

三原子 置換反應의 反應確率, 간단한 古典力學的 取扱

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(1975. 8. 1 接受)

Reaction Probabilities for Three-atom Rearrangement Reaction. $A+B-C=A-B+C$: An Idealized Classical Approach

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(Received Aug. 1, 1975)

요 약. 直線 衝突모형을 써서 三原子 置換反應 $A+B-C \rightarrow A-B+C$ 의 反應確率을 全體 에너지의 函數로 計算하였다. 使用한 포텐셜 에너지 亦是 極히 單純한 理想的인 것이다. 三原子的 質量이 모두 같은 경우에 대하여 數值로 結果를 얻어서 더욱 더 간단한 모형을 쓴 다른 研究者들의 結果와 比較하여 定性的으로 더 나음을 알았다.

ABSTRACT. An idealized linear collision model has been employed to calculate the reaction probabilities for the three-atom rearrangement reaction $A+B-C \rightarrow A-B+C$. Potential energy surface used is also a highly idealized one with constant values. Numerical results were obtained for the system in which the atomic masses of all three atoms are the same. Potentials were varied to see the effect of the magnitude of the opposing potential barrier on the reaction probabilities. Results obtained were compared with those obtained using different models.

1. INTRODUCTION

The reactive scattering of an atom by a diatomic molecule is of great importance in theoretical chemical dynamics. A model that is often used to study this problem is to restrict the atoms to lie on a nonrotating line throughout the collision and consider that the system is electronically adiabatic.

This model has extensively been studied both classically¹ and quantum mechanically² in relation with $H+H_2$ reaction. The studies performed so far can be classified into two major categories depending on the type of the potential energy surface used. The first class of studies are those which use one of the realistic potential energy surfaces such as Karplus³, London-Eyring-Polanyi⁴ or London-Eyring-Polanyi-Sato⁵ type. Because of the extreme mathematical difficulties

countered in this type of study, both classical and quantum mechanical calculations have been possible only with many simplifying approximations and also with the help of electronic computers.

The second type of studies are those which use a very idealized potential energy surface such as shown in Fig. 1 by heavy lines. The L-shaped channels are bound by infinite potential walls, and potentials inside the channels are constants. Even though this type of idealized potential energy surface is too naive to give practically useful results, it enables one to perform a relatively less laborious but rigorous analytical calculation, thus making it possible to study the general trends, and effects of atomic masses, heights of the potential barrier, and the initial vibrational energy of a diatomic molecule on the reaction probabilities.

Hulbert and Hirschfelder⁶ were the first to study this idealized problem, and the particular case they studied was $\alpha=90^\circ$, i. e., the case of a scattering center with infinite mass, with $V_I = V_{II} = V_{III} = 0$. Recently Robinson⁷ showed that the basis set of wave functions used by them was incomplete for a set of resonance energies for the same problem. Dion, Milleur, and Hirschfelder⁸ reexamined their results using Robinson's corrected basis set and obtained the quantum mechanical reaction probability at one particular value of the total energy of the system. Their result is in good agreement with that of Tang and his coworkers.⁹ Locker and Wilson¹⁰ also studied the same problem quantum mechanically for the system of DN colliding with H, D, and T. The system with potential barrier, i. e., $V_{II} > 0$, was studied by Rubin¹¹ and Shin¹² for $\alpha=90^\circ$ and $\alpha=45^\circ$, respectively. All works mentioned above employed quantum mechanical approach except the last two cases.

In 1959 Jepsen and Hirschfelder¹³ further in-

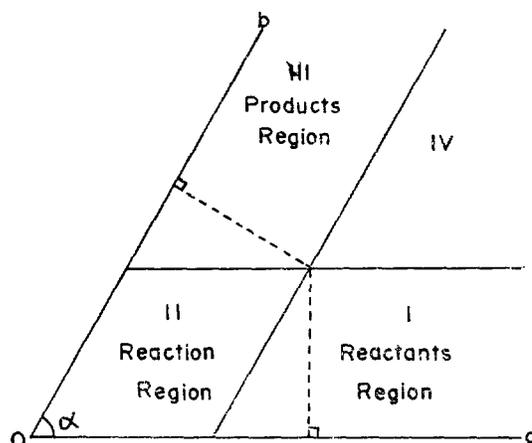


Fig. 1. Potential energy surface.

roduced a rather drastic simplification to avoid a difficulty that some of the particles which enter the diamond-shaped reaction region remain there too long, thus making the calculation very tedious. They take the lip of the reaction region perpendicular to the outside walls of the region of motion to give the potential energy surface shown in Fig. 1 by dotted lines.

