PROBLEMS

10–1. Calculate the fraction of hydrogen atoms ionized at 10,000°K when $\rho_{\mathrm{H}}^{0} = 0.01$ mole·liter^{-1}. (Page 185.)

10–2. Calculate the fraction of hydrogen molecules dissociated into atoms when $\rho_{\mathrm{H}_2}^{0} = 0.01$ mole·liter^{-1} and (a) $T = 1000$°K, (b) $T = 5000$°K. (Page 185.)

10–3. Repeat the argument of Section 10–2, but maximize the partition function $\Delta(N_A, N_B, p, T)$ [see Eq. (4–35)] at constant N, p, T instead of Q at constant N, V, T.

10–4. In the example of Section 10–3, show that

$$\overline{N_A N_B} - \overline{N_A}\,\overline{N_B} = -\frac{\overline{N_A}\,\overline{N_B}}{N}.$$

Why the negative sign?

10–5. Use the data in Table 8–1 to calculate K at 700°K for the reaction $2\mathrm{HI} \rightleftarrows \mathrm{H}_2 + \mathrm{I}_2$.

10–6. Calculate K at 1000°K for the reaction $\mathrm{I}_2 \rightleftarrows 2\mathrm{I}$ (see Section 4–4 and Table 8–1).

10–7. Calculate Θ_v for H_2, given that $\nu = 3770\ \mathrm{cm}^{-1}$ for HD.

10–8. Calculate Θ_v for H_2, given that, for H_2, $D_e = 4.722$ ev and $D_0 = 4.454$ ev.

10–9. Calculate K for the "water-gas" reaction at 1200°K using data in the text.

SUPPLEMENTARY READING

FOWLER and GUGGENHEIM, Chapter 5.
MAYER and MAYER, Chapter 9.
RUSHBROOKE, Chapter 11.

CHAPTER 11

THE RATE OF CHEMICAL REACTIONS IN IDEAL GAS MIXTURES

Strictly speaking, the subject indicated in the chapter title is outside the scope of this book, which is devoted to equilibrium statistical mechanics. However, Eyring's approximate absolute reaction rate theory has a quasi-equilibrium foundation: it is based on an application of the chemical equilibrium theory of the preceding chapter. For this reason, and because of its importance, it seems appropriate to include an account of the Eyring theory in the present work. But the treatment we give will be very brief, and we shall not consider any detailed special cases. The reader should consult the book by Glasstone, Laidler, and Eyring (see the Supplementary Reading list) for further details.

More exact approaches to this problem will not be discussed here, since they cannot be put in quasi-equilibrium form.

An example of a nonchemical application of Eyring's theory is presented in Section 11–3: the surface diffusion of a dilute, localized monolayer.

11–1 Potential surfaces. There are two distinct stages in the Eyring theory. The first is the purely quantum-mechanical one of calculating the ground-state electronic energy surface (potential surface, for short) for the reaction, and the second is the statistical-mechanical calculation of the reaction rate. This division is the same as that which we have encountered in calculating the thermodynamic functions of, say, an ideal polyatomic gas (Chapter 9). In this latter problem, we first have to find the potential surface of the molecule by quantum mechanics (or obtain equivalent information empirically from spectroscopy). This surface (see Section 9–1) determines the equilibrium structure of the molecule, the moments of inertia, the vibrational force constants and normal coordinates, and the depth of the potential well in the surface relative, say, to separated atoms as zero. With this information, we can then turn to the statistical-mechanical problem of deducing the thermodynamic functions.

We discuss the potential-surface part of the rate problem in this section, and the statistical-mechanical part in the next section.

For ease of visualization, let us consider a hypothetical one-dimensional reaction

