

## Steric Effects. I. Van der Waals Potential Energy Curves

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$$U = \frac{e^2}{r_{12}} - \frac{e^2}{2r_0} \times \sum_{n=0}^{\infty} [x_1^{2n} + x_2^{2n} + 2x_1^n x_2^n P_n(\cos\theta_{12})] \quad (31)$$

where  $\theta_{12}$  is the angle between the lines joining the two electrons to the center, and the  $P_n(\cos\theta_{12})$  are the ordinary Legendre functions.

If the one-electron problem is solved, the two-electron problem can be treated by perturbation theory with

$$\frac{e^2}{r_{12}} - \frac{e^2}{r_0} \sum_{n=0}^{\infty} x_1^n x_2^n P_n(\cos\theta_{12})$$

as the perturbation.

The extension to any number of charges is obvious.

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## Steric Effects. I. Van der Waals Potential Energy Curves

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Reliable van der Waals potential energy functions are available in only a limited number of cases. An approximate semi-empirical method is presented for estimating these curves in other cases, based on an extrapolation from the nature of the curves that are known. The relation of the above method to calculations of the type discussed by Westheimer and Mayer on the activation energy for racemization of substituted symmetrical diphenyls is considered.

### I

IN a number of problems, including studies on steric effects,<sup>1-4</sup> it is necessary to have expressions for the van der Waals interaction energy  $U$  between two atoms, molecules, or groups as a function of the interatomic or intermolecular distance  $r$ . Only a few such functions are available and it is necessary in most cases to make approximations.<sup>2</sup> It is the purpose of the present paper to examine available information on this question, and to suggest a semi-empirical and approximate method of extrapolation to new cases. The suggestions to be made here are, of course, based on the present state of our knowledge. Undoubtedly, it will be desirable in the future to modify many of the assumptions, constants, etc., used here.

It is proposed to formulate in the second paper of this series a rather general theoretical ap-

proach to the problem of the influence of the steric factor on rate and equilibrium in chemical reactions, and to discuss steric effects on molecular structure (for example, in  $H_2O$  and  $NH_3$ , and in *cis* butene). In a third paper, some applications to particular chemical reactions will be considered.

For studies on steric effects one is interested usually in values of  $r$  such that  $U$  is positive ( $U=0$  at  $r=\infty$ ). In this region (and, in fact, for the whole range in  $r$ ) one can use as a good approximation for spherical or effectively spherical non-polar molecules

$$U = -(\mu/r^6) + P \exp(-r/\rho), \quad (1)$$

where  $P$ ,  $\rho$ , and  $\mu$  are parameters. Unfortunately, it is relatively difficult to evaluate  $P$ ,  $\rho$ , and  $\mu$  (using both experimental and theoretical information) and apparently these parameters are available only for helium, neon, and argon. On the other hand, writing  $U$  in the form<sup>5</sup>

$$U = -2\epsilon(r^*/r)^6 + \epsilon(r^*/r)^{12}, \quad (2)$$

<sup>5</sup> For a general survey of this subject see R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (University Press, Cambridge, England, 1939), Chapter VII.

<sup>1</sup> F. H. Westheimer and J. E. Mayer, *J. Chem. Phys.* **14**, 733 (1946).

<sup>2</sup> F. H. Westheimer, *J. Chem. Phys.* **15**, 252 (1947).

<sup>3</sup> I. Dostrovsky, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.* 173 (1946).

<sup>4</sup> T. L. Hill, *J. Chem. Phys.* **14**, 465 (1946).

it is less difficult to evaluate the parameters (using the experimental second virial coefficient) but this form for  $U$  is not satisfactory when  $U \gg 0$ . It is clearly desirable, therefore, to be able to estimate  $P$ ,  $\rho$ , and  $\mu$  when  $r^*$  and  $\epsilon$  are known.  $\epsilon$  and  $r^*$  have been determined for helium, neon, argon, hydrogen, nitrogen, methane, and a few other gases.

By exhibiting a semi-empirical connection between the parameters  $P$ ,  $\rho$ , and  $\mu$  and the parameters  $r^*$  and  $\epsilon$  for helium, neon, and argon, and assuming that this connection has general validity, to a good approximation, for spherical non-polar gases, we shall be able to calculate  $P$ ,  $\rho$ , and  $\mu$  from  $r^*$  and  $\epsilon$  for hydrogen, nitrogen, and methane. A similar approximate procedure may be used to relate  $r^*$  and  $\epsilon$  to  $T_c$  and  $P_c$  (critical constants), and thus further extend the extrapolation.

