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Absolute Rates of Four-Atom Reactions

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Equipotential surfaces such as one encounters in valence problems and particularly in the calculation of absolute rates, are discussed in a "bond space" instead of configuration space, with much simplification resulting both in the general aspects and in the practical handling of such problems. The exchange part, as well as the so-called coulombic part, of the bond energies is seen to obey a simple vector addition rule. A complete treatment of a four-atom reaction without symmetry ($\text{H}_2 + \text{ICl} \rightarrow \text{HI} + \text{HCl}$) is carried out and results are compared with the existing experiments.

INTRODUCTION

THE simultaneous interaction of more than two atoms with each other is a complicated theoretical problem. Insofar as it manifests itself in chemical exchange reactions it can be described on the following four assumptions:

I. When an atom is joined by at least sufficiently many bonds to saturate its valence the lower potential energies will correspond to configurations which makes additional bonds to this atom as small as is possible without weakening the main bonds.

IIa. The energy of interaction of more than two atoms can be expressed as a function of single bond additive and exchange energies. Here we are using the word "bond" in a somewhat wider sense than usual, meaning electron pair energy which two atoms at any particular distance would exhibit in the absence of other atoms.

IIb. The interaction energy a of a pair of atoms consists of two parts: one part A arising from "classical" forces, which is purely additive, and a second α arising from quantum-mechanical electron exchange. This latter part is not simply additive and is responsible for the valence properties of atoms.

III. In the approximation considered here, the addition law for the latter type of binding is taken to be that following from perturbation theory calculations. For the case of three and four atoms the following well-known formula is obtained:¹

$$E = A + B + C - \left(\frac{1}{2} [(\alpha - \beta)^2 + (\beta - \gamma)^2 + (\gamma - \alpha)^2] \right)^{\frac{1}{2}}, \quad (1)$$

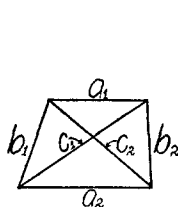


FIG. 1.

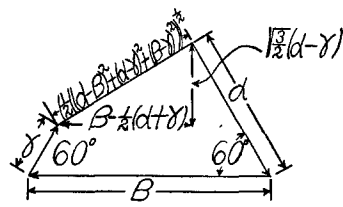


FIG. 2. Vector addition of exchange binding.

where $a = A + \alpha$, $b = B + \beta$, $c = C + \gamma$, are the bonds in the case of three atoms, while for four atoms (see Fig. 1),

$$\begin{aligned} a &= a_1 + a_2, & b &= b_1 + b_2, & c &= c_1 + c_2 \\ A &= A_1 + A_2, \text{ etc.}, \\ \alpha &= \alpha_1 + \alpha_2, \text{ etc.} \end{aligned}$$

IV. The actual amounts of additive and of exchange energy for each pair are taken to be constant fractions of the total interaction energy as represented by its Morse curve.

$$\begin{aligned} A_1 &= \lambda a_1, & \alpha_1 &= (1 - \lambda) a_1, \\ B_1 &= \lambda b_1, & \beta_1 &= (1 - \lambda) b_1, \\ C_1 &= \lambda c_1, & \gamma_1 &= (1 - \lambda) c_1. \end{aligned} \quad (2)$$

The assurance with which these four assumptions can be accepted probably decreases in the order in which they are quoted. It will naturally be very interesting to see to what extent these assumptions, taken separately, can be justified or improved upon by comparison with experiment. Even the most specific assumption IV has not been shown to be in disagreement with experiment for configurations near the activated state though for interatomic distances less than the equilibrium distance of two atoms the fraction λ certainly decreases with decreasing distance. When more experimental information is available we may find it desirable to replace the assumption of a percentage λ not varying with distance, by more general relations. There is nothing in our present procedure that would not be equally well adapted to such a generalization. We shall find that assumptions I and II, together with very much less specific assumptions than III and IV, permit us to draw conclusions based only on the potential curves of the atom pairs and on geometrical relations. In view of the semi-empirical basis of (1) it is desirable to carry the more firmly established assumptions to their farthest logical conclusions before making more specific assumptions about (1). For example, the

¹ F. London, *Zeits. f. Elektrochemie* **35**, 552 (1929); Eyring and Polanyi, *Zeits. f. Physik* **B12**, 19 (1931).

conclusions that activated complexes for three monovalent atoms should be linear and that activated complexes of four monovalent atoms are planar or more generally that configurations are more stable the smaller the exchange binding between the atoms not paired in the ordinary chemical sense rest on a more general basis than III and IV and yet these conclusions are sufficient to enable us to find the "best reaction surface" in bond space as we shall see.

We propose to describe the potential function E of a three or four-particle system in bond space instead of the usual configuration space. That is, we shall represent our system by using the three bond energies a , b , c as orthogonal coordinates. That this is possible for four atoms depends on the fact that the three pairs of bonds a_1 and a_2 , b_1 and b_2 , c_1 and c_2 enter into (1) only through their sums. Apparently it is generally true that the interaction energy of an even numbered particle system, $2n$, involves no more linearly independent combinations of bonds to express the energy than does the one for $(2n-1)$ atoms.

By abandoning the configuration space one sacrifices the foremost advantage of that treatment, namely that the configurational changes of the system in a reaction may be represented by a mass point subjected to the known potential E and obeying the laws of ordinary mechanics. But such a representation turns out to be not feasible for more than three particles, quite apart from the complications in visualizing which arise from the many dimensions.

The success and the simplicity of the new treatment depend on the following fact: In general, of the six parameters specifying a configuration of four particles in space, only two, say a and b , need be considered as actually independent and as determining a surface B which will include the best reaction path. This surface will be considered in detail later. A reaction may be described by saying that the system starts from a configuration where a has its maximum value and $b=c=0$, and proceeds to a final state where b is a maximum and $a=c=0$. By the "best reaction path" is meant that sequence of configurations by which this transition is accomplished in a way most economical of potential energy. Thus each of these configura-

tions must have a minimum potential energy in all directions except the one in which the reaction proceeds. The point of highest potential energy along this path represents the activated configuration. It is clearly true that for this point—a saddle point—the energy is stationary in all directions, a fact of fundamental importance in that it allows us to use the theory of small vibrations for setting up the partition function of the activated state. Mathematically, the activated configuration is thus determined as the point with the highest potential along the best reaction path for which $dE=0$.

It is characteristic of the theory of reaction rates that the original and the activated configuration are the only ones whose physical properties determine the rate of reaction. Only in the case of two saddle points of nearly equal heights is it necessary to consider both.

Since we propose to describe the progress of a reaction in bond space we must consider how points in bond space and in configuration space correspond to each other. In the case of three atoms, the three bonds are just sufficient to determine the configuration, except for a certain ambiguity which is readily disposed of.² In the case of four atoms, however, the situation is complicated by the fact that it takes six parameters to determine a configuration so that there exist in general ∞^3 configurations for a point (a, b, c) . On the other hand there are regions in bond space which are not attainable by a particular system owing to the obvious restriction on the greatest absolute value a bond can take, and also owing to the geometrical restrictions which prevail among the six distances between four atoms. It so happens that in spite of this general situation the best reaction path, because of the conditions on c , always lies on the boundary surface between the physically attainable and the unattainable region, and for this surface B there does exist a point to point correspondence between bond and configuration space.