$$A + BC \rightarrow AB + C. \tag{11–1}$$

Three atoms and (in one dimension) three nuclear coordinates are in-

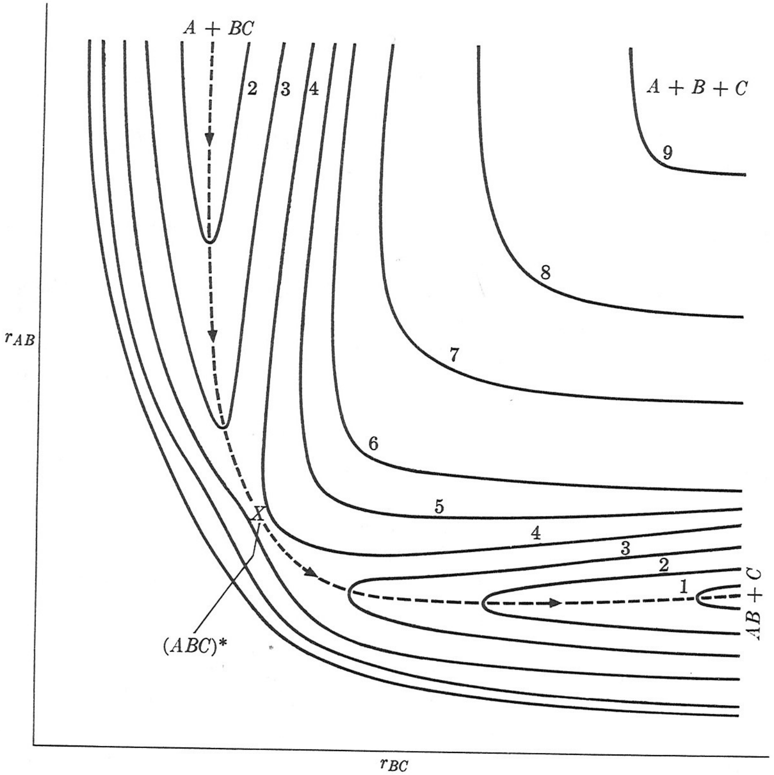

FIG. 11–1. Potential surface (u_e) in the form of a contour diagram for a hypothetical one-dimensional reaction $A + BC \rightarrow AB + C$. The numbers on the contours are values of u_e in arbitrary units.

volved. One coordinate is concerned with the center of mass and is therefore uninteresting for the above process. The other two coordinates determine the configuration of the three nuclei relative to each other (see Appendix V). For example, we might choose for these two coordinates the internuclear distances r_{AB} and r_{BC}. For given values of r_{AB} and r_{BC} the ground-state electronic energy $u_e(r_{AB}, r_{BC})$ is calculated. From a large number of such values of r_{AB} and r_{BC}, one can construct a potential surface in the form of a contour diagram, which in a typical case might appear as in Fig. 11–1. The valley at the upper left corresponds to an A atom and a diatomic BC molecule. (The curvature of the surface at the bottom of and perpendicular to the valley determines the vibrational frequency in BC; the depth of the valley is a measure of the energy of the bond BC.) The valley at the lower right corresponds to the state $AB + C$.

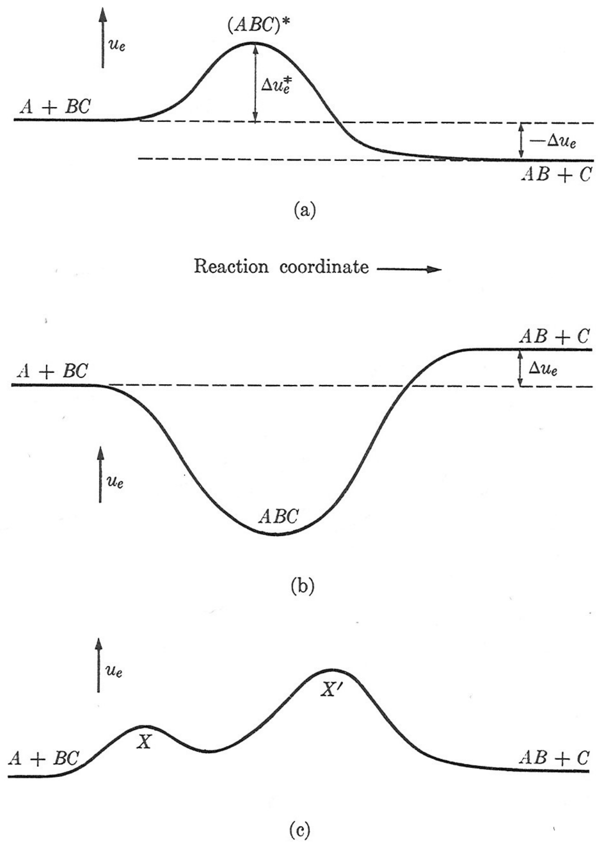

FIG. 11–2. (a) Potential energy (u_e) along the reaction path in Fig. 11–1. Note the potential barrier. (b) Corresponding curve from Fig. 11–3. Note the minimum in u_e (stable molecule, ABC). (c) Corresponding curve from Fig. 11–4.