They studied the $\alpha=60^\circ$ case (i. e., masses of three atoms are equal) and compared their results with those of Wall, Mazur, and Hiller's¹⁴. The agreement was not good except possibly at very high energy region.

The simplification introduced by Jepsen and Hirschfelder is physically too unrealistic and cause some undesirable features which will be discussed in other section.

The purpose of this study is to remove the Jepsen-Hirschfelder modification and study the explicit dependence of the reaction probability on the height of the potential, and effect of the initial vibrational energy of the diatomic molecule in overcoming the potential barrier. It is also hoped that comparison with the quantum mechanical study, which will be carried out later, will add some light on the applicability of classical mechanics in the chemical reaction pro-

blems.

2. MODEL

Collision Model. In this study we use a linear collision model which is shown in Fig. 2. Initially atom A impinges on a diatomic molecule BC; after collision, either particle A is reflected without achieving a rearrangement, or chemical reaction occurs yielding a new diatomic molecule AB and the new free atom C moving away.

If we skew the coordinates r_1 and r_2 as shown in Fig. 3, then¹⁴

$$r_1 = x - (\cot \alpha)y, \quad (1)$$

and

$$r_2 = \left\{ \left[\frac{m_a(m_b+m_c)}{m_c(m_a+m_b)} \right]^{\frac{1}{2}} \csc \alpha \right\} y \quad (2)$$

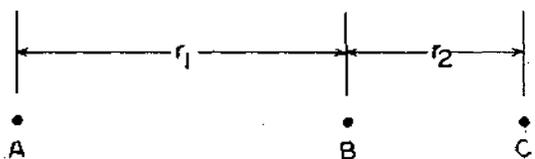


Fig. 2. Collision model.

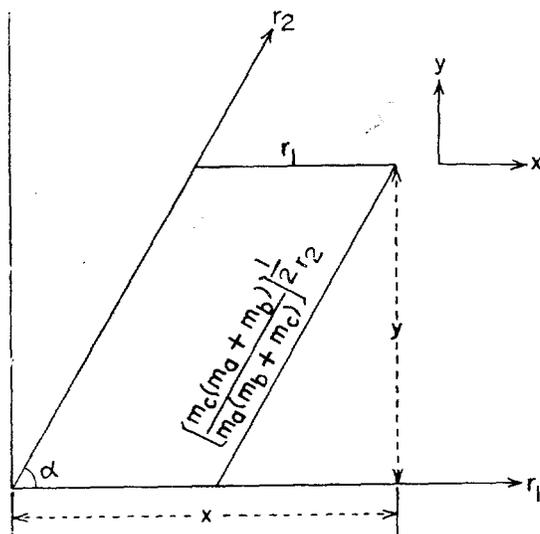


Fig. 3. Skewed coordination.

where

$$\csc \alpha = \left[\frac{m_a m_c}{(m_c + m_b)(m_b + m_c)} \right]^{\frac{1}{2}} \quad (3)$$

$$x = r_1 + \frac{m_c}{m_a + m_b} r_2, \quad (4)$$

and

$$y = \frac{1}{m_b + m_c} \left[\frac{m_b m_c (m_a + m_b + m_c)}{m_a} \right]^{\frac{1}{2}} r_2.$$

