Molecular Constants and Potential Energy Curves for Diatomic Molecules[1]

MAURICE L. HUGGINS, *Department of Chemistry, The Johns Hopkins University*
(Received April 26, 1935)

By using the function $U = Ce^{-a(r-r_e)} - C'e^{-a'(r-r_e)}$ with $C = 10^{-12}e^{-a(r_e-r_{12})}$, and taking $a = 6.0 \times 10^8$ cm^{-1}, r_{12} values calculated from the band spectrum constants are nearly the same (1.46A) for all except highly excited states of all diatomic molecules containing only elements in the first row of the periodic table and having 12 or more electrons. This indicates that the repulsive term is nearly the same in all of these cases. This relation enables one to calculate, from experimental values of two of the molecular constants (e.g., ω_e and $\omega_e x_e$) the magnitudes of others (e.g., r_e, B_e and α). Calculated values of $\omega_e y_e$ and $\omega_e z_e$ are invariably small but not zero. The dissociation energy is (empirically) about 0.8 $(C' - C)$, calculated using $a = 4.0 \times 10^8$ cm^{-1}.

INTRODUCTION

MORSE'S equation[2] for the potential energy of a diatomic molecule as a function of the internuclear distance has been found very useful by band spectroscopists and others. This equation may be written in the form

$$U = Ce^{-a(r-r_e)} - C'e^{-a'(r-r_e)} \qquad (1)$$

with $a = 2a'$ and $C' = 2C$. (Since at $r = r_e$

$$dU/dr = a'C' - aC = 0 \qquad (2)$$

these two relationships between the constants are not independent.)

By relating the constants in this way Morse was enabled to solve the wave equation, obtaining from the solution an equation for the energy levels,

$$E_v/hc = E_e/hc + \omega_e(v + \tfrac{1}{2}) - \omega_e x_e(v + \tfrac{1}{2})^2 \qquad (3)$$

agreeing approximately with that usually deduced from the spectra. Although additional terms, $\omega_e y_e(v + \tfrac{1}{2})^3$ and $\omega_e z_e(v + \tfrac{1}{2})^4$, are sometimes needed to represent the experimental data accurately, $\omega_e y_e$ and $\omega_e z_e$ are nearly always negligibly small in comparison with ω_e and $\omega_e x_e$.

The values of the constants in Morse's equation can be calculated from ω_e and $\omega_e x_e$ in which case the calculated dissociation energy, $C' - C$, is usually quite far from the true value as obtained in other ways. On the other hand the constants of the equation can be obtained from ω_e and the dissociation energy, the calculated value of $\omega_e x_e$ then being inaccurate. Apparently a single equation of the Morse type is not accurately correct over the whole range of distance from r_e to ∞. This is not surprising in view of the simplicity of the function and the somewhat arbitrary relation between the constants.

For different electronic states of the same diatomic molecule not only does the attractive potential vary widely but so also does the repulsive potential. It would seem more reasonable that the repulsion should vary but little from state to state. It may be noted that for the alkali halide crystals a repulsion term of the form $Ce^{-a(r-r_{12})}$ has been found[3] to be satisfactory for calculations of lattice energies and interatomic distances, with the same value of a for all these crystals. The constants r_{12} are different for different crystals but are additive.

Considerations such as the foregoing led the writer to derive and test a modification of Morse's equation, in which the repulsive term is the same for all electronic states of a particular molecule. In so doing, several interesting and useful relationships between the molecular constants have been deduced and compared with the experimental data.

SUMMARY OF METHODS AND RESULTS

Putting
$$C = ce^{-a(r_e - r_{12})} \qquad (4)$$

we have
$$Ce^{-a(r-r_e)} = ce^{-a(r-r_{12})}. \qquad (5)$$

---

[1] Preliminary reports of this work have been made at the Washington (1933), Cleveland (1934) and New York (1935) meetings of the American Chemical Society.
[2] P. M. Morse, Phys. Rev. **34**, 57 (1929).

[3] M. Born and J. E. Mayer, Zeits. f. Physik **75**, 1 (1932); J. E. Mayer and L. Helmholz, Zeits. f. Physik **75**, 19 (1932); M. L. Huggins and J. E. Mayer, J. Chem. Phys. **1**, 643 (1933).

TABLE I.

