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## Deuterium Isotope Effect in the Reaction of Hydrogen Molecules with Chlorine Atoms and the Potential Energy of the H<sub>2</sub>Cl Transition Complex<sup>\*</sup>

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The relative rates of reaction of  $H_2$  and HD with chlorine atoms have been measured over the temperature range of 243-350°K. In this temperature interval, the ratio of the second-order rate constants,

#### $R = k_{\rm H_2} / \Sigma k_{\rm HD},$

is equal to  $(1.24 \pm 0.03) \exp (490 \pm 6/RT)$ . A search was made for HD after an unequilibrated mixture of H<sub>2</sub> and D<sub>2</sub> was half converted to hydrogen chloride by photochemical reaction with Cl<sub>2</sub>. From the failure to detect 0.02% HD in the unreacted hydrogen, a lower limit is set for the ratio of the rate constants of the reactions

# $H+Cl_2\longrightarrow HCl+Cl \text{ and } H+HCl\longrightarrow H_2+Cl.$

It is shown that the pre-exponential factors in R for the HD experiments and in the analogous experiments on HT are in quantitative agreement with theoretical calculations for either linear or triangular transition states, subject to the sole restriction that  $k(HD+Cl\rightarrow HCl+D)$  is approximately equal to  $k(HD+Cl\rightarrow DCl+H)$ . An intercomparison is made between the experimental difference in activation energies between  $H_2$ , HD, HT, and  $D_2$  for reaction with chlorine atoms and theoretical calculations for linear and triangular transition states. With the most favorable potential function for H<sub>2</sub>Cl, the maximum deviation between  $\Delta E_{exp}$ ; and  $\Delta E_{theor}$ ; is fifteen percent. Inasmuch as there are more experimental data than parameters necessary to construct the potential function of H<sub>2</sub>Cl, the agreement between theory and experiment constitutes a positive test of the transition state formulation of the effect of isotopic substitution on the rates of chemical reactions.

#### I. INTRODUCTION

THE recent experiments of Jones<sup>1</sup> on the relative L rates of reaction of  $H_2$  and HT with chlorine atoms and the evaluation of the rate constant for the reaction of  $H_2$ +Cl as a function of temperature by Ashmore and Chanmugan<sup>2</sup> show that quantitative data for this reaction can be obtained by the use of competitive methods. It has been shown<sup>3</sup> that the ratio of rate constants for the isotopic reactions provides a method for the evaluation of the "symmetrical" stretching frequency of the H<sub>2</sub>Cl complex. The experimental activation energy of the reaction  $H_2$ +Cl may be used to evaluate the undetermined parameter which occurs in a recently proposed method<sup>4</sup> of constructing the energy surface for the reaction. Moreover, Pitzer<sup>5</sup> has shown that the absolute rate, the thermodynamic properties of hydrogen molecules and chlorine atoms, the geometry of the complex, and the "symmetrical" stretching frequency of the complex, can be combined to give a value for the bending frequency of the transition state. It is, therefore, evident that our knowledge of many of the details which contribute to the rate of

this reaction has reached a point where new independent experimental data will be useful as checks on various aspects of the theory of the rate of the reaction, the potential energy of the transition state, and even the transition-state theory itself.

From the point of view of the description of the kinetics of the reaction, it would seem desirable to evaluate in a more quantitative way the role of the back reaction  $H+HCl\rightarrow H_2+Cl$ , which has been discussed to some extent by Rollefson and Burton.<sup>6</sup> In Sec. IV of this paper new experimental data pertinent to this question are presented.

The measurement of the relative rates of reaction of  $H_2$  and another one of its isotopes as a function of the temperature constitutes an additional piece of independent experimental data. We have, therefore, measured the relative rates of reaction of H<sub>2</sub> and HD with chlorine atoms as a function of the temperature. The experimental results, when interpreted in terms of a theory of isotope effects on the rates of chemical reactions,<sup>7</sup> can provide a check on the zero point energy of the "symmetrical" stretching vibration in the H<sub>2</sub>Cl complex and its variation with isotopic substitution. A comparison is made between the experimental results and values calculated from four different potential functions in Sec. V.

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<sup>†</sup> Visiting Chemist (1956-1957) on leave from the Weizmann <sup>1</sup> W. M. Jones, J. Chem. Phys. **19**, 78 (1951). <sup>2</sup> P. G. Ashmore and J. Chanmugan, Trans. Faraday Soc. **49**,

<sup>254 (1953)</sup> 

J. Bigeleisen and M. Wolfsberg, J. Chem. Phys. 23, 1535 (1955)

<sup>&</sup>lt;sup>4</sup> S. Sato, J. Chem. Phys. 23, 592, 2465 (1955).

<sup>&</sup>lt;sup>5</sup> K. S. Pitzer, J. Am. Chem. Soc. 79, 1804 (1957).

<sup>&</sup>lt;sup>6</sup>G. K. Rollefson and M. Burton, Photochemistry and the Mech-

 <sup>&</sup>lt;sup>1</sup> Chemical Reactions (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1942), p. 305.
 <sup>7</sup> See J. Bigeleisen and M. Wolfsberg in Advances in Chemical Physics, I. Prigogine, editor (Interscience Publishers, Inc., New York, 1958), Vol. I, pp. 15–76.

### **II. EXPERIMENTAL METHOD**

The Nernst chain mechanism is widely accepted for the reaction path

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$$H_2+Cl\longrightarrow HCl+H$$
 slow (1)

$$H+Cl_2 \longrightarrow HCl+Cl$$
 fast. (1a)

In the case of a mixed molecule such as HD, HT, or DT two slow steps, which in principle need not be equal, must be considered

$$HD+Cl \longrightarrow DCl+H$$
 slow (2a)

$$DH+Cl\longrightarrow HCl+D$$
 slow. (2b)

The most convenient method for measuring the relative rates of isotopic reactions is the isotopic competetive method.<sup>8</sup> This is particularly true in the present case because of the experimental difficulties in reproducing the chain length. Unless it is possible to quench the reaction between hydrogen atoms and chlorine molecules, such an experiment will measure  $R = k_1(k_{2a} + k_{2b})$ . Measurements of the individual ratios  $k_1/k_{2a}$  and  $k_1/k_{2b}$ would be preferable.

In the isotopic competitive method, the ratio of rate constants can be obtained either by intercomparison of the isotopic composition of the product or the unreacted substrate at known amounts of reaction with that of the original substrate. In the case of HCl as product in small amount, extreme care is necessary to avoid isotopic dilution by exchange with water adsorbed on glass surfaces. Some preliminary experiments showed that it was possible to convert DCl to D<sub>2</sub>, without interfering dilution, for mass spectrometric analysis by reaction with zinc. However, DCl formed by the photochemical reaction with Cl<sub>2</sub> in our glass reaction vessel, to be described below, was considerably diluted. The experiments were carried far enough to show that, when deuterium exchange between HCl and water adsorbed on the wall of the reaction cell was eliminated, the results were in complete agreement with those obtained by the analysis of the unreacted hydrogen. Since hydrogen is inert to exchange with HCl and H<sub>2</sub>O, all the measurements were carried out by intercomparing the isotopic composition of the unreacted hydrogen at measured amounts of reaction with hydrogen of the original composition.

Two types of  $HD-H_2$  mixtures can be prepared, namely, systems either equilibrated or not with respect to the reaction  $H_2+D_2=2HD$ . Since the best methods of purifying hydrogen establish the equilibrium, the experiments were carried out with an initially equilibrated mixture. In such a mixture a correction, whose magnitude depends on the absolute deuterium content, must be made for the presence and reaction of  $D_2$ . In the derivation of a formula for this correction, we shall assume for the present, but prove later experimentally, that no significant quantities of  $H_2$  or HD are produced either by back reaction or by recombination of hydrogen atoms during the course of the reaction.