We now show that the best reaction path lies completely on the boundary surface. We start

² This ambiguity arises in the case of four, three and even two-atom systems, from the fact that two different distances are always associated with every negative value of E occurring in the diatomic potential curve. No complication arises from this fact since the reaction path never involves configurations where an interatomic distance is contracted beyond the equilibrium distance for that pair.

out by finding for every given pair of values, a, b , the smallest possible value of $|c|$ which is attainable by our system under its geometrical restrictions. The surface so defined in bond space will clearly be a boundary surface for the attainable region. Its equation can be set down as

$$d(c_1 + c_2)_{a, b} = 0. \quad (3)$$

On the other hand, if we restrict our attention to all those points (a, b, c) which for given values a, b , have their minimum value of E , then the surface so obtained must completely contain the best reaction path. But this condition can be written

$$(dE)_{a, b} = (\partial E / \partial c)(dc_1 + dc_2) = 0. \quad (4)$$

It should be borne in mind that the differentials dc_1 and dc_2 occurring in (3) and (4) are related to each other in a way depending upon the geometry of the system, i.e., on the specific values assigned to a_1, a_2, b_1, b_2 , and also involve the Morse curves of the individual atom pairs. But from (4) it follows that a stationary value of E corresponds to a stationary value of c , ignoring the unimportant singular cases where $\partial E / \partial c = 0$. Whether a minimum of E corresponds to a minimum or a maximum of c , is determined by the sign of $\partial E / \partial c$, which in the particular case of the London formula can be written as:

$$\partial E / \partial c = \lambda - (1 - \lambda)(c - \frac{1}{2}(a + b)) \times [\frac{1}{2}(a - b)^2 + (a - c)^2 + (b - c)^2]^{-\frac{1}{2}}. \quad (5)$$

This is negative if $|c|$ is the smallest of the bonds, as it is for the comparatively small values which λ assumes for nonmetallic elements. Thus we have shown that, to make E as low as possible for a given a and b , the value $|c|$ must be made a minimum, and thus the best reaction path lies in the boundary surface. Equations exactly similar to (3) and (4) can be discussed for a and b . If $|a|$ happens to be the largest of the three, then $\partial E / \partial a$ is positive so that a minimum value of E will now go with a maximum value for $|a|$. In some cases it is found more convenient to use this latter relationship. In the intermediate case where $|b|$ say, is neither the largest nor the smallest of the three $|b|$ should be made a minimum or a maximum depending on whether $\partial E / \partial b \leq 0$. A mechanical device which enables one easily to satisfy condition (3) will be described in a later section.

A VECTOR ADDITION RULE FOR BOND ENERGIES

After this more or less kinematical discussion of configurations in bond space we now turn to the question of the interaction energy of a system of atoms. In particular we shall consider the nature of the equipotential surfaces defined by (1) and (2). We now prove that the law of combination of exchange energies as expressed by the square root in (1) is equivalent to the following simple vector addition:

$$E_{ex} = (\frac{1}{2}[(\alpha - \beta)^2 + (\beta - \gamma)^2 + (\gamma - \alpha)^2])^{\frac{1}{2}} = |\alpha + \omega\beta + \omega^2\gamma|, \quad (6)$$

where ω and ω^2 are third roots of unity. This situation is also represented by the vector diagram Fig. 2 in terms of which the following simple proof can be given: If we plot the bond energies α, β, γ end-on making angles of 60° with each other as in Fig. 2, then the resultant has the horizontal and vertical components $(\beta - \frac{1}{2}(\alpha + \gamma))$ and $\frac{1}{2} \times 3^{\frac{1}{2}}(\alpha - \gamma)$. Thus its length turns out to be just E_{ex} . The existence of such a simple vector addition rule for bonds in three and four particle systems is significant and suggests the possibility of similar relations in more complicated cases. Its practical importance lies in the avoidance of practically all calculations in obtaining potential energies from the individual bonds, especially since the 60° triangular paper on the market is ideally suited for such purposes.

The equipotential surfaces in bond space likewise turn out to be strikingly simple. Transforming to new orthogonal coordinates by means of a rotation of the a, b, c axes,

$$\begin{aligned} x &= 1/\sqrt{2}(a - b), \\ y &= 1/\sqrt{6}(a + b - 2c), \\ z &= 1/\sqrt{3}(a + b + c), \end{aligned} \quad (7)$$

we find the expression for the energy of the system using (1) and (2) becomes:

$$E = \sqrt{3}(\lambda z - (1 - \lambda)(\frac{1}{2}(x^2 + y^2))^{\frac{1}{2}}) = \sqrt{3}[\lambda z - ((1 - \lambda)/\sqrt{2})r]. \quad (8)$$

Thus it is seen that the equipotential surfaces are circular cones with their axes along the z axis, and with their apex angle $2 \tan^{-1} \lambda / (1 - \lambda)$ depending only on the ratio of additive to exchange binding. The relation exhibited by (8) that E_{ex} is simply proportional to the distance r

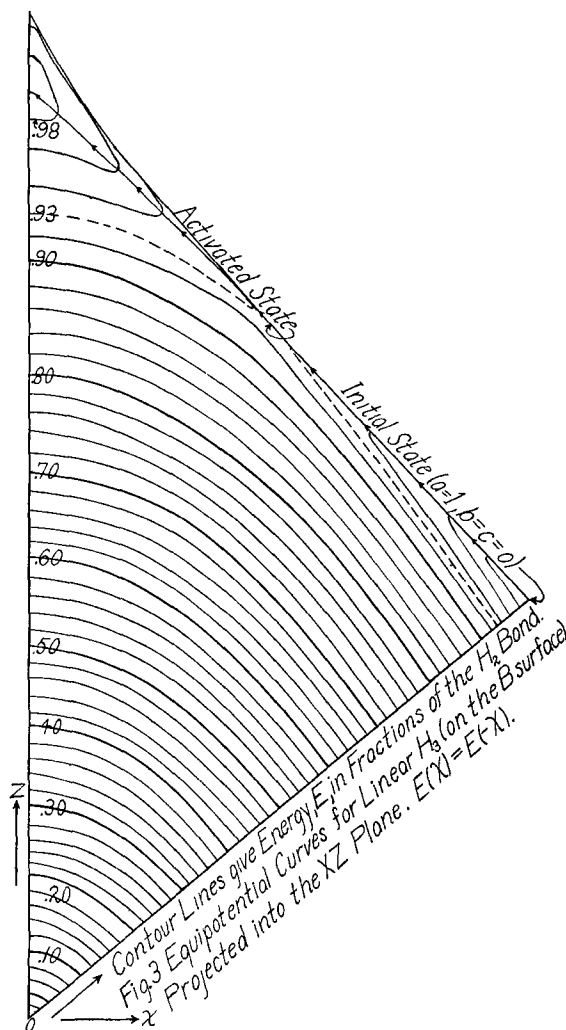


FIG. 3.

from the z axis provides an alternative proof of our previously given vector addition rule since the three valence bonds α , β , γ when plotted along their axes, a , b , c appear to make just the angles used in Fig. 2 to an observer looking down the z axis. The equipotential surfaces in bond space together with the boundary surface B determine completely the best reaction path: The intersection of the equipotentials with B traces a system of equipotential lines on B of much the same character as the system of equipotential lines found in the usual plots of a potential surface in configuration space for a three-atom problem.