The new coordinate x is the distance of atom A from the center of mass of the molecule B-C; and y is proportional to the amplitude of the vibration of molecule B-C. Therefore, the translational energy of the system (E_t) manifests as the x -component kinetic energy in the new coordinate system, and the vibrational energy of the diatomic molecule (E_v) as the y -component kinetic energy. In the new coordinate system, the kinetic energy expression becomes

$$T = \frac{1}{2} \mu (x^2 + y^2)$$

where $\mu = m_a(m_b + m_c)/M$, the reduced mass of the system. M is the total mass of the system, i. e.,

$$M = m_a + m_b + m_c.$$

Therefore, the collinear motion of three particles is equivalent to the motion of a fictitious particle with mass μ in the two-dimensional x - y surface. The skewed angle α in Fig. 3 is a function of masses. For example, for a system of equal masses as in $H + H_2 = H_2 + H$ reaction, $\alpha = 60^\circ$.

Potential Energy Surface Model. To complete the specification of the problem an idealized potential energy function is introduced. The reaction path is divided into three regions as shown in Fig. 1.

Region I represents the reactants particles A +

BC; region III the rearranged system $AB+C$; and region II the interaction of three particles $A\cdots B\cdots C$. Since we are dealing with the problem of scattering of an atom by a diatomic molecule, the region IV which corresponds to three free atoms A , B , and C is not available for the reaction, and is effectively eliminated by putting it at an infinite potential. Inside the L -shaped channel, the potential is V_I , V_{II} , and V_{III} in regions I, II, and III, respectively.

The outer boundary lines oa and ob represent the hard-sphere contacts of B and C , and A and B , respectively. At the point o , all three atoms are in hard-sphere contact.

Jepsen-Hirschfelder Potential Model. Because many works have been done by use of J-H potential energy surface, it will be discussed briefly. Essentially their model is same as ours except the fact that the lips of the diamond-shaped reaction region are perpendicular to the outside boundary lines oa and ob as shown in *Fig. 1*. This simplification has an advantage that it makes the classical calculation of the reaction probability very easy. In doing so, however, there arises several problems.

1. Except at $\alpha=90^\circ$ case for which there is no difference between two models, there always is a substantial increase in the area of the reaction region in J-H potential. Obviously the sharper the skewed angle α becomes, the larger the additional area is. Ratio of the additional area to the original reaction area is given by $\cos \alpha$.

2. As mentioned before, the vibrational energy of the diatomic molecule (E_v) manifests as the y -component of the kinetic energy of the fictitious particle. In the simplified J-H model this component of the kinetic energy is always parallel to the boundary line between the reactants region and the reaction region. Hence, the vibrational energy can never be utilized for crossing the potential barrier. Also, the vibrational-

translational energy transfer never occurs. Certainly this is not the real case as shown by Wall and his coworkers¹⁶.

3. Depending on the geometry and the energy of the trajectory, there is possibility that some trajectories that enter the product region can rearrange again and move back into the reactants region, and finally end up in the reactants region. Physically this redissociation is possible when the vibrational energy of the newly formed molecule $A-B$ is too great. In J-H model this backward rearrangement cannot occur, while in our model it is possible and indeed it occurs.

In our model above shortcomings can be corrected and more physically meaningful qualitative results can be obtained. For this study we consider only the $\alpha=60^\circ$ case, since the general features are expected to be same for other cases as long as the skewed angle α is not equal to 90° .

3. REACTION PROBABILITY

General Behavior of Trajectories. The reactant particles A and $B-C$ start their movement from a certain point in the reactant region. The corresponding configuration point (the fictitious representative particle with the reduced mass) exhibits a straight line motion, for the potential is assumed to be constant. Whenever the configuration point hits the boundary lines bc and ef shown in *Fig. 4*, it will be reflected elastically from the infinite potential walls. If the diatomic molecule has no vibrational energy at all, the trajectory of motion is parallel to the x -axis. On the other hand, if it has vibrational energy, the trajectory has an inclination angle ϕ .