From Eqs. (1) and (2), we can write

$$-[d(\mathbf{H}_2)/dt] = k_1(\mathbf{H}_2)(\mathrm{Cl}), \qquad (3)$$

$$-[d(HD)/dt] = (k_{2a} + k_{2b}) (HD) (Cl), \qquad (4)$$

which can be integrated directly to give

$$R = \frac{k_1}{k_{2a} + k_{2b}} = \frac{\ln(\mathrm{H}_2/\mathrm{H}_2^0)}{\ln(\mathrm{HD}/\mathrm{HD}^0)},$$
(5)

where  $(H_2/H_2^0)$  and  $(HD/HD^0)$  are the fractions of  $H_2$  and HD respectively unreacted after f of the chemical species, hydrogen, has reacted. We note that

$$1 - f = \frac{H_2}{H_2^0} \cdot \frac{(1 + \rho + \sigma)}{(1 + \rho_0 + \sigma_0)},$$
 (6)

where

$$\rho \equiv (HD/H_2)_f \quad \rho_0 \equiv (HD/H_2)_0,$$
 (7)

$$\sigma \equiv (D_2/H_2)_f \qquad \sigma_0 \equiv (D_2/H_2)_0.$$
 (8)

If the correction for the presence of  $D_2$  is to be made exactly, it is necessary to measure  $\sigma$ , since the unreacted hydrogen is not in exchange equilibrium with respect to the reaction  $H_2+D_2=2HD$ . The final  $D_2$  content cannot be calculated from  $\rho$  and the equilibrium constant. From Eqs. (5)-(8) one obtains

$$R = \frac{\left[\ln(1-f)\left(1+\rho_{0}+\sigma_{0}\right)/(1+\rho+\sigma)\right]}{\ln\left[\left(\rho/\rho_{0}\right)\left(1-f\right)\left(1+\rho_{0}+\sigma_{0}\right)/(1+\rho+\sigma)\right]}.$$
 (9)

If  $\rho$  and  $\rho_0$  can be measured in a concentration range with a precision independent of  $\rho$  and  $\rho_0$ , then it follows from Eq. (9) that low concentrations of deuterium minimize the errors in R resulting from errors in the absolute determination of  $\sigma$  and  $\sigma_0$ .

## III. EXPERIMENTAL PROCEDURE

The experimental procedure was similar in many respects to that described by Jones<sup>1</sup> in his experiments on HT. Conventional high-vacuum techniques were used and the apparatus for carrying out the measurements is shown schematically in Fig. 1. Commercially pure liquid chlorine from a tank was vaporized, after removal of air and other noncondensable gases, and the gas passed in sequence through calcium oxide powder, concentrated sulfuric acid, and phosphorus pentoxide powder supported on glass beads. A middle fraction was collected and stored at liquid nitrogen temperature in the storage vessel labeled "Cl<sub>2</sub>." A sample of hydrogen gas, containing approximated 0.7 atom percent deuterium,<sup>9</sup> was repurified by absorption on powdered uranium. The purified and equilibrated gas was stored

<sup>9</sup> J. Bigeleisen and A. Kant, J. Am. Chem. Soc. 76, 5957 (1954).

<sup>&</sup>lt;sup>8</sup> See reference 7, Sec. 5.





FIG. 1. Experimental apparatus (schematic).

under pressure in a small tank. The dissociation of uranium hydride serves as an effective, leak-proof compressor for hydrogen. An aliquot of the repurified  $H_2$ —HD mixture was stored on the vacuum line in the vessel marked "HD."

After evacuation of the vacuum manifold and vessels A, B, H, S, T, U, and V, chlorine from the storage vessel was allowed to vaporize into the calibrated dosing vessel S. The pressure in the dosing vessel was measured with a mercury manometer N by the use of the sickle gauge B as a null indicator. Stopcocks in this section of the line were lubricated with a grease of polymerized chlortrifluorethylene (Halocarbon Products Corporation), which is inert toward chlorine. The amount of chlorine to be transferred to the reaction cell need not be known accurately. In a typical experiment, the pressure in the reaction cell was 200-300 mm. The chlorine was transferred to the reaction cell V from the dosing vessel by condensation on a re-entrant thimble, which was filled with liquid nitrogen. A sample of the HD-H<sub>2</sub> mixture was transferred to the calibrated bulbs A and B for measurement and mercury was brought up to the fiduciary marks  $F_1$ and  $F_3$ . The pressure was measured with the mercury manometer M with the aid of a precision cathetometer. The hydrogen was then transferred to the reaction vessel by means of a Toepler pump T. In general, the amount of hydrogen was about one-half the amount of chlorine. The small amount of hydrogen remaining in the lines was recompressed into bulb A and its pressure measured in the manner described. The correction for gas imperfection is negligible for the present purpose.

The reaction vessel, approximately cyclindrical in shape, 6.0 cm in diameter  $\times 7.0$  cm long, was permanently submerged in a large, covered Dewar vessel, which served as a thermostat. The thermostat assembly was opaque to stray light. Methanol and water were used as thermostat fluids. Temperature was maintained

constant to  $\pm 0.01$  °C by means of heaters and/or refrigeration operated intermittently by a thermoregulator.

To carry out the reaction, the chlorine was allowed to vaporize by removal of the liquid nitrogen from the re-entrant thimble. Ten minutes were allowed for the system to come to thermal equilibrium and for the chlorine to mix with the hydrogen. The radiation of wavelength longer than 3900 A from a low-pressure mercury arc (General Electric Company AH-4) was isolated by means of a Corning No. 3391 filter and admitted by opening a shutter in the thermostat cover. The entire cross section of the reaction cell was illuminated along the cylinder axis. No effects due to nonuniform illumination were observable. After a suitable reaction time, the reaction was stopped by closing the shutter. The gases in the reaction vessel were then removed and the hydrogen fraction was separated from the chlorine and hydrogen chloride. Reaction from stray light was certainly less than 1%. To effect the separation, the irradiated reaction mixture was passed through the helical freeze-out trap H, which contained beads of platinum gauze and was cooled by liquid nitrogen. This trap removed all the chlorine and most of the hydrogen chloride. The gas then passed through tube U, filled with Ascarite to remove the last traces of hydrogen chloride, and the purified hydrogen, which was recovered quantitatively, was transferred into the calibrated bulb A by Toepler pump T. The volume of unreacted hydrogen was then measured. This ratio of the corrected volume of unreacted hydrogen to the corrected initial amount of hydrogen transferred to the reaction vessel is 1-f. A sample of the unreacted hydrogen was analyzed mass spectrometrically for HD/H<sub>2</sub>. The correction for  $\sigma$ and  $\sigma_0$  is negligible for the present experiments. Similar ratios were determined for the initial H<sub>2</sub>—HD mixture. Measurements were made by intercomparison with standards by the method in use in this laboratory.<sup>10</sup>

#### **IV. EXPERIMENTAL RESULTS**

The experimental results, calculated in accord with Eq. (9), are given in Table I as a function of temperature and the fraction of the hydrogen reacted, f.

No trend is found in the values of R, computed from the experimental data, as a function of f. This indicates that the gas mixing in the reaction cell is sufficiently rapid to eliminate any correction necessary for the self-shielding of the gas mixture from the actinic radiation. The radiation used to initiate the reaction was chosen in the region of low extinction coefficient to minimize such an effect. If the reaction mixture did not achieve a homogeneity of better than 90% by selfmixing, an effect from self-shielding could contribute a detectable trend for those experiments where the reaction is carried to more than 75% of completion.

