A New Method of Drawing the Potential Energy Surface

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Introduction

The calculation of the potential energy of a polyatomic system, which is necessary for the discussion of molecular structure or chemical reaction, is mathematically so difficult that the so-called "semi-empirical method" devised by Eyring and his collaborators has been widely used to interpret many chemical reactions[1]. The results obtained by this method, however, are found to have several weak points when being compared with the experimental data. In the present paper a new method of drawing the potential energy surface for the system of three atoms is proposed and compared with Eyring's method.

1) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes" McGraw-Hill Book Company, Inc., New York and London (1941).

Approximate Function for the Anti-bonding State of Two Atoms

When two atoms approach each other, there appear two energy states generally; the one is bonding and the other anti-bonding. The potential energy of the bonding state can be obtained experimentally as a function of the distance between two atoms. As is well known, the curves for many diatomic molecules are conveniently approximated by the Morse function[2],

$$E_{\text{bond}}=D_e\left[e^{-2\beta(r-r_e)}-2e^{-\beta(r-r_e)}\right]. \qquad (1)$$

For the anti-bonding state, however, the curves cannot be obtained experimentally and the function is not yet proposed. The present author researched the function and found that the equation

2) P. M. Morse, *Phys. Rev.* **34**, 57 (1929).

$$E_{\text{ant}}=\frac{D_e}{2}[e^{-2\beta(r-r_e)}+2e^{-\beta(r-r_e)}], \qquad (2)$$

where D_e, β and r_e are constants which appear in the equation (1), is in good agreement with results calculated by James-Coolidge-Present[3] and Hirschfelder-Linnett[4] for the $^3\Sigma_u$ state of hydrogen molecule, which is shown in Fig. 1. Their results seem to be

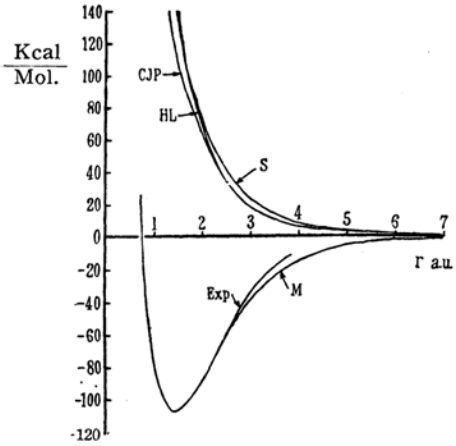

Fig. 1. Potential energy curve of hydrogen molecule.
Exp=Experimental; M=Morse curve; CJP = Coolidge, James and Present calculations; HL = Hirschfelder and Linnett calculations; S=Curve used by the present author.

the best ones at present. The applicability of this function for the anti-bonding states of other diatomic molecules cannot be ascertained because of no existing data. In the present method, one needs the energy curve for the anti-bonding state and the relation of (2) is assumed until the more suitable function is found.

Potential Energy for the System of Three Atoms

On the other hand, the potential energy curve of the system of two atoms A and B is approximated from the analogy of the well-known Heitler-London method for hydrogen molecule, as follows.

$$E_{\text{bond}}=(Q_{AB}+\alpha_{AB})/(1+S^2_{AB})$$
$$=(Q_{AB}+\alpha_{AB})/(1+k) \qquad (3)$$

and

$$E_{\text{ant}}=(Q_{AB}-\alpha_{AB})/(1-S^2_{AB})$$
$$=(Q_{AB}-\alpha_{AB})/(1-k) \qquad (4)$$

where $k=S^2_{AB}$ and Q_{AB}, α_{AB} and S_{AB} are Coulomb, exchange and overlap integrals respectively, all of which are functions of the distance between two atoms A and B.