In many triatomic reactions the smallest bond, c , remains very small throughout so that the

surface B can be approximated by the plane $c=0$. In this case the equipotential curves on B are simply a system of confocal ellipses generated by the intersection of the ab plane with the cones. The reaction path is then the line where either a or b has its most negative value, c being zero.

The other extreme where $|c|$ assumes comparatively large values for three-atom reactions is typified by the case of three H atoms. In Fig. 3 we have given the equipotential curves plotted on the B surface as they appear looking along the y direction in bond space. This particular projection was chosen because of the ease with which the construction can be carried out.

The potential diagram for $c=0$ is practically identical with the one for 3 H atoms in the region lying below the best reaction path indicated by arrows in Fig. 3.³ It has seemed desirable to give this brief discussion of two typical three-atom cases since the general features are just the same as for four-atom reactions.

LOCATING THE ACTIVATED CONFIGURATION OF FOUR ATOMS

It is in the application to four-atom reactions that the use of bond space instead of configuration space proves to be of real advantage. Even in the presentation of a symmetric case such as $H_2 + I_2$, the method of finding the activated state as well as the representation of the potentials in configuration space becomes extremely laborious. With the present method, a four-atom system with no symmetry at all such as $H_2 + ICl$ has been investigated and the reaction rate calculated with no unreasonable hardships.

A mechanical device for selecting configurations which, for a given pair of values a , b , have the smallest possible $|c|$ to go with it, is pictured in Fig. 4. Scales are provided on which the six interatomic distances between four atoms H, H, I, Cl are marked with their respective bond

³ As pointed out in reference 2, we are ignoring throughout configurations involving "contracted" bonds. However, if one wants to extend the B surface into this region, it results in making multiple-valued the present allowed portion of the B surface in the case when $c=0$. In the case $c \neq 0$, the extended B surface bends over completely in the direction of the z axis, crosses it and finally departs in the direction of infinite positive z .

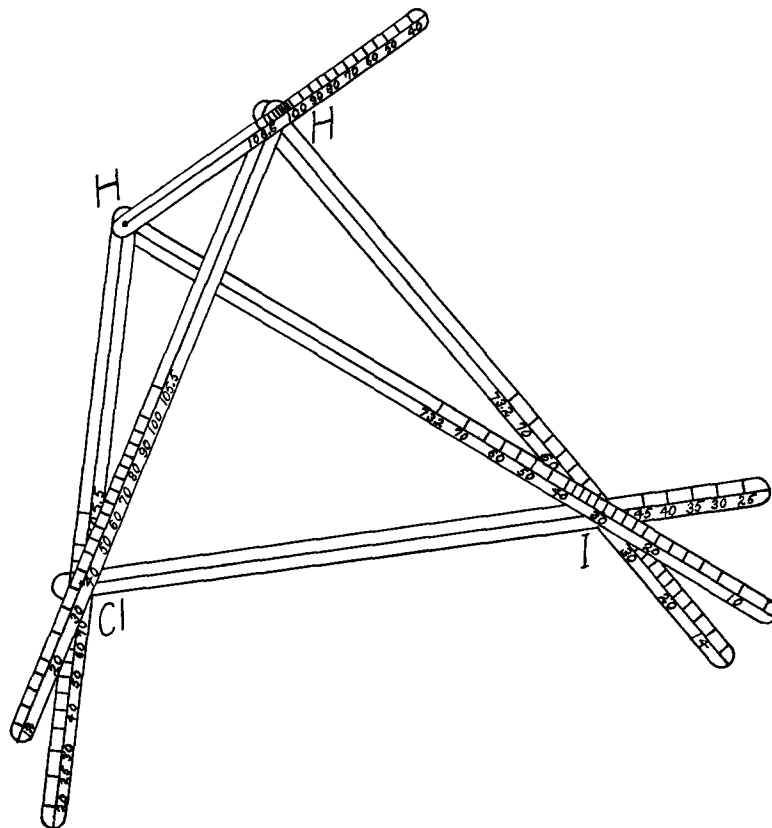


FIG. 4. Device for rapidly finding configurations which lie on the boundary surface, i.e., having the lowest sum, c , for the diagonal bonds for a given a and b . The activated configuration is the one shown.

energies and the scales so obtained attached to each other so as to present a model of the plane configurations of these four atoms. The scales are hinged by means of thumb-tacks in such a way that, without varying four of the six distances, the remaining two, let us say the diagonal ones, can be adjusted until the sum of their energies (absolute values) as read directly from their scales is a minimum. In doing this one must of course try various combinations of a_1 and a_2 which add up to the same a , and also various combinations for b , until an absolute minimum for $|c|$ is obtained. By way of emphasis we should like to point out that this method of variation leads to a unique configuration for fixed values of a and b thus establishing our previous statement that there exists a point-to-point correspondence between those points in three-dimensional bond space which lie on the surface B , and the points on the cor-

responding surface in six dimensional configuration space.

A point of the B surface can be found in a few minutes with the use of this device. A sufficient number of such combinations (a , b , c) must be found to map out the potential diagram on the B surface. A very pleasant feature of this procedure is that it enables us to describe the essential aspects of the potential surface in two-dimensional diagrams in spite of the fact that the number of parameters of the dynamical problem is six. The plot for the reaction, $\text{H}_2 + \text{ICl} \rightarrow \text{HI} + \text{HCl}$ is given in Fig. 5, showing the projection on the ab plane of the intersections of the boundary surface with the equipotential curves. An alternative way which is sometimes more satisfactory is to plot the xy projection.

Since the B surface does not depend on a particular potential law, the points (a , b , c) determined in the way described may be used for

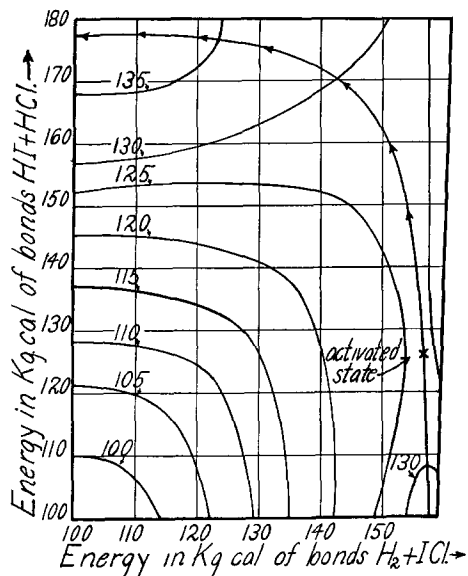


FIG. 5. Projection on the ab plane of the intersections of the equipotentials with the boundary surface B for the reaction $H_2 + ICl \rightarrow HI + HCl$.

different fractions λ of additive binding and indeed for different laws of interaction and the results compared with experiment. In this particular case we have located the activated point and determined the activation energy for 14, 17 and 20 percent of additive binding, with results given later in Table II.