In order to find the functional relations between  $P$ ,  $\rho$ , and  $\mu$  on the one hand, and  $r^*$  and  $\epsilon$  on the other (without expecting to get the correct constants of proportionality), let us adjust  $P$ ,  $\rho$ , and  $\mu$  so that (A)  $\mu$  is the same as the coefficient of  $-r^{-6}$  in Eq. (2) and (B) the minimum in Eq. (1) coincides with the minimum in Eq. (2) ( $U = -\epsilon$ ,  $r = r^*$ ). One finds easily

$$P = \epsilon e^{12}, \quad \rho = r^*/12 \quad \text{and} \quad \mu = 2\epsilon r^{*6}. \quad (3)$$

Now actually, if Eqs. (1) and (2) were used separately to fit experimental data in the range  $U < 0$  we would not, of course, expect conditions (A) and (B) above to hold exactly. But we might expect

$$P = c_1 \epsilon, \quad \rho = c_2 r^* \quad \text{and} \quad \mu = c_3 \epsilon r^{*6} \quad (4)$$

to hold, where  $c_1$ ,  $c_2$ , and  $c_3$  are more or less universal constants for spherical non-polar gases, with values not very far from  $c_1 = e^{12}$ ,  $c_2 = 1/12$ , and  $c_3 = 2$ .

In Table I we give the data for helium, neon,

TABLE I.\*

	$r^*$ in A	$\epsilon \times 10^{15}$ ergs	$P \times 10^{10}$ ergs	$\rho$ in A	$\mu \times 10^{10}$ ergs $\times \text{A}^6$	$c_1$	$c_2$	$c_3$	$\mu/P\rho^6$
Helium	2.95	0.827	8.71	0.216	0.0147	$10.53 \times 10^9$ $= e^{12.87}$	0.0732	2.70	16.6
Neon	3.08	4.89	25.7	0.235	0.090	$5.26 \times 10^9$ $= e^{12.17}$	0.0764	2.15	20.8
Argon	3.83	16.5	169.	0.273	1.02	$10.24 \times 10^9$ $= e^{13.84}$	0.0713	1.96	14.6

\*  $r^*$ ,  $\epsilon$ ,  $P$ ,  $\rho$ , and  $\mu$  from Fowler and Guggenheim, reference 5, based on work by Lennard-Jones and Buckingham.

and argon. The constants  $c_1 = P/\epsilon$ ,  $c_2 = \rho/r^*$ , and  $c_3 = \mu/\epsilon r^{*6}$  are seen to be fairly constant ( $c_3$  has the largest variation but is the least important in steric effects). Using average values (geometric mean<sup>6</sup> for  $c_1$  and  $c_3$ , and arithmetic mean for  $c_2$ ) for  $c_1$ ,  $c_2$ , and  $c_3$  from Table I we have then

$$\begin{aligned} P &= 8.28 \times 10^5 \epsilon, \\ \rho &= 0.0736 r^*, \\ \mu &= 2.25 \epsilon r^{*6}, \end{aligned} \quad (5)$$

as our approximate connection between  $P$ ,  $\rho$ , and  $\mu$  and  $r^*$  and  $\epsilon$ . Equations (5) imply the following connection between  $P$ ,  $\rho$ , and  $\mu$ :  $\mu = 17.1 P \rho^6$ . The separate values of  $\mu/P\rho^6$  are included in Table I. The minimum in

$$U = -2.25 \epsilon (r^*/r)^6 + 8.28 \times 10^5 \epsilon \exp(-r/0.0736 r^*) \quad (6)$$

occurs at  $r/r^* = 1.0076$  and  $U = -1.210\epsilon$ . Also,  $U = 0$  at  $r/r^* = 0.8937$  so that  $r(U = \min.)/r(U = 0) = 1.1274$ .

$P$ ,  $\rho$ , and  $\mu$  are estimated from  $r^*$  and  $\epsilon$ , in Table II, for hydrogen, nitrogen and methane using Eqs. (5).