This angle of inclination between the trajectory and the horizontal direction of motion is determined by the relation

$$\tan \phi = \frac{y}{x} = \left(\frac{E_v}{E_t} \right)^{\frac{1}{2}}. \quad (7)$$

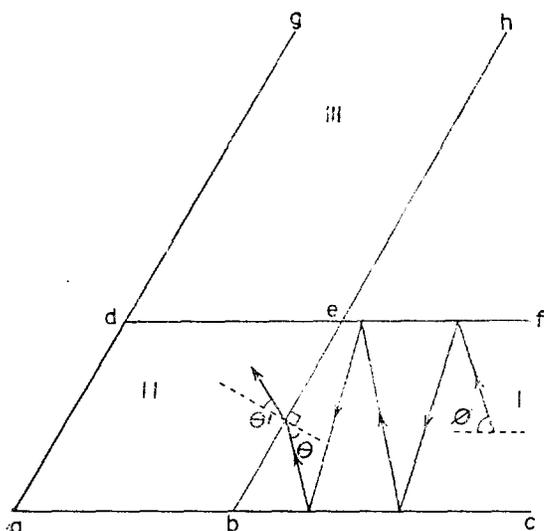


Fig. 4. Motion of a trajectory.

Total Reflection. When a trajectory hits the boundary line between two different regions in which the potentials are not equal, say, the line between the regions I and II, it either reflects back into the region in which it is travelling or refracts into the neighboring region. If the kinetic energy associated with the velocity component which is perpendicular to the boundary line (E_{\perp}) is greater than the potential to be overcome, the configuration point refracts into the neighboring region. For this case the normal velocity component is reduced by an amount related to the energy expended in crossing the potential barrier. If the kinetic energy component of the fictitious particle associated with the velocity component normal to the boundary line is less than the opposing potential, the particle is specularly reflected.

Before crossing the barrier the kinetic energy components which are perpendicular (E_{\perp}) and parallel (E_{\parallel}) to the boundary line are expressed as follows.

$$\begin{aligned} E_{\perp} &= E \cos^2 \theta \\ E_{\parallel} &= E \sin^2 \theta \end{aligned} \quad (8)$$

where E is the total kinetic energy, i. e., $E = E_{\perp} + E_{\parallel}$, and θ is the angle of incidence as shown in Fig. 4.

After crossing the boundary the parallel and perpendicular components of the kinetic energy, E_{\perp}' and E_{\parallel}' , respectively, become

$$E_{\perp}' = E_{\perp} - V = E \cos^2 \theta - V, \quad (9)$$

and

$$E_{\parallel}' = E_{\parallel}$$

where V is the magnitude of the opposing potential.

The angle of incidence, θ , and the angle of refraction, θ' , are related to the energy components as shown in Eq. 10.

$$\begin{aligned} \theta &= \tan^{-1} \left(\frac{E_{\parallel}}{E_{\perp}} \right)^{\frac{1}{2}} \\ \theta' &= \tan^{-1} \left(\frac{E_{\parallel}}{E_{\perp} - V} \right)^{\frac{1}{2}} \end{aligned} \quad (10)$$

Method of Calculation. In this model the calculation of the reaction probability is straightforward, and it can be done by analyzing the trajectories. If the particle is initially in the reactants region, but ends up in the products region and no backward rearrangement occurs, then the system has reacted to give the products.

If the laws of reflection and refraction are correctly carried out in Fig. 5, and if there is no possibility of a backward rearrangement of the products to give the reactants again, then it is apparent from the geometry that for a given total energy all trajectories striking the interface at points on the line be between e and b will be refracted back into the reactants region, and those striking at points between b and p will be transmitted to the product region, thus achieving successful rearrangement reaction. Therefore, the probability of a rearrangement occurring is

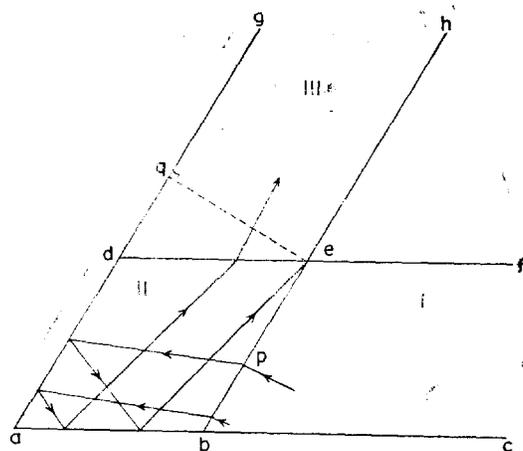


Fig. 5. Typical behavior of trajectories.

