^2}{4a} = \frac{Q}{RT}$ . It seems, however, that this solution cannot be the correct one, because if it were applied to two reciprocal reactions it would lead to an expression for the equilibrium constant  $K = \frac{k_1}{k_{-1}}$

$$K = \sqrt{\frac{a_2 J_2(l_2)}{a_1 J_1(l_1)}} = \frac{\nu_1 J_2(l_2)}{\nu_2 J_1(l_1)}$$

which is not identical with the classical value found on p. 6 eq. (7).

8. Therefore, we must consider the problem of two opposing reactions more closely.

If we have two types of molecules (1,2) transforming into each other, the resulting velocity becomes, as well known,

$$s = -\frac{dN_1}{dt} = k_1 N_1 - k_{-1} N_2 \quad (18)$$

from which we obtain by integration

$$\left. \begin{aligned} N_1 &= k_{-1} \frac{N}{k} + C \cdot e^{-kt} & (k \equiv k_1 + k_{-1}) \\ N_2 &= k_1 \frac{N}{k} - C \cdot e^{-kt}. \end{aligned} \right\} \quad (19)$$

This means obviously that we have to look for solutions of (11) of the types

$$\left. \begin{aligned} y_1 &= A + B_1 + \eta_1 \\ y_2 &= A + B_2 + \eta_2 \end{aligned} \right\}, \quad (20)$$

where  $A$  is constant in time and space, while  $B_1, B_2$  which are constant in space and  $\eta_1, \eta_2$  contain the common factor  $e^{-kt}$ . It is now the question, how to define the total "concentration" (number of particles per cm) or the density of probability  $c$  and the corresponding  $y$ , so that both  $c$  and  $s$  are continuous at the point of separation. The simplest procedure seems to be the following: We assume everywhere

$$c \varphi = y = A + \varphi [(B_1 + \eta_1) \varphi_1^{-1} + (B_2 + \eta_2) \varphi_2^{-1}], \quad (21)$$

where  $\varphi$  is the true value of  $\varphi$  everywhere, while  $\varphi_1$  and  $\varphi_2$  are defined as the functions valid in the two different regions corresponding to the two types of the molecule. In the harmonic case,  $\ln \varphi_1 = \frac{x_1^2}{4a_1}$ ,  $\ln \varphi_2 = \frac{x_2^2}{4a_2}$ , where  $x_1$  and  $x_2$  are the distances measured from the points  $A$  and  $C$  respectively on the potential curve (cf. Fig. 1).

It is supposed that  $\varphi$  coincides with  $\varphi_1$  or with  $\varphi_2$  in the main parts of the regions corresponding to the two types of the molecule, so that the expressions given below for the number of molecules of the two types remain essentially correct. Around the transition point itself we assume a difference, since here  $\varphi' = 0$  while  $\varphi_1'$  and  $\varphi_2'$  are different from 0. In order to preserve continuity, we assume  $\varphi_1 = \varphi_2$  at the same point; without further loss of generality we may place both equal to 1 at the same point. Thus, the number  $N_1$  of molecules of type 1 becomes with good approximation

$$N_1 = \int_{-\infty}^{l_1} c dx = (A + B_1) \int_{-\infty}^{l_1} \varphi_1^{-1} dx \equiv (A + B_1) P_1 \quad (22 a)$$

as we may assume  $\int_{-\infty}^{l_1} \eta_1 \varphi_1^{-1} dx$  and  $B_2 \int_{-\infty}^{l_1} \varphi_2^{-1} dx$  to be vanishingly small. Analogously,

$$N_2 = (A + B_2) \int_{-l_2}^{+\infty} \varphi_2^{-1} dx \equiv (A + B_2) P_2. \quad (22 b)$$

To calculate  $\dot{N}$ , we consider the flow  $s$  at the point of transition where it is equal to  $-\dot{N}$ . Generally, we have  $s = -D \varphi^{-1} y'$ ;  $y'$  at the mentioned point becomes

$$y' = \varphi \frac{d}{dx} [(B_1 + \eta_1) \varphi_1^{-1} + (B_2 + \eta_2) \varphi_2^{-1}]. \quad (23)$$

Furthermore, we shall introduce two conditions analogous to that used in the case of a onesided reaction viz.

$$B_1 + \eta_1 = 0; \quad B_2 + \eta_2 = 0, \quad (\text{at } x_1 = l_1, x_1 = -l_2); \quad (24)$$

hence, we get

$$-\dot{N}_1 = s = -D [\eta_1' \varphi_1^{-1} + \eta_2' \varphi_2^{-1}]. \quad (25)$$

Just as in the former case, we now assume approximately

$$\dot{y}_1 = C_1; \quad \dot{y}_2 = C_2, \quad (26)$$

where  $C_1$  and  $C_2$  both contain the factor  $e^{-kt}$  but are constant in space.