The high plateau is $A + B + C$. When reaction (11–1) occurs, the lowest possible path from reactants ($A + BC$) to products ($AB + C$) is the dashed line in Fig. 11–1. The highest point on this path is marked X in the figure. This is the "activated state," and the triatomic system A, B, C at this point is referred to as an "activated complex," denoted by $(ABC)^*$. If one plots the potential energy u_e along the dashed path of Fig. 11–1 as a function of the distance along the path (called the "reaction coordinate"), one obtains a curve as in Fig. 11–2(a). The height $\Delta u_e^{\ddagger}$ of the potential energy barrier which must be overcome is called the "activation energy."

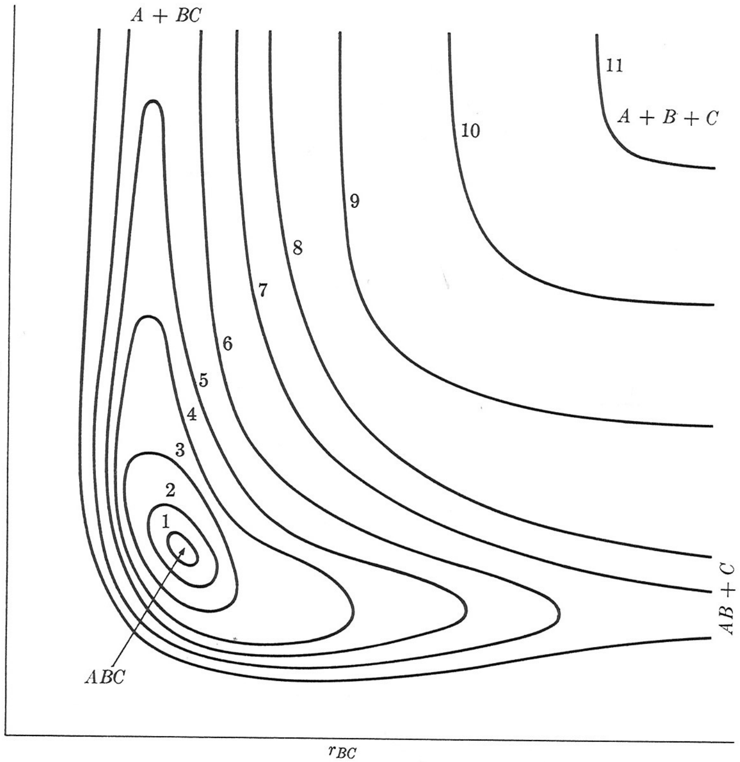

FIG. 11-3. Potential surface (u_e) in the form of a contour diagram in one-dimensional case where stable molecule ABC is formed.

For the reverse reaction,

$$AB + C \rightarrow A + BC, \tag{11–2}$$

the reaction path in Fig. 11–1 must be reversed in direction. In this example the activated state and complex (X in Fig. 11–1) are the same for forward (11–1) and reverse (11–2) reactions. Let

$$\Delta u_e = u_e(AB + C) - u_e(A + BC). \tag{11–3}$$

This is Δu_e for the reaction as written in (11–1) and has the same meaning as $\Delta\epsilon_{e1}$ in Eq. (10–32). In Fig. 11–1 it is determined by the difference in levels of the two valleys. In Figs. 11–1 and 11–2(a), Δu_e is negative. If $\Delta u_e^{\ddagger}$ is the activation energy for the forward reaction, $\Delta u_e^{\ddagger} - \Delta u_e$ is the activation energy for the reverse reaction.