The constants used in the Morse curves for the various bonds are given in Table I where the Morse curve is given by

$$E = D' [e^{-2a(r-r_0)} - 2e^{-a(r-r_0)}].$$

TABLE I.

	r_0 (Å°)	ω_0 (cm ⁻¹)	D (kcal.)	D' (kcal.)	a
H-H	0.74	4375	102.4	108.6	1.941
I-Cl	2.310	384.6	49.4	49.95	1.871
H-Cl	1.282	2840.8	101.5	105.5	1.781
H-I	1.616	2233	70.0	73.2	1.700

There is nothing in our procedure which limits us to the constant percentage rule as expressed by the constant λ in Eq. (2). We might equally well have replaced each of the energy scales in our model by a double scale giving the additive and the exchange part of the bond as separate functions of the distance.

The accuracy with which the activated configuration can be found using this easily improvised mechanical model (of a size no larger than is convenient) is more than sufficient for all practical purposes. But if greater accuracy is required, a rapidly converging mathematical procedure can be devised which renders the question of attainable accuracy merely one of how much numerical computation one is willing to bestow on the solution. Suppose that from the mechanical model we have obtained a configuration close enough to the activated one so as to make all the first derivatives $\partial E / \partial q_i$ small, and suppose that we are in possession of a complete set of second derivatives $\partial^2 E / \partial q_i \partial q_k$, taken with respect to all five "plane" coordinates q_i , for this configuration. Knowledge of these second derivatives is necessary anyway for the calculation of the characteristic vibrations, and the method for obtaining them will be described later in that connection. Denoting by Δq_i the differences of the coordinates of the true activated configuration minus the ones for the approximate one which was found, we can expand the first derivatives $\partial E / \partial q_i$ in the neighborhood of the activated point where $(\partial E / \partial q_i)_{q_0} = 0$, as follows:

$$(\partial E / \partial q_i)_{q_0 + \Delta q_i} = \sum_k (\partial^2 E / \partial q_i \partial q_k) (-\Delta q_k). \quad (9)$$

Solving this set of inhomogeneous linear equations for the quantities Δq_k and using five arbitrary quantities λ_k as multipliers, we can express our solution in a particularly condensed form as follows:

$$D \equiv \begin{vmatrix} -\sum \lambda_k \Delta q_k & \partial E / \partial q_1 & \partial E / \partial q_2 & \cdots & \partial E / \partial q_5 \\ \lambda_1 & \partial^2 E / \partial q_1 \partial q_1 & \partial^2 E / \partial q_1 \partial q_2 & \cdots & \partial^2 E / \partial q_1 \partial q_5 \\ \lambda_2 & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \lambda_5 & \partial^2 E / \partial q_5 \partial q_1 & \cdot & \cdots & \partial^2 E / \partial q_5 \partial q_5 \end{vmatrix} = 0. \quad (10)$$

TABLE II.

	Config.*	H-H r_1	I-Cl r_2	H-Cl r_3	H-I r_4	H-Cl r_5	H-I r_6	$\partial E/\partial q_1$	$\partial E/\partial q_2$	$\partial E/\partial q_3$	$\partial E/\partial q_4$	$\partial E/\partial q_5$
17%	1	.8033	2.335	1.597	2.264	2.214	2.475	2.966	-4.022	-3.831	-1.519	.795
	2	.8048	2.354	1.597	2.200	2.195	2.460	.395	-.399	.158	.200	-.513
20%	1	.791	2.346	1.564	2.372	2.166	2.548	1.071	.229	-1.050	-4.143	-1.415
	2	.792	2.345	1.564	2.330	2.190	2.508	.037	-.06	.80	.48	.06
14%	1	.830	2.39	1.61	2.08	2.24	2.41					

* 1 and 2 refer to the preliminary and the improved configuration. Distances are given in Å units.

From (10) a particular Δq_p is determined by putting the corresponding $\lambda_p = 1$ and all the other λ 's equal to 0. For practical computation it is very convenient to first reduce the determinant D to diagonal form except for the first row and the first column, thus obtaining all quantities Δq_i at once. These five quantities define a certain change in the originally assumed configuration, a change which can be carried out graphically with great ease and precision. For this new configuration the first derivatives $\partial E/\partial q_i$ may be recalculated and the improvement obtained in locating the activated point may be judged by the decreases simultaneously obtained in all five derivatives. The process has been applied to the activated configurations of $H_2 + ICl$ both for $\lambda = 17$ percent and 20 percent, with results tabulated in Table II. The simultaneous decrease of all five derivatives by approximately a factor 0.10 must be very striking to anyone who tries to improve the approximate configuration in a less systematic fashion. The activation energies E_c (see Fig. 6) for 14 percent and for 20 percent were found to be 41.2 and 24.9 kcal., respectively. By linear interpolation a percentage of 17 was indicated as giving $E_c = 33$. The experimental value of E is approximately 34 kcal.⁴ The activated point for 17 percent was then actually determined and gave an activation energy $E_c = 32.8$ kcal. The activated configuration for 14 percent was not determined with the same accuracy as for the other two cases. Sherman and Li⁵ have calculated a value of 24.6 kcal. using 14 percent

additive binding in agreement with the value given here.

THE VIBRATIONS OF THE ACTIVATED STATE (VIBRATIONS OF PLANE CONFIGURATIONS OF FOUR UNLIKE ATOMS)

Six of the twelve modes of motion of four atoms arranged in a plane involve a change in the relative positions of the atoms while the other six amount to rigid translations or rotations of the whole molecule, and proceed without change in the potential energy. Of the "internal" motions, five preserve the plane arrangement of the four atoms whereas the sixth involves displacements different in sign for adjacent atoms and at right angles to the plane of equilibrium. Since this plane is obviously a plane of symmetry for the molecule, this last mode belongs to a symmetry class different from the rest and the secular equation will split into two factors of first and fifth degree, respectively. There are no other symmetry conditions imposed on the activated configuration as there is in reactions of the type $H_2 + I_2 \rightarrow 2HI$ where the secular equation decomposes into $1+2+3$ degrees of freedom.⁶

We consider first the vibrations where the plane arrangement is preserved but ignore translational motions in this plane by keeping the center of gravity fixed at the origin. Tentatively we introduce 6 parameters the meaning of which is apparent from Fig. 7 and the following remarks: q_3 is the distance between the two centers of gravity of m_1 with m_2 and m_3 with m_4 . One of these centers of gravity separates q_1 into

⁴ Bonner, Gore and Yost, J. Am. Chem. Soc. **57**, 2723 (1935).

