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## Simple Potential Functions and the Hydrogen Halide Molecules

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Five simple molecular potential functions have been tested by comparison with spectroscopic data for the hydrogen halides. It is shown that when plotted on a "reduced" distance scale ( $r/r_e$ ), the potential curves for these molecules coincide closely up to  $\Delta(r) = 0.10r_e$ . Two electrostatic functions indicate  $\beta/r^n$  as the more satisfactory form of the repulsive term. Significant values of the effective polarizability and "fractional ionic character" are deduced. The latter are higher and more nearly constant than the uncorrected values currently quoted as showing changing bond type in these molecules. The results conform with Kirkwood's very successful treatment of HCl as a polarizable ion pair.

Of purely empirical functions, the Pöschl-Teller provides a slight improvement upon the simple Morse relation, and is only a little more cumbersome than the latter. The Rosen-Morse function is less satisfactory for these molecules. Simple expressions are given for evaluating the three parameters in these functions from spectroscopic data.

ONE of the central problems in molecular structure is the correct representation of the potential field binding the atoms in the molecule. The problem assumes its simplest form in the case of diatomic molecules where  $r$ , the distance apart of the nuclei, is the one independent variable. As yet, specific indications of the most appropriate general form of potential function are not provided by theory, as only for the simplest molecules, such as  $H_2$ , has quantum-mechanical theory been applied with precision. Further, it is more than likely that the type of potential function required for an accurate representation of the conditions, from equilibrium to dissociation, will vary with the nature of the molecule: the degree of polarity in the bond will clearly be one of the features leading to such variations. Currently quoted estimates<sup>1</sup> of the "percentage ionic character" give this as 43 percent in HF and 5 percent in HI, the former value being almost coincident with the figure for KI. With this point in mind the hydrogen halides would appear to provide reasonably wide ground for the testing of simple potential functions. These functions will be at least partly empirical.

The basis of the treatment lies in the expansion of  $U(r)$  near the equilibrium value  $U(r_e)$  as follows:

$$U(r) = \frac{1}{2}! \cdot U''(r_e)(r-r_e)^2 + \frac{1}{3}! \cdot U'''(r_e)(r-r_e)^3 + \frac{1}{4}! \cdot U^{iv}(r_e)(r-r_e)^4 \dots \quad (1)$$

TABLE I.

Molecule	$U''(r_e)10^{-6}$	$U'''(r_e)10^{-14}$	$U^{iv}(r_e)10^{-22}$	$D_e \cdot 10^{12}$	$\mu$	$\alpha_X \cdot 10^{18}$
HF	0.967	-7.53	57.8	10.65	1.91	0.96
HCl	0.515 <sub>8</sub>	-2.84 <sub>6</sub>	13.7 <sub>2</sub>	7.41	1.03	3.57
HBr	0.409 <sub>0</sub>	-2.07 <sub>3</sub>	8.7 <sub>9</sub>	6.34	0.78	4.99
HI	0.314 <sub>8</sub>	-1.55 <sub>3</sub>	6.8 <sub>6</sub>	5.21	0.38	7.57

<sup>1</sup> L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca 1939), p. 46; C. P. Smyth, *Frontiers in Chemistry*, Vol. 5 (Interscience Publishers, Inc., New York, 1948), p. 31.

$U'(r_e)$ , the value of the first derivative at  $r_e$ , is, of course, zero. Relations first deduced by Kratzer and modified for the above form of expansion<sup>2</sup> provide values of these derivatives in terms of the spectroscopic constants as follows:

$$\begin{aligned} U''(r_e) &= (2\pi c\omega_e)^2 \cdot m, \\ U'''(r_e) &= -(3U''(r_e))/(r_e)[(\alpha\omega_e/6B_e^2) + 1], \\ U^{iv}(r_e) &= 5/3 \cdot ([U'''(r_e)]^2)/(U''(r_e)) \\ &\quad - (8x_e \cdot \omega_e)/(B_e \cdot r_e^2) \cdot U''(r_e). \end{aligned}$$

In addition, there are available the energies of dissociation,  $D_e = D_0 + \frac{1}{2} \cdot h c \omega_e (1 - x_e/2)$ , and such factors as the dipole moments ( $\mu$ ), and polarizabilities of the halide ions ( $\alpha_X$ ).<sup>3</sup> The spectroscopic data have been taken from Herzberg<sup>4</sup> with the corrections to the  $D_0$  values for HBr and HI pointed out by Gaydon.<sup>5</sup> The dipole moments listed in Table I (see, for instance, reference 1) are in Debyes; the other items are in c.g.s. units, i.e.,  $D_e$  in erg./molecule, etc. An accuracy of at least one percent has been aimed at in most of the subsequent numerical work.  $U''(r_e)$ , of course, is identical with the force constant, the units above being dynes/cm. An interesting calculation is that of the work needed to increase the internuclear distance by, say, 1 percent or 10 percent of its equilibrium value. With the latter value of  $(r-r_e)$ , the third term in Eq. (1) is, at most, 5 percent of the first, so that the absence of higher terms is not serious at that extension. The work of stretching is given in Table II in units of  $10^{-14}$  erg/molecule, and then as the percentage of

<sup>2</sup> See, for instance, Jevons, *Report on Band Spectra of Diatomic Molecules* (Physical Society, London, 1932), p. 27.

