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THE NATURE OF ACTIVATION HEATS. A CALCULATION OF THE HEAT OF ACTIVATION FROM BAND SPECTRA DATA

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When one compares the heat of activation in a chemical reaction with the heats of dissociation of one of the reacting molecules into its component parts (*cf.* Tables I, II and III), the conclusion may be drawn that activation is not, in general, a dissociation but must be essentially an interaction between two molecules, in which both take part and which could not occur except for the presence of the second molecule. In the present paper this idea will be applied in detail to the hydrogen iodide decomposition, as the

TABLE I

DISSOCIATION ENERGETICS

Activation heats taken from Hinshelwood, "The Kinetics of Chemical Change in Gaseous Systems," Oxford, **1926**. Heats of dissociation calculated from data in Tables II and III. Value for Cl + ClO taken as one-half "atomic" heat of formation of Cl_2O. Value in parentheses for H + I indicated from convergence limit [Tingey and Gerke, THIS JOURNAL, **48**, 1838 (1926)], but uncorrected for the fact that absorbing molecules may be in a higher quantum state than the zero-th. Heat of activation for ammonia estimated (Hinshelwood, p. 93). Heat of activation for N_2O_5 decomposition given in parentheses corrected to ten degrees of freedom by formula

$$E_{\text{corr.}} = E_{\text{obs.}} + 2.303RT[((n/2) - 1)]$$

Substance	Products	Heat of dissociation, kg. cal.	Homogeneous heat of activation
N_2O_5	$N_2O_4 + O$	71	24.7
	$N_2O_3 + O_2$	20.2	
	$2NO + O$	251	
	$NO + NO_2 + O_2$	28.5	(30.4)
	$N_2O + 2O_2$	18.4	
	$N_2 + 2O_2 + O$	68	
N_2O	$N_2 + O$	48	59.4
	$N + NO$	110.5	
O_3	$O_2 + O$	35	26.0
Cl_2O	$Cl_2 + O$	52	21.4
	$Cl + ClO$	(55)	
HI	H + I	68.9 (64.4)	44.7
NH_3	$NH + H_2$	64.8	(70.0)

TABLE II

HEATS OF FORMATION OF THE ELEMENT MOLECULES

Substance	Kg. cal.	Reference
H_2	101	Witmer, *Proc. Nat. Acad. Sci.*, **12**, 238 (1926)
N_2	219	Mulliken, *Phys. Rev.*, **32**, 761 (1928) Birge, *Nature*, **122**, 842 (1928)
O_2	139	Herzberg, *Z. physik. Chem.*, **4B**, 223 (1929) Birge, *Trans. Faraday Soc.*, **25**, 707 (1929)
I_2	35.2	Kuhn, *Z. Physik*, **39**, 77 (1926)
Cl_2	58.5	Kuhn, *Z. Physik*, **39**, 77 (1926)
$C_{dia.}$	141	Kohn and Guckel, *Naturwissenschaften*, **12**, 139 (1924)

TABLE III

ATOMIC HEATS OF FORMATION (*i. e.*, FROM THE GASEOUS ATOMS)

Group	N_2O_5	N_2O_4	N_2O_3	NO	NO_2	N_2O	Cl_2O	HI	NH_3	NH	O_3
Heat, kg. cal.	565	494	406	157	240	267	110	68.9 (64.4)	274.1	108.3	174

References: Landolt-Börnstein, "Tabellen," Vol. V, pp. 1485, 1490, 1493, 1495, 1496; Hodgman-Lange, "Handbook of Chemistry and Physics," 13th ed., Chemical Rubber Publishing Co., Cleveland, Ohio, **1928**, p. 574; Villars, THIS JOURNAL, **51**, 2374 (1929).

experimental data[1,2] for this reaction are the most accurate, and it will be shown that we can account qualitatively for its heat of activation if we make use of certain simple principles taught by the quantum mechanics.

These principles are the following. First, Franck[3] has shown that the electronic excitation of a molecule takes place instantaneously compared to its vibrational period, and that the separation of the nuclei can be considered to remain unchanged during the light absorption.[4] Condon[5] extended this principle by assuming that, for most of the time, the nuclei occupied those positions at the extremities of their vibrations, as it was here that the velocity of their motions was least. He was successful in explaining certain peculiarities of the intensity distribution in band spectra which had been mystifying up to that time, and has since shown how these considerations are in harmony with the quantum mechanics.[6]

Second, one of the characteristic differences between the quantum mechanics and the classical mechanics has been that the former takes account of degeneracy introduced by the fact that an electron, for example, in the H_2^+ ion may belong as well to a second similar atom as to the first one and have the same energy value. This degeneracy causes a probability distribution of the electron between the two atoms; if we think of the separate atoms and not the molecule, as a whole, the electron can be considered as belonging to one atom at one moment; at a later moment it may

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[1] Bodenstein, *Z. physik. Chem.*, **29**, 295 (1899).

