The Transition State Method in Chemical Kinetics.

Contribution to a Discussion on The Transition State in Reaction Kinetics, held by the Chemical Society on February 4th,* 1937.

By C. N. Hinshelwood.

There can be no fundamental difference between the results of a kinetic treatment and those of a thermodynamic treatment. The object of the present contribution is to attempt to show that the transition state method and the kinetic method of treating reaction velocity problems are very much more similar than they might appear at first sight. Neither can be said to stand in opposition to the other. The thermodynamic method frequently has the advantage of a greater formal elegance of its equations and a greater generality. On the other hand, this quality is accompanied by the corresponding defect that the magnitudes operated with are often quite inaccessible to experimental control, and further, that the plausibility of certain assumptions cast in a mathematical form is less easy to assess at its face value than it would be with the corresponding assumptions of the alternative method. The most satisfactory attitude is to be willing to derive all the information possible by the impartial consideration of problems from both points of view. The interpretation of kinetic relations in terms of thermodynamics and vice versa is in any case

---

* A few additional remarks are added to what was said in the discussion itself.

a process worth while for its own sake, and seldom fails to enrich one's understanding of the workings of Nature.

In the following, I shall consider a number of problems from both points of view, and the comments will indicate what I consider to be the relative strengths and limitations of the two methods in various connexions.

The kinetic method is based upon the consideration of the equation, Reaction velocity $= PZe^{-E/RT}$, where Z is the number of encounters between the reactants, E the activation energy, and P a factor expressing the probability that other conditions, such as the orientation of all the molecules concerned, the relative motions of their atoms and electrons, and a favourable disposition of the surrounding solvent molecules, are fulfilled. The simple exponential form of this expression has to be modified if the activation energy resides in a considerable number of degrees of freedom. The extra temperature-variable terms could be included in P, which would then be temperature-dependent: whether or not we do so include them, or whether we replace the exponential by a more complicated expression and call P constant, is a matter of convenience only.*

To calculate Z we must know the collision diameters: the collision diameter is obviously not an absolutely sharply defined magnitude. But there is good sense in taking it as the value derived from viscosity (momentum transfer) experiments, and then enquiring what further conditions must be fulfilled. This is equivalent to assuming that we have a normal size for the transition state. The diameter of the transition complex has to be assumed in making calculations by the thermodynamic method also; and unless we assume it to be normal we do not know what value to assign to it. The diameter difficulty comes equally into both methods.

The transition state method sets out to calculate reaction velocities as follows. The statistical theory of equilibria is employed to calculate the equilibrium constant, K, of a transition complex of the reactants; K is then multiplied by a thermal velocity v and by a numerical factor of the order $\frac{1}{2}$, giving $\frac{1}{2}Kv$ for the rate. K is expressible as a product of partition functions for the activated state divided by a product of partition functions for the reactants, and the whole is multiplied by $e^{-E/RT}$. For v, Eyring uses kT/h.

It is instructive to compare the calculation of a reaction velocity by the two methods in the simplest possible case, and then to see in what manner the difficulties increase as we pass from the simplest to more complex cases. We shall see that they increase in a more or less parallel manner in both.

From the point of view of the kinetic theory, the simplest assumption that we can make is that the activation energy resides in two square terms, and that all the collisions with enough energy lead to reaction. This gives for the rate at unit concentrations

$$\left\{8\pi RT\left(\frac{1}{m_1}+\frac{1}{m_2}\right)\right\}^{\frac{1}{2}}\sigma^2$$

If we wish to make the calculation for more complex cases we must make assumptions about the number of degrees of freedom in which the activation energy resides, and about the orientations, and about the internal phases of the molecular motions, and so on. In general, we do not know what to assume about these, and all that we can do is to investigate whether they appear to change in the right direction when we pass from one example to another.