<sup>3</sup> K. Fajans, *Zeits. f. physik. Chemie* B24, 118 (1934); O. K. Rice, *Electronic Structure and Chemical Binding* (McGraw-Hill Book Company, Inc., New York, 1940), p. 178.

<sup>4</sup> G. Herzberg, *Molecular Spectra and Molecular Structure: Vol. I: Diatomic Molecules* (Prentice-Hall, Inc., New York, 1939), p. 482 et seq.

<sup>5</sup> *Nature* 161, 731 (1948). The correction arises from the non-gaseous standard state to which the thermal data for Br<sub>2</sub> and I<sub>2</sub> are referred (Gaydon, private communication).

the dissociation energy  $D_e$ . The degree of equality in the energy values measures the coincidence in the potential curves for these molecules near their minima when the curves are plotted in energy units against a "reduced" distance scale, i.e., in terms of  $r/r_e$ . An alternative numerical expression of the same result is found in the approximate constancy of  $U''(r_e) \cdot r_e^2$ . The markedly different values of  $D_e$  show that this coincidence occurs only in the neighborhood of  $r_e$ .

The subsequent calculations accept the values of the derivatives in Table I as being correct. This is only so within certain limits, depending upon the adequacy of the representation of the spectroscopic terms by the constants employed in calculating them. This, and other relevant points, are critically discussed in the work of Coolidge, James, and Vernon on the potential function for  $H_2$ .<sup>6</sup> In the present instance the approximations involved are quite adequate for the comparisons to be made.

### ELECTROSTATIC POTENTIAL FUNCTIONS

The first quantitative treatment of the hydrogen halide bonding<sup>7</sup> suggested on simple physical grounds the potential function

$$U(r) = -e^2/r - e^2 \cdot \alpha_{\text{eff}}/2r^4 + \beta e^2/r^n \dots \quad (2)$$

Writing  $a = (2n-8)e^2 \cdot \alpha_{\text{eff}}/r_e^3$ ,  $b = (n-1)e^2$ ;  $U'(r_e) = 0$ ,  $U''(r_e) = 1/r_e^3(a+b)$ ,  $U'''(r_e) = -3/r_e^4(2a+b)$ ,  $U^{iv}(r_e) = 6/r_e^5(7a+2b)$ . This corresponds to electrostatic binding between ions of charge  $e$ , the sum of whose effective polarizabilities is  $\alpha_{\text{eff}}$ .  $\beta$  and  $n$  are adjustable or arbitrary parameters in the form assumed for the repulsive term. Apart from the latter, Eq. (2) is precisely the form arrived at by Kirkwood<sup>8</sup> in his quantum-mechanical calculations of the molecular constants of the hydrogen halides. He was able to make very successful estimates of what are here adjustable parameters. Other calculations<sup>7,9</sup> have taken  $e = e = \text{electronic charge} = 4.80 \cdot 10^{-10}$  e.s.u. Even in the most polar molecule, HF, reasons can be advanced which suggest that at equilibrium the conditions may depart appreciably from those of a polarizable ion pair.<sup>10</sup> Thus, a more general approach to the conditions obtaining is to use the observed dipole moment to determine  $e$ .

$$\mu_{\text{observed}} = er_e(1 - \alpha_{\text{eff}}/r_e^3) = er_e(1 - s).$$

Three other relations are then needed to define  $\alpha_{\text{eff}}$ ,  $\beta$  and  $n$ . These can be taken as  $U'(r_e) = 0$ ,  $U''(r_e) = (2\pi c\omega_e)^2 m$ , and  $U(r_\infty) - U(r_e) = D_e$ .

<sup>6</sup> A. S. Coolidge, H. M. James, and E. L. Vernon, Phys. Rev. **54**, 726 (1938).

<sup>7</sup> M. Born and W. Heisenberg, Zeits. f. Physik **23**, 388 (1924).

<sup>8</sup> J. G. Kirkwood, Physik. Zeits. **33**, 259 (1932).

<sup>9</sup> G. Briegleb, Zeits. f. physik. Chemie **B51**, 9 (1941).

<sup>10</sup> L. Pauling, J. Am. Chem. Soc. **54**, 998 (1932).

TABLE II.