$$P = \frac{\overline{\delta p}}{b\delta} \quad (11)$$

The backward rearrangement is often possible when the trajectory enters the products region but reaches the dq portion of the hard-sphere repulsion line ag . In this case, depending on the total energy of the system and the geometry of the trajectory, some will reflect from the hard-sphere contact line and reach the interface between the products and reaction regions. If the trajectory has enough energy to overcome the barrier, then it refracts into the reaction region. For this case the reaction probability must be modified to incorporate this redissociation.

So, we define two types of reaction probability: the first is one that completely ignores the redissociation, and is designated as P_{uo} . Once a trajectory reaches the product region, it is accounted as a successful reaction. The second probability is one that considers fully the effect of redissociation, and is designated as P_w . As a consequence, P_w is less than or equal to, P_{uo} . The transmission coefficient, κ , is defined as

$$\kappa = \frac{P_w}{P_{uo}} \quad (12)$$

and this coefficient denotes the fraction of the trajectories which do not undergo the redissociation and achieve permanent reaction.

If the trajectory enters the products region and the first hard-sphere contact of newly formed $A-B$ molecule occurs beyond the point q , then, the reentry into the reaction region, hence the redissociation, is not possible.

4. NUMERICAL RESULTS

In this study we consider $\alpha=60^\circ$ case, i.e., $m_a=m_b=m_c$, and three different types of potentials.

Because all three atoms are identical in this study, the potential energy surface is symmetrical about the $r_1=r_2$ line. Thus V_I is equal to V_{III} and their values are set equal to zero. The value of V_{II} is determined by the nature of the reaction.

The actual values of the potential in region II are those which have been used by other workers⁹ in their simplified J-H model calculation.

1) Uniform potential:

$$V_I = V_{III} = 0, \quad V_{II} = 0$$

2) Potential well:

$$V_I = V_{III} = 0, \quad V_{II} = -1.5$$

3) Potential barrier:

$$V_I = V_{III} = 0, \quad V_{II} = +2.5$$

Note that the units of potential need not be specified as long as they are in energy units and are consistent with other energy terms. To compare with the result from the quantum mechanical treatment and to see the effectiveness of the vibrational energy in overcoming the potential discontinuities, the diatomic molecule $B-C$ before reaction is assumed to be in its ground vibrational state. The excited vibrational states are ignored since nearly all molecules are in their ground vibrational state at room temperature. This

assumption is especially good for small and stiff molecules. The vibrational energy of the di-

Table 1. Reaction probability, uniform potential ($V_I=V_{II}=V_{III}=0$).

	Total kinetic energy (E)	Reaction probability
a. P_w (Redissociation is considered.)	$1 \sim \frac{4}{3}$	1.0
	$\frac{4}{3} \sim 4$	$\frac{3 - \sqrt{3(E-1)}}{2(\sqrt{3(E-1)} + 1)}$
	$4 \sim \frac{28}{3}$	$\frac{\sqrt{3(E-1)} - 3}{\sqrt{3(E-1)} - 1}$
	$\frac{28}{3} \sim \infty$	$\frac{\sqrt{3(E-1)} - 2}{\sqrt{3(E-1)} + 1}$
b. P_{wo} (Redissociation is ignored.)	$1 \sim \frac{4}{3}$	1.0
	$\frac{4}{3} \sim 4$	$\frac{1}{\sqrt{3(E-1)} + 1}$
	$4 \sim \frac{28}{3}$	$\frac{3E - 7 - \sqrt{3(E-1)}}{3E - 4}$
	$\frac{28}{3} \sim \infty$	$\frac{\sqrt{3(E-1)} - 1}{\sqrt{3(E-1)} + 1}$

atomic molecule is thus fixed before reaction and is given the numerical value of unity.

