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**DIVIDING SURFACE IN TRANSITION STATE
THEORY OF REACTION RATES: NOTE
ON HORIUTI'S PAPER, "ON THE STATISTICAL
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ABSOLUTE RATE OF CHEMICAL REACTION"**

By

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Abstract

Horiuti's contribution to the variational theory of chemical reaction rates is briefly described. A simple example of variational calculation given by him [Bull. Chem. Soc. Japan, 13, 210 (1938)] is carefully re-examined, as a result of which its relation with the theory of ion-molecule reactions or free-radical recombination reactions given by Eyring, Hirschfelder and Taylor (1936) or by Gorin (1938) is revealed.

Introduction

Transition state theory, TS theory for short, has long played a central role in the theory of chemical reaction rates. During the last decade and half, the dynamical foundation of TS theory has been a subject of a large number of intense discussions (see below). One of key concepts in such discussions is dividing surface (also called critical surface by some authors^{1,2,3}) in the phase space of a reacting system; the surface divides the phase space into reactant and product regions. This concept was introduced as early as 1915 by Marcelin in his paper,² "Contribution à l'étude de la cinétique physico-chimique." At that time our knowledge of atoms, molecules, interatomic or intermolecular forces, *etc.* was very poor, which held up further development of his rate theory for many years. Perhaps we may say that the theory of reaction rates in the modern age of physical chemistry started with the important work by Pelzer and Wigner (1932),^{3,4} which subsequently developed into the well-known formulation of TS theory by Eyring (1935)^{5,6} and Evans and Polanyi (1935).⁷ The rate expression derived in TS theory of these authors may be viewed as evaluating the flux of representative

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T. NAKAMURA

points through a dividing surface in a phase space.^{1,3,8,9)}

A dividing surface, in a phase space consisting of momenta \mathbf{p} and coordinates \mathbf{q} , is described by an equation of the form,

$$S(\mathbf{p}, \mathbf{q}) = 0. \quad (1)$$

Very often a dividing surface expressed by an equation of the form,

$$S(\mathbf{q}) = 0 \quad (2)$$

is also considered. Of course (2) is a special case of (1).

There are a number of different ways, different mainly in appearance, of writing the rate equation of TS theory. For convenience let us consider the following expression^{10,9)} for the rate R :

$$R = \int_S d\sigma v_n \theta(v_n) \rho(\mathbf{p}, \mathbf{q}). \quad (3)$$

Here $\int_S d\sigma$ is the surface integral over the dividing surface S defined by (1) or (2), v_n is the normal component, normal to the surface S , of the generalized velocity \mathbf{v} of a representative point in the multi-dimensional phase space, θ is Heaviside's unit step function¹¹⁾ introduced to evaluate the positive flux, *i. e.*, the flux from the reactant region to the product region, of representative points through S , and $\rho(\mathbf{p}, \mathbf{q})$ is the probability density (distribution function) of representative points.

In 1937 Wigner,¹²⁾ in his theory of association reactions of the type,



made an important remark; *i. e.*, he pointed out that the rate calculated by (3) gives an upper bound to the "true" reaction rate, and hence the surface S should be varied so that the right hand side of (3) gives its lowest possible value. This minimization principle for (3) reminds us of the variational principle in quantum mechanical calculations of wave functions. Thus it is appropriate that rate calculations based on (3) plus this principle later became known as variational calculations.^{10,9)}

In 1938 Horiuti's interesting paper¹⁾ entitled "On the Statistical Mechanical Treatment of the Absolute Rate of Chemical Reaction" was published, where he discussed how the minimization or variational principle should be incorporated into conventional TS theory developed by Pelzer and Wigner,⁴⁾ Eyring,^{5,6)} and Evans and Polanyi.⁷⁾ It is to be noted that Wigner considered a dividing surface of the type (1) because he aimed at calculating the rate of the atomic association reaction (4), in which the disposal, by the third body M , of the energy (which is a function of \mathbf{p} and \mathbf{q}) of A_2 formed by

Dividing Surface in Transition State Theory

the association plays a crucial role. On the other hand Horiuti's surface is of the type (2), because in his theory as well as in the conventional TS theory, attention is directed to the structural change, *i. e.*, the change in nuclear configuration q of reacting systems.