 $^{10}$  R. E. Weston, Jr., and J. Bigeleisen, J. Chem. Phys. 20, 1400 (1952).

The spread in the experimental data at any temperature is consistent with that to be expected from the relation

$$\Delta \ln R = \left| \frac{R}{\ln(1-f)} \right| \left[ \left( \frac{R-1}{R} \frac{\Delta f}{1-f} \right)^2 + \left( \frac{\Delta(\rho/\rho_0)}{\rho/\rho_0} \right)^2 \right]^{\frac{1}{2}},$$
(10)

where  $(\Delta f/1-f) \sim 10^{-3}$  and  $[\Delta(\rho/\rho_0)/(\rho/\rho_0)] \sim 10^{-2}$ . Equation (10) is derived by neglecting the factor  $(1+\rho_0+\sigma_0)/(1+\rho+\sigma).$ 

A plot of  $\log R vs 1/T$  of the experimental data is given in Fig. 2. It is to be noted that, just as in the case of HT,  $\log R$  is linear in 1/T. Over the temperature range from 240 to 350°K,

$$R = (k_{\rm H_2}/\Sigma k_{\rm HD}) = (1.24 \pm 0.03) \exp(490 \pm 6/RT).$$

In the calculation of R from the experimental data it is important to establish that Eqs. (3) and (4) describe the relative rates of disappearance of  $H_2$  and HD. Particular attention must be paid to the possible production of HD by the reactions

$$H+DCl\rightarrow HD+Cl,$$
 (11)

$$D+HCI\rightarrow HD+CI.$$
 (12)

In reactions (11) and (12) hydrogen chloride competes with chlorine molecules for reaction with hydrogen atoms. Rather than rely on theoretical estimates, which would be somewhat uncertain in the present case, a direct experimental test was carried out.

A mixture of unequilibrated  $H_2$  and  $D_2$  (94%)  $H_2-6\%$  D<sub>2</sub>) was reacted with Cl<sub>2</sub> in the reaction vessel under conditions similar to the measurements in which R was determined. The reaction was carried to fifty percent of completion and the unreacted hydrogen was recovered and analyzed for  $D_2/H_2$  and formation of HD. Practically all of the HD found  $(HD/H_2 \sim 10^{-3})$ could be accounted for by partial equilibration of the  $H_2$  and  $D_2$  in the mass spectrometer ion source. A correction for the source equilibration was made with known mixtures and an upper limit,  $HD/H_2 < 2 \times 10^{-4}$ , was set for the production of HD during the photochemical reaction. This clearly establishes the fact that the measurement of R is not complicated by processes for the production of  $H_2$  or HD.

If we make the usual steady-state assumptions and neglect reactions of the type

$$M + H + H \rightarrow H_2 + M, \qquad (13)$$

 $M+Cl+Cl\rightarrow Cl_2+M$ , (14)

$$M+H+Cl\rightarrow HCl+M,$$
 (15)

then the upper limit for the production of HD from an irradiated mixture of  $H_2$  and  $D_2$  gives for the ratio

TABLE	Ι.	Ratio	of	rate	constants	for	the	reaction	of	$H_2$	and	HD
					with Cla	ator	ns.					

t°C	$10^{3}/T$	f	$\log_{10} R$	$\langle \log_{10} R \rangle$
77.5 <sub>0</sub>	2.840	0.8250 0.8379 0.6311	0.4117 0.3900 0.3973	0.400±0.009
75.00	2.872	$\begin{array}{c} 0.4584 \\ 0.7502 \\ 0.7271 \\ 0.6883 \\ 0.8002 \end{array}$	$\begin{array}{c} 0.4150 \\ 0.3990 \\ 0.3979 \\ 0.4043 \\ 0.4057 \end{array}$	0.404±0.006
50.00	3.094	$\begin{array}{c} 0.2543 \\ 0.5207 \\ 0.7166 \\ 0.4623 \\ 0.6686 \end{array}$	$\begin{array}{c} 0.4260 \\ 0.4286 \\ 0.4136 \\ 0.4276 \\ 0.4259 \end{array}$	0.424±0.005
25.0 <sub>5</sub>	3.353	0.2873 0.2821 0.5525 0.2256 0.6291	$\begin{array}{c} 0.4660 \\ 0.4553 \\ 0.4484 \\ 0.4708 \\ 0.4478 \end{array}$	0.457±0.009
0.00	3.661	$\begin{array}{c} 0.5051 \\ 0.1839 \\ 0.6279 \\ 0.5598 \\ 0.8168 \\ 0.9235 \end{array}$	$\begin{array}{c} 0.4914 \\ 0.4933 \\ 0.4942 \\ 0.4777 \\ 0.4826 \\ 0.4980 \end{array}$	0.489±0.007
-30.00	4.113	0.6737 0.7119 0.6837 0.6914	0.5344 0.5372 0.5298 0.5288	0.533±0.004

of the rate constants of the reactions

$$H+Cl_2 \rightarrow HCl+Cl, \tag{16}$$

$$\mathbf{H} + \mathbf{H} \mathbf{C} \mathbf{I} \rightarrow \mathbf{H}_2 + \mathbf{C} \mathbf{I}, \tag{17}$$

 $k_{16}/k_{17} \ge 2 \times 10^1$  at 298°K.<sup>11</sup> From the data of Ashmore and Chanmugan<sup>2</sup> and thermochemical data,<sup>12</sup>  $E_{17}$  is calculated to be 4500 cal mole<sup>-1</sup>. If we now assume with Morris and Pease<sup>13</sup> that the ratio of preexponential factors,  $A_{16}/A_{17}$ , is 10, then  $E_{16}$   $\ddagger < 4000$  cal mole<sup>-1</sup>. Morris and Pease made various estimates of  $E_{16}$ <sup>‡</sup> and concluded, using the ratio  $A_{16}/A_{17}$  equal to ten, that  $E_{16}$  ties in the range between 1600-4200 cal mole<sup>-1</sup>.

### V. DISCUSSION

The present experiments, when added to the previous work of Jones<sup>1</sup> on the relative rates of reaction of  $H_2$ and HT with chlorine atoms and the rate data on  $D_2$ 

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<sup>&</sup>lt;sup>11</sup> In arriving at this lower limit for  $k_{16}/k_{17}$  due account has been given to isotope effects on rates and equilibria. The latter are completely and exactly calculable in the present case. For the rate processes, experimental data have been used except for the reactions  $H+Cl_2\rightarrow HCl+Cl$  and  $D+Cl_2\rightarrow DCl+Cl$ . For the latter reaction we have estimated  $k_D/k_H\simeq 2$ . The accuracy of the esti-<sup>12</sup> "Selected Values of Chemical Thermodynamic Properties,"

Series III, National Bureau of Standards, Washington, D. C. <sup>13</sup> J. C. Morris and R. N. Pease, J. Chem. Phys. 3, 796 (1935).