For the potential energy of the system of three atoms A, B and C, London derived an equation by making some approximations and his equation has been used by Eyring et al. to interpret many simple chemical reactions[1]. The present author, by making a slightly different assumption $S^2_{AB}=S^2_{BC}=S^2_{CA}=k$, has derived the equation

$$E=\frac{1}{1+k}\left\{Q_{AB}+Q_{BC}+Q_{CA}\right.$$
$$\left.-\sqrt{\frac{2}{1}[(\alpha_{AB}-\alpha_{BC})^2+(\alpha_{BC}-\alpha_{CA})^2+(\alpha_{CA}-\alpha_{AB})^2]}\right\}, \qquad (5)$$

where Q_{ij}, α_{ij} and k have the same meanings as in equations (3) and (4). The London equation does not contain the term k, which corresponds to the square of overlap integral and may be so small compared with unity in the range of the internuclear separation under consideration that the equation (5) does not differ very much from London's equation.

Thus one can calculate the potential energy of the system of three atoms A, B and C as functions of r_{AB}, r_{BC} and r_{CA} from the above equations; assuming k as a constant for the system considered, one can obtain Q_{ij} and α_{ij} as functions of r_{ij} by substituting eqs. (1) and (2) in eqs. (3) and (4) respectively and these functions are substituted in the equation (5).

In Eyring's method Q_{ij} and α_{ij} are calculated by putting $k=0$ and by assuming that the Coulomb fraction ρ is a constant for the system of two atoms, while the present method is based on the relation of (2) and the assumption of k.

Potential Energy Surface for Hydrogen Atom-molecule Reaction

As a first attempt to make use of the method just described, the author has drawn the potential energy surface for hydrogen atom-molecule reaction, which has been already treated by Eyring's method[1].

The calculation for two configurations of an equilateral triangle (a) and a straight-line (b) indicates that the latter configuration is more stable than the former one as is seen from Fig. 2. Since only the lowest state is necessary for the present discussion, the surface has been drawn in the linear configuration. The result of calculation on the assumption of $k=0.18$ is given in Fig. 3,

3) H. M. James, A. S. Coolidge and R. D. Present, *J. Chem. Phys.*, 4, 187 (1936).
4) J. O. Hirschfelder and J. W. Linnett, *J. Chem. Phys.*, 18, 130 (1950).

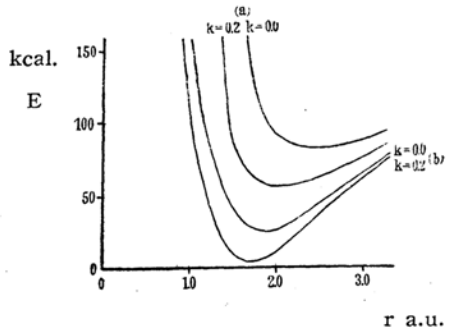

Fig. 2. Comparison of two configurations.
(a) equilateral triangle; (b) straight-line

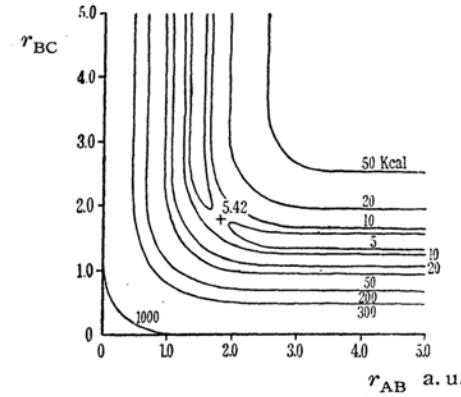

Fig. 3. Potential energy surface for the system of three hydrogen atoms in the linear configuration.

where r_{AB} is the distance between hydrogen atoms A and B and r_{BC} is the distance between B and C in the linear configuration of A-B-C. The vicinity of the saddle point in Fig. 3 is enlarged in Fig. 4. The diagram

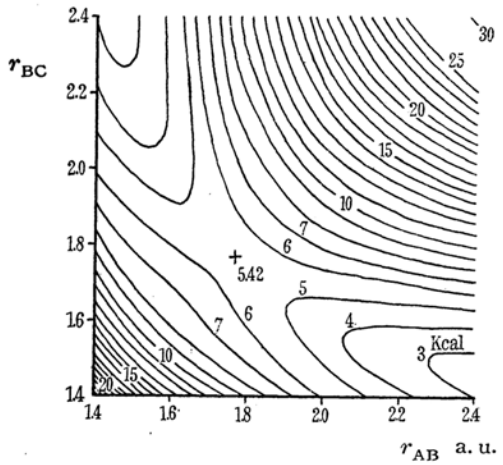

Fig. 4.

obtained differs essentially from Eyring's one which has two saddle points and a basin[1]; the present result has only one saddle point and no basin, coinciding with that of the non-empirical calculation[5]. The calculations with various values of k show the same situation, which seems, then, to be accompanied by the present method.