Wigner¹²⁾ suggested the possibility or desirability of varying the dividing surface but did not perform any variational calculation. Horiuti's work^{1,13)} provided fundamental ideas but did not go farther although he showed one very simple example of variational calculation,^{1,14)} which will be discussed in the next section. Thus it remained to be shown how variational calculations should be practically carried out for reacting systems of physical or chemical interest. But further progress was much retarded partly because of the heavy pressure of World War II. It was not until Keck¹⁰⁾ performed, in 1960, a variational calculation of the rate of the association reaction (4) that Wigner's or Horiuti's idea materialized.*)

In fact Keck's work (1960, 1967)^{10,9)} triggered a new interest in the variational calculations of reaction rates. Meanwhile in 1960s, with the advent of fast and large electronic computers, trajectory calculations, based on classical dynamics, of reacting systems became possible.¹⁵⁾ Stimulated by this new development, numerous investigations have been made on the foundation, capability and limitation of TS theory during the last decade and half. They include discussions on the recrossing problem,¹⁷⁾ which deals with multiple crossing of a trajectory through a dividing surface and has an important bearing on the Wigner-Horiuti-Keck variational theory.

Also, in 1970s a number of rate calculations for reactions of the type,



have been performed on the basis of the Wigner-Horiuti-Keck variational theory, and interesting results have been obtained.

However, it is not the purpose of the present paper to review or discuss these recent developments.**) In the next section the above-mentioned example of Horiuti^{1,14)} will be re-examined. It will be shown that this example as such is rather trivial but its re-examination leads to a few interesting results.

*) Thus it was not until 1960s that physical chemists' attention was drawn to Horiuti's paper, ref. 1, of which Keck was unaware when he published his variation theory paper in 1960 (private communication from Keck to Horiuti dated 18 January 1961). In an interesting paper (1974) on the variational theory, Koepl (ref. 16) re-examined and commented upon this ref. 1 by Horiuti.

**) See ref. 18 by Garrett and Truhlar, and some one hundred and twenty papers quoted therein. Particularly, recent important developments of the variational theory are described in this reference.

T. NAKAMURA

§ 1. Horiuti's Example

As an example of the application of his variational theory, Horiuti^{1,10} has considered the association reaction $A+B \rightarrow AB$, in which the interatomic potential U between the two atoms A and B is a function only of the internuclear separation r . His argument proceeds as follows.

In applying (3) to the above reaction, the 12-dimensional phase space of the two particles A and B is considered and the density $\rho(\mathbf{p}, \mathbf{q})$ is taken to be that of canonical distribution, *i. e.*,

$$\rho(\mathbf{p}, \mathbf{q}) = Z^{-1} \exp(-\beta H(\mathbf{p}, \mathbf{q})), \quad (5)$$

where β stands for $1/kT$, Z is the phase integral,

$$Z = \iiint d\mathbf{p} d\mathbf{q} \exp(-\beta H(\mathbf{p}, \mathbf{q})) \quad (6)$$

and the Hamiltonian function $H(\mathbf{p}, \mathbf{q})$ is written as

$$H(\mathbf{p}, \mathbf{q}) = \frac{1}{2(m_A + m_B)} (p_x^2 + p_y^2 + p_z^2) + \frac{1}{2\mu} \left(p_r^2 + \frac{p_\theta^2}{r^2} + \frac{p_\phi^2}{r^2 \sin^2 \theta} \right) + U(r). \quad (7)$$

On the right hand side of (7), the kinetic energy part is expressed in terms of the momenta conjugate to the center-of-gravity coordinates (X, Y, Z) and the internal motion coordinates (r, θ, ϕ) of the system A+B, and the reduced mass μ is given by $\mu = m_A m_B / (m_A + m_B)$, where m_A is the mass of A and m_B is that of B. The dividing surface appropriate for the above reaction is a sphere with its center at the center of the atom A. For this surface eq. (2) becomes

$$r - r_* = 0, \quad (8)$$

where r_* is the radius of the sphere.