1 Formula	2 State	3 ω_e EXP. (cm⁻¹)	4 $\omega_e x_e$ EXP. (cm⁻¹)	5 $\omega_e x_e$ CALC. FROM r_e (a=6) (cm⁻¹)	6 $\omega_e x_e$ CALC. FROM D_e (a=4) (cm⁻¹)	7 a' FROM $\omega_e x_e$ (a=6) (10³cm⁻¹)	8 D_e EXP. (e.v.)	9 $(C'-C)$ FROM $\omega_e x_e$ (a=6) (e.v.)	10 $0.8(C'-C)$ FROM $\omega_e x_e$ (a=4) (e.v.)	11 D_e FROM MORSE'S EQUA-TION (e.v.)	12 C' FROM $\omega_e x_e$ (a=6) (10⁻¹²erg)	13 C FROM $\omega_e x_e$ (a=6) (10⁻¹²erg)	14 r_{12} FROM $\omega_e x_e$ (a=7) (10⁻⁸cm)	15 r_{12} FROM $\omega_e x_e$ (a=6) (10⁻⁸cm)	16 r_{12} FROM $\omega_e x_e$ (a=4) (10⁻⁸cm)	17 r_e EXP. (10⁻⁸cm)	18 r_e FROM $r_{12}=1.46$ (a=6) (10⁻⁸cm)	19 α EXP. (cm⁻¹)	20 α FROM $\omega_e x_e$ (a=6) (cm⁻¹)	21 α FROM MORSE'S EQUATION (cm⁻¹)	22 REF.
C_2	$d\ ^1\Pi_g$	1832.45	34.01	10.7		4.33		2.9	1.8	3.0	16.3	11.75	1.47	1.66	imag	1.251	1.05	0.0255	0.034	0.035	
	$B\ ^3\Pi_g$	1792.55	19.35	10.0	(23)	2.02	(3.1)	5.9	3.8	5.1	14.1	4.74	1.41	1.52	2.45	1.261	1.20	.0173	.024	.024	
	$b\ ^1\Pi_u$	1608.31	12.10	6.9	(17)	.72	(3.4)	13.2	5.2	6.6	23.9	2.87	1.41	1.49	1.95	1.315	1.28	.0174	.019	.017	
	$A\ ^3\Pi_u$	1641.55	11.67	6.8	(12)	.64	(5.5)	15.5	5.7	7.1	27.6	2.94	1.40	1.49	1.94	1.308	1.28	.0149	.019	.016	
N_2^+	$B\ ^2\Sigma_u^+$	2419.84	23.190	17.1	49.0	3.30	3.1	7.6	5.8	7.8	26.8	14.75	1.36	1.52	imag	1.071	1.01	.025	.025	.025	2
		2173.2	10.43			.75		27.0	10.1		49.1	6.14					1.16		(.014)	(.013)	3
	$X\ ^2\Sigma_g^+$	2207.19	16.136	15.7	17.7	1.94	6.2	10.8	6.9	9.3	25.4	8.22	1.34	1.45	2.36	1.113	1.11	.02	.020	.019	2, 3
N_2	$C\ ^3\Pi$	2044.70	26.047	15.6		3.79		4.8	3.7	5.0	20.5	12.95	(1.40)	(1.57)	imag	(1.14)	1.03	(.032)	(.027)	(.027)	
	$B\ ^3\Pi_{reg}$	1732.84	14.437	14.7		1.60		8.1	4.8	6.4	17.5	4.67	1.35	1.46	2.13	1.201	1.20	.023	.020	.019	
	$a\ ^1\Pi_u$	1692.28	13.318	14.7	11.7	1.36	5.7	9.0	5.0	6.6	18.6	4.21	1.35	1.45	2.05	1.209	1.22	.021	.019	.018	3
	$A\ ^3\Sigma$	1460.39	13.929	10.3		1.48		6.2	3.5	4.7	13.1	3.24	1.39	1.48	2.10	1.289	1.26	.013	.019	.018	4
	$X\ ^1\Sigma_g^+$	2359.60	14.445	15.5	17.1	1.60	7.34	14.9	8.8	11.9	32.4	8.65	1.33	1.45	2.18	1.092	1.10	.018	.018	.017	3
O_2^+	$b\ ^4\Sigma_g^-?$	1198.1	17.8		(13)	2.78	(2.5)	2.5	1.8	2.5	7.5	3.47					1.25				
	$A\ ^4\Pi_u$	898.9	13.7	11.4	13.1	1.85	1.4	2.1	1.3	1.8	4.9	1.52	1.40	1.48	2.18	1.41	1.39	.014	.020	.019	
	$a\ ^4\Pi_u?$	1037.2	11.1		(10)	1.23	(2.6)	4.3	2.2	3.0	8.6	1.76					1.37				
	$X\ ^2\Pi_{g\,reg}$	1876.4	16.53	14.2	12.9	2.49	6.15	6.9	4.8	6.6	18.8	7.80	1.35	1.48	imag	1.14	1.12	.009	.019	.018	
O_2	b	1121	17			2.60		2.4		2.3	6.7	2.88					1.28				
	$B\ ^3\Sigma_u^-$	710.14	11.705	5.0	12.1	1.38	0.95	1.8	1.0	1.3	3.7	.85	1.51	1.57	2.04	1.599	1.49	.014	.017	.016	
	E	1454	12			1.45		7.1		5.4	15.0	3.62					1.25				
	D	1524	12			1.45		7.8		6.0	16.5	3.98					1.23				
	C	1494	12			1.45		7.5		5.7	15.8	3.83					1.24				