Molecule	HF	HCl	HBr	HI
$r_e \cdot 10^8 \cdot \text{cm}$	0.917	1.275	1.414	1.604
1 percent extension	0.396	0.410	0.400	0.395
10 percent extension	32.6	33.6	32.6	31.7
1 percent extension	0.037	0.055	0.063	0.076
10 percent extension	3.06	4.54	5.15	6.08
$U'''(r_e) \cdot r_e^2 \cdot 10^{10}$	0.813	0.839	0.818	0.811

Sufficient consistency with these equations is readily obtained by assuming a reasonable value for  $n$ , say  $n = 8.0$ , solving for  $s = \alpha_{\text{eff}}/r_e^3$  from  $U''(r_e)$ , and then calculating  $D_e$ . A few successive approximations will define  $n$  adequately. The resulting  $U(r)$  correctly reproduces  $r_e$ ,  $\omega_e$ ,  $D_e$ , and  $\mu$ . Further tests of the function are then provided by a comparison of the values calculated for  $U'''(r_e)$  and  $U^{iv}(r_e)$  with those in Table I; the latter, being based on spectroscopic data, are designated  $U_s'''(r_e)$  and  $U_s^{iv}(r_e)$ .

The summary in Table III shows the ratios of the calculated to the spectroscopic values of the higher derivatives. It is seen that the calculated derivatives, and hence the values of the further spectroscopic functions related to them, are only some 60 percent of the observed. This is not a satisfactory result. Briefly, two reasons can be advanced for these deficiencies. The assumed form of the potential function is not, of course, throughout consistent with the physical facts, as in the ground state these molecules dissociate into atoms. Secondly, the adjustment of the curve to give the correct  $D_e$ , i.e., to extrapolate to the correct asymptote at  $r_\infty$ , gives rise to slight departure from the true curvature at  $r_e$  which makes itself felt in the values of the third and fourth derivatives. An alternative mode of choosing the constants in (2), i.e., by equating to the "observed" values of  $U'(r_e)$ ,  $U''(r_e)$ ,  $U'''(r_e)$ , and  $\mu$ , leads to physically meaningless values of the constants—e.g., for HCl,  $a = 144 \cdot 10^{-20}$ ,  $b = -37 \cdot 10^{-20}$ .

TABLE III.

Molecule	HF	HCl	HBr	HI
$e \cdot 10^{-10}$ e.s.u.	3.27	2.98	2.88	2.69
$e/e$	0.68	0.62	0.60	0.56
$\alpha_{\text{eff}} \cdot 10^{24}$ cm <sup>3</sup>	0.280	1.51	2.28	3.77
$\alpha_{\text{eff}}/\alpha_X$	0.292	0.423	0.457	0.499
$n$	6.3	7.6	8.3	9.3
$\beta$	$6.9 \cdot 10^{-44}$	$2.55 \cdot 10^{-53}$	$1.57 \cdot 10^{-58}$	$6.1 \cdot 10^{-66}$
$U'''(r_e)/U_s'''(r_e)$	0.52	0.61	0.63	0.58
$U^{iv}(r_e)/U_s^{iv}(r_e)$	0.39	0.58	0.63	0.50

TABLE IV.

Molecule	HF	HCl	HBr	HI
$\alpha_{\text{eff}}$ : Table III	0.28	1.51	2.28	3.77
$\alpha_{\text{eff}}$ : Kirkwood	0.6	1.5	2.3	3.9
$\alpha$ for inert gas	0.394	1.65	2.54	4.11
$\alpha_{\text{eff}}/\alpha_{\text{inert gas}}$	0.71	0.92	0.90	0.92

These provide a better value for  $U^{\text{iv}}(r_e) = 1.21 U_s^{\text{iv}}(r_e)$ , but give a worthless figure for  $D_e$ .

Returning to Table III, the values deduced for  $n$ ,  $\alpha_{\text{eff}}/\alpha_X$ — and  $e/\epsilon$  are all physically acceptable. If the ratios  $\alpha_{\text{eff}}/\alpha_X$ — are divided by the corresponding ionic radii in angstroms,<sup>11</sup> the following figures result: 0.215; 0.233; 0.235; 0.231. The significance of this apparent constancy is not clear; it might mean that  $\alpha_{\text{eff}}$  is proportional to  $\alpha_X$ — and inversely proportional to the electrostatic potential which can be ascribed to the electrons at the “surface” of the ions:  $\alpha_{\text{eff}} = \text{const. } \alpha_X - / r^{-1}$ . But this is merely the simplest, and not a very helpful, hypothesis. Even if the quantitative agreement in this factor is regarded as accidental, it nevertheless serves to emphasize the reasonableness in the trend of  $\alpha_{\text{eff}}/\alpha_X$ —.

