Thermodynamics and the Kinetics of Gaseous Reactions

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IT is commonly recognized that the free energy change of a reaction mechanism gives no information as to the rate of the mechanism. In some cases the heat of the reaction is significant but the really important thing is the heat of activation which bears no relation to the change in energy for the reaction, except that it is usually equal to or greater in magnitude algebraically. This is little more than saying that it is usually a positive quantity. The heat of activation may be obtained (practically) independently of all assumptions, from the temperature coefficient of reaction rate but the rate may not be measured with any greater accuracy than the absolute rate of the reaction, and often with much less accuracy. It would be desirable to be able to estimate heats of activation from measurements of rate at a single temperature and *vice versa*.

The absolute rate of a reaction depends not only upon the heat of activation but upon certain additional terms which are analogous at least to entropies. This is a plausible analogy. If we assume that the energy of activation is required in the formation of an unstable complex, then the greater number of possible states for this complex, the more rapid the reaction. The complete equation for both heat and entropy of activation may be said to define a free energy of activation.
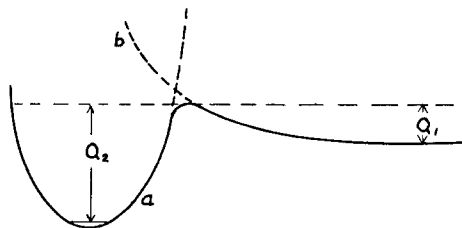

FIG. 1.

We may illustrate the aptness of these thermodynamic, analogies by considering a simple mechanism, the homogeneous bimolecular condensation of two unlike atoms to form a diatomic molecule.

$$A + B = AB. \tag{1}$$

Let us assume for purposes of generality that the potential energy of the molecule is represented by a curve of the type of Fig. 1 with a hump at the point of dissociation. We shall show later that the energy of formation of the molecule in the average vibrational state is

$$\Delta E = Q_1 + \tfrac{1}{2}RT - Q_2. \tag{2}$$

By a familiar equation of thermodynamics

$$\ln K = -(\Delta E - RT)/RT + \Delta S/R, \tag{3}$$

where K is the equilibrium constant of (1), which will be expressed in this paper in terms of numbers of molecules per cubic centimeter. For the Eq. (3)

$$\Delta S/R = S_{AB}/R - S_A/R - S_B/R \tag{4}$$

and from quantum statistical theory at unit concentration

$$S_A/R = \ln \ (2\pi m_1 kT/h^2)^{\tfrac{3}{2}} + 5/2, \tag{5}$$

$$S_B/R = \ln \ (2\pi m_2 kT/h^2)^{\tfrac{3}{2}} + 5/2, \tag{6}$$

$$S_{AB}/R = \ln \ (2\pi(m_1 + m_2)kT/h^2)^{\tfrac{3}{2}}$$
$$+ \ln \ (8\pi^2 IkT/h^2) + \ln \ (kT/h\nu) + 9/2. \tag{7}$$

In the foregoing equations m_1 and m_2 are the masses of the two atoms, I is the moment of inertia of the diatomic molecule, $(m_1 m_2/m_1 + m_2)r^2$, where r is the distance between centers of the atoms and ν is the characteristic frequency of vibration for the molecule. The other symbols have their usual significance. Eq. (9) does not make any allowance for the change of moment of inertia, or of vibrational frequency in the excited states. These effects could of course be taken care of by more elaborate expressions but the illustration does not lose any significance through the simplification.

Upon substitution from (2) and (5) (6) and (7) in (3) we have

$$\ln K = -(Q_1-Q_2)/RT+\ln\left[2^{\frac{3}{2}}\pi^{\frac{1}{2}}(m_1+m_2/m_1m_2)^{\frac{1}{2}}r^2(kT)^{\frac{1}{2}}\right]-\ln\nu. \tag{8}$$

Now the reaction toward the right is bimolecular and toward the left unimolecular. Hence for the rates of these two opposing reactions we may write

$$R_1 = k_1n_1n_2, \tag{9}$$

$$R_2 = k_2n_3, \tag{10}$$

where n_1, n_2 and n_3 are the concentrations of A, B and AB respectively. Since at equilibrium

$$R_1 = R_2 \tag{11}$$

we have

$$K = k_1/k_2 \tag{12}$$

and we may now write

$$\ln k_1/k_2 = -(Q_1-Q_2)/RT+\ln\left[2^{\frac{3}{2}}\pi^{\frac{1}{2}}(m_1+m_2/m_1m_2)^{\frac{1}{2}}r^2(kT)^{\frac{1}{2}}\right]-\ln\nu. \tag{13}$$