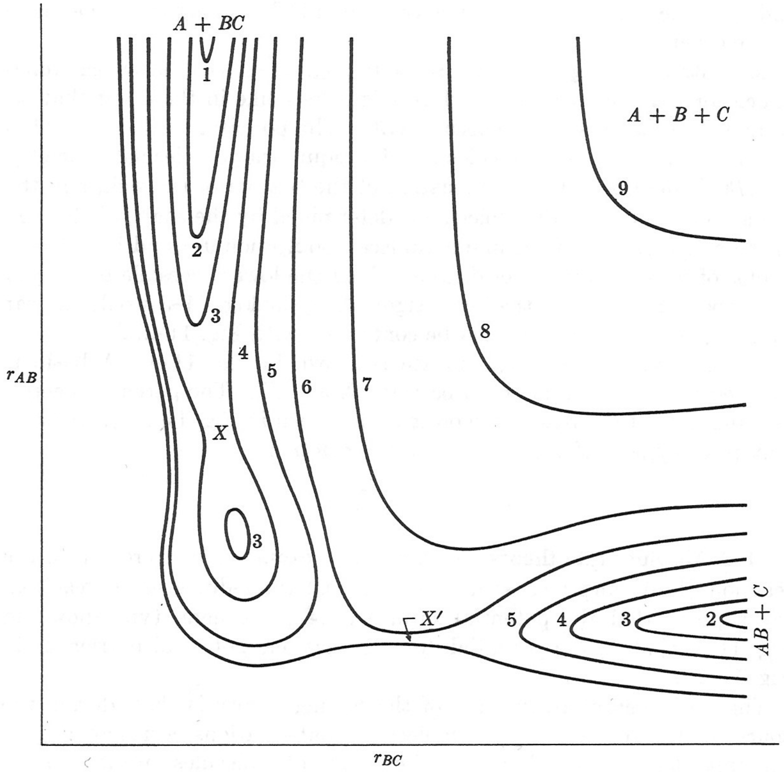

FIG. 11–4. Potential surface (u_e) in which a basin occurs between two potential barriers.

In a real (three-dimensional) triatomic reaction we would need a contour diagram in three-dimensional (r_{AB}, r_{BC}, r_{AC}) instead of two-dimensional space (or a surface in four-dimensional space). But the general concepts introduced above for a hypothetical one-dimensional reaction remain the same. Incidentally, it should be noticed that linear configurations of A, B, C are included in the potential surface (in fact, activated complexes in triatomic reactions are usually linear), and we recall that linear molecules have four, not three, vibrational coordinates. However, this is not contradictory to the statement that u_e is a function of the three variables r_{AB}, r_{BC}, and r_{AC} only, for two of the normal modes in a linear molecule are degenerate (i.e., of the same frequency). For example, the positions of the atoms in the two degenerate modes of CO_2 [shown preceding Eq. (9–3)] are expressible by the same sets of values of r_{AB}, r_{BC}, and r_{AC} (the triangle ABC is merely rotated 90° in going from one mode to the other).

In contrast to Fig. 11–1, we show in Fig. 11–3 what a typical (one-dimensional again) potential surface might look like in the event that A, B, and C formed a stable molecule ABC. The potential well in Fig. 11–3 is characteristic of a stable molecule. The equilibrium molecular geometry of ABC is determined by the location of the bottom of the well, and the vibrational motion of the molecule is determined by the shape of the well in the neighborhood of the minimum [see also Section 9–1 and Eq. (V–1)]. A plot of u_e as a function of distance along the lowest possible path from the upper left valley to the lower right valley in Fig. 11–3 would appear as in Fig. 11–2(b). This should be contrasted with Fig. 11–2(a).

Another type of potential surface is shown in Fig. 11–4. A basin is situated between two potential barriers, X and X'. The potential energy as a function of the reaction coordinate is shown in Fig. 11–2(c). A basin may possibly occur,* for example, in the reaction

$$\mathrm{H} + \mathrm{H}_2 \rightarrow \mathrm{H}_2 + \mathrm{H}.$$

11–2 Absolute rate theory. As a concrete example, let us return to the reaction (11–1) and discuss it now as a real three-dimensional reaction. We suppose that the potential surface is of the general type shown in Fig. 11–1; that is, the potential "profile" has one potential barrier, as in Fig. 11–2(a).

The fundamental assumption of the Eyring theory is that, during the course of the reaction (11–1), molecular configurations corresponding to the upper left valley in Fig. 11–1 (i.e., reactant molecules) are in thermodynamic equilibrium with molecular configurations corresponding to the neighborhood of the activated state X in Fig. 11–1 (i.e., activated complexes). This is an assumption which cannot be rigorously correct, but which is probably rather accurate in many cases. This assumption of equilibrium between reactant molecules and activated complexes makes it possible for us to use the methods of the preceding chapter on chemical equilibria to deduce the concentration (defined below) of activated complexes. From this knowledge, as we shall see, we can then calculate the number of reactants passing over the barrier, from upper left to lower right, per unit time and per unit volume of the system. This is the desired reaction rate.

An activated complex is very much like an ordinary stable molecule. It has a definite mass ($m_A + m_B + m_C$ in this example) and a definite nuclear configuration (corresponding to the position of the X in Fig. 11–1 at the top of the potential barrier). This configuration determines the moments of inertia and the symmetry number. Thus we can immediately write (assuming the potential surface is available) the translational and rotational partition functions for an activated complex, just as we did in Chapter 9 for a stable molecule.

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* See GLASSTONE, LAIDLER, and EYRING (Supplementary Reading list), p. 108, and R. E. WESTON, JR., *J. Chem. Phys.* **31,** 892 (1959).