FIG. 2. Plot of  $\log_{10}R$ ,  $R = k_{\rm H2}/2k_{\rm HD}$ , vs 1/T. The solid line, H<sub>2</sub>/HT, covers a portion of Jones' data.<sup>1</sup> The arrow with the limits 0.32 and 0.57 covers the range of the measurements of Farkas and Farkas, Naturwissenschaften 22, 218 (1934) in a mixture of H<sub>2</sub>, HD, and D<sub>2</sub>.

plus chlorine atoms,14 are pertinent to two fundamental questions. These are the quantitative adequacy of the theory of the effect of isotopic substitution on the rates of chemical reactions<sup>15</sup> and the nature of the potential energy surface in the neighborhood of the transition state. Inasmuch as the Bigeleisen theory<sup>15</sup> of the effect of isotopic substitution on the rates of chemical reactions is based on the quantum version of the transition state theory, a test of the Bigeleisen theory constitutes a test of those factors in the transition-state theory which are functions of the atomic masses. The number of quantitative tests of the transition theory is indeed small, and even a test limited to the effect of isotopic substitution is most welcome. Boato et al.,16 have recently reported a new set of measurements on the homogeneous exchange reaction between  $H_2$  and  $D_2$ ; their work has been discussed in some detail.<sup>17</sup> In connection with the present study the following points merit explicit mention. Bigeleisen and Wolfsberg<sup>3</sup> have shown that the relative rates of isotopic reactions of the type  $A+H_2 \rightarrow AH+H$ , where A is an atom, are sensitive primarily to the real stretching frequency in the transition state. In the work of Boato et al. this frequency is evaluated from the relative rates of conversion of parahydrogen and ortho-deuterium by hydrogen and deuterium atoms, respectively. However, the experimental errors in these rate constants (particularly that for the deuterium

reaction) are too large to permit a unique determination of the ratio. The stretching frequency, together with a pre-exponential factor (which is completely determined by atomic masses and statistical factors) and small corrections for the bending vibration and for tunneling, suffice to calculate the rates of the reactions  $H+D_2$  and  $D+H_2$ , which were investigated by Boato et al. The tunnel correction is of particular importance in the extrapolation of the rate constant to room temperature, where a comparison with the experimental value of Geib and Harteck<sup>18</sup> is made. Jones's experiments as well as the present ones have a higher accuracy in the measurement of the relative rates for the reactions of the type  $H_2+Cl$  than have been achieved to date for the  $H+H_2$  reactions.

In order to test the theory we must know the zeropoint energy associated with the stretching vibration in the transition state and how it changes with isotopic substitution. Small corrections are necessary for the bending vibrations and the tunneling. We shall assume no isotope effect on the transmission coefficient for these reactions. The remaining quantities: the vibrational frequencies of the isotopic hydrogen molecules and the atomic masses, are known. First we shall construct empirical potential surfaces, by a procedure similar to that used by Bigeleisen and Wolfsberg, using either  $R(H_2/HT)$  or  $R(H_2/HD)$ , and then we shall calculate the remaining ratios. Subsequently, we shall give a calculation based on the method of construction of the energy surface suggested by Sato.<sup>4</sup>

In the approximation that there is no isotope effect on the transmission coefficient, it is necessary that reactions of the type (2a) and (2b) have nearly equal rate constants so that  $\log R$  will be linear in 1/T, in accord with experiment. This is an important clue to the nature of the energy surface. The Wheeler, Topley, and Eyring<sup>19</sup> surface, with strong H--Cl bonding and a repulsive force between hydrogen atoms in the transition state, does not have this property and leads to poor agreement with experiment.<sup>1,3</sup> The empirical potential surfaces will also be formulated such that the Wigner tunneling correction will be adequate. Bigeleisen and Wolfsberg<sup>3</sup> found that an isosceles triangular model for the H<sub>2</sub>Cl transition state could be constructed to give good agreement with the HT data. The disagreement with Rollefson's D2 data was twice the experimental error. For the triangular model, a simple potential with a weak bending frequency and no interaction between stretching and bending frequencies leads to values of isotopic frequency ratios,  $\omega_1 \underset{\text{HTCl}}{\text{HTCl}} \frac{1}{2} / \omega_1 \underset{\text{H2Cl}}{\text{H2Cl}} \frac{1}{2}$ and  $\omega_{L \text{ HTCl}} \ddagger / \omega_{L \text{ H}_2 \text{Cl}} \ddagger$  which are insensitive to the bond angle. These ratios lead in turn to a pre-exponential factor for  $R(H_2/HT)$  in good agreement with Jones' experiments. This model also gives reasonable

<sup>&</sup>lt;sup>14</sup> (a) G. K. Rollefson, J. Chem. Phys. 2, 144 (1934); (b) A preliminary value at 298°K, consistent with Rollefson's data, has been obtained in the course of this research and is shown in Figs. 3 and 4.

<sup>&</sup>lt;sup>15</sup> J. Bigeleisen, J. Chem. Phys. 17, 675 (1949).

<sup>&</sup>lt;sup>16</sup> Boato, Careri, Cimino, Molinari, and Volpi, J. Chem. Phys. **24**, 783 (1956). <sup>17</sup> H. S. Johnston, Ann. Rev. Phys. Chem. **8**, 252 (1957).

<sup>&</sup>lt;sup>18</sup> K. H. Geib and P. Harteck, Z. physik. Chem. (Bodenstein Festband) 849 (1931).

<sup>&</sup>lt;sup>19</sup> Wheeler, Topley, and Eyring, J. Chem. Phys. 4, 178 (1936).

agreement with the pre-exponential factor for the HD data, namely 1.19 compared with the experimental value of  $1.24\pm0.03$ . A plot of  $\log R vs 1/T$  for the triangular model using the parameters given in Tables I and II of Bigeleisen and Wolfsberg is given in Fig. 3. We note that  $\log R_{eale}$  is too small for HD and too large for D<sub>2</sub>. The calculated values for D<sub>2</sub> can be brought into closer agreement with experiment by choosing the bending frequency of the complex larger than 200 cm<sup>-1</sup> and the imaginary frequency smaller than 720*i*. These changes would increase the discrepancy between  $R_{eale}$  and  $R_{exp}$  for HD. A comparison of the experimental and calculated differences in activation energies for reactions (1) and those of type (2) is given subsequently in Table VIII.

The relative rates are calculated from the relation<sup>15</sup>

$$\ln(k_1/k_2) = \ln(f/f_{N_p}\ddagger) + (1/24) (hc/kT)^2 (|\omega_{1L}\ddagger |^2 - |\omega_{2L}\ddagger |^2). \quad (18)$$

The symbols have been defined previously.<sup>3,15</sup> The partition function ratio f for the isotopic hydrogen molecules can be written in the form

$$f = (s'\omega/s\omega') \exp[3\Delta u_0 + 2(\sigma - \sigma')]/6.$$
(19)

The recent re-evaluation of the  $H_2$  spectrum given by Herzberg<sup>20</sup> is used to give the partition function ratios used,

$$f(HD/H_2) = 1.73228 \exp 405.61/T,$$
 (20)

$$f(HT/H_2) = 1.63349 \exp 555.91/T,$$
 (21)

$$f(D_2/H_2) = 0.70738 \exp 889.93/T.$$
 (22)