Numerical results of the reaction probabilities are collected in Table 1 through 3 as a function of total kinetic energy. They are also plotted

Table 2. Reaction probability, potential well ($V_I=V_{III}=0, V_{II}=-1.5$).

Total kinetic energy (E)	Reaction probability (P_{wo})
$1.0 \sim 1.197$	1.0
$1.197 \sim \frac{4}{3}$	$\left\{ \frac{1}{4} + \frac{3 - \sqrt{3(E-1)}}{4\sqrt{3E+4} + 2\sqrt{3(E-1)}} \right\} \times \frac{\sqrt{3(E-1)} + 1}{\sqrt{3(E-1)}}$
$\frac{4}{3} \sim 2.187$	$\frac{1}{4} + \frac{3 - \sqrt{3(E-1)}}{4\sqrt{3E+4} + 2\sqrt{3(E-1)}}$
$2.187 \sim 4.0$	$\frac{3 - \sqrt{3(E-1)}}{\sqrt{3E+4} + 2\sqrt{3(E-1)}}$
$4.0 \sim 4.23238$	$\frac{\sqrt{3(E-1)} - 3}{2\sqrt{3E+4} + 2\sqrt{3(E-1)}}$
$4.23238 \sim \infty$	$\frac{1}{4} + \frac{\sqrt{3(E-1)} - 3}{4\sqrt{3E+4} + 2\sqrt{3(E-1)}}$

Table 3. Reaction probability, potential barrier ($V_I=V_{III}=0, V_{II}=+2.5$).

	Total kinetic energy (E)	Reaction probability
a. P_w (Redissociation is considered.)	$1.0 \sim 2.55848$	0
	$2.55848 \sim 2.68750$	0.5
	$2.68750 \sim 7.75504$	$\frac{1}{4} + \frac{3 - \sqrt{3(E-1)}}{4\sqrt{3E-12} + 2\sqrt{3(E-1)}}$
	$7.75504 \sim 9.92425$	$\frac{\sqrt{3(E-1)} - 3}{2\sqrt{3E-12} + 2\sqrt{3(E-1)}}$
	$9.92425 \sim 11.2449$	$1.5 + \frac{\sqrt{3(E-1)} - 3}{2\sqrt{3E-12} + 2\sqrt{3(E-1)}} - \frac{\sqrt{3(E-1)} + 3}{2\sqrt{3E-12} - 2\sqrt{3(E-1)}}$
	$11.2449 \sim 16.6711$	$\frac{5}{4} + \frac{3\sqrt{3(E-1)} - 9}{4\sqrt{3E-12} + 2\sqrt{3(E-1)}} - \frac{3 + \sqrt{3(E-1)}}{2\sqrt{3E-12} - 2\sqrt{3(E-1)}}$
	$16.6711 \sim \infty$	$\frac{1}{4} + \frac{3\sqrt{3(E-1)} - 9}{4\sqrt{3E-12} + 2\sqrt{3(E-1)}}$
b. P_{wo} (Redissociation is ignored.)	$1 \sim 11.2449$	Same as P_w
	$11.2449 \sim 16.6710$	$\frac{3}{2} + \frac{\sqrt{3(E-1)} - 3}{2\sqrt{3E-12} + 2\sqrt{3(E-1)}} - \frac{3 + \sqrt{3(E-1)}}{2\sqrt{3E-12} - 2\sqrt{3(E-1)}}$
	$16.6710 \sim \infty$	$\frac{1}{2} + \frac{\sqrt{3(E-1)} - 3}{2\sqrt{3E-12} + 2\sqrt{3(E-1)}}$

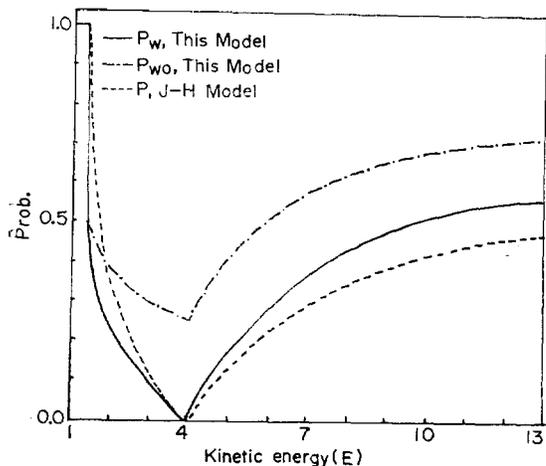


Fig. 6. Reaction probability for uniform potential ($V_I=V_{II}=V_{III}=0$).