Furthermore, we can carry out a normal-coordinate analysis for the vibrational frequencies, based on the shape of the potential surface in the neighborhood of the activated state. If the activated complex is linear, there will be $3n - 5$ normal vibrational modes, otherwise there will be $3n - 6$. The activated state is located at a saddle point in the potential surface. That is, although the activated state is a maximum point along the reaction coordinate, it is a minimum in other directions (e.g., in Fig. 11–1, in the direction perpendicular to the reaction coordinate). This feature will appear automatically in the normal-coordinate analysis when the potential energy u_e is expressed in terms of the normal coordinates ξ_i [see Eq. (V–13)]. Necessarily (i.e., by definition of a normal coordinate), u_e will be a sum of squared terms in the ξ_i, and the coefficients will be positive as usual (Eq. V–13) *except* for one coordinate, call it ξ, which will have a negative coefficient. This particular normal coordinate is the rigorous equivalent of what we have hitherto been loosely calling the reaction coordinate. The coefficient of ξ^2 in u_e is negative because the potential surface *falls off* on both sides of the activated state along this direction (and this direction only).

From the normal-coordinate analysis we thus obtain $3n - 6$ (linear) or $3n - 7$ (nonlinear) ordinary vibrational frequencies ν_i. The frequency associated with ξ is imaginary because the force constant (twice the coefficient of ξ^2) is negative. We can therefore construct, in the usual way, from the ν_i, a vibrational partition function for the activated complex—except we omit the factor belonging to the ξ-motion. Thus of the $3n$ nuclear degrees of freedom of an activated complex, $3n - 1$ can be handled just as with stable molecules. Only the reaction normal coordinate ξ requires special treatment.

Let q_v^* represent the vibrational partition function of the activated complex, omitting the ξ-factor. Also, let $q^{\ddagger} = q_t^{\ddagger} q_r^{\ddagger} q_v^{*} q_e^{\ddagger}$ be the complete partition function of the activated complex, just as for any polyatomic molecule—except, again, omitting the ξ degree of freedom.

We wish next to calculate the number of activated complexes per unit volume of the system which are in an infinitesimal range $d\xi$ of the reaction coordinate at the activated state. We shall call this number $\rho'\, d\xi$, so that ρ' is the number of activated complexes per unit volume and also per unit length along the reaction coordinate ξ at the activated state. We want the number $\rho'\,d\xi$ to include all activated complexes in $d\xi$ irrespective of the value of p_ξ, the momentum conjugate to ξ. For the element of phase space $d\xi\,dp_\xi$ in the coordinate ξ, the (classical) partition function is

$$\frac{1}{h}e^{-p_\xi^2/2m^*kT}\,d\xi\,dp_\xi, \tag{11–4}$$

where m^* is defined by $p_\xi = m^*\dot{\xi}$. It should be noted, incidentally, that there is always some arbitrariness in defining normal coordinates [see the constants C_i in Eqs. (V–12) and (V–14)], and so there is arbitrariness in m^* and ξ. But combinations of these quantities with physical significance (e.g., $p_\xi^2/2m^*$ or $d\xi\,dp_\xi$ above) are not arbitrary. Integration of (11–4) over p_ξ gives the ξ partition function for an activated complex in $d\xi$. The *complete* partition function for such an activated complex is then

$$q^{\ddagger}\left(\frac{2\pi m^*kT}{h^2}\right)^{1/2}d\xi. \tag{11–5}$$

With the assumption, already mentioned, of equilibrium between reactants (say A and BC, for concreteness) and activated complexes,

$$A + BC \rightleftarrows (ABC)^*, \tag{11–6}$$

we have, as in Eqs. (10–6) and (10–31),

$$\frac{\rho'\,d\xi}{\rho_A\rho_{BC}} = \frac{(q^{\ddagger}/V)(2\pi m^*kT/h^2)^{1/2}\,d\xi}{(q_A/V)(q_{BC}/V)}$$

$$= \frac{(q^{\ddagger\prime}/V)(2\pi m^*kT/h^2)^{1/2}\,d\xi}{(q'_A/V)(q'_{BC}/V)}\,e^{-\Delta u_e^{\ddagger}/kT}, \tag{11–7}$$

where q' means, as before, that q_e is omitted from q. The quantity $\Delta u_e^{\ddagger}$ is defined for the process (11–6) by analogy with (11–2) and (11–3). If the ground electronic states are degenerate, a factor $\omega_{e1}^{\ddagger}/\omega_{e1}(A)\omega_{e1}(BC)$ must be included in Eq. (11–7) ($\omega_{e1}^{\ddagger}$ being the degeneracy of the activated complex).