Inasmuch as we shall consider potential functions involving stiffer bending vibrations than those considered by Bigeleisen and Wolfsberg, we cannot utilize the  $\Delta u_b t^2/24$  approximation. Instead we use the expansion recently given<sup>21</sup> for the function

$$\ln \left[ \frac{u_{i}}{u_{i}'} \exp\left(\Delta u_{i}/2\right) \frac{\left[1 - \exp\left(-u_{i}'\right)\right]}{(1 - \exp\left(-u_{i}\right)}\right]$$
$$= \sum_{j=1}^{\infty} (-1)^{j+1} \frac{B_{2j-1} \delta u_{i}^{2j}}{2j(2j)!} \left[u_{i}' < 2\pi\right], \quad (23)$$

where  $B_{2j-1}$ 's are the Bernoulli numbers 1/6, 1/30, 1/42,  $\cdots$  etc., and  $\delta u_i^{2j}$  is defined as  $u_i'^{2j} - u_i^{2j}$ . With the use of Eq. (23) for the bending vibrations,  $\ln f_{N_n} \ddagger$ 



becomes in the harmonic approximation

$$\ln f_{N_{p}} \ddagger = \ln \frac{s_{1} \ddagger (\omega_{1} \ddagger \omega_{L} \ddagger)_{D,T}}{s_{2} \ddagger (\omega_{1} \ddagger \omega_{L} \ddagger)_{H_{2}C_{1}}} + \Delta u_{1} \ddagger / 2 + g_{n} \left( \frac{1}{24} \delta u_{\phi} \ddagger^{2} - \frac{1}{2880} \delta u_{\phi} \ddagger^{4} + \frac{1}{181440} \delta u_{\phi} \ddagger^{6} \cdots \right),$$
(24)

where  $s_1^{\ddagger}$  and  $s_2^{\ddagger}$  are the symmetry numbers of H<sub>2</sub>Cl and an isotopic species respectively,  $\omega_1^{\ddagger}$  is the real stretching frequency,  $\omega_L^{\ddagger}$  is the imaginary stretching frequency, and  $u_{\phi}^{\ddagger}$  is (hc/kT) times a  $g_n$ -fold degenerate bending frequency. The factor

$$\ln[1-\exp(-u_i\ddagger)]/[1-\exp(-u_1\ddagger)],$$

arising from the excitation of the real stretching fre-

<sup>&</sup>lt;sup>20</sup> G. Herzberg, Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1950), second edition, p. 532. (The frequencies, moments of inertia, and anharmonicities of HD, D<sub>2</sub>, and HT have been calculated from the data on H<sub>2</sub>. The tabulated values do not obey the isotope relationships.)

<sup>&</sup>lt;sup>21</sup> J. Bigeleisen in *Proceedings of the International Symposium on Isotope Separation*, Kistemaker, Bigeleisen, and Nier, editors (North-Holland Publishing Company, Amsterdam, 1958), p. 148.

			Fi	equency ratio	s <sup>b</sup>	
Force constants <sup>a</sup>	Frequencies (H <sub>2</sub> Cl)	HTCl	THCl	HDCl	DHCl	$D_2Cl$
$ \begin{array}{c} f_1(\text{H}-\text{H}) = 0.445 \\ f_2(\text{H}-\text{Cl}) = 1.313 \\ f_{12} = 0 \end{array} $	$\omega_1 \ddagger 1335 \text{ cm}^{-1}$ $\omega_L \ddagger 1000i$ $\omega_{\phi} \ddagger 540$	0.6253 0.9476 0.7225	0.9660 0.6134 0.9018	0.7412 0.9666 0.8011	0.9764 0.7337 0.9273	0.7217 0.7111 0.7082

TABLE II. Parameters for a WTE type potential for H<sub>2</sub>Cl (linear).

<sup>a</sup> In units of 10<sup>5</sup> dynes/cm.

<sup>b</sup>  $\omega_i \ddagger / \omega_i \ddagger (H_2 Cl)$ .

TABLE III. Parameters for H<sub>2</sub>Cl (linear) potential with H-H bonding.

			Fi	requency ratio	Sp	
Force constants <sup>a</sup>	Frequencies (H <sub>2</sub> Cl)	HTCl	THCl	HDCl	DHCl	$D_2Cl$
$f_1 = 0.50 f_2 = -0.10 f_{12} = -0.05$	$\omega_1 \ddagger 1327 \text{ cm}^{-1}$ $\omega_L \ddagger 300i$ $\omega_4 \ddagger 540$	0.8117 0.7300 0.7225	0.8117 0.7300 0.9018	0.8638 0.8294 0.8011	0.8638 0.8294 0.9273	0.7074 0.7233 0.7082

\* In units of 10<sup>5</sup> dynes/cm.

 $^{\mathrm{b}}\omega_{i}$ ‡/ $\omega_{i}$ ‡(H<sub>2</sub>Cl).

quency of the transition state, is negligible in the temperature range of interest.

The best Wheeler, Topley, and Eyring type potential, i.e.  $f_1(H-H) < 0$ ,  $0 < f_2(H-Cl) < 5.2 \times 10^5$  dynes/cm (force constant of HCl),  $f_{12}=0$ , for a linear molecule, consistent with the equations for the frequencies of a linear triatomic molecule, has the parameters given in Table II. The pertinent equations for the stretching and bending frequencies of a linear XYZ molecule are

$$\lambda_1 + \lambda_L = (\mu_x + \mu_y)f_1 + (\mu_y + \mu_z)f_2 - 2\mu_y f_{12}, \quad (25)$$

$$\lambda_1 \lambda_L = (\mu_x \mu_y + \mu_x \mu_z + \mu_y \mu_z) (f_1 f_2 - f_{12}^2), \quad (26)$$

$$(\omega_{\phi}/\omega_{\phi}') = (MI/M'I')^{\frac{1}{2}}\Pi_{i}(m_{i}'/m_{i})^{\frac{1}{2}}, \qquad (27)$$

where  $\mu_x$  is the reciprocal mass of atom x, and m, M, and I refer to the atomic masses, molecular weights, and moments of inertia, respectively. The bending frequency of  $H_2Cl$  was taken to be 540 cm<sup>-1</sup> in accord with Pitzer's calculation.<sup>5</sup> His geometry has also been used to calculate the moments of inertia. The calculated values of  $\log R$  from this potential are compared with the experimental data in Fig. 3. The absolute deviation is at most 10%, but the curvature in the plots of  $\log R$  vs 1/T for the unsymmetrical molecules, HT and HD, casts some doubt on this form of a potential. This conclusion is subject to the stated assumption of no temperature-dependent difference in transmission coefficients for the isotopic molecules. The difficulty arises from the large zero-point energy differences between pairs of the type HTCl and THCl. The results are similar to those of the linear model considered previously.3

From the definition of R, we can write

$$\ln R = \ln (k_1/k_{2a}) - \ln (1 + k_{2b}/k_{2a}).$$
(28)

We define

$$k_{2b}/k_{2a} \equiv 1 + 2\epsilon. \tag{29}$$

The subscripts can always be assigned such that  $0 < k_{2b}/k_{2a} < 1$ . Expansion of  $\ln(1+\epsilon)$  gives

$$\ln R = \ln (k_1/2k_{2a}) - \epsilon + \epsilon^2/2 + \cdots$$
 (30)

Inasmuch as  $\ln(k_1/2k_{2a})$  and  $\epsilon$  are expected theoretically to be essentially linear in 1/T, the experimental data on HT and HD show that the term in  $\epsilon^2/2$  cannot contribute more than two percent to the ratio of rate constants, R, at 225°K. From Eqs. (25) and (26), this fact suggests a potential with  $f_1 > 0 > f_2$ . We shall arbitrarily choose  $f_2 = 2f_{12} = -0.2f_1$ . Such a potential will give a small value of  $\lambda_L$ , and  $\lambda_1$  will be the same for a pair of isotopic isomers such as HDCl and DHCl. A considerable variation in  $f_2$  and  $f_{12}$  will have little effect on the ultimate comparison of  $R_{calc}$  with the experimental data. The parameters leading to the best fit with the experimental data for this type of potential are given in Table III. A comparison with the experimental data is shown in Fig. 4. The mean deviation of all the experimental data, HD, HT, and D<sub>2</sub>, from the calculated values is approximately fifteen percent. The calculated values utilize one parameter only,  $f_1$ , evaluated from the experimental data. We shall now show that these discrepancies between the calculated and experimental values in the present case contain no temperature-independent terms.