Thus the rate equation (3) is rewritten as

$$R = \frac{1}{Z} \iiint d\mathbf{p} d\mathbf{q} \delta(r - r_*) \frac{-p_r}{\mu} \theta(-p_r) \exp(-\beta H(\mathbf{p}, \mathbf{q})), \quad (9)$$

where δ is the delta function. Carrying out the integrations in (9) and (6) we readily have

$$R = V^{-1} (8\pi kT/\mu)^{3/2} r_*^2 \exp(-\beta U(r_*)), \quad (10)$$

where V is the volume of the gaseous mixture of A and B in which the

Dividing Surface in Transition State Theory

association reaction takes place. To determine the optimum value of r_* , the variation requirement for a minimum of R is invoked; *i. e.*, r_* is obtained from the condition,

$$\frac{\partial R}{\partial r_*} = 0, \quad (11)$$

which implies

$$\frac{\partial U(r_*)}{\partial r_*} = \frac{2kT}{r_*}.$$

The interatomic potential $U(r)$ is of the form shown in Fig. 1. Thus no potential barrier occurs along the reaction coordinate, which implies that conventional TS theory can not be applied to this particular problem (see however § 3 of the present paper). Horiuti^{1,10} has claimed that his theory is free of such a difficulty in the sense that the condition (11) based on the variational principle uniquely determines the critical surface (dividing surface) and the critical state (transition state) for the above reaction.

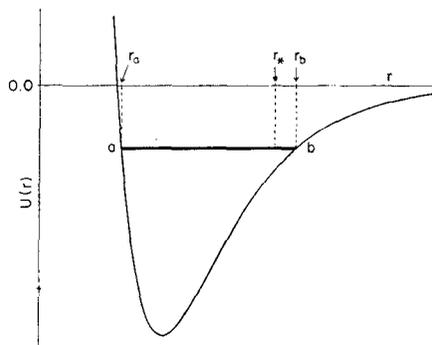


Fig. 1. The potential energy $U(r)$. The line a-b represents the energy level of a typical bound state (diatomic molecule AB). If $r_a < r_* < r_b$, where r_* is the radius of the spherical dividing surface, then the trajectory of this bound state crosses the dividing surface and contributes to the rate R .

§ 2. Comments

It is interesting to see why there occurs the optimum value of r_* , which corresponds to a minimum value of R and is determined from the condition (11). In so doing we consider the combined effect of two factors involved in (10), namely, r_*^2 and the exponential factor $\exp(-\beta U(r_*))$.

T. NAKAMURA

For large values of r_* , the exponential factor is almost unity and can be ignored (see Fig. 1). Then R given by (10) is proportional to r_*^2 , *i. e.*, proportional to the area of the spherical dividing surface, $4\pi r_*^2$. Hence R becomes just the probability of the collision of A and B provided that the collision cross section is taken to be πr_*^2 . To see this, remember that the frequency per unit volume of such collisions is given by the well-known expression,¹⁹⁾

$$\pi r_*^2 \left(\frac{8kT}{\pi\mu} \right)^{\frac{1}{2}} \frac{N_A}{V} \frac{N_B}{V} = \frac{1}{V} \left[\frac{1}{V} \left(\frac{8\pi kT}{\mu} \right)^{\frac{1}{2}} r_*^2 \right] N_A N_B, \quad (12)$$

where N_A and N_B are the numbers of the atoms A and B, respectively, in the volume V . It is to be noted that the right hand side of (10) is, except for the exponential factor, equal to the quantity in the square brackets on the right hand side of (12).

In the neighborhood of $r=r_e$, the exponential factor is considerably larger than unity, especially so at lower temperatures. The exponential factor in (10) represents the contribution to R from bound states of A+B, namely, diatomic molecules AB (see Fig. 1); at lower temperatures, the relative population of diatomic molecules increases.