TABLE II.\*\*

	$r^*$ in A	$\epsilon \times 10^{15}$ ergs	$P \times 10^{10}$ ergs	$\rho$ in A	$\mu \times 10^{10}$ ergs $\times \text{A}^6$
H <sub>2</sub>	3.28	4.25	35.2	0.241	0.119
N <sub>2</sub>	4.17	13.25	109.7	0.307	1.57
CH <sub>4</sub>	4.29	20.5	169.5	0.316	2.86

\*\*  $r^*$  and  $\epsilon$  for H<sub>2</sub> and N<sub>2</sub>: Same reference as in Table I. For CH<sub>4</sub>: Beattie and Stockmayer, J. Chem. Phys. 10, 473 (1942).

When  $r^*$  and  $\epsilon$  are not known they may be estimated from  $T_c$  and  $P_c$ , and hence  $P$ ,  $\rho$ , and  $\mu$  may be estimated also. Using a hard sphere model with an attractive energy varying as  $r^{-6}$ , one can get a connection between  $\epsilon$  and  $r^*$  on the one hand, and  $T_c$  and  $P_c$  on the other, via the van der Waals constants:<sup>7</sup>

$$\begin{aligned} r^{*3} &= (3/16\pi)(kT_c/P_c), \\ \epsilon &= (27/8)kT_c, \end{aligned} \quad (7)$$

<sup>6</sup> In this paper we use the arithmetic mean in combining distances and the geometric mean in combining energies, as suggested by what is apparently a successful procedure in dealing with mixtures of gases. See, for example, Hirschfelder and Roseveare, J. Phys. Chem. 43, 15 (1939). We use the geometric mean for  $c_3$  rather arbitrarily.

<sup>7</sup> See, for example, Mayer and Mayer, *Statistical Mechanics* (John Wiley and Sons, Inc., New York, 1940), p. 268. Equations (8) follow from the general law of corresponding states with the constants unspecified. See reference 5, page 344. That is, a particular model (e.g., van der Waals) need not be used.

or

$$r^* = c_5(T_c/P_c)^{\frac{1}{2}}, \quad (8)$$

$$\epsilon = c_4 T_c,$$

with  $c_4 = 0.466 \times 10^{-15}$  erg per degree and  $c_5 = 2.011 A$ -atmos. $^{\frac{1}{2}}$  degree $^{-\frac{1}{2}}$  from this model. This suggests, as above, finding empirical constants to replace those just given. Such constants are obtained in Table III for neon, argon, nitrogen,

TABLE III.

	$r^*$ in A	$\epsilon \times 10^{15}$ ergs	$T_c$ °K	$P_c$ atmos.	$c_4 \times 10^{15}$ ergs-degree $^{-1}$	$c_5$ A-atmos. $^{\frac{1}{2}}$ degree $^{-\frac{1}{2}}$
Neon	3.08	4.89	44.4	25.9	0.1101	2.574
Argon	3.83	16.5	151.1	48.0	0.1092	2.613
N <sub>2</sub>	4.17	13.25	126.0	33.5	0.1052	2.681
CH <sub>4</sub>	4.29	20.5	190.6	45.8	0.1074	2.665

and methane. Helium and hydrogen are omitted because their critical constants are influenced by Bose-Einstein degeneracy. Using average values of  $c_4$  and  $c_5$  (geometric mean and arithmetic mean, respectively) from Table III, we have

$$\epsilon(\text{ergs}) = 0.1080 \times 10^{-15} T_c, \quad (9)$$

$$r^*(A) = 2.633 [T_c/P_c(\text{atmos.})]^{\frac{1}{2}}.$$

Carrying the approximation one step further, Eqs. (9) may be used together with Eqs. (5) to find  $P$ ,  $\rho$ , and  $\mu$  from  $T_c$  and  $P_c$ :

$$P(\text{ergs}) = 0.894 \times 10^{-10} T_c,$$

$$\rho(A) = 0.1938 [T_c/P_c(\text{atmos.})]^{\frac{1}{2}}, \quad (10)$$

$$\mu(\text{ergs} - A^6) = 81.0 \times 10^{-15} [T_c^3/P_c^2(\text{atmos.})]$$

It is interesting to note that the diatomic gas nitrogen and the polyatomic gas methane behave in the same way as do the monatomic gases, neon and argon, as far as Table III is concerned. Aside from other considerations, this leads one to have some confidence in the application, as an approximation, of the constants  $c_1$ ,  $c_2$ , and  $c_3$  found from Table I to non-polar polyatomic molecules which are spherically symmetrical or effectively so because of rotation.