We thus get

$$\left. \begin{aligned} 2 a_1 \eta_1'' - x_1 \eta_1' &= \frac{2 a_1}{D} C_1 \\ 2 a_2 \eta_2'' - x_2 \eta_2' &= \frac{2 a_2}{D} C_2 \end{aligned} \right\} \quad (27)$$

from which

$$\left. \begin{aligned} \eta_1 &= -\frac{C_1}{D} \left[ \int_{-\infty}^{x_1} \varphi_1^{-1} J_1 dx - J_1 \int_{-\infty}^{x_1} \varphi_1^{-1} dx \right]; \quad \eta_1' = \frac{C_1}{D} \varphi_1 \int_{-\infty}^{x_1} \varphi_1^{-1} dx \\ \eta_2 &= -\frac{C_2}{D} \left[ \int_{+\infty}^{x_2} \varphi_2^{-1} J_2 dx - J_2 \int_{+\infty}^{x_2} \varphi_2^{-1} dx \right]; \quad \eta_2' = \frac{C_2}{D} \varphi_2 \int_{+\infty}^{x_2} \varphi_2^{-1} dx \end{aligned} \right\} \quad (28)$$

$-\dot{N}_1 = s$  at the transition point  $x_1 = l_1$ ;  $x_2 = -l_2$  thus becomes

$$\begin{aligned} s &= -C_1 \int_{-\infty}^{l_1} \varphi_1^{-1} dx - C_2 \int_{+\infty}^{-l_2} \varphi_2^{-1} dx = -C_1 \int_{-\infty}^{l_1} \varphi_1^{-1} dx + C_2 \int_{-l_2}^{+\infty} \varphi_2^{-1} dx \\ &= -C_1 P_1 + C_2 P_2. \end{aligned}$$

The condition that  $\dot{y} = 0$  is fulfilled on account of the two conditions (24) introduced above. From these we get

$$\left. \begin{aligned} DB_1 + C_1 J_1(l_1) P_1 &= 0 \\ DB_2 + C_2 J_2(-l_2)(-P_2) = DB_2 + C_2 J_2(l_2) P_2 &= 0. \end{aligned} \right\} \quad (29)$$

Thus

$$s = D \left( \frac{B_1}{J_1} - \frac{B_2}{J_2} \right). \quad (30)$$

From the equations (22)

$$N_1 = (A + B_1) P_1$$

$$N_2 = (A + B_2) P_2$$

we get by addition

$$N_1 + N_2 = N = A(P_1 + P_2) \quad (31)$$

as the total number of molecules must be independent of time, and the  $B$ 's are time dependent. Therefore,

$$B_1 = \frac{1}{P_1} \frac{N_1 P_2 - N_2 P_1}{P_1 + P_2}$$

$$B_2 = -\frac{1}{P_2} \frac{N_1 P_2 - N_2 P_1}{P_1 + P_2}$$

Substitution in (30) gives

$$s = -\dot{N}_1 = D \frac{N_1 P_2 - N_2 P_1}{P_1 + P_2} \left( \frac{1}{P_1 J_1} + \frac{1}{P_2 J_2} \right). \quad (32)$$

By comparison with

$$-\dot{N}_1 = k_1 N_1 - k_{-1} N_2 \quad (33)$$

we get

$$k_1 = D \left( \frac{1}{P_1 J_1} + \frac{1}{P_2 J_2} \right) \frac{P_2}{P_1 + P_2}$$

$$k_{-1} = D \left( \frac{1}{P_1 J_1} + \frac{1}{P_2 J_2} \right) \frac{P_1}{P_1 + P_2}$$

and

$$k = k_1 + k_{-1} = D \left( \frac{1}{P_1 J_1} + \frac{1}{P_2 J_2} \right), \quad (34)$$

while

$$\frac{k_1}{k_{-1}} = \frac{P_2}{P_1} = K. \quad (35)$$

According to their definitions, the products  $PJ$  in the expression for  $k$  are independent of the choice of the zero point for the potential energy, and they are equal to  $\sqrt{4\pi a} \int_0^l e^{\frac{x^2}{4a}} dx = \sqrt{4\pi a} \cdot j$ . In experiments on a reaction of the first order we actually measure  $k = k_1 + k_{-1}$ , and the expression (34) is thus generally valid. The value of the equilibrium constant is identical with the classical expression, as may be seen from the following.