	$A\ ^1\Sigma_u^-?$	1432.615	13.925	25.7	13.4	1.90	3.47	5.3	3.4	4.5	12.4	3.92	1.35	1.45	2.26	1.223	1.23	.0188	.018	.018	
	$X\ ^3\Sigma_g^-$	1584.91	11.645	23.9	11.4	1.35	5.09	9.1	5.0	6.7	18.7	4.22	1.34	1.44	2.05	1.204	1.22	.016	.015	.015	
F_2	$^1\Sigma$	977	141	2		21.6		.3	0.3	.2	−	.2	.6	imag	imag	imag	1.45		.050	.049	5
	$^1\Pi$	1139.8	9.7	11.7		1.34		5.6	3.2	4.1	11.6	2.06	1.35	1.44	1.99	1.28	1.30	.014	.013	.012	5
CN	$B\ ^2\Sigma^+$	2164.15	20.25	14.9	16.9	2.45	6.30	7.6	5.3	7.2	20.4	8.33	1.37	1.50	imag	1.148	1.11	.02215	.024	.024	
	$A\ ^2\Pi_{inv}$	1788.66	12.883	11.4	12.8	1.05	5.74	12.1	5.8	7.7	19.8	4.07	1.37	1.47	2.01	1.236	1.23	.01746	.018	.017	
	$X\ ^2\Sigma^+$	2068.70	13.176	14.0	14.1	1.11	7.09	15.3	7.6	10.0	25.0	5.51	1.35	1.45	2.03	1.169	1.18	.0173	.018	.017	
BeO	$E\ ?^2\Sigma$	1006	10	>12		.24		14.8	2.7	3.1	24.6	.98	>1.41	>1.47	>1.79	>1.47	1.46		<.022	<.020	7
	$D\ ?^2\Sigma$	1136	10			.24		19.0	3.4	4.0	31.4	1.26					1.42				
	$C\ ^1\Sigma^+$	1370.81	7.76	10.2	7.8	−.19	7.5	−35.	7.5	7.5	−53.8	1.70	1.38	1.45	1.78	1.358	1.37	.016	.018	.013	7
	$B\ ^1\Pi$	1127.77	8.401	1.8	8.1	−.07	4.7	−64.	4.4	4.7	−100.6	1.17	1.50	1.49	1.81	1.468	1.43	.01607	.019	.015	7
	$A\ ^1\Sigma^+$	1486.87	11.70	10.8	10.0	.57	5.8	13.7	4.6	5.8	24.0	2.28	1.39	1.47	1.89	1.327	1.32	.0189	.021	.018	7
BO	$B\ ^2\Sigma^+$	1280.3	10.07	17.4	(12)	.51	(3.26)	12.9	4.1	5.0	22.4	1.91	1.33	1.41	1.81	1.301	1.35	(.017)	.020	.017	
	$A\ ^2\Pi_{inv}$	1297.13	11.61	13.2	(11)	.70	(3.7)	9.0	3.5	4.5	16.3	1.90	1.37	1.45	1.87	1.343	1.35	.0211	.021	.019	8
		1260.42	10.94	12.7	(11)	.70	(3.7)	9.1	3.5	4.5	16.4	1.90	1.37	1.45	1.87	1.342	1.35	.0196	.019	.017	8
	$X\ ^2\Sigma^+$	1940.26	12.48	14.1	(13)	.87	(6.6)	16.3	7.2	9.3	30.3	4.39	1.35	1.45	1.96	1.203	1.21	.0177	.019	.017	8
		1885.44	11.77	13.4	(13)	.86	(6.6)	16.5	7.2	9.3	30.6	4.39	1.35	1.45	1.96	1.202	1.21	.0165	.018	.016	8
CO⁺	$B\ ^2\Sigma^+$	1722.1	24.33	20.6	25.4	3.31	2.68	3.8	2.9	3.8	13.4	7.38	1.35	1.49	imag	1.16	1.13		.030	.030	
	$A\ ^2\Pi_{inv}$	1564.53	14.07	14.9	12.4	1.39	4.58	7.4	4.1	5.4	15.3	3.56	1.36	1.45	2.05	1.24	1.25		.020	.019	
	$X\ ^2\Sigma^+$	2212	15.17	16.7	15.6	1.61	7.1	12.8	7.5	10.0	27.7	7.43	1.33	1.44	2.17	1.11	1.13		.019	.018	
CO	$F\ ^1\Pi?$	2112	198		(404)	21.8	(0.6)	.9	.9	.7	−.5	−1.89		imag					.042	.042	
	$B\ ^1\Sigma$	2182	50	16.6	(43)	7.37	(2.8)	2.7	2.5	2.9	−19.1	−23.4	1.63	imag	imag	1.118		.028	.042	.042	
	$A\ ^1\Pi$	1516.7	17.24	17.2	26.7	2.11	2.0	4.6	3.1	4.1	11.2	3.95	1.35	1.46	2.37	1.232	1.23	.024	.024	.023	
	$a'\ ^3\Sigma?$	1182	9		9.0	.39	3.9	15.0	4.0	4.8	25.6	1.66					1.38				
	$a\ ^3\Pi$	1739.3	14.5	15.3	17.1	1.55	4.0	8.2	4.8	6.4	17.6	4.54	1.35	1.45	2.11	1.202	1.21	.02	.020	.019	9
	$X\ ^1\Sigma^+$	2169.32	13.278	15.4	11.1	1.30	10.0	15.2	8.2	10.9	30.9	6.68	1.33	1.44	2.07	1.127	1.14	.01738	.018	.017	10