Turning now to the transition state method, we must write down K. For the transition

* The objection has been made that the kinetic method assumes P to be a constant, whereas the thermodynamic method shows it to be related to an entropy, which, being expressible as the integral of specific-heat terms divided by temperature, may be temperature-variable. This objection amounts to comparing the first approximation of one theory with the second approximation of another. For if the specific-heat terms are of importance, the activation energy will vary with temperature. Variation of activation energy with temperature means that there are different probabilities of reaction for different states within the range of what might be called the spectrum of activated states. In this case the simple exponential form no longer expresses the reaction velocity: or, if it is made to do so formally, then a temperature-variable residuum has to be included in P. This state of affairs has long been familiar in connexion with theories of unimolecular reactions.

complex we shall have a product of three translational partition functions, one rotational (3-dimensional) partition function, and a whole series of vibrational partition functions; for the reactants, we have a product of three translational partition functions for each molecule concerned, a rotational function for each, and a whole series of vibrational ones. In the simplest case, say the union of two atoms to form a molecule, the expression for the K reduces to the form $T_a^3 . R_a/T^6$, where T_a^3 means a product of three translational partition functions for the activated state.

Putting in the values for the different kinds of partition function, and multiplying by kT/h and by $e^{-E/RT}$, we obtain for the rate.

$$\frac{\left\{\frac{2\pi(m_1+m_2)kT}{h^3}\right\}^{\frac{3}{2}} . \frac{8\pi^2 IkT}{h^2} . \frac{kT}{h}}{\frac{(2\pi m_1 kT)^{\frac{3}{2}}}{h^3} . \frac{(2\pi m^2 kT)^{\frac{3}{2}}}{h^3}} . e^{-E/RT}$$

We must now put in the value for the moment of inertia. If this is written as $\mu\sigma^2$, where σ is the sum of the normal radii of the reactants, then we have made an assumption not very different from that of the simple kinetic theory. If we wish to assume a very different value, then we are doing something which must be equivalent to making the assumption of an abnormal target area in the kinetic theory. In one method as in the other it is difficult to know what value we should take, if for any reason we believe the normal one to be inadmissible. There will be, of course, small differences according to whether we take σ to be the diameter of the product or that of the unchanged pair of reactants, but it is no exaggeration to say that the difference is well within the limits of the other uncertainties. Taking σ as the normal value, we obtain for the rate the expression :

$$(8\pi kT)^{\frac{1}{2}}\left(\frac{m_1+m_2}{m_1 m_2}\right)^{\frac{3}{2}} . I$$

Since $I = \frac{m_1 m_2}{m_1 + m_2} . \sigma^2$, this becomes $\left\{8\pi kT\left(\frac{1}{m_1}+\frac{1}{m_2}\right)\right\}^{\frac{1}{2}}\sigma^2$

which agrees with that obtained the other way. This is a very neat example of the inter-relation of kinetic theory and thermodynamics.

In more complicated cases the partition products do not reduce to the simple form. We obtain products involving a number of vibrational and rotational partition functions for the activated state divided by a similar product for the reactants. The closer study of these products reveals several interesting things. If we are dealing with an association reaction there will be a number of vibrational partition functions for the activated state divided by rotational functions for the reactants. In general, the numerical values of the former are smaller than those of the latter; the result is a small value of K and a correspondingly small reaction rate. This corresponds to a small value of the factor P. The kinetic interpretation of this is clearly that in an association reaction rotational degrees of freedom disappear and new linkages appear with associated vibrations, and that this process can only take place when the mutual orientations of the reactants are suitable, and when the relative motions of various atoms are also suitable for the creation of the new bonds. Each method of statement illuminates the other. As regards the possibility of making quantitative calculations, from the kinetic point of view it is evident at once that to specify the orientations and phases correctly is a very difficult task. To write down the appropriate partition functions may sound formally a matter capable of treatment with greater precision. But this can hardly be true in actual practice. The vibrational partition function depends upon the frequency of the vibration in question, and can easily vary by one or two powers of 10. A product of several can thus vary by many powers of 10. The value of the frequency depends upon the strength of the binding, and precisely in an activated complex, where some bonds are being broken and others formed, we are likely to be very much in the dark as to the appropriate values to take. It is probably not unfair to say that our chances of writing down the correct values of the partition functions correctly are about the same as those of specifying the orientations and phases correctly.