⁵ Sherman and Li, J. Am. Chem. Soc. **58**, 690 (1936).

⁶ Wheeler, Topley and Eyring, J. Chem. Phys. **4**, 178 (1936).

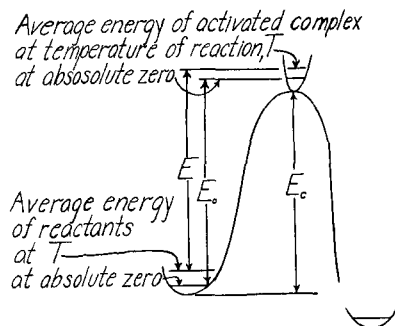


FIG. 6. Activation energies: E is the usual difference in average energies at temperature of reaction; E_0 = activation energy at absolute zero; E_c = "classical" activation energy at absolute zero. All are useful quantities in the theoretical treatment of reaction rates.

two parts in the ratio $\rho : (1-\rho)$ and the other separates q_2 in the ratio $\sigma : (1-\sigma)$. These six coordinates not only describe the relative positions of the four particles but also the angular position φ of the whole system relative to a reference line R fixed in the plane. Thus the kinetic energy, when expressed in all six parameters, includes a part arising from rotations in the plane which can be separated from the rest because such a motion involves no changes in the potential energy.

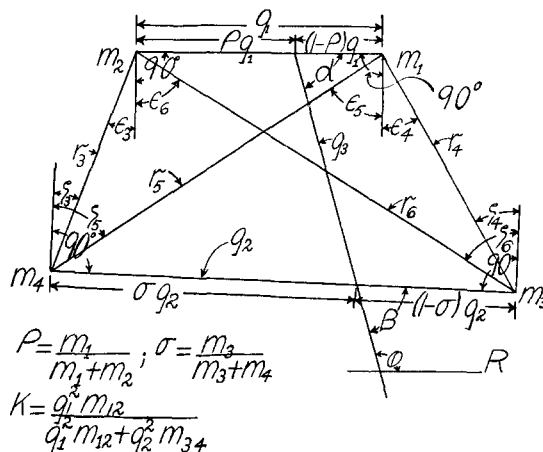


FIG. 7. Notation used in treating four atoms.

The final coordinates were chosen in such a manner as to give a sum of square terms for the kinetic energy. This determines the coordinates, of course, only to within an orthogonal transformation, but the rotational coordinate Φ is uniquely determined by the requirement that it be normal to all the other coordinates none of which can involve the parameter φ .

The expression for the kinetic energy in terms of the parameters defined in Fig. 7 is easily calculated to be:

$$2K = m_{12}\dot{q}_1^2 + m_{34}\dot{q}_2^2 + m_{1234}\dot{q}_3^2 + a\dot{\varphi}^2 + b(2\dot{\varphi}\dot{\alpha} + \dot{\alpha}^2) + c(2\dot{\varphi}\dot{\beta} + \dot{\beta}^2), \quad (11)$$

where m_{12} , m_{34} and m_{1234} are reduced masses of m_1 with m_2 , m_3 with m_4 , $m_1 + m_2$ with $m_3 + m_4$ respectively, and where a , b , c stand for

$$a = \sum_1^4 m_i R_i^2, \quad b = q_1^2 m_{12}, \quad c = q_2^2 m_{34}.$$

The R 's measure distances from the center of gravity of the system. The last three terms of (11) are easily transformed into a sum of squares if we substitute

$$\dot{u} = \dot{\varphi}(a - b - c)^{1/2}, \quad \dot{v} = b^{1/2}(\dot{\alpha} + \dot{\varphi}), \quad \dot{w} = c^{1/2}(\dot{\beta} + \dot{\varphi}),$$

which property is preserved under any orthogonal transformation, in particular the following one:

$$\begin{aligned} U &= a^{-1/2}((a - b - c)^{1/2}u + b^{1/2}v + c^{1/2}w), \\ V &= [(a - b - c)/(a(b + c))]^{1/2}[-(b + c)/(a - b - c)^{1/2}u + b^{1/2}v + c^{1/2}w], \\ W &= (b + c)^{-1/2}(c^{1/2}v - b^{1/2}w). \end{aligned} \quad (12)$$

Substituting for these variables in terms of the original parameters φ , α , β and also for a , b , c we obtain:

$$2K = m_{12}\dot{q}_1^2 + m_{34}\dot{q}_2^2 + m_{1234}\dot{q}_3^2 + \left[\frac{q_1^2 m_{12} + q_2^2 m_{34}}{\sum m_i R_i^2} \right] \dot{q}_4^2 + \frac{q_1^2 q_2^2 m_{12} m_{34}}{q_1^2 m_{12} + q_2^2 m_{34}} \dot{q}_5^2 + \frac{\dot{\Phi}^2}{\sum m_i R_i^2}, \quad (13)$$

where $q_4 = k\alpha + (1-k)\beta = (q_1^2 m_{12}\alpha + q_2^2 m_{34}\beta)(q_1^2 m_{12} + q_2^2 m_{34})^{-1}$, $q_5 = \alpha - \beta$,

$$\dot{\Phi} = \sum m_i R_i^2 \dot{\varphi} + q_1^2 m_{12} \dot{\alpha} + q_2^2 m_{34} \dot{\beta}. \quad (14)$$

The newly defined coordinates q_4 and q_5 do not involve the angle φ and are thus orthogonal to the rotations of the system as a whole. The rotational coordinate is thus Φ ; since it does not enter into the potential function for the system, it may be omitted from further consideration.

As was stated previously there exists but one internal degree of freedom which carries the four particles out of their plane of equilibrium $z=0$. Indeed, of the four independent motions involving displacements z_i at right angles to the equilibrium plane we may choose two as the rotations r_x and r_y , and a third as the translation t_z , and represent them by the following coordinates:

$$\begin{aligned} r_x &= \sum m_i z_i x_i = q_1 m_{12} \sin \alpha (z_1 - z_2) + q_2 m_{34} \sin \beta (z_3 - z_4), \\ r_y &= \sum m_i z_i y_i = (q_3 / \sum m_i) \{ -(m_3 + m_4)(m_1 z_1 + m_2 z_2) + (m_1 + m_2)(m_3 z_3 + m_4 z_4) \}, \\ t_z &= \sum m_i z_i. \end{aligned}$$

The internal motion is then completely determined by the requirement that its coordinate q_6 be orthogonal to r_x , r_y , t_z . Let q_6 be a linear function of the z displacements $q_6 = \sum \sigma_i z_i$, then the following relations must hold among the σ 's:

$$\sum_{i=1}^4 m_i \sigma_i x_i = 0, \quad \sum_{i=1}^4 m_i \sigma_i y_i = 0, \quad \sum_{i=1}^4 m_i \sigma_i = 0.$$