TABLE I. (Continued.)

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22
FORMULA	STATE	ω_e EXP. (cm^{-1})	$\omega_e x_e$ EXP. (cm^{-1})	$\omega_e x_e$ CALC. FROM r_e ($a=6$) (cm^{-1})	$\omega_e x_e$ CALC. FROM D_e ($a=4$) (cm^{-1})	a' FROM $\omega_e x_e$ ($a=6$) (10^8 cm^{-1})	D_e EXP. (e.v.)	$(C'-C)(C'/-C)$ FROM $\omega_e x_e$ ($a=6$) (e.v.)	$0.8(C'-C)$ FROM $\omega_e x_e$ ($a=4$) (e.v.)	D_e FROM MORSE'S EQUATION (e.v.)	C' FROM $\omega_e x_e$ ($a=6$) (10^{-12} erg)	C FROM $\omega_e x_e$ ($a=6$) (10^{-12} erg)	r_{12} FROM $\omega_e x_e$ ($a=7$) (10^{-8} cm)	r_{12} FROM $\omega_e x_e$ ($a=6$) (10^{-8} cm)	r_{12} FROM $\omega_e x_e$ ($a=4$) (10^{-8} cm)	r_e EXP. (10^{-8} cm)	r_e FROM $r_{12}=1.46$ ($a=6$) (10^{-8} cm)	α EXP. (cm^{-1})	α FROM $\omega_e x_e$ ($a=6$) (cm^{-1})	α FROM MORSE'S EQUATION (cm^{-1})	REF.[1]
NO	D $^2\Sigma^+$	2351	27		(13)	4.28	(9.5)	5.9		6.3	32.9	23.5					.93				
	C $^2\Pi_{rg}$	2358.6	15.8	15.9	(13)	2.10	(9.5)	12.1	4.8	10.8	29.5	10.35	1.33	1.46	2.56	1.07	1.07		.018	.018	11
	B $^2\Pi_{rg}$	1038.6	7.46	7.1	(9)	2.19		26.6	7.9	4	43.7	1.35	1.40	1.46	1.80	1.413	1.41	.015	.014	.012	
	A $^2\Sigma^+$	2375.3	16.52	16.7	(13)	2.25	(1.0)	11.4	7.5	10.5	29.1	10.92	1.33	1.46	imag.	1.060	1.06	.016	.019	.019	
	X $^2\Pi_{rg}$	1906.5	14.44	15.3		1.80	(6.1)	9.2	5.7	7.7	21.0	6.29	1.34	1.45	2.24	1.146	1.15	.0182	.018	.018	12
BeF	A $^2\Pi_{rg}$	1172.6	8.78	11.2	(16)	.11	(1.9)	46.9	4.3	4.8	75.9	1.39	1.38	1.45	1.78	1.390	1.40	.01610	.019	.015	
	X $^2\Sigma^+$	1265.6	9.12	12.5	(8)	.18	(6.0)	33.4	4.7	5.4	53.6	1.64	1.34	1.44	1.80	1.357	1.38	.01685	.019	.016	12

1 Except as otherwise noted, the experimental data are from W. Jevons, *Report on Band Spectra of Diatomic Molecules*, The University Press, Cambridge, England, 1932.
2 D. Coster and H. H. Brons, Zeits. f. Physik 73, 747 (1932).
3 W. W. Watson and P. G. Koontz, Phys. Rev. 46, 32 (1934). For the first N$_2^+$ state listed, r_e=1.16A was assumed in calculating the values of α.
4 S. M. Naudé, Proc. Roy. Soc. A136, 114 (1932).
5 H. G. Gale and G. S. Monk, Astrophys. J. 69, 77 (1929). $\omega_e x_e$ was assumed to be equal to $\omega_0 x_0$ and ω_e to $\omega_0 + \omega_0 x_0$. If

$\omega_e x_e$ is large, as indicated by the calculated values for the ^{12} state, the $\omega_e x_e$ values given (and also other quantities derived therefrom) are not accurate. The "experimental" r_e value for this state was calculated from B_0 and the value of α in col. 20, r_0=1.48A.
6 H. Bürwald, G. Herzberg and L. Herzberg, Ann. d. Physik 20, 569 (1934), give 4.8, 6.8 and 9.7 electron volts, respectively, for D_e for the 3 states of CN listed.
7 L. Herzberg, Zeits. f. Physik 84, 571 (1933).
8 F. A. Jenkins and A. McKellar, Phys. Rev. 42, 464 (1932).

9 G. H. Dieke and J. W. Mauchly, Phys. Rev. 43, 12 (1933).
10 D. N. Read, Phys. Rev. 46, 571 (1934).
11 As a first approximation, $B_e \approx B_0$ =1.955, $r_e \approx r_0$=1.072, and $\omega_e x_e^0$=2.447. By Eqs. (27), (28) and (29), $\omega_e x_e \approx$ 15.74. Using (30), $\omega_e \approx$ 2355. Recalculation of $\omega_e x_e$ by Eqs. (27), (28) and (29) then gives 15.64. By means of Eqs. (15) and (21), $\alpha \approx$ 0.0183, from which B_e =1.964 and r_e =1.071. Using this r_e then gives $\omega_e x_e$=15.77, from which α =0.0185.
12 The values given are averages for the doublets.