Comparison of the Two Methods

According to the theory of absolute reaction rates, the energy value at the saddle point, after allowing for zero-point energies, corresponds to the activation energy of hydrogen atom-molecule reaction. The results calculated by the two methods are given in Table I together with the experimental data.

TABLE I
ACTIVATION ENERGY OF HYDROGEN ATOM-MOLECULE REACTION

(kcal./mol.)

Observed	Calculated					
	Eyring			Present		
	ρ	E_c[a]	E_a[b]	k	E_c	E_a
5.0±0.5[5]	0.14	14	...	0.0	23.8	...
				0.1	13.4	...
7.0±0.5[7]	0.20	7.63	8.50	0.18	5.42	4.99
				0.2	3.59	...

a) without allowing for zero-point energies.
b) after allowing for zero-point energies.

Inspecting the table one can easily find that if $\rho>0.20$ is used in Eyring's method the better value may be obtained. If this is done, however, the minimum of the basin which appears in Eyring's diagram becomes lower than the minimum of the hydrogen molecule. This result might suggest the possibility of a stable linear complex H-H-H which has not been observed. Moreover Eyring's method cannot be applied in the range of $r<1.0$ a.u., as is seen from Fig. 5,

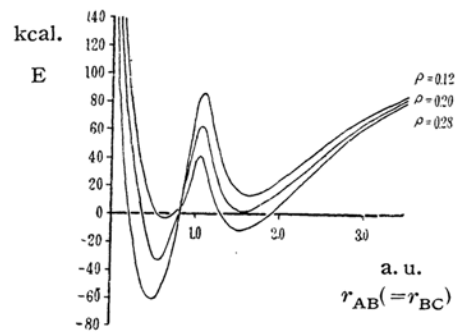

Fig. 5. Potential energy curves along the diagonal section of the surface for various values of ρ by Eyring's method.

5) J. O. Hirschfelder, H. Diamond and H. Eyring, *J. Chem. Phys.* 5, 697 (1937).
6) A. Farkas and L. Farkas, *Proc. Roy. Soc.* (London) *A*152, 124 (1935).
7) K.H. Geib and P. Harteck, *Z. physik. Chem.* (Bodenstein Festband) 849 (1931).

which shows the potential energy curves along the diagonal section of the surface for the various values of ρ. The minimum of the curves at 1.5 a.u. in Fig. 5 corresponds to the basin described above.

On the other hand, the present method gives a more reasonable value for the activation energy of hydrogen atom-molecule reaction and is bearable even in the range of $r<1.0$ a.u., as in seen from Fig. 6.

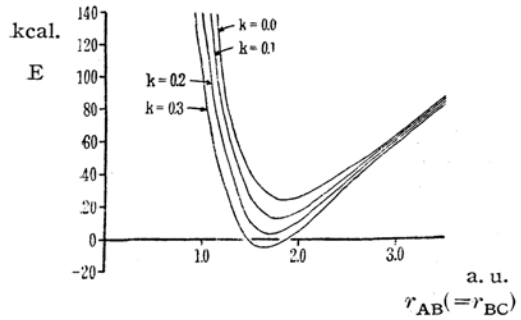

Fig. 6. Potential energy curves along the diagonal section of the surface for various values of k by the present method.

Summary

A new method of drawing the potential energy surface has been devised and compared with Eyring's semi-empirical method. The points different from the latter method are that an appropriate function for the anti-bonding state of a diatomic molecule is assumed and the overlap integral is not ignored. The so-called Coulomb fraction in Eyring's method is not used and the London equation has been slightly modified.

As an example the activation energy of hydrogen atom-molecule reaction has been calculated. So far as this reaction is concerned, the present method gives more reasonable value than Eyring's method.

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