The experimental ratios of rate constants can be written in the form,

$$R = A \exp(B/T), \tag{31}$$

in the temperature range  $230^{\circ}-350^{\circ}K$ , which is a significant temperature variation. For any linear

transition state for H<sub>2</sub>Cl in which  $k_{2a} \sim k_{2b}$ , we can write from Eqs. (18), (19), (24), (26), and (30),

$$A = [(M/M')_{\rm H_2}(M'/M)_{\rm H_2C1}]^{\frac{1}{2}}, \qquad (32)$$

where  $(M/M')_{H_2}$  is the ratio of the *molecular* weights of the isotopic hydrogen molecules and  $(M'/M)_{H_2C1}$  is the inverse ratio of the *molecular* weights of the isotopic H<sub>2</sub>Cl molecules. We use the usual convention that the prime stands for the light molecule. A more general derivation of Eq. (32) is given elsewhere.<sup>22</sup> We note that the pre-exponential factor in the ratio of the rate constants derived under the assumption that  $k_{2\alpha} \sim k_{2b}$  for a linear molecule is identical with the ratio of the collision frequencies, assuming equal collision cross sections. A comparison with the experimental



FIG. 4. Intercomparison of theoretical and experimental values of log R. Theoretical lines: \_\_\_\_\_\_ linear H<sub>2</sub>Cl complex with H—H bonding (cf. Table III), ---- linear H<sub>2</sub>Cl complex with interaction between stretching modes (cf. Table VII). Circles are experimental data.

<sup>22</sup> J. Bigeleisen, Second International Conference on Peaceful Uses of Atomic Energy, Geneva (September, 1958).

TABLE IV. Intercomparison of experimental and theoretical preexponential factors in the relative rates.

	$A_{exptl}$	$A_{\mathrm{theoret}}$
$H_2/HD$	$1.24 \pm 0.03$	1.21
$H_2/HT$ $H_3/D_3$	$1.35 \pm 0.03$	$1.38 \\ 1.38$

values is given in Table IV. The agreement between the theoretical and experimental pre-exponential factors in the relative rates is excellent. The theoretical values for the temperature independent factors are a direct consequence of the theory of the relative rates of reaction of isotopic molecules and their evaluation does not utilize any arbitrary parameters. Under the assumption of a linear transition state, the close agreement shows that there are no temperature-independent factors, such as transmission coefficients, which have been omitted from Eq. (18).

It can be shown that, in the framework of the present calculations, no change in the parameters given in Table III will reduce the relative discrepancy between the HT and HD values. It is possible to change  $f_1$  so as to give better agreement with either the HT or HD data, but not both. If the choice is made to change  $f_1$  to arrive at a better agreement for the HD data, then the fit for HT will be poorer but that for  $D_2$  will be better. The converse holds if the adjustment is made to fit the HT data more closely. There are two assumptions made in Eqs. (18) and (24) which may contribute to the discrepancy. These are the harmonic approximations and the neglect of the transmission coefficients; we have already shown that any possible contribution from the transmission coefficients can have no temperature-independent component. The anharmonic correction would in fact be a pure temperature-dependent term. Its nature would have to be such as to add to rather than to subtract from the sum of the squares of the stretching frequencies,  $\lambda_1 + \lambda_L$ . If  $f_2$  or  $f_{12}$  had been chosen somewhat larger than the choice made in Table III and either or both of them showed the usual anharmonicity, the calculated values of  $R_{(H_2/HT)}$  and  $R_{(H_2/HD)}$  would be closer to the experimental data. This is a very reasonable supposition, but any detailed calculation would be an ad hoc one, and one would end up with a number of adjusted parameters equal to the number of independent experimental data. The potential parameters given in Table III involve essentially only one parameter,  $f_1$ , and give a reasonable fit to three independent sets of data which span a range of one order of magnitude. Therefore, we may conclude that the temperature dependence of the theory of the relative rates of reaction of isotopic molecules, in the approximations stated, is nearly correct on a quantitative scale. However, the potential of the form considered, viz., Table III, might be expected to lead to a rather high value for

			Fi	requency ratio	sp	
Force constants <sup>a</sup>	Frequencies (H <sub>2</sub> Cl)	HTCl	THCl	HDCl	DHCl	$D_2Cl$
$\begin{array}{c} f_1(\text{H}-\text{H}) & 0.572 \\ f_2(\text{H}-\text{Cl}) & 1.559 \\ f_{12} & 1.499 \end{array}$	$\omega_1 \ddagger 1348 \text{ cm}^{-1}$ $\omega_L \ddagger 1497i$ $\omega_{\phi} \ddagger 727$	0.9096 0.6524 0.7130	0.6542 0.9070 0.9099	0.9407 0.7621 0.7944	0.7648 0.9373 0.9332	0.7241 0.7094 0.7085

TABLE V. Parameters for the Sato potential for a linear H2Cl complex.

<sup>a</sup> In units of 10<sup>5</sup> dynes/cm.

<sup>b</sup>  $\omega_i \ddagger / \omega_i \ddagger (H_2 Cl)$ .

the absolute activation energy. In this potential the H-H force constant is appreciably smaller than that for the hydrogen molecule and the hydrogen-chlorine force constant is negative.

Since the isosceles triangular model proposed by Bigeleisen and Wolfsberg and shown in Fig. 3 shows a similar behavior to the linear model with  $k_{2a} \sim k_{2b}$ , we may confidently expect that any bent model with a potential such that  $k_{2a} \sim k_{2b}$  will lead to a similar result. Thus, we find that essentially independent of geometry the pre-exponential factors are calculated from the theory in excellent agreement with experiment by the choice of a potential which leads to  $k_{2a} \sim k_{2b}$ . However, the assumption of simple harmonic potentials and the neglect of isotope effects on the transmission coefficients do lead to discrepancies between the experimental and observed differences in activation energies.

Recently Sato<sup>4</sup> has proposed a modification of the Eyring-Polanyi method for calculating the activation energy of a reaction of the type  $A + BC \rightarrow AB + C$ . The method is not an absolute one since one parameter is evaluated from the activation energy. For the reactions of the isotopic hydrogen molecules with chlorine atoms, the energy surface can be obtained from the known Morse curves for H<sub>2</sub> and HCl and Ashmore and Chanmugan's<sup>2</sup> value for the activation energy (5.50 kcal) for the reaction  $H_2$ +Cl, after correction for the zero-point energies of  $H_2$  and  $H_2Cl$ . These lead to a value for k, the Sato parameter, of 0.177, which is not much different from Sato's value. However, we find that the use of an invariant value of k from system to system does not lead to good values of the activation energies for reactions of the type A+BC, as Sato suggests. The Sato method is subject to the same types of criticism that Coolidge and James<sup>23</sup> brought to the Eyring-Polanyi method of calculating energy surfaces. For the present we shall use Sato's method as an empirical one for the calculation of the energy surface from the activation energy. The harmonic vibrational parameters of the Sato potential for a linear complex are given in Table V.

Apart from the tunnel correction, the parameters of the Sato potential are such that  $k_{2a} \sim k_{2b}$  and  $\log R$ will be linear with 1/T. Since the pre-exponential factors in Eq. (31) are independent of the potential for a linear complex in which  $k_{2a} \sim k_{2b}$ , they need not be recalculated and can be taken from Table IV. We note that the imaginary frequency for H<sub>2</sub>Cl has a value of 1497*i*, which means that the Wigner tunnel correction is not applicable at room temperature. It is valid at 600°K and the absolute rate at this temperature calculated from the Sato potential agrees within 5% with the experimental data.