A further feature of the above  $\alpha_{\text{eff}}$ 's is their concurrence with those values calculated by Kirkwood and given, in units of  $10^{-24}$  cm<sup>3</sup>, in Table IV. With the exception of HF, the coincidence is practically complete, although it should be noted that Kirkwood's  $\alpha_{\text{eff}}$ 's are based on older values of  $\alpha_X$ — which have all now been increased by about 10 percent. Debye pointed out many years ago<sup>12</sup> that to account for the observed dipole moments of the hydrogen halides in terms of an ionic structure, an effective polarizability only slightly different from that of the inert gas with the same number of electrons as  $X^-$  is needed. This relation is retained by the present values of  $\alpha_{\text{eff}}$ , as is shown by the last row in Table IV. The reason for this relation is also unknown.

The ratio  $e/\epsilon$  can be taken as an estimate of the “fractional ionic character” derived from the dipole moment after correction for polarizability. A small but reasonable trend is seen. Without discussing the significance of the “fractional ionic character” (a term which arises in the resonance treatment of the molecular bond), it is certain that these figures provide far more reliable estimates of this factor than those<sup>13</sup> having no correction for polarizability. These uncorrected values are, from HF to HI, 0.43, 0.17, 0.11, 0.05—showing a different order of variation from that suggested here and tending to give an entirely false impression of changes in the nature of the hydrogen halide bonds. The present much higher and roughly constant values of this factor are

in conformity with the fact that Kirkwood's quantitative treatment of the bond in HCl on the basis of purely ionic character met with considerable success.

An electrostatic potential function of the type treated here has proved satisfactory in calculating the energy of interaction leading to  $[F \cdots H - F]^-$ .<sup>14</sup>

The repulsive term in (2) is of the arbitrary power form. It has been known since the work of Born and Mayer<sup>15</sup> that better results are found for ionic lattices by using a repulsive term of an exponential form which is also indicated by quantum mechanics. The simplest version of this type,  $b \cdot e^{-r/\rho}$ , contains the two constants  $b$  and  $\rho$  which now replace  $\beta$  and  $n$  of Eq. (2). It seemed of interest to examine whether the new function, Eq. (3), provided any improvement upon Eq. (2).

$$\begin{aligned}
 U(r) &= -e^2/r - e^2 \cdot \alpha_{\text{eff}}/2r^4 + b \cdot e^{-r/\rho} \dots, \quad (3) \\
 U'(r_e) &= 0 \quad \text{gives} \quad (b/\rho) \cdot e^{-r_e/\rho} = e^2/r_e^2(1+2s), \\
 U''(r_e) &= e^2/r_e^2 \{ (1/\rho) - (2/r_e) + 2s((1/\rho) - (5/r_e)) \}, \\
 U'''(r_e) &= -2e^2/r_e^3 \{ (1/\rho) - (3/r_e) \\
 &\quad + 5s((1/\rho) - (6/r_e)) \}, \\
 U^{\text{iv}}(r_e) &= 6e^2/r_e^4 \{ (1/\rho) - (4/r_e) \\
 &\quad + 10s((1/\rho) - (7/r_e)) \}, \\
 D_e &= e^2/r_e \{ 1 - (\rho/r_e) + (s/2)(1 - (4\rho/r_e)) \}.
 \end{aligned}$$

$U'(r_e)$ ,  $U''(r_e)$ ,  $D_e$ , and  $\mu$  are used to evaluate the constants, a process which is again effected most readily by successive approximations from a value of  $\rho$  near  $0.15 \cdot 10^{-8}$  cm. The results are summarized in Table V.

Comparison of the last two rows with the similar entries in Table III shows that the new form of the repulsive term has caused a marked deterioration in the calculated values of  $U'''(r_e)$  and  $U^{\text{iv}}(r_e)$ . However, the values of  $e/\epsilon$  and  $\alpha_{\text{eff}}/\alpha_X$ — are practically unchanged, so that the comments previously made on the basis of these ratios need no modification. It is not a justifiable conclusion that in such potential functions the power form of the repulsive term will generally be the more acceptable, even when the attractive energy is written as a power series, for the exponential form is superior in ionic lattice calculations. Solution of (3) from the spectroscopic values of  $U'(r_e)$ ,  $U''(r_e)$ ,  $U'''(r_e)$ ,  $U^{\text{iv}}(r_e)$  leads, for HF, to

TABLE V.