Equation (11–7) provides us with an explicit equation for ρ', the number of activated complexes per unit volume of the system and per unit length along ξ at the activated state. Our next task is to calculate the number of activated complexes per unit volume which cross the potential barrier X per unit time in the direction of reaction (left to right in Fig. 11–1). Assuming all of these complexes become products, this is the rate of the reaction. Consider those activated complexes with values of $\dot{\xi}$ between $\dot{\xi}$ and $\dot{\xi} + d\dot{\xi}$. The fraction of all activated complexes which are in this class is, from (11–4),

$$f(\dot{\xi})\,d\dot{\xi} \equiv \frac{e^{-m^*\dot{\xi}^2/2kT}\,d\dot{\xi}}{\int_{-\infty}^{+\infty} e^{-m^*\dot{\xi}^2/2kT}\,d\dot{\xi}} = \left(\frac{m^*}{2\pi kT}\right)^{1/2} e^{-m^*\dot{\xi}^2/2kT}\,d\dot{\xi}.$$

Suppose ξ increases as the activated state is approached from the reactant (left) side in Fig. 11–1. Then an activated complex with $\dot{\xi} > 0$ is proceeding along the reaction coordinate in the direction required for the reaction to take place. We note that activated complexes with a given value of $\dot{\xi} > 0$ will cross the potential barrier in unit time if they start at a distance from X not greater than a length of magnitude $\dot{\xi}$. The number of activated complexes per unit volume and per unit length along ξ having values of $\dot{\xi}$ in the interval $d\dot{\xi}$ is $\rho' f(\dot{\xi})\,d\dot{\xi}$. The number of activated complexes per unit volume in the length $\dot{\xi}$ along ξ having $\dot{\xi}$ in the interval $d\dot{\xi}$ is then $\dot{\xi}\rho' f(\dot{\xi})\,d\dot{\xi}$. This is the number of complexes per unit volume with $\dot{\xi}$ in $d\dot{\xi}$ which cross the barrier per unit time. To get the total number of complexes per unit volume crossing the barrier per unit time, we have to integrate $\dot{\xi}$ over the range $0 \le \dot{\xi} \le +\infty$:

$$\rho' \int_0^{\infty} \dot{\xi} f(\dot{\xi})\,d\dot{\xi} = \rho'\left(\frac{m^*}{2\pi kT}\right)^{1/2}\left(\frac{kT}{m^*}\right)$$

$$\equiv \mathbf{k}\rho_A\rho_{BC}, \tag{11–8}$$

which is the defining equation for $\mathbf{k}$. The quantity $\mathbf{k}\rho_A\rho_{BC}$ is the rate of the reaction, and $\mathbf{k}(T)$ is called, conventionally, the rate constant. If ρ' is obtained from Eq. (11–7), we find

$$\mathbf{k} = \frac{kT}{h}\,\frac{(q^{\ddagger\prime}/V)e^{-\Delta u_e^{\ddagger}/kT}}{(q'_A/V)(q'_{BC}/V)}\cdot \tag{11–9}$$

If only a fraction κ (called the transmission coefficient) of complexes passing the potential barrier in the right direction actually proceed to products, then κ must be inserted as a factor on the right-hand side of Eq. (11–9). This situation arises, for example, in cases such as Fig. 11–4, where the system passes over a barrier (X) but then finds itself in a basin. The system may leave the basin (via X') to form products or return (via X) to reactants. In the reaction $H + H_2 \rightarrow H_2 + H$, the basin is symmetrical (if it exists), and it is usually assumed that $\kappa = 1/2$.

Equation (11–9) furnishes a straightforward statistical-mechanical recipe for calculating the rate constant $\mathbf{k}$. The potential surface must be available, however, and this is a very serious practical obstacle. Because of this, it is difficult to test the theory in a really satisfactory way. Of course, one does not expect exact agreement between theory and experiment, as the argument used to deduce Eq. (11–9) is not rigorous—the assumption of equilibrium between reactants and activated complexes being especially questionable. Also, if a transmission coefficient must be used, this introduces a somewhat nebulous feature into the theory since κ is in general difficult to evaluate.