[2] Kistiakowsky, THIS JOURNAL, **50**, 2315 (1928).

[3] Franck, *Trans. Faraday Soc.*, **21**, 536 (1926).

[4] *Cf.* also Villars, *Nature*, **123**, 240 (1929).

[5] Condon, *Phys. Rev.*, **28**, 1182–1201 (1926).

[6] Condon, *ibid.*, **32**, 858 (1928); *Proc. Nat. Acad. Sci.*, **13**, 462 (1927).

change its allegiance to the other atom, although it does not change its position nor its energy. This idea may be extended to a system of atoms and it is just as reasonable to expect that two of these atoms may change their allegiance, provided the energy of the second state is equal to that of the first. Thus, in the decomposition of hydrogen iodide, if two molecules, H_aI_a and H_bI_b collide, two kinds of allegiance exchange are possible. After the collision, H_a may owe allegiance to I_b and H_b to I_a. This is similar to the case mentioned above of the molecular hydrogen ion. The energy perturbation arising in this case of degeneracy will account, in part, for the van der Waals attraction between the two molecules. But a second case is possible, where H_a may owe its allegiance to H_b and I_a to I_b. If this occurs, a chemical reaction has taken place.[7]

Our picture, then, of chemical activation, or rather of chemical reaction, for activation is concomitant with reaction, is that of a collision in which the nuclear separations of the atoms are such that the latter can change allegiance without changing their total energy content. Expressed in an equation, chemical reaction can occur only when

$$x + y - 1.4 = a + b \tag{1}$$

where x and y are the internal energies of the two colliding hydrogen iodide molecules, a and b the internal energies of the hydrogen and iodine molecules, respectively, and -1.4 is the heat of reaction.[8] In the following calculations these energies are considered as representing vibrational energy only; they are the values obtaining at the moment just before and just after the exchange and do not account for any attractive or repulsive force between the hydrogen iodide molecules. Kinetic energy of the molecules after collision is considered equal to that before collision, since the probability of energy transfer by a collision of the second kind rapidly diminishes with increasing difference in the total kinetic energies.[9] Obviously, the energy of activation is

$$A = x + y + F \tag{2}$$

where F is the potential energy due to repulsion of two hydrogen iodide molecules.

The calculation itself was a cut and try process. The vibrational potential energy curves were plotted for hydrogen, iodine and hydrogen iodide. The iodine nucleus defined the origin in the hydrogen iodide curve and was considered to be at rest. A one-dimensional collision was then depicted (Fig. 1) by bringing a templet of a second hydrogen iodide curve up within a definite distance of the first, corresponding to a possible nuclear

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[7] The same conclusion has been drawn independently by Langer, *Phys. Rev.*, **34**, 92 (1929).

[8] Landolt-Börnstein, "Tabellen," Vol. V, p. 1489.

[9] Beutler and Josephy, *Naturwissenschaften*, **15**, 540 (1927); Webb and Wang, *Phys. Rev.*, **33**, 329 (1929); Kallmann and London, *Naturwissenschaften*, **17**, 226 (1929); *Z. physik. Chem.*, **2B**, 207 (1929).

separation of the iodine molecule. The energy value of b was read from the iodine curve (Fig. 2). Then, by means of a pair of dividers, the separations of the two hydrogen atoms, consistent with Equation 1 were found for different values of y ranging from 0 to 60 kg. cal.