The constant c is arbitrary; in this paper it will be taken as 10^{-12} erg, the value used for the alkali halide crystals. The distances r, r_e, r_0 and r_{12} will be measured in Angstrom units and a and a' in reciprocal Angstroms (10^8 cm^{-1}).

We shall consider in this paper only diatomic molecules composed of elements in the first row of the periodic table, and except from consideration the Li$_2$ molecule, since it contains a much smaller number of electrons than the others for which data are available.

From the band spectrum constants ω_e, $\omega_e x_e$, r_e and α a rough values of a (in most cases) be calculated. For the molecules being considered a is usually about 6. For any assumed value of a, all the other constants a', C', C and r_{12} are obtainable from ω_e, $\omega_e x_e$ and r_e.

The assumption that a is exactly 6 in all cases leads to approximately the same value of r_{12}, not only for different electronic states of the same molecule but also for different molecules. (See col. 15, Table I.) In the highest energy state of each molecule for which data are available, the calculated r_{12} values are usually higher than for the lower energy states. All values of r_{12} for the C_2 molecule are also a little high, perhaps on account of the smaller number of electrons. Otherwise, in all cases but one for which data are available, the calculated r_{12} values are within 0.02A of 1.46A. This means that, to this same degree of approximation, the r_e values can be calculated from ω_e and $\omega_e x_e$, assuming exactly the same repulsive term for all of these molecules in all but highly excited states. (See cols. 17 and 18.)

Calculations of $\omega_e y_e$ and $\omega_e z_e$ show them to be small in all cases. The agreement with experiment is apparently as good as with Morse's equation (giving $\omega_e y_e = \omega_e z_e = 0$) but still not good in the cases where the experimental constants are large. This probably means that this form of potential function, like Morse's, is not a very good approximation for large values of r.

Further evidence to the same effect is afforded by the fact that the values of $C'-C$ do not agree well with the values of dissociation energy (col. 8) where the latter are known. Better agreement is obtained using $a=4.0$ and the empirical relationship

$$D_e = 0.8(C'-C), \qquad (6)$$

the quantity in parenthesis being calculated with the a value just mentioned, is fairly accurate (col. 10). D_e values calculated in this way are as a rule more accurate than those calculated by means of Morse's equation (col. 11).

Calculation of the rotational constant α gives practically the same degree of agreement with the experimental values as obtained from Morse's equation (cols. 19, 20 and 21).

Rough values of $\omega_e x_e$ are obtainable from $\omega_{\frac{1}{2}}$, r_e or r_0 and the assumption that $r_{12}=1.46$A, with $a=6.0$ (col. 5).

CALCULATION OF a', C AND C' FROM ω_e, $\omega_e x_e$ AND a

Expanding the exponentials of Eq. (1) and collecting corresponding terms, one obtains an equation of the form[4]

$$U=E_e+c_2(r-r_e)^2+c_3(r-r_e)^3+c_4(r-r_e)^4+\cdots \quad (7)$$

with

$$c_2=aC(a-a')/2=aa'(C'-C)/2, \quad (8a)$$

$$c_3=-aC(a^2-a'^2)/2\cdot 3, \quad (8b)$$

$$c_4=aC(a^3-a'^3)/2\cdot 3\cdot 4, \quad \text{etc.} \quad (8c)$$

The values of c_2, c_3 and c_4 are given in terms of the band spectrum constants by the equations[5]

$$c_2=2\pi^2c^2\omega_e^2\mu, \quad (9a)$$

$$\omega_e=(c_2/2\pi^2c^2\mu)^{\frac{1}{2}}, \quad (9b)$$

$$c_3=-(c_2/r_e)(\alpha\omega_e/6B_e^2+1), \quad (10a)$$

$$\alpha=-(c_3r_e/c_2+1)(6B_e^2/\omega_e), \quad (10b)$$

$$c_4=5c_3^2/4c_2-2\omega_e x_e c_2/3B_e r_e^2, \quad (11a)$$

$$\omega_e x_e=(15c_3^2/8c_2^2-3c_4/2c_2)B_e r_e^2. \quad (11b)$$

Substituting Eqs. (8a) and (8b) in Eq. (11b),

$$\omega_e x_e=(1/24)(2a^2+7aa'+2a'^2)B_e r_e^2, \quad (12)$$

$$a'=(33a^2/16+12\omega_e x_e/B_e r_e^2)^{\frac{1}{2}}-7a/4. \quad (13)$$

Since $\quad B_e r_e^2=10^{16}h/8\pi^2c\mu=16.78/M \quad (14)$

where M is the reduced mass in atomic weight units

$$a'=(33a^2/16+96\pi^2c\mu\omega_e x_e/10^{16}h)^{\frac{1}{2}}-7a/4$$

$$=(2.0625a^2-0.7154M\omega_e x_e)^{\frac{1}{2}}-1.7500a. \quad (15)$$

[4] Jevons, reference 1, Table I, p. 23.
[5] Jevons, reference 4, p. 27. The additional correction terms in the corresponding equations derived by J. L. Dunham, Phys. Rev. **41**, 721 (1932) are of negligible magnitude.