A point which is relevant here is the question of the identity of the two molecules which constitute the transition complex in a bimolecular reaction. It may be said that the collision theory postulates that their identity is preserved: this, however, is hardly to be insisted on, since we postulate for reaction a state of affairs where the energy exceeds E, where the orientation of the two molecules is between certain limits, and where the phase of their internal motions is also defined. We thus contemplate a structure as specialised as the new species which the thermodynamic method calls the transition state.

In the simplest of cases most of the vibrational degrees of freedom of the reactant molecules might persist more or less unchanged in the transition complex. The corresponding partition functions in the numerator and the denominator of K would cancel. In this case we should be justified in saying that these internal degrees of freedom ought not to be invoked in explaining the reaction rate. But in many cases the activation process must be rather complex: and several, or even many, degrees of freedom in the activated complex possess frequencies very different from those of the normal reactants. If the frequencies are very much smaller, which corresponds to a great loosening of the binding, then the corresponding product of partition functions becomes very great. This corresponds to a large value of P. Here there seems to be no reason why a number of degrees of freedom should not contribute to the activation energy, as in the well-known theories of unimolecular reactions.

These reflexions arise in an interesting way in the question of the effect of solvation on reaction velocity in solution. It has been pointed out that if the transition state is more solvated than the reactants, the temperature-independent factor in the reaction velocity will tend to be small, and vice versa. This follows from considerations of the entropy of activation. The corresponding kinetic statements seem to be as follows. If the activated state is more solvated, it means that the actual reaction process involves the collecting round the reactants of the appropriate number of suitably orientated solvent molecules. The probability of this is small so that P is small. In the converse case we start with solvated reactants: by hypothesis they must become desolvated in the process of activation. From the thermodynamic point of view, the entropy increases when the ordered solvated systems pass into the disordered scattered components with their independent translational and rotational energies. The activation process involves the loosening of the solvated molecules. The frequencies of the links binding them to the reactants become very small in the activated state: this makes the partition function product great, and P great. Kinetically, P is great because the very necessity for loosening the solvate appendages involves the placing of energy in many links; and this, as in the unimolecular reaction theories, causes the expression giving the activation rate to be greater than $Ze^{-E/RT}$ by a large factor.

As I have been invited to contribute to this discussion, I will state my personal view in concluding this section, that the great value of the transition state method is in causing us to think more deeply about the inter-relation of thermodynamic and kinetic magnitudes, rather than in providing us with an essentially more accurate calculus. It must certainly be said that sometimes the answer to a problem may be seen more easily from one point of view than from the other: we can then translate the answer into the language which we prefer.

Another field of usefulness of the transition state method is even more directly thermodynamical. The transition state is regarded as a definite molecular species possessing assignable thermodynamic properties, so that the various thermodynamic relations of common utility can be applied to the equilibrium constant K, enabling one to predict the influence of various factors on rates of reaction.

This leads to many elegant relations, which are formally more satisfying than any which a direct kinetic approach could yield. On the other hand, these relations involve the assignment of values to thermodynamic properties of the transition state, and this is only possible if we know a good deal about the transition state already. In view of the fact that we do not in general know a great deal about the transition state, it is probably best to invert the obvious procedure, and to use empirical facts about reaction velocity to discover the thermodynamic properties of the transition state. This may lead to valuable generalisations.

One of these may be mentioned as particularly suitable for this method of treatment. Polanyi and Evans, from a study of the influence of pressure on reaction velocity, justify the conclusion that the volume of the transition state is intermediate between that of the reactants and that of the products.

Other cases might be equally simple : some must be less so. For example, we know that the energy of the transition state is not intermediate between that of the reactants and products. When we are thinking of assigning values to thermodynamic properties of the transition state on the basis of analogy with ordinary molecular species, we must remember that the properties of the latter represent averages over the whole of configuration space, while those of the former refer to limited and specialised regions only. Thus it would seem dangerous to apply empirical laws about solubility, or about activity coefficients to the activated state, without special investigations to justify such a procedure. (The fact that the various Brønsted activity coefficient relationships hold is no answer to this demand for caution. The Brønsted relation refers to the influence of Coulomb forces in ionic reactions : nobody would suppose that the total charge on a transition complex is other than the sum of the charges on its constituents.)