Molecule	HF	HCl	HBr	HI
$e \cdot 10^{10}$ e.s.u.	3.21	2.96	2.83	2.67
$e/\epsilon$	0.67	0.62	0.59	0.56
$\alpha_{\text{eff}} \cdot 10^{24}$ cm <sup>3</sup>	0.27 <sub>1</sub>	1.51	2.27	3.76
$\alpha_{\text{eff}}/\alpha_X$ —	0.28 <sub>2</sub>	0.42 <sub>4</sub>	0.45 <sub>6</sub>	0.49 <sub>7</sub>
$\rho \cdot 10^8$ cm	0.122 <sub>5</sub>	0.145	0.149	0.155
$b \cdot 10^8$ erg	0.454	1.26	2.04	3.78
$U'''(r_e)/U_s'''(r_e)$	0.275	0.37 <sub>6</sub>	0.39 <sub>6</sub>	0.37 <sub>6</sub>
$U^{\text{iv}}(r_e)/U_s^{\text{iv}}(r_e)$	0.086	0.53	0.245	0.217

<sup>11</sup> See reference 1, L. Pauling, p. 326.

<sup>12</sup> P. Debye, *Polar Molecules* (The Chemical Catalogue Company, New York, 1929), p. 62.

<sup>13</sup> See reference 1, Pauling and Smyth.

<sup>14</sup> Mansel Davies, *J. Chem. Phys.* **15**, 739 (1947).

<sup>15</sup> P. M. Morse, *Phys. Rev.* **34**, 57 (1929).

$\rho = 0.530 \cdot 10^{-8}$ ,  $s = 0.160$ , but a negative value for  $e^2$  and a similarly impossible value of  $D_e$ .

### MORSE FUNCTION

A remarkably simple and successful general potential function is the well-known one of Morse.<sup>15</sup> This may be written as

$$U(r) = D_e \cdot [1 - \exp(-a(r - r_e))]^2.$$

Both the attractive and repulsive terms are now of an exponential character. The function expresses  $U'(r_e) = 0$  implicitly and has the two constants  $a$  and  $D_e$ . The derivatives take the very simple forms:

$$U''(r_e) = 2a^2 \cdot D_e, \quad U'''(r_e) = -6a^3 \cdot D_e, \\ U^{iv}(r_e) = 14a^4 \cdot D_e.$$

To test the adequacy of this relation in the same manner as the earlier one, we take the values of  $D_e$  and  $U''(r_e)$  from Table I and then calculate  $a$  and the other derivatives. These results are collected in Table VI. The Morse curve reproduces  $U'''(r_e)$  and  $U^{iv}(r_e)$  a good deal more accurately than the simple electrostatic functions. One of the associated factors in its satisfactory performance is the fact that the Morse function when inserted in the Schrödinger equation leads to the explicit form

$$E_{vib} = h\omega_e(v + \frac{1}{2}) - x_e h\omega_e(v + \frac{1}{2})^2$$

for the vibrational energy levels. This relation is the exact expression used to represent the results for low vibrational quantum numbers, and from it the experimental values of  $\omega_e$ ,  $x_e$  are deduced. Thus, any divergence between the true and the spectroscopic values of the derivatives  $U'''(r_e)$  and  $U^{iv}(r_e)$  is the less likely to appear in testing the Morse function.

Some adjustment or extension of the Morse curve is a likely line of improvement for these empirical potential functions. An extended form of the function with an arbitrary number of terms can be used where the data warrant it,<sup>6</sup> but there are obvious practical advantages in restricting the number of adjustable parameters. This restriction is maintained in the two following alternative and somewhat generalized forms of the Morse expression; no more data are required for their definition than for the simple Morse equation.

### ROSEN-MORSE FUNCTION

The first of these is the Rosen-Morse function,<sup>16</sup> which we take in the simple version:

$$U(r) = A \cdot \tanh(r/d) - C \cdot \text{sech}^2(r/d) \cdots \quad (4)$$

TABLE VI.

Molecule	HF	HCl	HBr	HI
$a \cdot 10^{-8}$	2.13 <sub>2</sub>	1.86 <sub>6</sub>	1.79 <sub>7</sub>	1.73 <sub>9</sub>
$U'''(r_e)/U_s'''(r_e)$	0.82 <sub>2</sub>	1.01 <sub>2</sub>	1.06 <sub>6</sub>	1.06 <sub>6</sub>
$U^{iv}(r_e)/U_s^{iv}(r_e)$	0.53 <sub>2</sub>	0.91 <sub>6</sub>	1.05 <sub>1</sub>	0.97 <sub>3</sub>

<sup>16</sup> N. Rosen and P. M. Morse, Phys. Rev. **42**, 210 (1932).

TABLE VII.