Curves showing the variation of a' with $M\omega_e x_e$ for $a=6.0$ and 4.0 are shown in Fig. 1.

From Eqs. (8a), (9a) and (15) we obtain (in 10^{-16} erg)

$$(C'-C)=\frac{2c_2}{aa'}=\frac{4\pi^2c^2\mu\omega_e^2}{aa'}=\frac{0.0585M\omega_e^2}{aa'}$$

$$=\frac{0.0585M\omega_e^2}{(33a^2/16+12\omega_e x_e/B_e r_e^2)^{\frac{1}{2}}a-7a^2/4}. \quad (16)$$

From Eq. 2,

$$C=(C'-C)/(a/a'-1). \quad (17)$$

C' is of course the sum of $(C'-C)$ and C. Thus, by means of Eqs. (15) and (17) we can obtain, from ω_e and $\omega_e x_e$ the constants a', C and C' for any given value of a. The calculated values for $a=6.0$ are given in columns 7, 12 and 13 of Table I.

CALCULATION OF r_{12} AND r_e

Assuming Eq. (4), with $c=10^{-12}$ erg,

$$(r_{12}-r_e)=(2.303/a)\log(10^{12}C). \quad (18)$$

The values of r_{12} computed by adding to the observed r_e values the values of $(r_{12}-r_e)$ obtained in this way are given in columns 14, 15 and 16 for $a=7.0$, 6.0 and 4.0. The constancy of the values calculated for $a=6.0$ has already been noted. Nearly as good constancy is obtained for $a=7.0$, r_{12} being then approximately 1.35A in

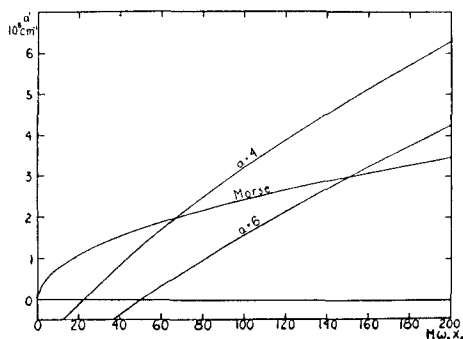
FIG. 1. The relationship between $M\omega_e x_e$ and a', for $a=4$, for $a=6$ and assuming Morse's equation.

practically all cases. Such agreement would seem to be ample evidence for the approximate constancy of the repulsive term, i.e., for the approximate correctness of Eq. (4) (at distances not far removed from r_e), with a constant value of a.

The calculated r_{12} values show a definite trend for each type of molecule, from a minimum of 1.44A or 1.45A (for $a=6.0$) for the normal state to much higher values for the higher energy states (low values of $(C'-C)$ and of D_e). For the latter the assumptions involved in Eqs. (1) and (4), with constant a and r_{12} are certainly inaccurate.

The approximate constancy of a and r_{12} for 1st row elements makes possible the calculation of r_e in cases where it is not known. To indicate the accuracy to be expected, the values in col. 18, calculated on the assumption that $a=6.0$, can be compared with the experimental values of col. 17. For states of high energy (low D_e) the calculated r_e values should be considered only as minimum values. Better agreement is of course obtained when allowance is made for the trend of r_{12} with D_e or $(C'-C)$.

CALCULATION OF $\omega_e y_e$ AND $\omega_e z_e$

To calculate $\omega_e y_e$ and $\omega_e z_e$ we may use equations derived by Dunham.[6] His constants a_1, a_2, etc., are related to those used in this paper by the equations

$$a_1/r_e = c_3/c_2 = -(a+a')/3, \tag{19a}$$

$$a_2/r_e^2 = c_4/c_2 = a^2 + aa' + a'^2/3\cdot4, \tag{19b}$$

$$a_3/r_e^3 = c_5/c_2$$
$$= -(a^3+a^2a'+aa'^2+a'^3)/3\cdot4\cdot5, \quad (19c)$$

$$a_n/r_e^n = c_{n+2}/c_2$$
$$= 2(-1)^n(a^n+a^{n-1}a'+\cdots+a'^n)/(n+2)!. \quad (19d)$$

By using these and Eqs. (9a) and (13) one can calculate, for an assumed value of a, $\omega_e y_e$ and $\omega_e z_e$ as functions of a', M and ω_e.

Values of $\omega_e y_e$ for the molecules listed in Table I have been calculated for $a=4.0$ and $a=6.0$. In both cases they are all very small, in agreement with the usual experimental obser-
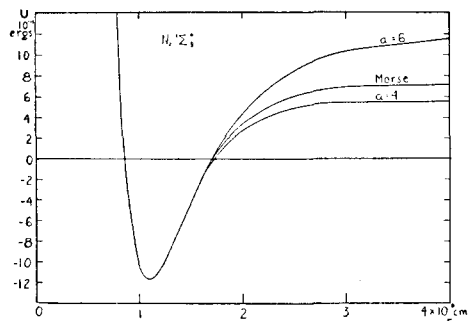
---

[6] J. L. Dunham, reference 5.