TABLE IV.\*\*\*

	$T_c$ °K	$P_c$ atmos.	$r^*$ in A	$\epsilon \times 10^{15}$ ergs	$P \times 10^{10}$ ergs	$\rho$ in A	$\mu \times 10^{10}$ ergs $\times A^6$
Krypton	210.1	54.	4.14	22.7	188.	0.305	2.52
Cl <sub>2</sub>	417.1	76.1	4.64	45.0	373.	0.342	10.15
Br <sub>2</sub>	584.1	102.	4.71	63.1	522.	0.347	15.52
(CH <sub>3</sub> ) <sub>2</sub>	305.2	48.8	4.85	33.0	273.	0.357	9.67

\*\*\* Critical constants for Br<sub>2</sub>: Scheffer and Voogd, Rec. Trav. chim. 45, 214 (1926).

As illustrations, we estimate in Table IV  $r^*$ ,  $\epsilon$ ,  $P$ ,  $\rho$ , and  $\mu$  from Eqs. (9) and (10) for krypton, chlorine, bromine, and ethane.

## II

In studies on steric effects it is necessary to approximate the potential energy  $U_a$  between two atoms or groups, alike or unlike, that are not bonded to each other but are, nevertheless, bonded. Let  $r_a^*$  and  $\epsilon_a$  represent the interaction parameters for a pair of such atoms or groups. In general, the values of  $r_a^*$  and  $\epsilon_a$  will differ depending on the nature of the bonds involved.

There is one special case that deserves particular mention. In principle, the interaction characterized by  $r^*$  and  $\epsilon$  for two identical symmetrical diatomic molecules can be separated, at least approximately, into four interactions characterized by  $r_a^*$  and  $\epsilon_a$  between pairs of bonded atoms that are not bonded to each other. Actually, such an analysis would be very complex. The approximate analysis used by Eyring<sup>8</sup> for two hydrogen molecules approaching with axes perpendicular to each other and to the line joining the centers of mass cannot be very accurate because it leads to the unsatisfactory result  $r_a^* > r^*$  (Table V). Approximate van der

TABLE V.

	$r^*$ in A	$\epsilon \times 10^{15}$ ergs	$r_a^*$ in A	$\epsilon_a \times 10^{15}$ ergs
H <sub>2</sub>	3.28	4.25	3.0	(2.06)
Cl <sub>2</sub>	4.64	45.0	3.7	(21.8)
Br <sub>2</sub>	4.71	63.1	3.9	(30.6)
(CH <sub>3</sub> ) <sub>2</sub>	4.85	33.0	[4.29]	[20.5]
			4.0	(16.0)
H (to C)			2.4	(2.92)
Cl (to C)			3.7	(21.8)
Br (to C)			3.9	(30.6)

Waals radii (that is,  $r_a^*/2$ ) are available<sup>9,10</sup> in a number of cases, and are given for some diatomic molecules (considering ethane as a "diatomic" molecule) in Table V. According to the data summarized by Stuart,<sup>9</sup> the value of  $r_a^*$  for the interaction of two hydrogen atoms is significantly smaller for hydrogen bonded to hydrogen than

<sup>8</sup> H. Eyring, J. Am. Chem. Soc. 54, 3191 (1932).

<sup>9</sup> H. A. Stuart, *Molekülstruktur* (Julius Springer Verlag, Berlin, 1934), p. 48. In listing the van der Waals radii in Table V we do not try to distinguish between  $r_a^*$  and  $1.0076 r_a^*$  (Eq. (6)).