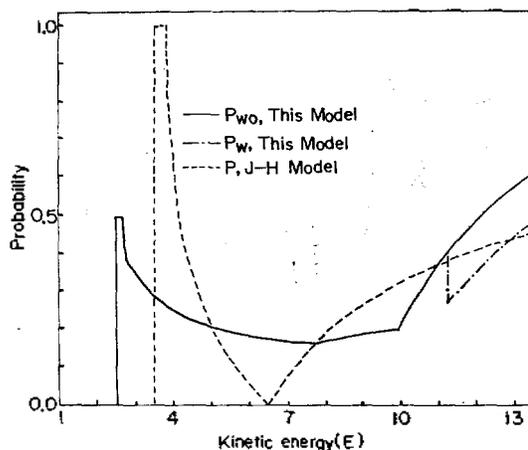


Fig. 8. Reaction probability for potential barrier ($V_I=V_{III}=0, V_{II}=+2.5$).

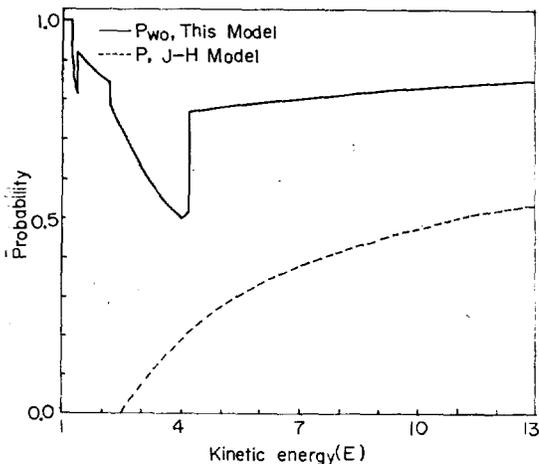


Fig. 7. Reaction probability for potential well ($V_I=V_{III}=0, V_{II}=-1.5$).

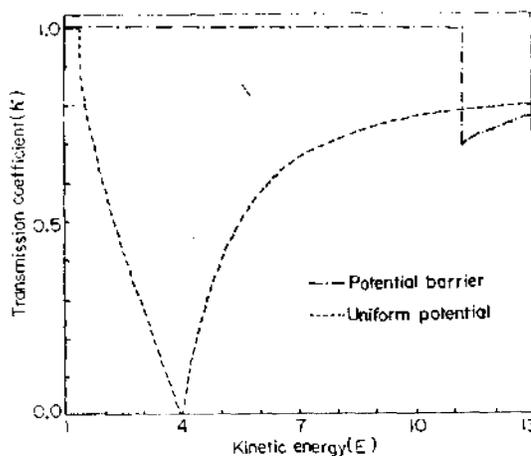


Fig. 9. Transmission coefficient.

in Fig. 6, 7, and 8.

Values obtained by Tang and his coworkers using the J-H model are also shown for comparison purpose. Transmission coefficients are also plotted as a function of total kinetic energy in Fig. 9.

5. DISCUSSION

As shown in Fig. 6, 7, and 8, reaction probabilities for this model are quite different from Vol. 19, No. 5, 1975

those for Jepsen-Hirschfelder model. The most distinct feature is the discontinuity in the values of reaction probabilities.

Uniform Potential 1. Our result is generally lower than that of Tang and his coworkers for small energies, namely for $E \leq 4$, and is generally higher than their result for $E > 4$. This difference is primarily due to the change in the boundary lines.