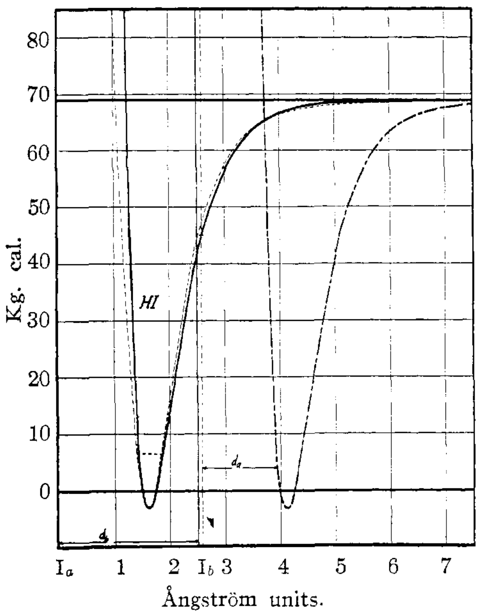

Fig. 1.—Vibrational potential energy curves of two colliding hydrogen iodide molecules. Heavy lines, Morse function. Dotted right branch, inverse power function. Dotted left branch, harmonic force function. Minimum distance of separation of iodine nuclei at collision d_b, is equivalent to b = 4 kg. cal., vibrational energy of I_2 molecule (See I_2 curve). In case first HI molecule has 45 kg. cal. vibrational energy ($y = 45$), second HI molecule must have x = 4 kg. cal., in order for relation $x - a = 1.4 + b - y$ and distance apart of H nuclei, d_a (equivalent to $a = 43.5$—see H curve) to be compatible. $A' \equiv x + y = 49$. First vibrational quantum level represented by dotted line. Band spectra constants used from Czerny, *Z. Physik*, **44**, 250 (1927). $\omega_0'' = 2272 \text{ cm.}^{-1}$, $I_0'' = 4.309 \times 10^{-40}$ g. cm.^{2}; $r_0'' = 1.616 \times 10^{-8}$ cm.

Potential energy curves for hydrogen, iodine and hydrogen iodide were plotted by making use of band spectra constants which give us the various derivatives of the curve at the equilibrium position of the nuclei.[10]

By expressing the potential energy in the form of an inverse power series

$$V = (a_6/r^6) + (a_7/r^7) + (a_8/r^8) + (a_9/r^9) + (a_{10}/r^{10}) \quad (3)$$

one can readily obtain the constants and calculate points for large nuclear separations.[11] This series is no longer convergent for small nuclear separations; the curve actually has several minima, some of which are lower than that corresponding to the stable state of the molecule. When data for iodine are substituted in the equations, the constant a_6 turns out to be positive, which is impossible.[12]

Morse[13] has proposed a new function

$$V = A + De^{-2a(r - r_e)} - 2De^{-a(r - r_e)} \quad (4)$$

which has the advantage of having only one minimum point (at $r = r_e$), is of a form similar to those required by Heitler and London and

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[10] Born and Hückel, *Physik. Z.*, **24**, 1 (1925).

[11] Kemble and Zener, *Phys. Rev.*, **33**, 532 (1929).

[12] Professor Kemble has kindly written me that this is quite likely due to inaccuracy in the value of α'' as reported by Loomis, *ibid.*, **29**, 119 (1927).

[13] Morse, *ibid.*, **34**, 57 (1929).

others, and the Schroedinger equation of which gives energy levels corresponding to those empirically observed. In this function, A is the heat of dissociation of the molecule, D the heat of dissociation plus the half quantum of vibrational energy associated with the lowest state of the molecule, r_e is the equilibrium separation of the nuclei in Ångström units, and

$$a = 2\pi\omega_e \sqrt{\frac{\mu}{2D}\frac{c}{h}} = 0.006547\ \omega_e \sqrt{M/D}$$

where ω_e is in cm.$^{-1}$, M the reduced mass in atomic weight units, and D is in kg. cal. This function has been used throughout these calculations and compares very favorably with the inverse power function (see Figs. 1 and 2).

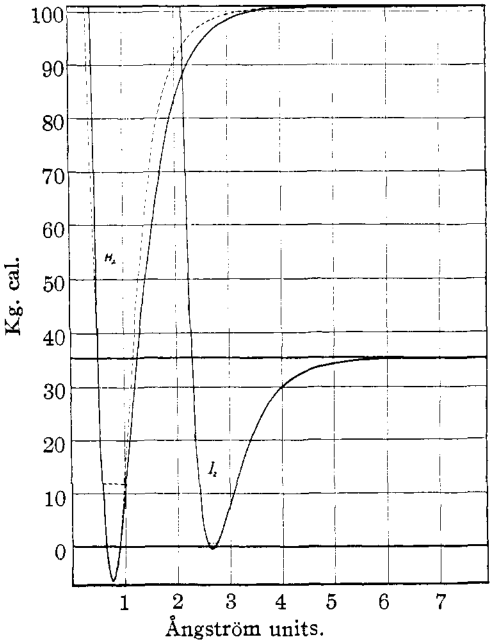

Fig. 2.—Vibrational potential energy curves for hydrogen and iodine. Heavy lines, Morse function. Dotted right branch, inverse power function. Dotted left branch, ascending powers function. First vibrational quantum level represented by dotted line. Band spectra constants used: Hydrogen [Hori, *Z. Physik*, **44**, 834 (1927)]—$\alpha'' = 2.7$; $\omega_0'' = 4415.2$ cm.$^{-1}$; $I_0'' = 0.467 \times 10^{-40}$ g. cm.^{2}; $r_0'' = 0.75 \times 10^{-8}$ cm.; Iodine [Loomis, *Phys. Rev.*, **29**, 119 (1927)]—$\alpha'' = 0.00012$; $\omega_0'' = 213.9$ cm.$^{-1}$, $I_0'' = 742 \times 10^{-40}$ g. cm.^{2}, $r_0'' = 2.66 \times 10^{-8}$ cm.