<sup>10</sup> L. Pauling, *Nature of the Chemical Bond* (Cornell University Press, Ithaca, 1945), p. 189.

for hydrogen bonded to carbon (saturated).<sup>11</sup> To within the accuracy of the data, this does not seem to be the case for chlorine and bromine. For these halogen atoms bonded to carbon we have, approximately,  $r_a^* = 3.7\text{\AA}$  ( $2 \times 1.87$ , Stuart) and  $3.9\text{\AA}$  ( $2 \times 1.95$ , Pauling), respectively. For the halogen in the diatomic molecule, we have, approximately,  $r_0 = 3.3\text{\AA}$  ( $2 \times 1.65$ , Stuart) and  $3.4_3\text{\AA}$  ( $1.78 + 1.65$ , Stuart), respectively, where  $r_0$  is the value of  $r_a$  at which  $U_a = 0$ . Now, from Eq. (2) or Eq. (6), the connection between  $r_a^*$  and  $r_0$  is  $r_a^* \cong 1.13r_0$ , which gives  $r_a^* = 3.7_3\text{\AA}$  and  $3.8_8\text{\AA}$ , respectively, as compared to  $3.7\text{\AA}$  and  $3.9\text{\AA}$  above for halogen bonded to carbon.

### III

Westheimer<sup>2</sup> has made the suggestion that it may prove desirable to use the rates of racemization of optically active diphenyl derivatives to determine the parameters in  $U_a$ . This would provide a check on some of the very uncertain values in Table V, discussed in the Appendix, when experimental activation energies are available.

For the interaction between a bromine atom (bonded to carbon—we shall not try to distinguish between aliphatic and aromatic carbons) and a hydrogen atom (bonded to carbon) Westheimer used

$$U_a = 2450 \times 10^{-10} \exp(-r_a/0.165) \text{ ergs.} \quad (11)$$

This expression is an approximation, in the range of interest, to the complete function and includes attraction. Hence, we cannot compare directly the parameters in Eq. (11) with our  $P$  and  $\rho$ .

On the assumption that Eq. (6) is approximately correct not only for helium, neon, and argon, but also for other van der Waals interactions between non-polar and effectively spherical atoms, molecules, bonded atoms, or bonded groups, we proceed now to estimate  $U_a$  from the present point of view for the hydrogen-bromine interaction mentioned above. Eq. (6) can be rewritten as

$$U/\epsilon = -(2.25/\alpha^6) + 8.28 \times 10^5 \exp(-\alpha/0.0736), \quad (12)$$

where  $\alpha = r/r^*$ . In Table VI, the attractive and

TABLE VI.

$\alpha$	Attraction	Repulsion	$U/\epsilon$	$\ln(U/\epsilon)$	$\frac{d \ln(U/\epsilon)}{d\alpha}$
0.50	144.0	929.4	785.4	6.666	13.88
0.55	81.28	471.2	389.9	5.966	14.14
0.60	48.22	238.8	190.6	5.250	14.49
0.65	29.83	121.1	91.24	4.514	15.01
0.70	19.12	61.38	42.25	3.744	15.86
0.75	12.64	31.12	18.48	2.916	17.41
0.80	8.583	15.78	7.192	1.973	20.99
0.85	5.966	7.996	2.031	0.708	32.77

repulsive terms,  $U/\epsilon$ ,  $\ln(U/\epsilon)$ , and  $-d \ln(U/\epsilon)/d\alpha$ , are given as functions of  $\alpha$ , as calculated from Eq. (12). The values of  $\alpha$  of interest (activated complex) in computations on the activation energy for racemization of 2,2'-dibromo-4,4'-dicarboxy-diphenyl are in the range  $0.70 < \alpha < 0.75$ . It is clear that in this range the attractive term is by no means negligible compared to the repulsive term. Furthermore, if  $U/\epsilon$  is to be approximated in a given range of values of  $\alpha$  by an expression of the form

$$U \cong P' \exp(-r/\rho') \quad (13)$$

or

$$U/\epsilon \cong (P'/\epsilon) \exp(-\alpha r^*/\rho'), \quad (14)$$

or

$$\ln U/\epsilon \cong \ln(P'/\epsilon) - (\alpha r^*/\rho'), \quad (15)$$

the quantity  $d \ln(U/\epsilon)/d\alpha$ , calculated from Eq. (12), must be effectively constant over the range. The variation in this derivative apparent in Table VI indicates that such an approximation can only be used over a rather small range in  $\alpha$  when  $\alpha > 0.5$ . For  $\alpha < 0.5$ ,  $-d \ln(U/\epsilon)/d\alpha$  varies more slowly and approaches the limiting value 13.587.