Bell<sup>24</sup> has recently given a treatment for the tunneling through a one-dimensional parabolic barrier which should be valid even when the tunneling is large. The solution utilizes the approximation that the permeability of the barrier G(W) is given by

$$G(W) = [1 + \exp(\beta y)]^{-1}, \qquad (33)$$

where

$$\beta = 2\pi^2 a \left(2mE\right)^{\frac{1}{2}}/h,\tag{34}$$

$$y=1-W/E,$$
 (35)

and E and 2a are the height and width of the barrier, respectively, while W is the thermal energy of the particle. Integration of (33) over the energy spectrum leads to the following quantum correction for tunneling.

$$Q = \frac{\pi \alpha / \beta}{\sin \pi \alpha / \beta} - \frac{\alpha e^{\alpha - \beta}}{\beta - \alpha} \left( 1 - \frac{\beta - \alpha}{2\beta - \alpha} e^{-\beta} + \cdots \right) \left[ \alpha < \beta \right], \quad (36)$$

where

$$\alpha = E/kT. \tag{37}$$

We note that

$$u = 2\pi\alpha/\beta = -ih\nu/kT. \tag{38}$$

Bell's solution reduces to Wigner's  $u^2/24$  correction for small tunneling. In the use of Bell's correction for the tunneling one should use the best parabolic fit to the barrier over the energy region for which there is appreciable tunneling, rather than the harmonic frequency obtained from the curvature at the top of the barrier.

To obtain a parabolic approximation to the Sato barrier the energy surface was calculated at intervals of 0.01 A over the range H—H 0.75-1.30 A and H—Cl 1.25-1.80 A. A portion of the energy contours is shown in Fig. 5. The energy as a function of the reaction

<sup>24</sup> R. P. Bell, Trans. Faraday Soc. 55, 1 (1959).

<sup>&</sup>lt;sup>23</sup> A. S. Coolidge and H. M. James, J. Chem. Phys. 2, 811 (1934).

coordinate was obtained by a Hirschfelder type plot<sup>25</sup> and is shown in Fig. 6. The parabolic barrier with a curvature six-tenths that at the top of the barrier gives a reasonable approximation to the Sato barrier over the energy range for which there is appreciable tunneling. The tunnel corrections found for H<sub>2</sub> and D<sub>2</sub> are given in Table VI. Even though high accuracy cannot be claimed for this treatment of the tunneling, the results indicate that the tunnel correction is very large and that the barrier calculated by the Sato method is too narrow. With a tunnel correction of the magnitude of that given in Table VI one would find a



FIG. 5. Energy contours for the three atom system H—H—Cl calculated by the Sato method. Contour lines at E = -(100+x) kcal.

non-Arrhenius dependence in both the absolute and relative rates. This is not in accord with the experimental facts. Subsequently, in Table IX, we shall compare experimental values of B, the difference in activation energies of the isotopic molecules, with calculated ones. The ones calculated by the Sato method without any tunnel correction are low by 30–100°K. If a tunnel correction of the magnitude of that given in Table VI were to be added to these values of B, the relative rates calculated from the Sato potential would be in poor agreement with experiment.

<sup>26</sup> See Glasstone, Laidler, and Eyring, *The Theory of Rate Proc*esses (McGraw-Hill Book Company, Inc., New York, 1941), pp. 100 ff.



FIG. 6. Energy barrier for the three atom system H—H—Cl calculated by the Sato method (solid line). Dashed lines are parabolic barriers: — — harmonic force constant  $f = -1.32 \times 10^{6}$  dynes/cm,  $---f = (0.6) (-1.32) \times 10^{5}$  dynes/cm.

It is significant to note that the Sato method of calculating the energy surface gives a large positive value for the interaction force constant,  $f_{12}$ . The nongenuine vibration, or the energy barrier, arises from the condition that  $f_{12}^2$  is greater than  $f_1f_2$ . In many respects this method is therefore similar to the procedure suggested and used by Johnston and co-workers.<sup>26</sup> These workers have utilized flat-topped barriers obtained from the condition  $f_{12}^2 = f_1f_2$ . Their method of estimating  $f_1$  and  $f_2$  leads to very high values for the real stretching frequencies in the different isotopic H<sub>2</sub>Cl molecules. As a result the calculated differences in activation energy are in poor agreement with experiment.

We note that both the semiempirical energy surface, whose parameters are given in Table III, and the Sato method give an H—H force constant in the transition state of about  $0.5 \times 10^5$  dynes/cm. A force constant of this magnitude is necessary to obtain a reasonable fit with the experimental data. If we add the requirement that the tunnel correction be sufficiently small so that both the absolute and relative rates follow an Arrhenius type relation ( $\omega_L \ddagger (H_2 Cl) \sim 600i \text{ cm}^{-1}$ ), we obtain then for a potential of the form  $f_{12} > f_1 f_2$  the parameters given in Table VII. The differences in

TABLE VI. Tunnel correction for the reaction of hydrogen molecules with chlorine atoms.

Τ°K	$Q_{\mathbf{H}_2}$	$Q_{\mathbf{D}_2}$	$Q_{\mathrm{H}_2}/Q_{\mathrm{D}_2}$
300	5.57	2.16	2.58
400	2.36	1.48	1.59

<sup>20</sup> Herschbach, Johnston, Pitzer, and Powell, J. Chem. Phys. 25, 736 (1956); D. J. Wilson and H. S. Johnston, J. Am. Chem. Soc. 79, 29 (1957).

			F	requency ratio	os <sup>b</sup>	
Force constant <sup>a</sup>	Frequencies (H <sub>2</sub> Cl)	HTCl	THCl	HDCl	DHCl	$D_2Cl$
$f_1 = 0.50$ $f_2 = 2.00$	$\omega_1 \ddagger 1340$ $\omega_1 \ddagger 600i$	0.821	0.754	0.891 0.802	0.775	0.726
$f_{12} = 1.10$	$\omega_{\phi}$ ‡ 540	0.723	0.902	0.801	0.927	0.708

TABLE VII. Potential constants and frequency ratios for a linear H<sub>2</sub>Cl complex with stretching interaction.

<sup>a</sup> In units of 10<sup>5</sup> dynes/cm.

 $^{b}\omega_{i}\ddagger/\omega_{i}\ddagger(H_{2}Cl).$ 

activation energies calculated from these constants are compared with experiment in Table IX and with the relative rates in Fig. 4. The agreement is slightly better than that obtained from the simpler potential given in Table III. Furthermore we note that any anharmonicity associated with the interaction between the two stretching motions will bring the calculated values of  $R_{(\rm H_2/HT)}$  and  $R_{(\rm H_2/HD)}$  into even better agreement with the experimental data.

We now wish to intercompare the experimental values of B, the difference in activation energies of the isotopic  $H_2$  molecules as expressed in Eq. (31), with the theoretical values obtainable from the potential functions given in Tables I and II of Bigeleisen and Wolfsberg<sup>3</sup> and Tables II, V, and VII of the present paper.