In the calculation procedure outlined above, there is a certain arbitrariness. One may note that rotation has been left out of consideration. This was done mostly to avoid complication, the postulate being made that the total rotational energy (as well as kinetic energy of translation) be the same after as before the collision. When we recall that hydrogen iodide molecules have a dipole moment,[14] it is seen that a rotation from the considered orientation at collision, I^--$H^+ \longleftarrow I^-$-H^+, through 180° to I^--$H^+ \longleftarrow H^+$-I^- would require the transformation of some of the available energy into orientation energy. This would have to be corrected for. Moreover, the faster the rotation, the less time is going to be spent by the molecule in those particular positions where reaction is favored, and hence the probability of reacting under such circumstances becomes negligibly small. A few cases were calculated corresponding to this 180° orientation away from the natural posi-

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[14] C. T. Zahn, *Phys. Rev.*, **24**, 400 (1924); **27**, 455 (1926).

TABLE IV

CALCULATED HEATS OF ACTIVATION FOR HI DECOMPOSITION

$x - a$ must $= 1.4 + b - y$

I-H $\longleftarrow$ I-H

d_b	x	y	a	b	A'	d_b	x	y	a	b	A'	d_b	x	y	a	b	A'
2.3	69	20	53	35	89	2.35	59	20	57.5	20	79	2.4	67	14.5	67	13	81.5
	45	30	39		75		39.5	30	48		69.5		55	20	60.5		75
	32.5	36.4	32.5		69		15.5	40	34		55.5		35	30	50.5		65
	22	40	25.6		62		5	45	28.5		50		14	40	39.5		54
	12	45	19.5		57		0	50	31–21		50		0	50	25–36		50
	0	50	13.5		50								5	45	35.5		50
2.45	62	15	68	7.5	77	2.5	63	15	72	4	78	2.6	63	15	76.5	0	78
	52	20	63		72		52	20	66.5		72		55	20	73.5		75
	33	30	54		63		33	30	57.5		63		35	30	63.5		65
	13	40	44		53		14	40	48.5		54		17.5	40	56		57.5
	0	50	41–30		50		4	45	43.5		49		6.5	45	50		51.5
	5	45	41		50		0	50	45–33		50		0	50	52–43		50
2.7	68	15	81	0	83	2.8	65	20	82	1.6	85	2.9	37	40	71	4.5	77
	60	20	78.5		80		49	30	76		79		26	45	65		71
	40.5	30	69		70.5		30	40	67		70		15	50	59		65
	21.5	40	60		61.5		18	45	60		63		1.5	55	50.5		56.5
	11.5	45	55		56.5		8	50	55		58		63.5	25	82.5		88.5
	1.5	50	50		51.5		0	55	54–45		55		55.5	30	79.5		85.5
3.0	69	25	85	7.5	94	3.1	68	30	85.5	11	98	3.2	66	35	85.5	14	101
	61	30	82		91		52	40	79.5		92		59	40	83.5		99
	44.5	40	75.5		84.5		30	50	67.5		80		38	50	72.5		88
	34	45	70		79		0	60	48–57				7	60	51.5		67
	22	50	63		72												
	8	55	54		63												
	0	60	40–49														

TABLE IV (*Concluded*)

d_b	x	y	a	b	A'	d_b	x	y	a	b	A'	d_b	x	y	a	b	A'
3.3	65	40	85.5	18	105	3.4	69	40	88	19.5	109	3.5	66	45	87.5	22	111
	47	50	77.5		97		52	50	81		102		46	55	77.5		101
	15	60	55.5		75		20	60	59		80		28	60	64.5		88
													0	65	42–50		65
							I-H ← H-I										
2.3	36_i	20_o	19.5	35	56	2.35	18_i	10_o	6.5	20	28	4.2	65_i	0_o	32	31.5	65
	8.5_o	30_i	2		38.5		20_o	20_i	18.5		40		30_o	10_i	7		40
	41_i	$_o$	34.5		71		21.5_i	$_o$	20		41.5		30_i	$_o$	7		40
	29_o	40_i	33		69		39.5_o	30_i	48		69.5		13_o	20_i	0		33
	50_i	$_o$	53.5		90		26_i	$_o$	34.5		56		64_o	$_o$	51		84
	46_o	50_i	59.5		96		51.5_o	40_i	70		91.5		10_o	30_i	7		40
	57_i	$_o$	70.5		107		31.5_i	$_o$	50		71.5		40_o	$_o$	37		70
	32.5_i	10_o	6		42.5		62_o	50_i	90.5		112		15_i	$_o$	12		45
	13_o	30_i	6.5		43		39.5_i	$_o$	68		89.5		7.5_o	40_i	14.5		47.5
													59_i	$_i$	66		99
													63_o	$_o$	70		103
													50_i	$_o$	57		90