The equations derived by Westheimer and Mayer,<sup>1,2</sup> to be used in computing the activation energy  $E_0$  for racemization of symmetrical diphenyl derivatives, are based on a potential function of the form of Eq. (13). We wish to emphasize that, in general, on the basis of Eq. (6) and Table VI, one cannot use an equation such as (13) and expect that  $P'$  and  $\rho'$  will be very constant over an appreciable range in  $\alpha$ , when  $\alpha > 0.5$ . It is fairly obvious intuitively and can easily be shown rigorously that the method of minimizing and the final equations obtained by Westheimer and Mayer,<sup>1</sup> treating  $P'$  and  $\rho'$  as constants, are still valid in the case we are

<sup>11</sup> The relation of these remarks to the problem of accounting for restricted rotation in ethane is considered in the Appendix.

discussing where  $P'$  and  $\rho'$  actually vary with  $\alpha$ , provided that the constant values of  $P'$  and  $\rho'$  chosen happen to be just those that make  $U$  (Eq. (13)) =  $U$  (Eq. (1)) and  $dU/dr$  (Eq. (13)) =  $dU/dr$  (Eq. (1)) for that value of  $r$ ,  $r=r'$ , which obtains in the activated complex. This, it may be noted, will require a method of successive approximations in numerical calculations, illustrated below for 2,2'-dibromo-4,4'-dicarboxy-diphenyl. However, when  $P'$  and  $\rho'$  vary with  $\alpha$ , the calculation or interpretation of quantities of interest for configurations other than the activated complex ( $r \neq r'$ ) using Eq. (13) will lead to incorrect results.

From Table V we take  $r_a^* = (3.9 + 2.4)/2 = 3.15\text{\AA}$  for the  $\text{H} \leftrightarrow \text{Br}$  interaction, in agreement with Westheimer.<sup>2</sup> Westheimer found  $r_a' = 2.31\text{\AA}$  so that we guess, as our first approximation, that  $\alpha = 2.31/3.15 = 0.733$  in the activated complex. For  $\alpha = 0.733$ , we find from Eq. (12) that  $U_a/\epsilon_a = 24.69$ ,  $\ln(U_a/\epsilon_a) = 3.207$  and  $d \ln(U_a/\epsilon_a)/d\alpha = -16.76$ . So our straight-line equation, in essentially the form of Eq. (15), which gives the correct  $U_a$  and  $dU_a/d\alpha$  at  $\alpha = 0.733$ , is

$$\ln(U_a/\epsilon_a) - 3.207 = -16.76(\alpha - 0.733) \quad (16)$$

or

$$U_a = 5.347\epsilon_a \times 10^6 \exp(-r_a/0.1879), \quad (17)$$

having put  $r_a^* = 3.15\text{\AA}$ . The experimental energy of activation is not known yet but it is about<sup>2,12</sup> 19 kcal./mole. Using Westheimer's equations and tables one can now find by numerical calculation the value of  $\epsilon_a$  in Eq. (17) which leads to  $E_0 = 19$  kcal./mole. The result is  $\epsilon_a = 9.44_5 \times 10^{-15}$  erg and, hence,

$$U_a = 505 \times 10^{-10} \exp(-r_a/0.1879) \text{ ergs.} \quad (18)$$

From Eq. (18) and the value of  $Z$ ,  $Z = 2.30_4$  (we refer to the papers of Westheimer and Mayer<sup>1,2</sup> for the definition of  $Z$ ), one finds easily  $r_a' = 2.31\text{\AA}$  and, hence, our original guess hap-

pened to be correct, so that the calculation is completed. If the original guess were not correct, the calculation would have to be repeated starting with the new  $\alpha = r_a'/r_a^*$ . As a matter of fact, not only here but in several other (unpublished) calculations it was found that  $r_a'$  was very insensitive to the parameters in Eq. (13), provided they were chosen so that  $E_0 \cong 19$  kcal./mole. Equation (18) should be compared with Westheimer's function, Eq. (11), which leads to  $E_0 = 18.3$  kcal./mole. In the present procedure the van der Waals radii dictate the value  $\rho' = 0.188\text{\AA}$ , as compared to  $\rho' = 0.165\text{\AA}$  used by Westheimer. In summary, our procedure has been to obtain  $r_a^*$  from van der Waals radii and  $\epsilon_a$  from the experimental activation energy, using Westheimer's normal coordinate analysis.