To continue the comparison of the two methods, we will now consider a special problem, namely, that of the logarithmic relation between velocity constants of certain series of related reactions.

If we have two series of reactions with velocity constants k_1^a, k_1^b . . . and k_2^a, k_2^b . . . , all members of series 1 and all members of series 2 being chemically analogous among themselves respectively, and the members *a*, *b* . . . of a given series differing in the structure of one or other of the reactants or in the substituents present, then we may find a relation of the following form :

$$\log k_1 = \alpha \log k_2 + \text{const.} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where α is the same for all the members of the series *a*, *b* . . . . For example, such a relation may be found by plotting the logarithm of the velocity constant for the hydrolysis of benzoic esters with a series of nuclear substituents against log *k* for the benzoylation of aromatic amines with the same series of substituents.

Another form which the relation may take is

$$\log k = \alpha \log K + \text{const.}$$

where log *k* refers to the velocity constant of a reaction and log *K* to the equilibrium constant of another reaction in which one of the reactants can participate. The best known example of this kind is the Brønsted relation between the catalytic coefficient for the action of a series of acids on a given substrate and the dissociation constant in water of the same series of acids.

Log *K* is proportional to the free energy of the reaction, and log *k* can be regarded as proportional to the free energy of the reaction by which the reactants pass to the transition state. If we introduce the thermodynamic equation $d \log k/d\chi = (\beta_1 - \beta_\tau)/RT$ where β is the differential coefficient of the free energy with respect to some variable χ, we can connect the experimental relations referred to above with the thermodynamic properties of the transition state by a simple algebraical elimination.

To account for the linear logarithmic relations we must assume, first, that all the various β's are constants, and secondly, that if the influence of change in structure or substituents is represented by a parameter χ, then the ratio (χ for reaction 1)/(χ for reaction 2) is a constant for all the members *a*, *b* . . . of the series. In other words, we translate the experimental relationship into a statement of the kind that certain thermodynamic quantities maintain a constant ratio throughout a series. When we have seen this we have tidied our ideas. The only danger to guard against is the introduction of such a statement as a self-evident truth, which we may be tempted to do simply because we have not enough intuitive feeling about the quantities in question to see how much assumption such a statement may contain.

Writing the reaction rate in the form

$$\log k = \log PZ - E/RT$$

we may see what the corresponding assumptions of the collision theory must be if equation (1) is to hold. For variations among members of a given series, we have

$$\Delta \log k = \Delta \log PZ - \Delta E/RT.$$

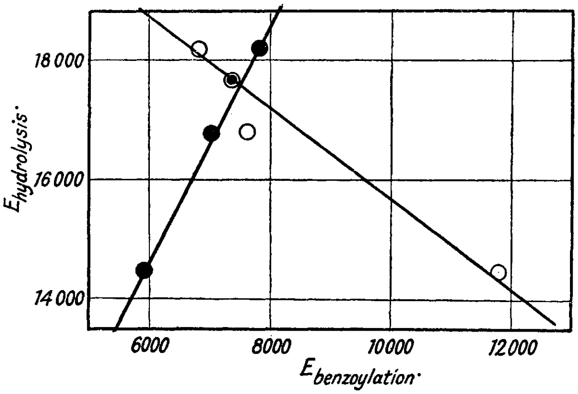
Two cases arise. In the simplest, PZ is constant for a given series, and equation (1) simply requires $\Delta E_1 = \alpha \Delta E_2$. Since PZ often remains nearly constant through a series, this case is of some importance, and is worth examining in more detail. Suppose we are studying the effect of the same series of substituents on two reactions. Let us suppose schematically that one particular bond in each type of molecule is principally influenced by the substituents, their effect on the rest of the molecule being in the first approximation negligible for the purpose of the reaction. If in one case the bond in question is a strong one requiring considerable activation while in the other case it is very weak or requires no activation, we may evidently have ΔE_2 finite but ΔE_1 nearly equal to zero, *i.e.*, $\alpha = 0$. At the other extreme we shall have the bond of approximately equal strength and requiring the same amount of activation in each reaction and $\Delta E_1 = \Delta E_2$ with $\alpha = 1$. In between we shall have fractional values of α. The condition that the fractional value shall be a constant for the series is that the effect of the substituent on the bond strength shall not be an absolute magnitude but one proportional to the original strength of the bond. Alternatively, we may suppose that ΔE_1 is much smaller than ΔE_2 because the effect of the substituent is not wholly transmitted to the part of the molecule where it will influence the activation energy; in this case we must assume, in order to arrive at a constant α, that a constant fraction of the maximum effect is transmitted for all members of the series.