Let us now arbitrarily separate Eq. (13) into two parts

$$\ln k_1 = -\frac{Q_1}{RT}+\ln\left[2^{\frac{3}{2}}\pi^{\frac{1}{2}}\left(\frac{m_1+m_2}{m_1m_2}\right)^{\frac{1}{2}}r^2(kT)^{\frac{1}{2}}\right], \tag{14}$$

$$\ln k_2 = -Q_2/RT+\ln\nu \tag{15}$$

or omitting logarithms

$$k_1 = \left[2^{\frac{3}{2}}\pi^{\frac{1}{2}}\left(\frac{m_1+m_2}{m_1m_2}\right)^{\frac{1}{2}}r^2(kT)^{\frac{1}{2}}\right]e^{-Q_1/RT}, \tag{16}$$

$$k_2 = \nu e^{-Q_2/RT}. \tag{17}$$

When we write

$$R_1 = k_1(n_1n_2) \tag{18}$$

we see that the rate of formation of the molecule AB is put equal to the number of collisions between atoms A and B in which the kinetic energy in the line of centers is greater than Q_1. This is of course plausible. Likewise we may write

$$R_2 = k_2n_3 = \nu n_3e^{-Q_2RT}, \tag{19}$$

which is the rate of dissociation of activated molecules, assuming that dissociation takes place at the end of the first vibration as is known to be the case in the phenomenon of predissociation.

The number of collisions calculated in (16) is of course dependent upon the value used for r hence in general we shall need a "steric factor" for "efficiency" of collisions in (16), but the same factor must be introduced in (17) if (13) is to be true. k_1 and k_2 are constants since the probabilities of reactions in collision are not dependent upon the existence of a state of equilibrium but rather determine the equilibrium itself. If the reaction were between two like atoms the symmetry factor of $\frac{1}{2}$ which would appear in the

entropy of the diatomic molecule would be identified with the factor $\frac{1}{2}$ in the expression for the number of collisions between like atoms.

At this point we may justify Eq. (2). If we differentiate Eqs. (16) and (17) we obtain

$$d\ln k_1/dT = (Q_1+\tfrac{1}{2}RT)/RT^2, \tag{20}$$

$$d\ln k_2/dT = Q_2/RT^2. \tag{21}$$

$Q_1+1/2RT$ and Q_2 are the heats of activation as defined by Tolman.[1] The heat of activation is taken to be the difference between the average energy of the activated molecules and the average energy of all molecules.

Eq. (19) is interesting since it gives us the rate of a unimolecular reaction, the dissociation of a diatomic molecule in terms of the number of activated molecules and the frequency of vibration. Since ν is large the concentration of activated molecules $n_3e^{-Q_2/RT}$ must be small. The only way activated molecules can be formed accord to Eq. (1) is by collision of A and B and an activated molecule is formed at every collision of A and B which takes place with sufficient violence. That is to say the equations here developed take account only of the two opposing mechanisms postulated in (1). They take no account of the combination of A and B in triple collisions or the activation of the molecule AB by collision with another atom or molecule.

It is not surprising that for an idealized model that the results of simple kinetic theory should agree with thermodynamics. It is important to consider whether the behavior described above may be expected in real molecules. The constancy of the frequency ν at high levels is only possible if

[1] Tolman, *Statistical Mechanics*, Chem. Catalog Co., New York (1927).

the hump in Fig. 1 is very sharp. In this case there is also the possibility of the molecule dissociating by "leaking" through the hump. Aluminum hydride appears to be an example of a molecule with flat hump. Many examples[2] of such humps are to be found in excited states of molecules. It seems likely that the nitrogen[3] molecule in the metastable A state comes to equilibrium with nitrogen atoms by a reversible predissociation mechanism which is of the type (1) discussed above, and for which a constant frequency ν would be significant.

In any event we may say that since the average molecule dissociates with an excess (kinetic) energy kT that the average life period of an activated diatomic molecule is short and of a period comparable to $1/\nu$. It seems probable that the negative temperature coefficient observed in some third order reactions is caused by the decrease in the average life period of some unstable complex with increasing kT, as is predicted by the above reasoning.

The Theory of Unimolecular Reactions

The rate of most unimolecular reactions may be represented by an expression of the form of Eq. (19) where Q_2 is the heat of activation and ν has a value of 10^{11} to 10^{13}, which corresponds roughly to the infrared frequency of the molecule. The heats of activation are usually not very large and in most cases certainly much less than the heat of dissociation to be expected for a bond.

Some years ago the author attempted an explanation[4] of this fact. It seems desirable to restate the ideas presented in that paper in the light of our present knowledge of the behavior of vibrating molecules. The author postulated exactly the mechanism of activation of molecules by collisions which has been discussed at length by Kassel, Rice and others.[5] An N_2O_5 molecule, for example, acquires by collision an energy in excess of the critical energy required for dissociation. This activated molecule has an average life period of the order of 10^{-6} seconds. If collision occurs before this time the molecule will be de-

activated but if collision does not occur soon enough the energy will become concentrated in some one bond (probably any one of a number of different bonds) and the molecule dissociates, perhaps at the end of the first vibration as in the case of the diatomic molecule. The author did not discuss the possibility of a decrease in rate at low pressures because it seemed unlikely that this could be observed in the case of nitrogen pentoxide and as a matter of it is only observed at pressures so low that the results are subject to considerable experimental uncertainty. Also he did not consider the possibility of a complete interchange of energy in a collision because at that time it was not known to be either necessary or possible. The case of nitrogen pentoxide is unique in this respect because of the symmetrical structure of the molecule and the possibility of dissociation taking place in various ways. The author considered the molecule as a loose complex of atoms within which energy is transferred by collisions between adjacent atoms.