Thus we find by a simple elimination process, that q_6 is proportional to:

$$q_6 \sim \begin{vmatrix} z_1 & z_2 & z_3 & z_4 \\ q_1 m_{12} \sin \alpha & -q_1 m_{12} \sin \alpha & q_2 m_{34} \sin \beta & -q_2 m_{34} \sin \beta \\ q_1 m_{12} \cos \alpha - m_1 q_3 \frac{m_3 + m_4}{\sum m_i} & -q_1 m_{12} \cos \alpha - m_2 q_3 \frac{m_3 + m_4}{\sum m_i} & q_2 m_{34} \cos \beta + m_3 q_3 \frac{m_1 + m_2}{\sum m_i} & -q_2 m_{34} \cos \beta + m_4 q_3 \frac{m_1 + m_2}{\sum m_i} \\ m_1 & m_2 & m_3 & m_4 \end{vmatrix}.$$

One possible way of describing the internal motion connected with q_6 is the following:

$$\begin{aligned} \Delta z_1 &= \Delta q_6 \left[\frac{\cot \alpha - \cot \beta}{q_3(m_1 + m_2)} + \frac{1}{q_1 m_1 \sin \alpha} \right], & \Delta z_3 &= \Delta q_6 \left[\frac{-\cot \alpha - \cot \beta}{q_3(m_3 + m_4)} - \frac{1}{q_2 m_3 \sin \beta} \right], \\ \Delta z_2 &= \Delta q_6 \left[\frac{\cot \alpha - \cot \beta}{q_3(m_1 + m_2)} - \frac{1}{q_1 m_2 \sin \alpha} \right], & \Delta z_4 &= \Delta q_6 \left[\frac{-\cot \alpha - \cot \beta}{q_3(m_3 + m_4)} + \frac{1}{q_2 m_4 \sin \beta} \right]. \end{aligned} \quad (15)$$

The displacements (15) comply with the three conditions:

$$\sum m_i x_i \Delta z_i = 0, \quad \sum m_i y_i \Delta z_i = 0, \quad \sum m_i \Delta z_i = 0,$$

as can be readily established. Thus they are orthogonal to the three rigid motions (Δr_x , Δr_y , Δt_z), and of course also to the other modes which do not involve z_i . Using (15), the kinetic energy K_6 associated with q_6 is then

$$2K_6 = \dot{q}_6^2 \left[\left(\frac{\cot \alpha - \cot \beta}{q_3} \right)^2 \left(\frac{1}{m_1 + m_2} + \frac{1}{m_3 + m_4} \right) + \left(\frac{1}{q_1 \sin \alpha} \right)^2 \frac{1}{m_{12}} + \left(\frac{1}{q_2 \sin \beta} \right)^2 \frac{1}{m_{34}} \right].$$

The next problem is the computation of the force constants of the activated configuration. Since the activated configuration, like a stable configuration of atoms, has a stationary value of the interaction energy, it is actually in stable equilibrium in all degrees of freedom except the one along which

the reaction proceeds. That means that all first derivatives $\partial E/\partial q_\alpha$ are 0 and that for small displacements from the activated configuration the energy function can be expanded:

$$dE = \sum_{\alpha\beta} \frac{\partial^2 E}{\partial q_\alpha \partial q_\beta} dq_\alpha dq_\beta. \quad (16)$$

The second derivatives in (16) are force constants for small displacements from equilibrium. When transformed into a sum of squares, only one force constant in (16) will exhibit a negative sign.

It has been preferable here to follow an explicit analytical procedure in deriving numerical values for the force constants rather than the previously followed methods which though applicable in simpler cases become excessively laborious for more degrees of freedom. One other fact should be borne in mind. The present method of second derivatives gives the force constants for infinitesimal vibrations so that in case of considerable anharmonicities they may not give the correct frequencies of finite vibrations.

Formulas necessary for the calculation of the second derivatives are presented in Tables III, IV and V. Formulas in IV and V are of course perfectly general and depend only on the geometry of the quadrilateral (Fig. 7). They give only first derivatives since tabulation of all second derivatives would require too much space; however, calculation of the second derivatives $\partial^2 r_i/\partial q_\alpha \partial q_\beta$ from IV, V requires no further consideration of Fig. 7.

The second derivative $\partial^2 E/\partial q_6^2$ remains to be calculated. We have

$$\frac{\partial^2 E}{\partial q_6^2} = \sum_i \frac{\partial^2 E}{\partial r_i \partial r_i} \frac{dr_i}{\partial q_6} \frac{dr_i}{\partial q_6} + \sum_i \frac{\partial E}{\partial r_i} \left\{ \frac{\partial^2 r_i}{\partial z_i^2} \left(\frac{\partial z_i}{\partial q_6} \right)^2 + \frac{dr_i}{dz_i} \frac{\partial^2 z_i}{\partial q_6^2} \right\}, \quad (17)$$

which reduces to

$$\frac{\partial^2 E}{\partial q_6^2} = \sum_i \frac{\partial E}{\partial r_i} \frac{\partial \alpha_i}{\partial r_i} \frac{1}{r_i} \left[\frac{d}{dq_6} (z_{i2} - z_{i1}) \right]^2 \quad (18)$$

since all the derivatives $\partial r_i/\partial q_6$ are zero on account of the symmetry character of this mode of motion (all the r 's are minima in the plane arrangement) and since

$$\frac{\partial^2 z_i}{\partial q_6^2} = 0 \quad \text{and} \quad \frac{\partial^2 r_i}{\partial z_i^2} = \frac{1}{r_i}.$$

Here the z_i in (17) refer to the z projections of the distances r_i and the quantities z_{i1} and z_{i2} in (18) refer to the two end-points of the interatomic distances r_i . Thus the force constant is given by (18) and all the mixed derivatives involving q_6 vanish identically.

THE VIBRATION FREQUENCIES FOR THE REACTION $\text{H}_2 + \text{ICl} \rightarrow \text{HI} + \text{HCl}$

In evaluating the terms for the kinetic and the potential energy using 17 percent additive binding we are led to the following secular equations for the five normal vibrations in a plane:

$$\begin{vmatrix} (402.82 - .25X) & 5.29 & 93.30 & 107.33 & .87 \\ 5.29 & (246.10 - 13.86X) & 5.72 & 34.54 & 7.78 \\ 93.30 & 5.72 & (-62.70 - .9879X) & -78.64 & -20.12 \\ 107.33 & 34.54 & -78.64 & (112.37 - 3.99X) & 39.50 \\ .87 & 7.78 & -20.12 & 39.50 & (29.86 - .161X) \end{vmatrix} = 0.$$

The twisting vibration out of the plane is given by the equation $272.88 - 1.5788X = 0$. Here the force constants are in units of kcal. per mole \AA^{-2} and in the kinetic energy mass is expressed in molecular weights and distance in angstroms (where distance occurs). The six characteristic frequencies ν_i for

TABLE III.