These interpretations are to be compared with the thermodynamic statements made above. They are not in themselves more or less probable than those. They have the disadvantage of being less general, but the advantage of being more easily appraised or verified.

Substituent.	Alkaline hydrolysis of benzoic esters in 85% alcohol. (Ingold and Nathan.)	Benzoylation of nuclear-substituted anilines.	Benzoylation of aniline with substituted benzoyl chlorides.
		(Williams and Hinshelwood.)	
Me	18,200	6,800	7800
H	17,700	7,350	7350
NO_2	14,500	11,800	5900
Cl	16,800	7,600	7000

The above table gives the activation energies for three reactions influenced by para-substituents in the benzene nucleus. The figure shows that the variations in activation energy may well be nearly proportional to one another, and that the values of ΔE decrease in the order : substituted amines, esters, substituted acid chlorides. This may well be due to the fact that the transmission of the effect of the substituent is less efficient in the case of the amines than with the esters, while with the acid chloride the effect is produced in a molecule which does not in any case need much activation, most being required in the other reaction partner.

When PZ varies considerably in the series of reactions, the matter is more complicated. In order to preserve relation (1) we most simply assume that $\Delta \log P_1Z_1 = \alpha \Delta \log P_2Z_2$. There are examples where in a series of reactions $\log PZ$ increases linearly with E, so that $\Delta \log P_1Z_1 = \rho_1 \Delta E_1$ and $\Delta \log P_2Z_2 = \rho_2 \Delta E_2$, and we now have $\rho_1 = \rho_2$ In other words, the at the moment unknown factor which makes PZ increase with E must be one operating equally in the case of both series of reactions. In many cases ρ tends to zero, and it must of course be remembered that the smaller ρ, the less accurately need $\rho_1 = \rho_2$ for relation (1) to be fairly well obeyed. An interesting special case must be mentioned here. At least one example is known in which there are rather irregular, though not very marked, variations in PZ in a series of basic catalyses, and the Brønsted relation is obeyed with great accuracy. The deviations of PZ from constancy seem therefore to be due to a factor which affects the dissociation of an acid and its catalytic power equally. An abnormally great PZ for a given acid of the series means that the reaction goes more easily than we should expect from the activation energy. Since the Brønsted relation is obeyed, we infer that that same acid also has an abnormally great tendency to give up a proton to water. If we attribute any anomalous behaviour to that part of the reaction mechanism connected with the giving up of the proton, rather than to any other kind of activation of the reaction partner, then we can see how the anomaly may show itself in the P–E relation while not appearing in the Brønsted relation. An examination of various facts from this point of view can provide clues to the nature of P–E correlations.



The law connecting the exponential and non-exponential terms of the reaction velocity equation will not be dealt with further here, as it is the subject of another communication from Fairclough and the author (this vol., p. 538).

Nothing has so far been said about the types of reaction to which the transition state method is applicable. It is no criticism of the method itself to mention that it can hardly be applied to chain reactions, or to reactions in which removal of energy from the products is a rate-determining factor. But the wide-spread occurrence of, at least, the former of these two categories shows that special investigation of each given example is necessary.