2. Note the discontinuity at $E=4/3$. This particular energy corresponds to the trajectory which has the inclination angle of 60° which is

also the skewed angle of the potential energy surface. In this model, the trajectories which have ϕ greater than or equal to 60° always hit the boundary line between the reactants and reactions upwardly. If the angle ϕ is less than 60° the trajectories hit the boundary line downwardly. So there is a sudden change in the reaction probabilities.

3. At $E=28/3$, there is also a discontinuity which is not present in J-H model. This is due to a characteristic angle ϕ (about 19.1°) which is peculiar in this model.

4. At $E=4$ both models have zero reaction probability. Their reasons, however, are entirely different. In J-H model no trajectory with $E=4$ can reach the products region. In our model half of upward trajectories can reach the products region, but they all are refracted back into the reactants region. So P_{wo} is 0.25 and P_a is zero. This is an example of the backward rearrangement mentioned in Section 2.

Potential Well. 1. The reaction probabilities in this study is always larger than those for J-H model. This is mainly due to the effectiveness of the downward trajectories. In our model the downward trajectories always achieve the rearrangement.

2. Because the potential in the reaction region is smaller than that for the products and reactants regions, the trajectories can always enter the reaction region from the reactants region. When the trajectories move to the products or reactants regions from the reaction region, however, total reflection is possible at the boundary lines. The discontinuities at $E=2.187$ and $E=4.2328$ are due to the total reflections. In J-H model this total reflection occurs at $E=2.5$.

3. Again the discontinuity at $E=4/3$ can be accounted for by the sudden change in the behavior of the trajectories. That is to say, the trajectories with $E=4/3$ are all upward moving

trajectories.

4. Because all downward trajectories always succeed in achieving the rearrangement, the reaction probabilities are always greater than equal to 0.5.

5. The trajectories which are reflected at the boundary between the reaction and the products regions usually undergo several hard-sphere repulsions inside the reaction region before ultimately refract into either the reactants region or the products region.

Potential Barrier. Reaction probabilities are markedly different for two models. Among other things, following differences merit some explanation.

1. The minimum energy required for successful rearrangement reaction is 2.55848 in our model, whereas that in J-H model is 3.5. In J-H model, the vibrational energy cannot be used in overcoming the potential barrier, so that the translational energy must be equal to or greater than the barrier height. Hence, the minimum total energy required is the sum of the barrier height and the vibrational energy, which is 3.5 in this case. In our model, however, part of the vibrational energy can be used to overcome the barrier. The minimum energy (2.55848) has the normal component kinetic energy of 2.5 which is just the barrier height. In general, when the total energy is slightly larger than the barrier height, the reaction becomes possible. Also, it is apparent that the vibrational energy is very effective in overcoming the barrier, since almost all of the vibrational energy is used.

2. In the vicinity of the minimum energy the reaction probability is maximum and has the value of 0.5. This is because, at these energies, the upward trajectories achieve the reaction without fail, while the downward trajectories are totally ineffective.

3. Discontinuity at $E=7.75504$ and $E=$

16. 6711

At these energies the upward trajectories for $E=7.75504$ and downward trajectories for $E=16.6711$ exhibit a similar behavior as the $E=28/3$ trajectories in the uniform potential case.

4. Discontinuity at $E=9.92425$

From this energy the downward trajectories start to succeed in achieving the rearrangement.

5. Discontinuity at $E=11.2449$

This is due to the partial redissociation of the products. This backward rearrangement is not possible if the energy is less than 11.2449, always possible if $E \geq 12.613$, and only partially possible if the energy is between the above two values.

6. Summary

The simplification introduced by Jepsen-Hirschfelder to the idealized potential is removed to get physically meaningful results, at least in the qualitative sense. The results we obtained show that several features previously ignored in the Jepsen-Hirschfelder model can be reascertained in our model. They are the availability of the vibrational energy in overcoming the potential barrier, the redissociation of the products, and the occurrence of translation-vibration energy transfer.

Quantitatively too, our results agree with those obtained by Wall and his coworkers much better than Tang's results obtained by use of Jepsen-Hirschfelder model.

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