The values  $r_a^* = 3.15\text{\AA}$  and  $\epsilon_a = 9.44_5 \times 10^{-15}$  erg give, from Eqs. (5),

$$10^{10}U_a = -(0.208/r_a^6) + 78.2 \exp(-r_a/0.2318) \text{ ergs.} \quad (19)$$

as the approximate potential function for the  $\text{H} \leftrightarrow \text{Br}$  interaction for all values of  $r_a$ .

The above discussion has been given to show how a potential function of the form of Eq. (13), as used by Westheimer and Mayer, can be included in the present method. However, it is not necessary in practice to use the method of successive approximations described above because equations of the type derived by Westheimer and Mayer from Eq. (13) can also be obtained by use of Eq. (1). By following the argument in Eqs. (7)–(12) of the paper by Westheimer and Mayer<sup>1</sup> but using Eq. (1) as the potential function, one finds (using the notation of Westheimer and Mayer)

$$E_0 = \frac{2Z_0^2}{\rho^2} \sum + 2E_{d0}' \exp(-2Z_0 \sum / \rho^2) - \frac{2\mu}{[d_0 + (2Z_0 \sum / \rho)]^6}, \quad (20)$$

where  $Z_0$  is defined as

$$Z_0 = E_{d0}' \exp(-(1/\rho) \sum_i b_i q_i^0) - \frac{6\mu\rho}{(d_0 + \sum_i b_i q_i^0)^7}. \quad (21)$$

<sup>12</sup> The experimental free energy of activation,  $\Delta F^*$ , is 19.5 kcal (see reference 2).  $E_0$  is the energy of activation at 0°K neglecting zero-point energies. Let  $E_0'$  be the value of  $E_0$  corrected for zero-point energies. Then  $\Delta F^* = E_0' - RT \ln f^*/f$ , where  $f^*$  is the partition function of the activated complex (omitting the degree of freedom associated with the reaction coordinate) and  $f$  is the usual partition function for the normal molecule. Also,  $\Delta E^* = E_{\text{exp}} - RT$ , where  $E_{\text{exp}}$  is the customary experimentally determined energy of activation. In other words, in a more refined treatment, one would have to distinguish carefully between  $E_0$ ,  $E_0'$ ,  $\Delta F^*$ ,  $\Delta E^*$ , and  $E_{\text{exp}}$ . In this footnote all energies are molar energies.

$Z_0$  is calculated by numerical solution of

$$Z_0 = E_{d_0'} \exp(-2Z_0 \sum / \rho^2) - \frac{6\mu\rho}{[d_0 + (2Z_0 \sum / \rho)]^7}. \quad (22)$$

In the above equations,

$$E_{d_0'} = P \exp(-d_0/\rho) \quad (23)$$

and

$$\sum = \sum_i B_i^2/a_i.$$

In applying Eqs. (20)–(23) and Eqs. (5) to the  $H \leftrightarrow Br$  interaction in 2,2'-dibromo-4,4'-dicarboxydiphenyl, we have first  $\rho = 0.0736 \times 3.15 = 0.2318\text{\AA}$ . The procedure is then to find the value of  $P$  that will give  $E_0 = 19$  kcal./mole (when  $P$  is assigned,  $\mu$  is determined by  $\mu = 17.1P\rho^6$ ). Of course one finds just the parameters in Eq. (19).  $E_0$  is divided as follows: deformations, 12.3 kcal./mole; van der Waals attraction, 3.9 kcal./mole; van der Waals repulsion, 10.6 kcal./mole.

## APPENDIX

We present here some very tentative calculations based on uncertain extrapolations. However, the results obtained may prove useful until more satisfactory data are available.