$E = \lambda(a+b+c) - (1-\lambda)R.$					
Here	$R = [\frac{1}{2}((a-b)^2 + (b-c)^2 + (c-a)^2)]^{\frac{1}{2}}$ and $a = a_1 + a_2, \quad b = b_1 + b_2, \quad c = c_1 + c_2$				
	$\frac{\partial^2 E}{\partial q_\alpha \partial q_\beta} = \sum_i \frac{\partial E}{\partial r_i} \frac{\partial^2 r_i}{\partial q_\alpha \partial q_\beta} + \sum_{i,k} \frac{\partial^2 E}{\partial r_i \partial r_k} \frac{\partial r_i}{\partial q_\alpha} \frac{\partial r_k}{\partial q_\beta}$		$\frac{\partial E}{\partial a_1} = \frac{\partial E}{\partial a_2} = \lambda - \frac{3}{2} \frac{(1-\lambda)}{R} a + \frac{1}{2} \frac{(1-\lambda)}{R} (a+b+c)$		
	$\frac{\partial E}{\partial r_i} = \frac{\partial E}{\partial \alpha_i} \frac{\partial \alpha_i}{\partial r_i} = \frac{\partial E}{\partial a_i} \frac{\partial a_i}{\partial r_i}$		$\frac{\partial^2 E}{\partial a_1^2} = \frac{\partial^2 E}{\partial a_2^2} = \frac{\partial^2 E}{\partial a_1 \partial a_2} = -\frac{3}{4} \frac{1-\lambda}{R^3} (b-c)^2$		
	$\frac{\partial^2 E}{\partial r_i \partial r_k} = \frac{\partial^2 E}{\partial a_i \partial a_k} \frac{\partial a_i}{\partial r_i} \frac{\partial a_k}{\partial r_k} + \delta_{i,k} \frac{\partial E}{\partial a_i} \frac{\partial^2 a_i}{\partial r_i \partial r_k}$		$\frac{\partial^2 E}{\partial a_i \partial b_i} = -\frac{3}{4} (1-\lambda) \left[\frac{(a-b)^2}{R^3} - \frac{1}{R} \right] = \frac{\partial^2 E}{\partial c_i^2} + \frac{3}{4} \frac{(1-\lambda)}{R} \quad i=1, 2.$		

TABLE IV. Formulas $\partial r_i / \partial q_i$ valid for any configuration of four atoms in a plane. Notation as in Fig. 7.

	q_1	q_2	q_3	q_4	q_5
r_1	1	0	0	0	0
r_2	0	1	0	0	0
r_3	$-\rho \sin \epsilon_3$	$\sigma \sin \zeta_3$	$\sin (\alpha - \epsilon_3)$	$q_3 \cos (\alpha - \epsilon_3)$	$-\rho(1-k)r_1 \cos \epsilon_3 - \sigma k r_2 \cos \zeta_3$
r_4	$-(1-\rho) \sin \epsilon_4$	$(1-\sigma) \sin \zeta_4$	$\sin (\alpha + \epsilon_4)$	$q_3 \cos (\alpha + \epsilon_4)$	$(1-\rho)(1-k)r_1 \cos \epsilon_4 + (1-\sigma)k r_2 \cos \zeta_4$
r_5	$(1-\rho) \sin \epsilon_5$	$\sigma \sin \zeta_5$	$\sin (\alpha - \epsilon_5)$	$q_3 \cos (\alpha - \epsilon_5)$	$(1-\rho)r_1(1-k) \cos \epsilon_5 - \sigma k r_2 \cos \zeta_5$
r_6	$\rho \sin \epsilon_6$	$(1-\sigma) \sin \zeta_6$	$\sin (\alpha + \epsilon_6)$	$q_3 \cos (\alpha + \epsilon_6)$	$-\rho(1-k)r_1 \cos \epsilon_6 + (1-\sigma)k r_2 \cos \zeta_6$

TABLE V. Derivatives of ϵ_i , α and β with respect to the coordinates q_k .

	q_1	q_2	q_3	q_4	q_5
ϵ_3	$-\frac{\rho}{r_3} \cos \epsilon_3$	$\frac{\sigma}{r_3} \cos \zeta_3$	$-\frac{1}{r_3} \cos (\alpha - \epsilon_3)$	$\frac{q_3}{r_3} \sin (\alpha - \epsilon_3)$	$\frac{1}{r_3} [\rho r_1(1-k) \sin \epsilon_3 + \sigma r_2 k \sin \zeta_3] + 1 - k$
ϵ_4	$-\frac{1-\rho}{r_4} \cos \epsilon_4$	$\frac{1-\sigma}{r_4} \cos \zeta_4$	$\frac{1}{r_4} \cos (\alpha + \epsilon_4)$	$-\frac{q_3}{r_4} \sin (\alpha + \epsilon_4)$	$-\frac{1}{r_4} [(1-\rho)r_1(1-k) \sin \epsilon_4 - (1-\sigma)r_2 k \sin \zeta_4] - 1 + k$
ϵ_5	$\frac{1-\rho}{r_5} \cos \epsilon_5$	$\frac{\sigma}{r_5} \cos \zeta_5$	$-\frac{1}{r_5} \cos (\alpha - \epsilon_5)$	$\frac{q_3}{r_5} \sin (\alpha - \epsilon_5)$	$-\frac{1}{r_5} [(1-\rho)r_1(1-k) \sin \epsilon_5 + \sigma r_2 k \sin \zeta_5] + 1 - k$
ϵ_6	$\frac{\rho}{r_6} \cos \epsilon_6$	$\frac{1-\sigma}{r_6} \cos \zeta_6$	$\frac{1}{r_6} \cos (\alpha + \epsilon_6)$	$-\frac{q_3}{r_6} \sin (\alpha + \epsilon_6)$	$\frac{1}{r_6} [\rho r_1(1-k) \sin \epsilon_6 - (1-\sigma)r_2 k \sin \zeta_6] - 1 + k$
α	0	0	0	1	$1 - k$
β	0	0	0	1	$1 - k$

The corresponding derivatives for the angle ζ_i follow from the same table as the ϵ_i by use of the identities: $\epsilon_i - \zeta_i = \pm(\alpha - \beta)$ $i=3, 4, 5, 6$, where the plus sign goes with $i=3, 5$ and the minus sign goes with $i=4, 6$. The geometrical significance of the symbols is given in Fig. 7.

TABLE VI.

Activated configuration for	Moments of Inertia (gram atom, A^2)			Frequencies of char. vibrations				(cm ⁻¹)		Act. Energy E_c (kcal.)
	A_3	B_3	C_3	ν_1	ν_2	ν_3	ν_4	ν_5	ν_n	
17%	152.95	5.81	158.76	4391.	1580.	1426.	481.	435.	11128	32.8
20% additive binding	158.54	6.00	164.54	4696.	1522.	1344.	550.	442.	933	24.9

17 percent additive binding are given in Table VI in wave numbers. They are obtained from the six roots X_i of the secular equations by the simple relationship $\nu_i = 108.46X_i^{\frac{1}{2}}$.