Molecule	HF	HCl	HBr	HI
$d \cdot 10^8$	0.84 <sub>2</sub>	0.99 <sub>2</sub>	1.04 <sub>0</sub>	1.10 <sub>2</sub>
$(-A) \cdot 10^{12}$	413	629	730	872
$C \cdot 10^{12}$	259	367	417	486
$U'''(r_e)/U_s'''(r_e)$	0.73	0.95	1.01	0.98
$U^{iv}(r_e)/U_s^{iv}(r_e)$	0.36	0.72	0.86	0.96

This leads to:

$$\tanh(r_e/d) = -A/2C.$$

And writing

$$1/C^2 \cdot (4C^2 - A^2)^2 = f, \\ U''(r_e) = f/8d^2C, \\ U'''(r_e) = 3Af/8d^3C^2, \\ U^{iv}(r_e) = (9A^2 - 8C^2)f/8d^4C^3, \\ D_e = (A + 2C)^2/4C.$$

As previously, the constants are chosen to fit  $U'(r_e)$ ,  $U''(r_e)$ , and  $D_e$ .  $A$  and  $C$  have the dimensions of erg/molecule, and  $d$  is in cm. Table VII summarizes the constants and their testing. Except for HI and possibly HBr, the curvature in the neighborhood of  $r_e$  is reproduced no better than by the Morse function. There is, however, a steady improvement in the accuracy of the function in going to the molecules of smaller apparent polarity, and the degree of agreement for HI is probably not far short of the accuracy of testing. The evaluation of the constants can also be made on the basis of  $U'(r_e)$ ,  $U''(r_e)$ , and  $U'''(r_e)$ , but this method is particularly unsatisfactory in practice, because of the very slow variation and closeness to unity of  $\tanh(r_e/d)$ , when  $r_e/d \sim 2$ . Thus for HF and HI, respectively, it yields values of  $D_e$  calc./ $D_e$  obs. = 0.17 and 0.25, and for  $U^{iv}(r_e)/U_s^{iv}(r_e)$  2.7 and 3.5, i.e., widely divergent from the results of alternative methods. Even more direct is the evaluation of  $A$ ,  $C$ , and  $d$  from  $U''(r_e)$ ,  $U'''(r_e)$ , and  $U^{iv}(r_e)$ , using the relations

$$(C/A)^2 = 9/8 \{1 - U^{iv}(r_e) \cdot U''(r_e) / [U'''(r_e)]^2\}, \\ d = 3A/C \cdot U''(r_e) / U'''(r_e).$$

This latter is virtually the method described by Kronig<sup>17</sup> for fitting the Rosen-Morse curve, but the above relations are far more convenient for numerical evaluation. They do not, however, lead to satisfactory parameters. The ratios  $D_e$  calc./ $D_e$  obs. for the same two molecules, HF and HI, now have the values 1.74 and 1.60, for which the most that can be said is that they are an improvement on those deduced via  $U'(r_e)$ ,  $U''(r_e)$ , and  $U'''(r_e)$ . Whilst not improbable values of  $d$  are given by this method, the ratio  $-A/2C$ , which should equal  $\tanh(r_e/d)$ , assumes the impossible values of 3.98 and 1.47. Incidentally, the Kronig version of the Rosen-Morse

<sup>17</sup> R. de L. Kronig, *The Optical Basis of the Theory of Valency* (Cambridge University Press, Cambridge, England, 1935), p. 88.

TABLE VIII.

Molecule	HF	HCl	HBr	HI
$D_{\text{Morse}}/D_e$	0.88	1.16	1.21	1.21
$D_{\text{Lotmar}}/D_e$	1.73	1.35	1.32	1.56
$D_{\text{RM}}/D_e$	0.53	0.70	0.73	0.77

curve, i.e., in Kronig's notation,

$$U(\rho) = -a \cdot \tanh((\rho+c)/d) - b \cdot \text{sech}^2((\rho+c)/d),$$

which has four adjustable parameters, is no improvement, in the present circumstances, upon Eq. (4). Solved on the basis of  $U'(r_e)$ ,  $U''(r_e)$ ,  $U'''(r_e)$ , and  $U^{iv}(r_e)$ , it leads to precisely the same results as the latter, with the meaningless equation for  $c$ ,  $\tanh((0.917+c)/3.08) = 3.98$ .

Lotmar<sup>18</sup> has discussed the use of the Rosen-Morse curve and has given the solutions for  $A$ ,  $C$ , and  $d$  on the basis of  $U''(r_e)$ ,  $U'''(r_e)$ , and  $D_e$ . This, then, is a fourth way of fitting the constants. That it is not a suitable treatment for the present cases is shown by the results for HF where it leads to  $\tanh(r_e/d) = 1.56$ ; thus, it fails to define a real value for  $r_e$ , the equilibrium internuclear distance. Lotmar also gives an independent formula for  $D_e$ ; this is based on the value obtained for  $\omega_e x_e$  when the Rosen-Morse potential is inserted in the Schrödinger equation for a vibrator. Although it is a somewhat clumsy expression, it appeared of interest to test it and, in particular, to compare it with the value of  $D_e$  calculated in the same way from the Morse function, i.e.,  $D_{\text{Morse}} = \omega_e/4x_e$ . Lotmar indicates too an empirical expression for  $D_e$  which arose from Rosen and Morse's solution of the Schrödinger equation but which was in error by a numerical factor. This empirical value,  $D_{\text{RM}}$ , whilst better than  $D_{\text{Lotmar}}$ , is not, contrary to what Lotmar suggests, any improvement upon  $D_{\text{Morse}}$ . These values are compared in Table VIII by their ratios to the correct  $D_e$ .