Referring back to Section II we may note that for one of the molecules in Table V there is some information about  $\epsilon_a$ . The values of  $r_a^*$  and  $\epsilon_a$  in square brackets are for methane (from Table II). These should be rather close to the values for the methyl group. This is seen to be the case for  $r_a^*$ . We can estimate (using an intuitive argument)  $\epsilon_a$  for the methyl group as follows: Consider 4.29 as a weighted mean between 4.85 and 4.0 (see Table V). Then assume that  $\ln 20.5$  is a weighted mean with the same weights between  $\ln 33.0$  and  $\ln (\epsilon_a \times 10^{15})$ . One finds  $\epsilon_a \times 10^{15} = 16.0$  ergs. One is tempted to go one step further and assume that the ratio  $\epsilon/\epsilon_a$  for symmetrical diatomic molecules is roughly constant. Using  $\epsilon/\epsilon_a = 33.0/16.0$ , one finds the values of  $\epsilon_a$  in parentheses for  $H_2$ ,  $Cl_2$ , and  $Br_2$ . Since the values of  $r_a^*$  for chlorine and bromine are apparently little changed on being bonded to a carbon atom, we assume the same is true for  $\epsilon_a$ .

We can now estimate  $\epsilon_a$  for  $H$  (to C)  $\leftrightarrow H$  (to C) as follows:

$$\begin{aligned} \epsilon_a(H \leftrightarrow Br) &= 9.44_s \times 10^{-15} \text{ erg} \\ &= [\epsilon_a(H) \times \epsilon_a(Br)]^{\frac{1}{2}} \\ &= [\epsilon_a(H) \times 30.6 \times 10^{-15}]^{\frac{1}{2}}, \end{aligned}$$

so that

$$\epsilon_a(H) = 2.92 \times 10^{-15} \text{ erg}.$$

Using Table V, one can now estimate  $\epsilon_a$  and  $r_a^*$  and, hence,  $P$ ,  $\rho$ , and  $\mu$  for various pairs such as, for example  $H$  (to C)  $\leftrightarrow CH_3$  and  $H$  (to C)  $\leftrightarrow Cl$  (to C) (see Table VII).

TABLE VII.

	$r_a^*$ in A	$\epsilon_a^* \times 10^{15}$ ergs	$P \times 10^{10}$ ergs	$\rho$ in A	$\mu \times 10^{10}$ ergs $\times A^4$
H (to C) $\leftrightarrow$ Br (to C)	3.15	9.44	78.2	0.232	0.208
H (to C) $\leftrightarrow$ Cl (to C)	3.05	(7.98)	(66.1)	0.224	(0.145)
H (to C) $\leftrightarrow$ CH <sub>3</sub> (to C)	3.20	(6.84)	(56.6)	0.236	(0.165)

Table V can be extended, of course, by similar arguments to other atoms and groups not included here. Experimental measurements of  $E_0$  for the racemization of diphenyl derivatives, and other similar measurements, may be an effective way of removing some of the considerable uncertainties in Tables V and VII.

It is of interest to calculate the steric potential barrier hindering rotation in ethane using  $P$ ,  $\rho$ , and  $\mu$  calculated from  $r_a^*$  and  $\epsilon_a$  in Table V for  $H$  (to C). One finds a barrier of 66 cal./mole. This result is to be anticipated qualitatively from the van der Waals radius  $r_a^*/2 = 1.2\text{\AA}$ . Any reasonable assignment of  $P$  and  $\mu$  will lead to a very small barrier because the distances between hydrogen atoms on different methyl groups are just of the order of 2.4\AA. Let  $\theta$  be the angle between two C—H bonds on different carbon atoms looking along the C—C axis. Then the distances between the two hydrogen atoms, calculated from the standard bond angles and distances, are:  $\theta = 0^\circ$ ,  $r = 2.27\text{\AA}$ ;  $\theta = 60^\circ$ ,  $r = 2.49\text{\AA}$ ;  $\theta = 120^\circ$ ,  $r = 2.89\text{\AA}$ ; and  $\theta = 180^\circ$ ,  $r = 3.06\text{\AA}$ . With  $r_a^* = 2.4\text{\AA}$ , all of these distances correspond to attraction. If the van der Waals radius and these distances are correct, the barrier of 3 kcal./mole in ethane does not receive an appreciable contribution from steric effects of the type considered here. Eyring<sup>8</sup> found an appreciable steric contribution because he used a potential curve with  $r_a^* = 3.9\text{\AA}$ . This leads to a repulsion for all the interatomic distances in ethane that are mentioned above. In fact, the constants  $r_a^* = 3.0\text{\AA}$  and  $\epsilon_a = 2.06 \times 10^{-15}$  erg, given for  $H$  (to H) in Table V, lead to a barrier of 744 cal./mole.