It seems possible at present to give these ideas a much more precise form in the light of our present knowledge of potential energy curves for molecules.

It seems reasonable to assume that when two adjacent atoms in a complex molecule are separated beyond a certain critical distance that the two portions of the molecule, each rearrange with a decrease in total potential energy and the complete rupture of the bond. Such a rearrangement bears a close analogy to the change to another electronic state that is assumed to take place in predissociation or the Auger effect. This point has been discussed at length by Kassel.[5] This situation would be represented by Fig. (1) if we consider the hump as defined by the dotted lines. The curve b represents a repulsive state for the two parts of the molecule. This comes about through a rearrangement of the valence forces to form two approximately saturated molecules which have very little residual attraction for each other. The hump will now have a sharp peak, and the peak will lie much below the energy of dissociation for the bond. Hence the mechanical frequency of vibration at the peak will not differ greatly from ν_0 the fundamental frequency of the bond.

If the foregoing conditions obtain the rate of

[2] Hulthén and Rydberg, Nature **131**, 471 (1933).

[3] Kaplan, Phys. Rev. **37**, 1407 (1931).

[4] Rodebush, J. Am. Chem. Soc. **45**, 606 (1923).

[5] Kassel, *Kinetics of Homogeneous Gas Reactions*, Chem. Catalog Co., New York (1932).

dissociation will be given by the expression

$$\nu n e^{-Q_2/RT}$$

provided that an equilibrium concentration of molecules is maintained and that dissociation takes place at the end of the first vibration. Even if the equilibrium concentration is not maintained the rate may still be given by the above expression as the following reasoning will show. Since Q_2 is large, corresponding to a high vibrational state there is a high probability that some energy will be transferred to some other part of the molecule at the end of a single vibration. This would mean that the bond would be deactivated at the end of the first vibration and the rate of deactivation must be equal to rate of activation. Now if every activated molecule dissociates the rate of dissociation will be given by the rate of activation and this will of course be unaffected by the fact that the molecules previously activated have dissociated. This is essentially the argument given by the author in his original paper.

The foregoing picture is of course much too simple since we are treating the vibration of a single bond as for a diatomic molecule whereas we are dealing with the complex vibrations of a polyatomic molecule. It seems probable that certain factors need to be introduced which might make the rate less or greater than that given above.

For example, it seems likely that the equilibrium concentration of activated molecules may be maintained owing to the fact that the bond does not break at the end of the first vibration. There may be a probability much less than unity that the molecule will transform from the state a to the state b when it is at the point of intersection. The transformation may take place by leaking through the hump. This possibility has been discussed by Bourgin[6] and there seems to be nothing against it except that it is not known to be required as an explanation. Finally, of course, the expression $e^{-Q_2/RT}$ is the fraction of the total number of harmonic oscillators with energy in excess of a certain critical amount. The fraction

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[6] Bourgin, Proc. Nat. Acad. Sci. **15**, 357 (1929).

of the total number of molecules with vibrational energy in a certain bond in excess of the critical amount may be much different for polyatomic molecules, due to weight factors different from unity for the various energy states.

The number of bonds susceptible of rupture differs in different molecules. It is surprising therefore that the rate of so many unimolecular reactions may be represented by an equation such as (19) with such a small range of values for ν.

BIMOLECULAR MECHANISMS

A bimolecular metathesis $A+BB=AB+B$ may be treated by the methods used in discussing the mechanism (1) in the beginning of this chapter, if we assume that the intermediate step in the reaction is the formation of the complex ABB. Eq. (13) should hold but there will now be two steric factors involved in the formation of the complex from $A+BB$ and $AB+B$, respectively, and these factors need not be equal. The kinetic theory is not adequate for the discussion of collisions between complex molecules. The method used here involves the assumption of complex formation. Kassel has discussed the relative merits of the two methods and has shown that they amount to the same thing in the end. The application of thermodynamics seems likely to be of greater utility since it may be possible to calculate the entropy of intermediate complexes, especially when we have more experimental data to give us information about steric factors. The difficulty with the entropy of activation is similar to the difficulty with the heat of activation. The entropy of activation bears no relation to the total entropy change of the reaction. The energy is assumed to be a maximum for the intermediate complex. The entropy of the intermediate complex, however, will in general be neither a maximum nor a minimum nor so far as one can predict any unique value. It seems possible to define the intermediate complex in such a way that the steric factors for the reaction in the two directions will be equal. This result would be apparently an extension of the principle of microscopic reversibility. It is not certain however that this definition would correspond to the unique definition required for the heat of activation.