### PÖSCHL-TELLER FUNCTION

From the alternative approaches explored here it appears that the Rosen-Morse function is no improvement upon the simpler Morse equation for these molecules. The clearest expression of this unsuitability is the tendency for  $\tanh(r_e/d) > 1$ . Lotmar indicates that this will occur when the real

TABLE IX.

Molecule	HF	HCl	HBr	HI
$d \cdot 10^8$	0.93 <sub>8</sub>	1.07 <sub>2</sub>	1.11 <sub>0</sub>	1.15 <sub>2</sub>
$M \cdot 10^{12}$	18.03	36.6 <sub>4</sub>	46.5 <sub>4</sub>	66.1
$N \cdot 10^{12}$	56.4	77.0	87.2	108.3
$U'''(r_e)/U_s'''(r_e)$	0.86	1.03 <sub>1</sub>	1.09	1.06
$U^{iv}(r_e)/U_s^{iv}(r_e)$	0.63	0.98 <sub>3</sub>	1.12	0.99

<sup>18</sup> W. Lotmar, Zeits. f. Physik **93**, 528 (1935).

potential curve is more unsymmetrical than that given by the Morse function. In such instances, the appropriate hyperbolic form is that given by Pöschl and Teller.<sup>19</sup> Thus we write

$$U(r) = M \cdot \text{csch}^2(r/d) - N \cdot \text{sech}^2(r/d).$$

And the following relations are found:

$$\tanh^4(r_e/d) = M/N = y^4, \text{ (say).}$$

$$U''(r_e) = 8N/d^2 \cdot (1-y^2)^2,$$

$$U'''(r_e) = -24N/yd^3 \cdot (1-y^2)(1-y^4),$$

$$U^{iv}(r_e) = 8/d^4 \cdot \{15(MN)^{1/4} \cdot ((1-y^4)/y^2)^2 - 32N(1-y^2)^2\},$$

$$D_e = N(1-y^2)^2.$$

In terms of the observed  $r_e$ ,  $U''(r_e)$ , and  $D_e$ , explicit solution follows readily from

$$d^2 = 8D_e/U''(r_e),$$

$$y = \tanh(r_e/d),$$

$$N = D_e/(1-y^2)^2.$$

The values thus calculated are given in Table IX. Apart from those for HBr, the figures in the last two rows show, on the average, slightly better concordance than is obtainable with the simple Morse equation. This suggests that the Pöschl-Teller function is able to represent the spectroscopic constants, up to the stage considered, somewhat more accurately than any of the other relations tested here. It should be emphasized that the function contains no more arbitrary constants than the simple Morse equation and, although its higher derivatives are more cumbersome, its numerical handling is not difficult. Substituted in the Schrödinger equation it leads to practically the same satisfactory solution for the vibrational energy levels as the simple Morse function. Thus it would scarcely be distinguishable from the latter by the test made in Table VIII. In this respect again it is nearer the experimental relations than the Rosen-Morse function, for which the expansion of  $E_v$  in terms of  $(v+\frac{1}{2})$ —see Lotmar—does not close with the  $(v+\frac{1}{2})^2$  term.

Although the foregoing is numerically the easiest and, partly for that reason, the most satisfactory means of fitting the simple version of the Pöschl-Teller function to the present data, the results of an alternative method may also be given. With the values of  $d$  quoted in Table IX as a first approximation, successive adjustment of that factor can be made to provide values of the parameters which satisfy the observed  $U'(r_e)$ ,  $U''(r_e)$ , and  $U'''(r_e)$ . The two terms  $D_e$  and  $U^{iv}(r_e)$  then provide independent tests of the constants so chosen. The same process can, of course, be applied to the simple Morse function itself, i.e.,  $a$  and  $D_e$  can be calcu-

<sup>19</sup> G. Pöschl and E. Teller, Zeits. f. Physik **83**, 143 (1933).

lated from  $U'''(r_e) = 2a^2 \cdot D_e$ ;  $U''''(r_e) = -6a^3 \cdot D_e$ . The first five rows in Table X refer to the Pöschl-Teller function treated in this way, and the last three rows to the Morse function. Compared on this basis, the Pöschl-Teller function reproduces  $U^{iv}(r_e)$ , and, hence, the curvature near  $r_e$  the more accurately, but there is the suggestion (HCl and HBr) that it extrapolates to a slightly poorer value of  $D_e$  than the simple Morse equation. Part of this second result is probably due to the poorer self-consistency of the  $P-T$  curve constants when determined by the (at most two) successive approximations used here, but some of the superiority of the Morse  $D_e$ 's based on  $U'(r_e)$ ,  $U''(r_e)$ , and  $U'''(r_e)$  in HCl and HBr is real.