FIG. 2. Potential energy curves for the ground state of N_2, assuming $a=4$, $a=6$, and Morse's equation. These curves are all made to agree at $r=r_e$. The true curve approaches the line $U=0$ asymptotically as r approaches infinity.

vations. In only 2 cases are the calculated values greater than 0.13 cm^{-1} for $a=6.0$ or 0.07 for $a=4.0$. Comparison with such $\omega_e y_e$ values as have been determined experimentally shows but little better agreement (if any) than is obtained with Morse's function. The assumed potential function is obviously far from accurate (at least in these cases) for interatomic distances far from r_e.

CALCULATION OF THE DISSOCIATION ENERGY D_e

If Eq. (1) were strictly true for all values of r, the dissociation energy D_e would be equal to $(C'-C)$. However the choice of $a=6.0$, which gives good agreement between r_{12} values for different molecules and electronic states and which we may assume gives a potential function approaching the truth quite closely for r not far from r_e, give $(C'-C)$ values which, like Morse's, are much too high. (Compare columns 8, 9 and 11 of Table I.)

An attempt was made to determine what value of a would give agreement with the otherwise determined dissociation energies, for those first row molecules for which values of the latter (not in parenthesis) are given by Jevons. Eliminating a' from Eqs. (15) and (16) one obtains

$$(2.0625a^2+0.7154M\omega_e x_e)^{\frac{1}{2}}a-1.750a^2$$
$$=0.0585M\omega_e^2/(C'-C). \quad (20)$$

Out of 10 cases, in only one is any value of a

possible which will satisfy this equation, using Jevons' values of D_e, ω_e and $\omega_e x_e$. In all cases, however, the closest approach to agreement is obtained with a in the neighborhood of 3.5 to 4.0. Comparison between columns 8 and 10 of Table I shows that approximately

$$D_e = 0.8(C' - C) \qquad (6)$$

if $(C' - C)$ is computed on the assumption that $a = 4.0$. The average deviation (not counting the D_e values given in parenthesis by Jevons) is less than 0.7 electron volt.

CALCULATION OF α

Eq. (10b) furnishes a method of calculating the rotational constant α. Substituting for c_2 and c_3,

$$\alpha = (2B_e^2/\omega_e)[(a + a')r_e - 3]. \qquad (21)$$

The values in column 20 of Table I were calculated in this way, taking $a = 6.0$. Calculations assuming $a = 4.0$ lead to but slightly different results. The α so computed averages 0.0015 cm^{-1} less, the maximum difference being 0.004 (not counting the exceptional $^1\Sigma$ state of F_2, where the difference is 0.04 cm^{-1}). The average deviation between the observed values of α and those calculated, assuming either a value, is less than 0.003 cm^{-1}.

In the instances in which B_0 was known but not B_e, the former was used to obtain an approximate value of α; this was then employed in calculating B_e from the relation

$$B_e = B_0 + \alpha/2 \qquad (22)$$

and finally a more exact value of α was computed from this B_e.

The expression for α derived by Dunham[6] leads to an equation of the form of (21) except for the addition of a complicated correction term. The magnitudes of the correction terms for the $^1\Sigma$ state of F_e and the F $^1\Pi$ state of CO (probably the worst cases), assuming $a = 6.0$, are about 2×10^{-5} and 10^{-6} cm^{-1}, respectively.

Assuming Morse's equation,

$$a' = a/2 = (8\pi^2 c\mu\omega_e x_e/10^{16}h)^{\frac{1}{2}}. \qquad (23)$$

Substituting in Eq. (21),

$$\alpha_M = 6B_e^2/\omega_e[(8\pi^2 c\mu\omega_e x_e/10^{16}h)^{\frac{1}{2}}r_e - 1]$$
$$= 6B_e^2/\omega_e[(\omega_e x_e/B_e)^{\frac{1}{2}} - 1]. \qquad (24)$$

This is equivalent to the equation

$$\alpha = 2x_e B_e[3(B_e/\omega_e x_e)^{\frac{1}{2}} - 3(B_e/\omega_e x_e)] \qquad (24a)$$

derived by Pekeris.[7]

The figures (col. 21) obtained by means of Eq. (24) closely parallel those (col. 20) obtained from Eq. (21), as might be expected.

CALCULATION OF a FROM α, ω_e, $\omega_e x_e$ AND r_e

From Eqs. (15) and (22) one obtains

$$a + a' = \alpha\omega_e/2B_e^2 r_e + 3/r_e$$
$$= (33a^2/16 + 0.7154M\omega_e x_e)^{\frac{1}{2}} - 3a/4. \qquad (25)$$

Solving for a,

$$a = /F2 \pm (11F^2/12 - 0.4769M\omega_e x_e)^{\frac{1}{2}}, \qquad (26)$$

where $$F = \alpha\omega_e/2B_e^2 r_e + 3/r_e. \qquad (26a)$$

Calculations of a using this relationship lead to imaginary values in 10 cases out of 36 for which the data are available. Either the method is too sensitive to experimental inaccuracies or else the assumed equations are not sufficiently valid. It is perhaps significant however that the average of the 26 other cases is 6.0, the value found to give such uniform values of r_{12}, with an average deviation of 0.9.