For the reverse reaction (11–2), the rate constant is

$$\mathbf{k}' = \frac{kT}{h}\,\frac{(q^{\ddagger\prime}/V)e^{-(\Delta u_e^{\ddagger}-\Delta u_e)/kT}}{(q'_{AB}/V)(q'_C/V)}. \qquad (11\text{–}10)$$

The equilibrium constant K for the reaction (11–1) is then

$$K = \frac{\mathbf{k}}{\mathbf{k}'} = \frac{(q'_{AB}/V)(q'_C/V)}{(q'_A/V)(q'_{BC}/V)}\,e^{-\Delta u_e/kT}, \qquad (11\text{–}11)$$

in agreement with Eqs. (10–6) and (10–31).

11–3 A nonchemical application of the Eyring theory. The fundamental ideas in Eyring's theory of the rate of chemical reactions can be and have been applied to many physical rate processes as well. Merely to illustrate the possibilities, we consider here a particularly straightforward example, namely, the rate at which monatomic molecules adsorbed at localized sites on a surface jump from one site to another. This rate is of course closely related to the coefficient of surface diffusion. The model we consider is essentially that already discussed in Sections 7–1 and 9–6. We have a lattice of equivalent surface sites for adsorption, but we need not specify the lattice type. The number of adsorbed molecules is small, so that each one behaves independently. The potential in which a molecule moves is $U_0(x, y)$ [see, for example, Eq. (9–19)]. The potential wells in $U_0(x, y)$ are the sites for adsorption. The partition function for an adsorbed molecule at a site is given by Eq. (7–3).

To move from a given site to a nearest-neighbor site, a molecule must pass over a potential barrier of height V_0. The top of the barrier is the activated state for this process:

$$A \text{ (site)} \rightarrow A^* \text{ (top of barrier)} \rightarrow A \text{ (neighboring site)}.$$

Let ξ and η be the normal coordinates at the activated state, which is a saddle point in the surface U_0. We take ξ as the "reaction coordinate." That is, the coefficient of ξ^2 in the expansion of U_0 in powers of ξ and η about the activated state is negative, while the coefficient of η^2 is positive. Thus a molecule at the top of a potential barrier vibrates in the usual way in the z-direction (perpendicular to the surface) and also in the η-direction (perpendicular to the direction of passage from one site to the other, i.e., perpendicular to ξ), but not in the ξ-direction. We denote the z and η vibrational partition functions at the activated state by $q_z^{\ddagger}$ and $q_\eta^{\ddagger}$.

The partition function for a molecule in the element of length $d\xi$ at the top of a barrier is [see Eq. (11–5)]

$$q_z^{\ddagger} q_\eta^{\ddagger} \left(\frac{2\pi mkT}{h^2}\right)^{1/2} d\xi\, e^{-(U_{00}+V_0)/kT}. \qquad (11\text{–}12)$$

Let $N'\,d\xi$ be the equilibrium number of molecules in a length $d\xi$ at the top of barriers, and let N be the equilibrium number of molecules in sites. Then, from Eq. (10–5), the ratio of these two numbers is

$$\frac{N'\,d\xi}{N} = \frac{q_z^{\ddagger} q_\eta^{\ddagger} (2\pi mkT/h^2)^{1/2}\, d\xi\, e^{-V_0/kT}}{q_x q_y q_z} \times \frac{M^{\ddagger}}{M}, \qquad (11\text{–}13)$$

where $M^{\ddagger}/M$ is the ratio of the number of activated states to the number of sites (this ratio is two for a square lattice). By the same argument as in the preceding section (Eq. 11–8),

$$N' \left(\frac{m}{2\pi kT}\right)^{1/2} \left(\frac{kT}{m}\right) \qquad (11\text{–}14)$$

is the number of molecules crossing a barrier (or the number of jumps being made from one site to another) per unit time, where N' is given by Eq. (11–13). We are assuming here that there are no "rebounds": $\kappa = 1$. If τ is the mean time a molecule spends at a site between jumps, then a second expression for the number of jumps occurring in unit time is N/τ. If we set N/τ equal to (11–14), we find

$$\frac{1}{\tau} = \frac{kT}{h} \cdot \frac{M^{\ddagger} q_z^{\ddagger} q_\eta^{\ddagger} e^{-V_0/kT}}{M q_x q_y q_z}. \qquad (11\text{–}15)$$

This is the analog of Eq. (11–9). That is, $1/\tau$ is the rate constant for this process.