Inasmuch as the experimental values of A, the preexponential factors in Eq. (18), agree within twice the experimental error with the theoretical values in each case we shall rewrite the experimental equation for Rto give exact agreement for the preexponential factor. This procedure magnifies the discrepancies between theory and experiment. From Eqs. (18,) (19), (23), (24), and (30) we can write

$$B = (hc/2k) \left[ (\omega_e' - \omega_e) + \frac{1}{2} (x_e' \omega_e' - x_e \omega_e) \right]_{\mathbf{H}_2} + (h^2/24\pi^2 k) (1/I - 1/I')_{\mathbf{H}_2} - (hc/2k) (\omega_1' \ddagger - \omega_{1a} \ddagger) - (g_n/24) (hc/k)^2 (\omega_{\phi'} \ddagger^2 - \omega_{\phi a} \ddagger^2) \langle (1/T) \rangle + (g_n/2880) (hc/k)^4 (\omega_{\phi'} \ddagger^4 - \omega_{\phi a} \ddagger^4) \langle (1/T)^3 \rangle - (\Delta/2) - (\Delta^2/8) + T (\omega_L' \ddagger, \omega_{La} \ddagger) + \cdots$$
(39)

TABLE VIII. Intercomparison of theoretical and experimental values for the effect of hydrogen isotope substitution on the activation energy for the reaction  $H_2$ +Cl. Isosceles triangular transition state.

Isotopic substitution	$B_{expt1}$	$B_{eale}$
$\begin{array}{c} H_2 - HD \\ H_2 - HT \\ H_2 - D_2 \end{array}$	259±2°K 278±2 (606±30)°	216°K (278) <sup>b</sup> 724

\* Parameters from Tables I and II of reference 3.

<sup>b</sup> This value has been used to fix  $\omega_1$ <sup>‡</sup>(H<sub>2</sub>Cl).

° Obtained from the value of R at 298°K and the theoretical value of the pre-exponential factor A.

where

$$T(\omega_L'\ddagger, \omega_{La}\ddagger) = (1/24) \left( hc/k \right)^2 \left( \omega_L'\ddagger^2 - \omega_{La}\ddagger^2 \right) \left\langle (1/T) \right\rangle$$

$$\tag{40}$$

when the Wigner tunnel correction is used, but

$$T(\omega_{L}'\ddagger, \omega_{La}\ddagger) = (1/24) (hc/k)^{2} (\omega_{L}'\ddagger^{2} - \omega_{La}\ddagger^{2}) \langle (1/T) \rangle$$
  
+ (1/2880) (hc/k)^{2} (\omega\_{L}'\ddagger^{4} - \omega\_{La}\ddagger^{4}) \langle (1/T)^{3} \rangle + \cdots (41)

when the Bell approximation is used. The quantity  $\Delta$ occurs only in those reactions involving the asymmetrical molecules HD and HT and is defined by the relation

$$\Delta = -(g_n/24) (hc/k)^2 (\omega_{\phi b} \ddagger^2 - \omega_{\phi a} \ddagger^2) \langle (1/T) \rangle + (g_n/2880) (hc/k)^4 (\omega_{\phi b} \ddagger^4 - \omega_{\phi a} \ddagger^4) (\langle 1/T)^3 \rangle + T(\omega_{Lb} \ddagger, \omega_{La} \ddagger) + \cdots. \quad (42)$$

The correction to B from nonclassical rotation of the transition state is negligible.

The intercomparison of the calculated and experimental values of B are given in Tables VIII and IX. The areas of agreement between  $B_{cale}$  and  $B_{exptl}$  have been discussed previously and the present tabulation gives the results in quantitative form.

#### VI. CONCLUSION

1. For models of the transition state complex,  $H_2Cl_1$ ,

TABLE IX. Intercomparison of theoretical and experimental values for the effect of hydrogen isotope substitution on the activation energy for the reaction  $H_2+Cl$ . Linear transition states.

Isotopic substitution	$B_{\mathrm{exptl}}$	B <sub>III</sub> <sup>a</sup>	$B_{\rm Sato}{}^{ m b}$	Bvii°
$\begin{array}{c} \mathrm{H_2-HD} \\ \mathrm{H_2-HT} \\ \mathrm{H_2-D_2} \end{array}$	256±2°K	245	193	219
	272±2	336	245	316
	(594±30)	543	489	586

<sup>a</sup> This value of B is calculated with the parameters in Table III. The number of independent calculated values is one less than the number tabulated since one value of  $B_{III}$  is required to fix  $\omega_1$ ‡(H<sub>2</sub>Cl).

<sup>b</sup> Calculated from the parameters in Table V. The calculated

values of B do not include a correction for tunneling. <sup>o</sup> Calculated from the parameters in Table VII. Essentially two experimental values of B are utilized to fix the potential.

such that there is approximately equal probability for the reaction of the head or tail of a mixed molecule, HT or HD, with chlorine atoms, a straightforward and rigorous calculation of the temperature-independent factor of the ratio of rate constants of the isotopic  $H_2$ molecules is in quantitative agreement with the experimental data. The calculation, which is independent of the geometry of the transition state, is based on the transition state formulation of the theory of isotope effects in reaction rates and neglects possible isotope effects which may arise from the transmission coefficient. The latter, therefore, makes no contribution to the temperature-independent part of the relative rate constants of isotopic molecules in the reaction of hydrogen molecules and chlorine atoms. The preexponential factors calculated from the transition state theory are in the present case identical with those predicted by the collision theory.

2. It is possible to construct a Wheeler-Topley-Eyring type of potential function for the H<sub>2</sub>Cl complex which accurately predicts the relative rates of reaction of HD and HT with chlorine atoms. This potential surface, cf. Table II, corresponds to an attractive force between hydrogen and chlorine atoms and a repulsive force between hydrogen atoms. It predicts a nonlinear dependence of log R, the ratio of rate constants of isotopic hydrogen molecules, on 1/T in the range 225– 400°K when a symmetrical hydrogen molecule, e.g.,  $H_2$ ,  $D_2$ , is compared with an unsymmetrical one, e.g., HD, HT. The predicted curvature is in disagreement with experiment and may result from the neglect of a small temperature dependent contribution to  $\log R$  from the transmission coefficient.

3. Three potential functions, one triangular and two linear ones, have been found which predict  $\log R$  linear in 1/T for the reactions of all the isotopic hydrogen molecules with chlorine atoms. Detailed calculations have been made for the linear structures in the harmonic approximation. Good agreement is found between the theoretical and experimental ratios of rate constants of H<sub>2</sub> to its isotopic molecules. However, the prediction of the relative rate constants of HD and HT is in less satisfactory agreement with the experimental data. It is shown that the Sato modification of the Eyring-Polanyi method of constructing the energy surface leads to an excessively narrow barrier with large tunneling. To the extent of the agreement between the experimental data and the calculations based on the empirical energy surfaces, these results may be considered as a quantitative confirmation of the transition state theory of the effects of isotopic substitution on the rates of chemical reaction formulated by Bigeleisen.

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## Determination of Intermolecular Potentials from Thermodynamic Data and the Law of Corresponding States\*

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It is shown that in classical statistical mechanics the second virial coefficient in the virial expansion of the equation of state of a gas uniquely determines the intermolecular potential provided that the potential is monotonic (i.e., everywhere repulsive or everywhere attractive). This result leads to a partial verification of a conjecture of H. Kammerlingh-Onnes and W. H. Keesom concerning the Law of Corresponding States. An explicit formula for the potential is also obtained. If the potential is not monotonic it is not uniquely determined by the second virial coefficient. All potentials corresponding to a given second virial coefficient are determined explicitly.

## INTRODUCTION

**S**TATISTICAL mechanics provides a method for the determination of the equation of state and the other thermodynamic properties of a gas in terms of its intermolecular potential. We consider the inverse

\* This work was performed under the auspices of the U. S. Atomic Energy Commission during the summer of 1958 while the authors were at Brookhaven National Laboratory. problem of determining the intermolecular potential from the equation of state or from other thermodynamic data. On the basis of classical statistical mechanics, we will deduce the following partial solution to this problem: if the potential is monotonic (i.e., everywhere repulsive or everywhere attractive) then it is uniquely determined by the second virial coefficient in the equation of state. We will also obtain an explicit for-