The corresponding secular equations for 20 percent additive binding are:

$$\begin{vmatrix} (465.07 - .25X) & -2.48 & 76.26 & 81.46 & -2.11 \\ -2.48 & (252.68 - 13.86X) & 11.65 & 38.50 & 6.60 \\ 76.26 & 11.65 & (-47.14 - .9878X) & -46.41 & -19.00 \\ 81.46 & 38.50 & -46.41 & (148.57 - 3.99X) & 34.62 \\ -2.11 & 6.60 & -19.00 & 34.62 & (26.96 - .1565X) \end{vmatrix} = 0$$

and $250.08 - 1.631X = 0$.

THE RATE OF REACTION

The general expression for the rate of a reaction of this type has been given.^{7, 6} Thus we have the equation

$$k_1 = \kappa \left(\frac{m_3'}{m_1' m_2'} \right)^{\frac{1}{2}} \frac{\sigma_1 \sigma_2}{\sigma_3} \frac{5.785 \times 10^{14}}{T} \frac{(A_3' B_3' C_3')^{\frac{1}{2}}}{I_1' I_2'} \frac{\left(2 \sinh \frac{h\nu_1}{2kT} \right) \left(2 \sinh \frac{h\nu_2}{2kT} \right)}{\prod_{i=1}^5 \left(2 \sinh \frac{h\nu_i}{2kT} \right)} \times \left(1 - \frac{1}{24} \left(\frac{h\nu_n}{kT} \right)^2 \right) \exp \left(-\frac{E_c}{kT} \right). \quad (19)$$

Here the subscripts 1 and 2 refer to the hydrogen and iodine chloride molecules, respectively, and 3 to the activated complex. κ , m_i' , σ_i and ν_i refer to the transmission coefficient which we take equal to unity, the mass of the i th molecule, the rotational symmetry number and the frequency respectively. $A_3 B_3 C_3$ are the three principal moments of inertia of the activated complex and I_1' and I_2' the moments of inertia of the hydrogen and iodine chloride molecules respectively. ν_n is the imaginary mode of vibration normal to the barrier. The primes indicate that masses are to be taken in molecular weight units and lengths in angstroms in which case k_1 is given in the units cc moles⁻¹ sec.⁻¹.

If, as is usual we define the energy of activation as

$$E = kT^2 d \log (k/T^{\frac{1}{2}}) / dT$$

$$\text{we have} \quad E = E_0 + \sum_{i=1}^5 \frac{h\nu_i}{\exp(h\nu_i/kT) - 1} - \frac{h\nu_1}{\exp(h\nu_1/kT) - 1} - \frac{h\nu_2}{\exp(h\nu_2/kT) - 1} - \frac{3}{2}kT$$

$$\text{and} \quad E_0 = E_c + \sum_{i=1}^5 \frac{1}{2}h\nu_i - \frac{1}{2}(h\nu_1 + h\nu_2).$$

⁷ Eyring, J. Chem. Phys. **3**, 107 (1935), Eq. (7).

We thus obtain for 17 percent additive binding $E_c = 32.8$; $E_0 = 37.85$ and $E = 36.62$ at 503.2° . For 20 percent additive binding $E_c = 24.9$; $E_0 = 30.29$; $E = 29.04$. Now defining three A 's by the following equations

$$k = A_c e^{-E_c/kT} = A_0 e^{-E_0/kT} = A e^{-E/kT}$$

we obtain Table VII.

These values are to be compared with the experimentally obtained specific reaction rate of Bonner, Gore and Yost.⁴ We change k from their units to cc mole⁻¹ sec.⁻¹ and so obtain $k = .52 = 1.64 \times 10^{15} e^{-33,900/k478.2}$; $2.8 = 1.49 \times 10^{15} e^{-33,900/k503.2}$ and $5.8 = 1.60 \times 10^{15} e^{-33,900/k513.2}$

By inspection of Table VII we see that A is independent of whether 20 percent or 17 percent additive binding is used. This is important since this means it is uniquely fixed by the potential function and depends on no arbitrary constant. If the percentage additive binding were raised to a fraction over 20 percent E would be lowered by a calorie to 28 kcal. and k would then agree rather well with the experimental values. The theoretical k would, however, not increase with temperature as fast as the experimental value does. Thus, if Bonner, Gore and Yost are, as they

TABLE VII.

% additive	T	k	$A_c \times 10^{10}$	$A_0 \times 10^{13}$	$A \times 10^{12}$
17	478.2	7.44×10^{-5}	7.36	1.50	4.11
17	503.2	5.12×10^{-4}	9.06	1.46	4.16
17	513.2	1.03×10^{-3}	9.64	1.37	4.09
20	478.2	2.28×10^{-1}	5.51	1.60	4.30
20	503.2	1.01	6.61	1.46	4.17
20	513.2	1.79	7.26	1.43	4.21

believe, actually measuring the reaction rate here calculated and if their values of k are dependable then our calculated A is too small by a factor of ≈ 350 . A would be increased by this amount if the three lowest frequencies are actually around 50 wave numbers instead of the calculated values. Such a change would also reduce the excess ($E_0 - E_c$) of the zero-point energy in the activated state over that in the initial state to practically zero. More experiments seem necessary before any of these quantities can be assigned from experiment with assurance. The corresponding isotopic reactions will also be useful in calculating $E_0 - E_c$. Extensive accurate data on reactions of this type will be particularly valuable in determining the accuracy and in suggesting methods for improving the calculation of potential functions of activated complexes.

The Diamagnetic Anisotropy of Aromatic Molecules

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Values of the diamagnetic anisotropy of benzene and other aromatic hydrocarbon molecules are calculated on the basis of the assumption that the p_z electrons (one per aromatic carbon atom) are free to move from carbon atom to adjacent carbon atom under the influence of the impressed fields. When combined with the assumed values for the contributions of the other electrons (-2.0×10^{-6} for hydrogen, -4.5×10^{-6} for aromatic carbon, -6.0×10^{-6} for aliphatic carbon) these lead to principal diamagnetic susceptibilities of molecules in approximate agreement with the available experimental data. The diamagnetic anisotropy of graphite is also discussed.

CERTAIN diamagnetic crystals, such as bismuth and graphite, show pronounced diamagnetic anisotropy, the susceptibility being of normal magnitude in the basal plane and abnormally large in the direction perpendicular to this plane. A similar phenomenon is shown by

crystals of aromatic substances. It has been pointed out by Krishnan and his collaborators¹ that the magnitudes and orientations of the principal axes of the susceptibility ellipsoid of

¹ (a) K. S. Krishnan, Proc. Ind. Sci. Cong., Madras Session, January, 1929; (b) K. S. Krishnan, B. C. Guha and S. Banerjee, Phil. Trans. Roy. Soc. **A231**, 235 (1933); (c) K. S. Krishnan and S. Banerjee, *ibid.* **A234**, 265 (1935).

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