To obtain an estimate of the order of magnitude of τ in Eq. (11–15), we set $M^{\ddagger}/M = 2$, $q_\eta^{\ddagger} = q_y$ [as would be the case with Eq. (9–19)], $q_z^{\ddagger} = q_z$, and $q_x = kT/h\nu_x$ (classical). Then

$$\frac{1}{\tau} = 2\nu_x e^{-V_0/kT}. \qquad (11\text{–}16)$$

This equation has the following approximate interpretation: $2\nu_x$ is the number of "attempts" per second the molecule makes to leave its site; $e^{-V_0/kT}$ is the probability that any particular attempt will be successful; and hence $1/\tau$ is the actual number of jumps a molecule makes from one site to another per second. If we take $\nu_x = 3 \times 10^{11}\ \mathrm{sec}^{-1}$, $V_0 = 500$ cal·mole^{-1}, and $T = 80$°K, then $e^{-V_0/kT} = 0.043$ and $\tau = 3.9 \times 10^{-11}$ sec.

Equation (11–15) also provides a theoretical equation for the coefficient of surface diffusion D, since D is related to τ (from the theory of random walks) by $D = Ca^2/\tau$, where a is the distance between nearest-neighbor sites and C is a constant of order unity which depends on the lattice type.

Problems

11–1. Write out the explicit forms for the partition functions in Eq. (11–9), assuming the triatomic complex $(ABC)^*$ is linear. Insert typical orders of magnitudes for the masses, frequencies, bond distances, etc., to estimate a magnitude for $\mathbf{k}$.

11–2. Derive an equation for $d \ln \mathbf{k}/dT$ from $\mathbf{k}$ in Problem 11–1.

11–3. Discuss the rate of diffusion of impurity atoms in a monatomic crystal from the point of view of Eyring's theory.

11–4. Consider the rate of evaporation of a dilute localized monatomic monolayer into the gas phase. (a) Use Eyring's method to derive an equation for $1/\tau_s$, where τ_s is the mean time a molecule spends on the surface before evaporating. (b) Derive the same expression for $1/\tau_s$ by equating the number of molecules condensing on the surface per unit area and per unit time with the number evaporating, at equilibrium:

$$\frac{p}{(2\pi mkT)^{1/2}} = \frac{(N/\mathcal{A})}{\tau_s},$$

where p is the equilibrium gas pressure and $N/\mathcal{A}$ is given by Eq. (7–10) in the limit as $\theta \to 0$.

Supplementary Reading

Fowler and Guggenheim, Chapter 12.

Frenkel, J., *Kinetic Theory of Liquids.* New York: Dover, 1955.

Glasstone, S., Laidler, K. J., and Eyring, H., *The Theory of Rate Processes.* New York: McGraw-Hill, 1941.

CHAPTER 12

IDEAL GAS IN AN ELECTRIC FIELD

Our principal object in this chapter is to deduce the thermodynamic properties of a very dilute gas in an electric field. In Chapter 15, this study will be extended briefly to slightly imperfect gases.

In Section 12–1 we give some necessary thermodynamic background, and in Section 12–2 we develop general statistical-mechanical equations (canonical ensemble). The material in the first two sections is quite general and would apply to any fluid (or isotropic) dielectric. The dilute-gas special case is then considered in Section 12–3. Finally, in Section 12–4, we discuss a somewhat related problem: a lattice of noninteracting magnetic dipoles in a magnetic field. This problem turns out to be formally the same as that of the ideal lattice gas in Chapter 7. The interacting magnetic dipole case (the Ising model for ferromagnetism) is included in Chapter 14.

12–1 Thermodynamic background. A number of alternative and equivalent thermodynamic formulations can be devised for a dielectric fluid in an electric field. Koenig[*] has given a very full discussion of this subject. The corresponding treatment for magnetic systems is contained in a paper by Guggenheim.[†] We confine ourselves here to the one particular formulation that is most convenient in the statistical mechanics of gases in an electric field. For condensed systems, there are some advantages to other choices.

Consider the parallel plate condenser in Fig. 12–1. The plate surface charge densities are $+\sigma$ and $-\sigma$, as indicated. The condenser is assumed to have a large enough plate area so that edge effects can be ignored. The volume V contains the dielectric fluid whose properties we are interested in. For simplicity, we take the fluid as one component with N molecules, but it could as well be multicomponent. The same is true in Section 12–2. One wall of the fluid container, parallel to the condenser plates, serves as a piston to vary the volume V. The equilibrium pressure on the piston is p. The regions between the fluid container and the condenser plates are evacuated. As a consequence of polarization of the dielectric in the field of the condenser plates, there are induced surface-charge densities $-\sigma'$

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[*] F. O. Koenig, *J. Phys. Chem.* **41**, 597 (1937).

[†] E. A. Guggenheim, *Proc. Roy. Soc.* **155A**, 49, 70 (1936).