Thus we see that the optimum value of r_* , which is somewhat larger than r_e , occurs as a compromise to satisfy the following two requirements: (1) r_* should be considerably larger than r_e to make the contribution to R from the bound state trajectories negligible; (2) r_* should be smaller to make the contribution to R from dissociated state trajectories smaller by decreasing the area of the dividing surface. Incidentally it is to be noted that if the value of r_* is considerably larger than its optimum value, the majority of the trajectories passing through the dividing surfaces and contributing to R computed by (3) are nothing but small-angle deflections as seen in Fig. 2.

So far we have considered how the optimum value of r_* and the minimum value of R occur. A crucial question is: "Does this minimum R have any bearing on the rate of the association reaction $A+B \rightarrow AB$ mentioned in §1?" Of course the answer is negative. The Hamiltonian function (7) is too simple to describe this reaction (see §4 however); it involves no

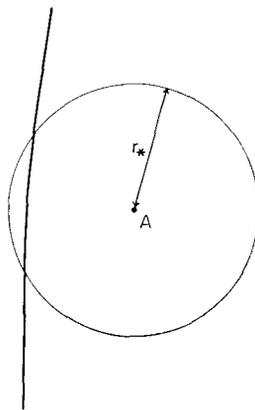


Fig. 2. This trajectory crosses the spherical dividing surface centered at A, but is nothing but a small-angle deflection.

Dividing Surface in Transition State Theory

mechanism for the energy disposal (*e.g.*, the third body), which is essential for the recombination of the dissociated atoms A and B. We have to turn to Wigner's or Keck's theory mentioned in Introduction in order to treat this kind of reactions.

In that sense Horiuti's example is rather trivial, but in § 3 we shall see that it deserves careful re-examination and a slight modification of the above treatment leads to some interesting results of pedagogical value.

§ 3. Modification

In what follows Horiuti's treatment in § 1 is slightly modified. In this modification the dividing surface is given by

$$r - r_*(l) = 0, \quad (13)$$

which is the same as (8) except that the radius of the dividing surface (sphere) r_* in (13) is a function of l , where l is the magnitude of the angular momentum vector of the two-particle system A+B. The new equation (13) determining the dividing surface involves the coordinate r and the momentum l ; hence (13) is a special example of (1) rather than (2). To determine the functional relation between r_* and l , the variational requirement is invoked. It will be shown that this modified treatment leads to a rate equation derived by Eyring *et al.*²¹⁾ and by Gioumousis and Stevenson²²⁾ for ion-molecule reactions, and to a rate equation derived by Gorin²³⁾ for recombination reactions of free radicals.

We start with the calculation of

$$R_0(l') = \frac{1}{Z} \iint d\mathbf{p} d\mathbf{q} \delta(l - l') \delta(r - r_*) \frac{-p_r}{\mu} \theta(-p_r) \exp(-\beta H(\mathbf{p}, \mathbf{q})). \quad (14)$$

The right hand side of (14) is obtained by inserting the delta function $\delta(l - l')$ into the right hand side of (9). Thus $R_0(l')$ is "partial rate" in the sense that the right side of (14) evaluates the contribution to R from those trajectories whose angular momentum l is equal to a particular value l' and $R_0(l')$ is related to the rate R by

$$R = \int_0^\infty dl' R_0(l'). \quad (15)$$

Evidently the angular momentum l is conserved, *i.e.*, $dl/dt = 0$, on each trajectory. Since

$$l^2 = p_\theta^2 + (p_\phi/\sin \theta)^2 \quad (16)$$

T. NAKAMURA

and

$$\int_{-\infty}^{\infty} dp_{\theta} \int_{-\infty}^{\infty} dp_{\phi} = 2\pi \sin \theta \int_0^{\infty} dl l,$$

we have, writing l for l' ,

$$R_0(l) = \frac{1}{V} \left(\frac{8\pi}{\mu^3 kT} \right)^{\frac{1}{2}} l \exp(-\beta U_{eff}(r_*)), \quad (17)$$

where U_{eff} is the well-known effective potential energy²⁴⁾ consisting of the kinetic energy (centrifugal energy) $l^2/2\mu r^2$ and the potential energy U , *i. e.*,

$$U_{eff}(r) = \frac{l^2}{2\mu r^2} + U(r). \quad (18)$$

This $U_{eff}(r)$ depends on the angular momentum l ; a typical example corresponding to the potential $U(r)$ of Fig. 1 is displayed in Fig. 3, where the occurrence of a rotational barrier²⁴⁾ is observed.