(i = inner branch)
(o = outer branch)

tion. It may be seen that sometimes the sum $A' \equiv x + y$ is smaller than the experimental heat of activation, but the difference is of the proper order of magnitude to be accounted for by the dipole repulsion.

Besides the repulsive force originating from a re-orientation of the molecule, there is a van der Waals attractive force between the molecules. The order of magnitude of the corresponding energy may be very roughly estimated from the latent heats of vaporization and fusion. The former is 4.7 (at −36°) kg. cal. and the latter 0.7[15] (at −51°). The density of the liquid at the boiling point is 2.799; this corresponds to an average separation of the molecules of 4.23 Å. A rough estimate of the separation of the molecules in the crystal lattice yields the same value.

The final results are summarized in Table IV. According to Bodenstein[1] the experimental heat of activation is 44 kg. cal. The minimum calculated values of A' lie in the neighborhood of 50 kg. cal. If we take $F = -5$ kg. cal., the agreement is very gratifying. In those cases where the vibrational quantum number of one of the molecules is very small, inaccuracies are especially prone to creep in, as the displacement of the nuclei has a much wider probability range than usual. The reader has, of course, recognized that quantization of vibration has also been neglected. In those cases of 180° relative orientation where some of the potential energy curves run parallel, it is especially difficult to pick the correct displacements, for here a small error makes a large energy difference. When we remember how rough the Condon working principle is, that the molecule spends all its time at the two extremities of vibration, the agreement in the calculated minimum values of A is very good and indicates that we have gained a better insight into chemical processes than has hitherto been possessed.

That enough molecules of these high vibrational energies exist to account for the observed reaction rate can be demonstrated by Hinshelwood's calculation.[16] He, it is true, made this on the assumption that it was translational energy alone (two degrees of freedom) which effected activation. One need only re-interpret his equations to mean vibrational energy alone and the same calculations hold.

Note of January 25, 1930.—Polyani has found some generalizations in regard to activation energies in reactions involving free atoms,[17] which may be understood in the light of the above theory. According to him, an exothermic reaction between a molecule and an atom demands no activation energy; on the other hand, an endothermic reaction between a

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[15] Giauque and Wiebe, THIS JOURNAL, **51,** 1446 (1929).

[16] Hinshelwood, "The Kinetics of Chemical Change in Gaseous Systems," Oxford, **1926,** p. 92.

[17] *Cf.* also Nernst, "Die Grundlagen des neuen Wärmesatzes," Wilhelm Knapp, Halle, **1918,** p. 133; Herzfeld, *Z. Elektrochem.*, **25,** 301 (1919); *Ann. Physik*, **59,** 635 (1919), in regard to bimolecular metatheses involving a free atom.

molecule and an atom will proceed with an activation energy equal to the heat of reaction. Thus, in the reaction

$$\begin{aligned} H + \overset{69}{HI} &= \overset{101}{H_2} + I + 32 \\ y + 32 &= a \end{aligned}$$

it is easy to find a collision distance at which the above equation will hold for $y = 0$.

On the other hand, in the reaction

$$\begin{aligned} I + \overset{69}{HI} &= H + \overset{35}{I_2} - 34 \\ y - 34 &= b \end{aligned}$$

it is obvious that in order for b to have positive values $y > 34$, and it is again easy to find a collision distance at which this equation will hold. The difference between this case and that taken up in the body of the paper lies in the extreme limitations to which we are subjected when we must satisfy the geometry of the *second* molecule taking part in the process.

Summary

Chemical reaction is most probable when the kinetic energy of the resulting molecules equals that of the reacting molecules, and will occur only in those cases where the sum of the potential energies of the colliding molecules plus the heat of reaction equals the sum of the potential energies which the resulting molecules would have if their respective nuclei undergo no change in position during the change in allegiance. The heat of activation, then, is the sum of the vibrational energies of the colliding molecules plus their heat of repulsion at the distance at which collision occurs. The foregoing principles have been applied to the hydrogen iodide decomposition with satisfactory numerical results.

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