Nearly all the spectroscopic constants for these molecules are based on limited series of rotational and vibrational features in the infra-red; the  $D_e$  values are derived via a number of thermal measurements and may possibly be in error by some parts

TABLE X.

Molecule	HF	HCl	HBr	HI
$d \cdot 10^8$	0.78 <sub>3</sub>	1.10 <sub>6</sub>	1.21 <sub>0</sub>	1.22 <sub>6</sub>
$M \cdot 10^{12}$	33.4	32.4	33.7	51.6
$N \cdot 10^{12}$	72.3	72.2	73.1	92.4
$D_e(\text{calc})/D_e(\text{obs.})$	0.70	1.06	1.18	1.13
$U^{iv}(r_e)/U_e^{iv}(r_e)$	0.83	0.94	0.97	0.91
$a(\text{Morse}) \cdot 10^{-8}$	2.59 <sub>6</sub>	1.84 <sub>1</sub>	1.69 <sub>0</sub>	1.64 <sub>6</sub>
$D_e(\text{Morse})/D_e(\text{obs.})$	0.67	1.03	1.13	1.12
$U^{iv}(r_e)/U_e^{iv}(r_e)$	0.79	0.89	0.93	0.87

per thousand, if not by more than one percent. Thus a more detailed comparison of the present or of more elaborate potential functions is probably not justified in these instances by the over-all accuracy of the data or of the assumptions involved in the treatment. It is clear that the simple Morse and the Pöschl-Teller functions are far the most satisfactory, with the latter holding a slight advantage.

## Hydrogen Peroxide in the Thermal Hydrogen Oxygen Reaction I. Thermal Decomposition of Hydrogen Peroxide

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The decomposition of hydrogen peroxide (at partial pressures of one to two millimeters of mercury) was studied in the presence of one atmosphere of oxygen or nitrogen by the use of a flow system. The concentration of H<sub>2</sub>O<sub>2</sub> was measured photometrically, using the continuous ultraviolet absorption of this compound. Determination by this means was more rapid, and offered less chance for errors of manipulation than conventional chemical analysis. A first order reaction with an activation energy of 40 kcal./mole was found in the neighborhood of 520°C. Evidence is presented to support the conclusion that the reaction is partly, at least, homogeneous in boric acid treated vessels at temperatures in the 470 to 540°C range.

### I. INTRODUCTION

**H**YDROGEN peroxide was first found as one of the products of combustion of hydrogen in 1882 by Schuller.<sup>1</sup> In 1930, Pease<sup>2</sup> showed that this compound appeared among the frozen-out products of the near third limit steady reaction of hydrogen and oxygen, and in 1947, Holt and Oldenberg<sup>3</sup> detected it, spectroscopically in the smoothly reacting mixture of these gases at temperatures near 540°C. This was surprising in view of the low thermal stability of this compound, and hence it aroused interest in a determination of the lifetime of hydrogen peroxide at these temperatures. It also became desirable to find out as much as possible about the

reaction of hydrogen peroxide with hydrogen gas and to see whether decomposing hydrogen peroxide could initiate chains in the near third limit hydrogen oxygen reaction as suggested by von Elbe and Lewis.<sup>4</sup> Papers on the last two topics will be submitted in the near future.

A search of the literature revealed a considerable amount of work done on the thermal decomposition of hydrogen peroxide vapor; however, in no case was any homogeneous reaction observed. Baker and Ouellet,<sup>5</sup> Mackenzie and Ritchie,<sup>6</sup> and Giguère,<sup>7</sup> who did the most recent and extensive work, confirmed the reports of other investigators that this reaction showed an extreme sensitivity to the character of the surface of the reaction vessel, and found

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<sup>2</sup> R. N. Pease, J. Am. Chem. Soc. **52**, 5106 (1930).

<sup>3</sup> R. B. Holt and O. Oldenberg, Phys. Rev. **71**, 479 (1947).

<sup>4</sup> G. von Elbe and B. Lewis, J. Chem. Phys. **10**, 366 (1942).

<sup>5</sup> Baker and Ouellet, Can. J. Research **23B**, 167 (1945).

<sup>6</sup> Mackenzie and Ritchie, Proc. Roy. Soc. **A185**, 207 (1946).

<sup>7</sup> Giguère, Can. J. Research **25B**, 135 (1947).