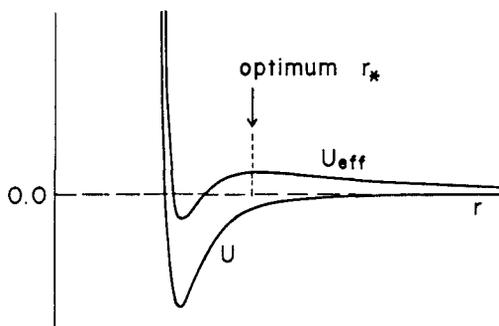


Fig. 3. The potential energy $U(r)$ and the effective potential energy $U_{eff}(r)$.

Now what we are going to do is to apply the variational requirement to the partial rate $R_0(l)$. In other words the optimum value of r_* is determined from the condition,

$$dR_0(l)/dr_* = 0. \quad (19)$$

Thus we at once find from (19) and (17) that the optimum value is equal to the value of internuclear separation r at maximum U_{eff} (see Fig. 3). Consequently the dividing surface is located at the position of the rotational barrier. Therefore the relation between the present variational treatment and the above-mentioned work by Eyring *et al.*²¹⁾ and Gorin²³⁾ is obvious. In their treatments the rate at which the system passes over the rotational barrier is calculated by means of conventional TS theory. In fact their

Dividing Surface in Transition State Theory

results can be derived from (17), (18), (19) and (15).

Following Eyring *et al.*²¹⁾ and Gorin²³⁾ let us take

$$U(r) = -C/r^m, \quad m = 4 \text{ and } 6. \quad (20)$$

where C is a constant. Using (18) and (20), and the optimum value of r_* determined from (19) and (17), we have

$$U_{eff}(r_*) = l^4/16C\mu^2 \quad \text{and} \quad U_{eff}(r_*) = l^3/(54C\mu^3)^{\frac{1}{2}}. \quad (21)$$

Combining (15), (17) and (21), we find

$$R = V^{-1} 2\pi(2C/\mu)^{\frac{1}{2}} \quad \text{and} \quad R = V^{-1}(8\pi/\mu)^{\frac{1}{2}}(4C^2kT)^{\frac{1}{6}} \Gamma(2/3), \quad (22)$$

where Γ is the gamma function. If the numbers of the atoms A and B in the volume V are N_A and N_B , the frequency of the reaction is $RN_A N_B = RV^2(N_A/V)(N_B/V)$; therefore the rate constant (per unit volume) equals RV . Hence the rate constants corresponding to (22) are

$$k = 2\pi(2C/\mu)^{\frac{1}{2}} \quad \text{and} \quad k = (8\pi/\mu)^{\frac{1}{2}}(4C^2kT)^{\frac{1}{6}} \Gamma(2/3), \quad (23)$$

which completely agree with the result obtained by Eyring *et al.*²¹⁾ or Gorin.²³⁾

§ 4. Further Comments

From (15) and (17) of § 3, we have

$$R = V^{-1}(8\pi/\mu^3 kT)^{\frac{1}{2}} \int_0^{\infty} dl l \exp(-\beta U_{eff}(r_*)), \quad (24)$$

which is to be compared with Horiuti's expression (10). In the integral on the right hand side of (24), r_* is to be understood as being a function of l , as explained in § 3. It is readily shown that if r_* is taken to be independent of l , (24) reduces to (10).