As we have made  $\varphi_1 = \varphi_2 = 1$  at the point of transition

$$\ln \varphi_1 = \frac{x_1^2}{4a_1} - V_1 \quad \text{where} \quad V_1 = \frac{Q_1}{RT} = \frac{l_1^2}{4a_1}$$

and

$$\ln \varphi_2 = \frac{x_2^2}{4a_2} - V_2 \quad \text{where} \quad V_2 = \frac{Q_2}{RT} = \frac{l_2^2}{4a_2}$$

Thus  $K = \frac{P_2}{P_1} = \sqrt{\frac{a_2}{a_1}} \cdot e^{V_2 - V_1} = \frac{\nu_1}{\nu_2} \cdot e^{-(V_1 - V_2)}$  which is identical with the classical expression.



9. In the numerous cases in which the reaction is practically irreversible, i. e.  $K \gg 1$  or  $V_2 > V_1$ ,  $j_2$  will be large as compared to  $j_1$ , and then we get the expression (17)

$$k = \frac{D}{\sqrt{4\pi a}} \cdot \frac{1}{j}.$$

In the special case of an experiment on racemisation  $j_1 = j_2$  and  $P_1 = P_2$  so that

$$k = 2k_1 = \frac{D}{\sqrt{\pi a}} \cdot \frac{1}{j}, \quad K = 1.$$

Using the approximation

$$j = \frac{2a}{l} \cdot e^{+\frac{l^2}{4a}}$$

we get in the former case

$$k = \frac{D}{2a} \cdot \frac{l}{\sqrt{4\pi a}} \cdot e^{-\frac{l^2}{4a}}.$$

By means of  $\frac{\alpha}{m} = 4\pi^2\nu^2$  and  $2a = \frac{RT}{\alpha}$  we may introduce  $\nu$  and get

$$k = \frac{4\pi m D}{RT} \cdot \nu^2 \sqrt{\pi} \sqrt{\frac{Q}{RT}} \cdot e^{-\frac{Q}{RT}}.$$

If it were literally true that  $4\pi m D = h$ , which at least is not impossible as  $D$  signifies an intramolecular diffusion constant, the frequency factor  $f$  would be  $\nu \sqrt{\pi} \cdot \frac{h\nu}{RT} \cdot \sqrt{\frac{Q}{RT}}$ , hence of the same order of magnitude as  $\nu$ , i. e. about  $10^{14}$  and this is the order of magnitude of  $f$  found empirically in numerous cases. It is also seen that this factor depends on  $T$  and on  $Q$ , however, their powers are far too small to account for the dependence found empirically.

10. In this connection it should be mentioned that in the case of strong interaction between the displaced particle and its surroundings, the "potential energy" must be replaced by "the free energy" given as a function of the position of the particle. Thus, it becomes possible to understand that thermodynamic relations can successfully be applied to problems in kinetics,

as shown repeatedly by M. POLANYI and his school, apart from several earlier authors.

So we may say that considerations based on classical statistical mechanics in connection with the assumption of EINSTEIN's equation for diffusion in a force field, which may also be called "classical", lead to an expression which contains the unknown quantity  $D$ , but otherwise seems to be reasonably consistent with the experimental facts. It should be emphasized that H. A. KRAMERS<sup>1</sup> discussed the application of the diffusion theory to the problem of chemical reactions more generally. KRAMERS came to the following result: if it is assumed that a "damping" of the oscillations arising from the interaction between the solute and the solvent molecules is very strong, which means that the acceleration forces may be neglected, EINSTEIN's diffusion equation may be applied. Actually this assumption was our starting point.

For the evaluation of the diffusion constant, one might of course resort to a procedure similar to that used in the kinetic theory of gases. We want a mechanism which is sufficiently effective to maintain the normal thermal distribution. Such a mechanism would demand the assumption of very numerous collisions as present in liquids, and the problem can hardly be solved with any reasonable degree of accuracy. Furthermore, one would be inclined in this case to expect a rather narrow parallelism between the viscosity of the solvent and the velocity of unimolecular reactions; however, such a parallelism does not seem to exist. It may be mentioned in this connection that in a few cases the same reaction has been studied as gas-reaction and in different solvents, but no appreciable difference was found between the frequency factors obtained with different solvents.

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<sup>1</sup> Cf. ref. 1) p. 8.

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