CALCULATION OF $\omega_e x_e$ FROM ω_i AND r_e

From Eq. (18) we have

$$C = 10^{-12} \log^{-1}[a(r_{12} - r_e)/2.303], \qquad (27)$$

from Eqs. (16) and (17)

$$a' = a - 0.0585M\omega_e^2/aC, \qquad (28)$$

and from Eqs. (12) and (13)

$$\omega_e x_e = (1/M)(1.398a^2 + 4.89aa' + 1.398a'^2). \qquad (29)$$

Assuming $a = 6.0$ and $r_{12} = 1.46$, values of $\omega_e x_e$ are readily computed by means of Eqs. (27), (28) and (29) from r_e and ω_e. As a first approximation ω_i can be used in place of ω_e, the approxi-

---

[7] C. L. Pekeris, Phys. Rev. **45**, 98 (1934).

mate $\omega_e x_e$ so obtained being then used to calculate ω_e:

$$\omega_e = \omega_{\frac{1}{2}} + \omega_e x_e/2. \qquad (30)$$

A second approximation can then be made if desired. In most cases, however, the second approximation is only about 0.2 cm^{-1} lower than the first approximation and the calculated values are rarely that accurate. (Compare columns 4 and 5 of Table I.) They are especially inaccurate for highly excited states and for states having r_e, not very different from r_{12}.

CALCULATION OF $\omega_e x_e$ AND OTHER CONSTANTS FROM $\omega_{\frac{1}{2}}$, a AND $(C'-C)$

As already pointed out, $(C'-C)$ is not in general equal to the dissociation energy, for any assumed value of a. Taking $a=4.0$ however, one can obtain approximate $(C'-C)$ values by Eq. (6) and from these by Eqs. (16) and (29) $\omega_e x_e$ may be calculated. As in the computation of this quantity from $\omega_{\frac{1}{2}}$ and r_e one can use $\omega_{\frac{1}{2}}$ in place of ω_e for a rough calculation, later, if desired, using ω_e obtained by means of Eq. (30).

Values of $\omega_e x_e$ obtained in this way are given in col. 6 of Table I for comparison with the experimental values in col. 4.

Knowing $\omega_e x_e$ and ω_e, one can of course then calculate r_e, B_e, α, etc., assuming $a=6.0$ and $r_{12}=1.46$, if these are not already known.

POTENTIAL CURVES FOR LARGE VALUES OF r

Comparison of the experimental values of $\omega_e y_e$ and D_e with those calculated indicates a closer agreement, when r is much larger than r_e, if a is taken as 4.0 than if it is given a higher value. To obtain the equation of a potential curve conforming reasonably well to the actual curve for r large, it is suggested that one use this smaller value of a and Eqs. (6), (16) and (17) to obtain a', C and C' from the dissociation energy (if known) and ω_e (or $\omega_{\frac{1}{2}}$).

Entropy and the Absolute Rate of Chemical Reactions. II. Unimolecular Reactions

O. K. RICE AND HAROLD GERSHINOWITZ,[1] *Chemical Laboratories, Harvard and Princeton Universities*
(Received April 8, 1935)

In this paper the considerations of the previous paper have been developed further and compared with the theory of reaction rates as formulated in terms of a specifically defined activated complex by Eyring. The theory has been applied to a discussion of various unimolecular reactions. A number of cases have been treated by considering the reverse bimolecular or trimolecular association and discussing the extent to which rotational degrees of freedom must be frozen out in order for the associations to occur. Other cases have been treated by the activated complex method, which involves discussion of the number of free rotations and the frequency of the vibrations in the complex. It has been shown that it is possible to account for the rates of a considerable number of unimolecular reactions by making reasonable assumptions and that there is a considerable class of unimolecular reactions which conform to what is designated as the "hypothesis of exact orientation," the only necessary assumption being that the rotational degrees of freedom of the fragments which recombine in the reverse reaction must be frozen out just sufficiently so that they correspond as regards their entropy terms to the resulting vibrational degrees of freedom of the molecule formed.

1. GENERAL CONSIDERATIONS

IN a recent paper[2] (referred to hereafter as Part I) we have developed a method for the discussion of the rates of reactions which do not involve any change in the electronic states of the system. Since the publication of Part I, there has appeared an interesting paper by Eyring[3] in which the same problem is treated by a method which has many features in common with our procedure, though the viewpoint and the termi-

---

[1] Parker Traveling Fellow of Harvard University.
[2] O. K. Rice and Gershinowitz, J. Chem. Phys. **2**, 853 (1934).

[3] Eyring, J. Chem. Phys. **3**, 107 (1935).