As shown in § 3 the rate formulas (23), which have been obtained by Eyring *et al.*²¹⁾ for ion-molecule reactions such as $\text{Ar}^+ + \text{H}_2 \rightarrow \text{ArH}^+ + \text{H}$ or by Gorin²³⁾ for free-radical recombination reaction such as $\text{CH}_3 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_6$, can be derived from (24) and (20). In other words, the rate formulas (23) for the above reactions result from a dynamical treatment of the two particles A and B interacting with the potential energy (20), which represents long-range attractive interaction energy proportional to r^{-m} ($m=4$ for induction energy between an ion and a molecule, or $m=6$ for dispersion energy between two free radicals). Evidently the expression (20) for the potential energy is valid only when the separation r between A and B is not too

T. NAKAMURA

small, *i. e.*, only when the overlap of the charge clouds of A and B is negligible. Because at least one of A and B is polyatomic in the above reactions, the interaction potential is far more complicated than (20) in the region of smaller separations. This region of r will be called the reaction zone (Fig. 4), where the reaction (ion-molecule reaction or free-radical recombination) is supposed to take place.

Thus the treatment in § 3 as well as the theory of Eyring *et al.*²⁰ or Gorin²³ calculates the probability of the system A+B entering the reactions zone but tells us nothing about what happens in the reaction zone. The modified dividing surface, which has been considered in § 3 and is implicit in the theory of the above authors, is used to sort the trajectories according

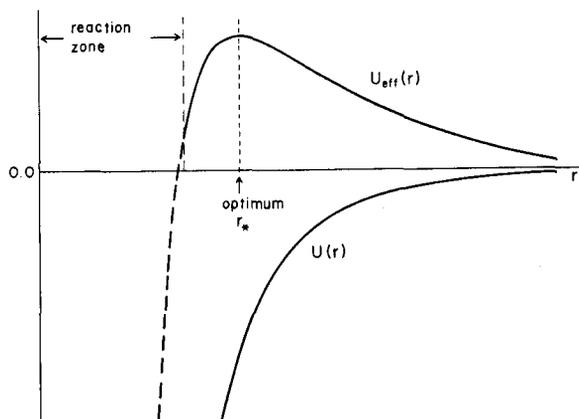


Fig. 4. The potential energy $U(r) = -C/r^4$ and the corresponding effective potential energy $U_{\text{eff}}(r)$.

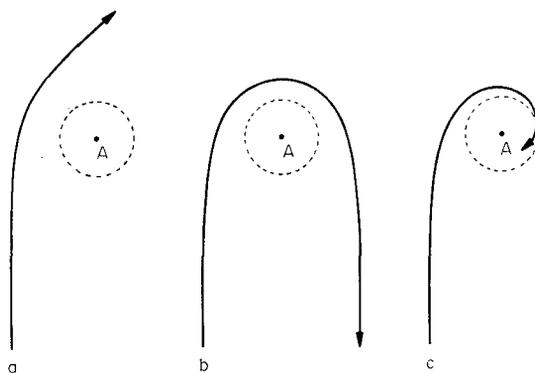


Fig. 5. Trajectories a and b do not enter the reaction zone but trajectory c does.

Dividing Surface in Transition State Theory

to whether or not they enter the reaction zone.*) Passing through the dividing surface is equivalent to passing over the rotational barrier and entering the reaction zone (Figs. 4 and 5), provided that the barrier occurs outside the reaction zone.

On the assumption***) that once the system A+B enters the reaction zone the reaction takes place with certainty, can we claim that the formulas in (23) correctly give the rate of the above mentioned ion-molecule reactions or free-radical recombination reactions.

Evidently the rate R computed with the modified dividing surface (13) in §3 is lower than the rate R computed with Horiuti's dividing surface (8) in §1. Hence, from the variation theoretical point of view, the modified surface (13) is a better dividing surface than the surface (8). A more important thing is however the "physics" of the modified dividing surface, *i. e.*, the way it sorts out trajectories, which has been discussed above.

§ 5. Concluding Remarks

As early as 1938 the late Professor Juro Horiuti suggested that the dividing surface in transition state theory of chemical reactions should be determined *variationally*. It gives us great pleasure to witness the blossoming in recent years¹⁸⁾ of variational calculations of reaction rates.

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*) Such sorting of trajectories has been discussed by Gioumousis and Stevenson in their paper (ref. 22) on the theory of ion-molecule reactions.

**) In these reactions, at least one of A and B is polyatomic, which implies that an energy disposal mechanism is built-in. On the contrary the recombination of two atoms needs the help of a third body M as mentioned in §2.

T. NAKAMURA

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