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Citation: *J. Chem. Phys.* **4**, 308 (1936); doi: 10.1063/1.1749845

View online: <http://dx.doi.org/10.1063/1.1749845>

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Molecular Constants and Potential Energy Curves for Diatomic Molecules. II

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(Received February 19, 1936)

The potential energy expression $U = e^{-a(r-r_{12})} - C'e^{-a'(r-r_e)}$ previously applied to diatomic molecules containing only first row elements is now applied to other types. For most of them the same value of a ($6.0 \times 10^8 \text{ cm}^{-1}$) can be used satisfactorily, the r_{12} values then being additive and depending only on the row of the periodic table in which the atoms occur. Molecules containing but few electrons require different values of a and r_{12} . Values of the equilibrium distance r_e , calculated from ω_e , $\omega_e x_e$ and these constants, are in most cases within 0.02 or 0.03 Å of the experimentally determined distances (see Table V). The relation between Badger's empirical equation for the calculation of r_e and the equations used in this paper is discussed.

INTRODUCTION

IN the previous paper of this series¹ the assumption that the potential energy of a diatomic molecule (not too far from equilibrium) obeys an expression of the form

$$U(\text{in } 10^{-12} \text{ erg}) = e^{-a(r-r_{12})} - C'e^{-a'(r-r_e)} \quad (1)$$

was applied to the band spectrum data for compounds containing only elements in the first row of the periodic table and containing 8 or more electrons. It was found that by taking a (in 10^8 cm^{-1}) as 6.0 and r_{12} (in 10^{-8} cm) as 1.46, for all such molecules in all states but highly excited ones, values of r_e and of various other constants could be calculated which are in quite good agreement with the experimental values. This agreement is taken to indicate that for these molecules the repulsive term in the energy expression is practically independent of the kinds of atoms in the molecule and of the electronic state. The attractive term however varies widely from molecule to molecule and from state to state.

An equation, based on the above energy expression, was given for the calculation of a directly from experimental values of ω_e , $\omega_e x_e$ and r_e . The calculation is quite sensitive to inaccuracies in the assumed constants however; in 10 cases out of 36 an imaginary result is obtained. The values computed in the other cases average close to 6.0, although, as shown in Table I here, there seems to be a trend from lower to higher values as the number of valence electrons (or the sum of the kernel charges) increases. It is

quite possible that the relatively poor agreement obtained in calculations of r_e for the C_2 molecule is due to the assumption of too high a value of a .

In this paper the same type of potential function, but, in general, with different values of a and r_{12} , is assumed to hold for other diatomic molecules than those previously considered. On the whole the data are neither so extensive nor so accurate as for the molecules containing only first row elements, hence the calculations of a and r_{12} are less sure. As one consequence, the agreement between calculated and experimental values of r_e , although on the whole satisfactory, is not quite so good as shown in the earlier paper.

THE CALCULATION OF a , r_{12} AND r_e

The results of calculations of rough values of a by the method mentioned in the second paragraph above are collected in Table I. The equation² used is

$$a = F/2 + (11F^2/12 - 0.4769M\omega_e x_e)^{1/2}, \quad (2a)$$

$$\text{where} \quad F = \alpha\omega_e/2B_e^2 r_e + 3/r_e. \quad (2b)$$

M is the reduced mass in atomic weight units. The other symbols have their usual significance. In the case of the hydrogen molecule r_e values were calculated from the r_0 values by the method described in the previous paper, taking $a = 5.0$. The assumption of $a = 4.0$ or 6.0 for this purpose makes but little difference.

It is evident from the figures in Table I that, if the assumed type of potential function is ap-

² Eqs. (15) and (26) of the previous article contain typographical errors. The correct equations are given here as (3a) and (2a).

¹ Huggins, J. Chem. Phys. 3, 473 (1935).

TABLE I.³ Calculated values of a .

SUM OF KERNEL CHARGES	8	9	10	11	12	14
	BeO 5.2 5.7 4.6 C ₂ 4.8	BeF 4.3 4.8 5.4 CN 5.1 4.8	CO 6.3 5.5 8.5 7.6 N ₂ ⁺ 6.0 6.1	NO 8.4 4.6 6.2 5.9	O ₂ 6.6 6.5	F ₂ 7.0
Average	5.1	4.9	6.5	6.3	6.6	7.0

SUM OF KERNEL CHARGES	2	3	4	7	8
	NaH 1.7	BeH ⁺ 3.1 3.5 BeH 2.7 3.1 MgH ⁺ 1.4 3.5 MgH 2.3 CaH 2.5 2.7	AlH 3.6	HO 6.2	HF 6.1 6.0 6.1 HCl ⁺ 2.3 HCl 4.7
Average	1.7	2.8	3.6	6.2	5.1

SUM OF KERNEL CHARGES	2	9	10	12	14
	Li ₂ 1.5 Na ₂ 1.2	AlO 4.9 3.9	P ₂ 3.5 6.0 TiO 4.6 PbO 2.8 SiO 4.7 SiN 4.3	SO 5.2 5.3	Cl ₂ 5.5 Br ₂ 6.3 ICI 7.1 7.0 I ₂ 2.9 3.5
Average	1.4	4.4	4.3	5.3	5.4

SUM OF KERNEL CHARGES	2	3	6	2
	CuH 3.8 4.1 AgH 6.1 3.8 AuH 2.7	ZnH ⁺ 2.4 4.2 CdH ⁺ 3.1 2.7 CdH 3.9 5.5 5.3 HgH ⁺ 5.0 2.7 HgH 4.1	BiH 4.7 4.7	H ₂ 7.4 4.8 3.5 6.5 6.4
Average	4.1	3.9	4.7	5.7

plicable throughout, a gradually increases as the strength of bond (in the normal molecule) increases. Thus, considering hydrides and other molecules separately, a increases as the sum of the kernel charges (or the number of valence electrons) increases. Also, the hydrides of Zn, Cd and Hg (all sub-group elements) seem to have a higher value of a than those of Be, Mg and Ca, in the corresponding main group of the periodic table. There is some indication also of a slightly higher value of a for the first row elements than for corresponding elements in the second and lower rows.

Using these results as a rough guide, calculations of r_{12} from the experimental r_e data have been made for various values of a to find the value or range of values of a for each molecule which leads to nearly the same values of r_{12} for all of its different states for which the data are available. The equations used are as follows:

³ Most of the data used in the preparation of Tables I, III and IV were obtained from Jevons, *Report on Band Spectra of Diatomic Molecules* (University Press, Cambridge, England, 1932). Results are included for all molecular states for which he gives the requisite data (not in parenthesis), except that the 26 states for which the data lead to imaginary values of a are omitted from Table I. For references, other than to Jevons, for work on molecules containing only Be, B, C, N, O and F, see the previous paper of this series. In Tables III and IV, although the values of r_e (calc.) - r_e (exp.) are given to 3 decimal places (except when less are given for r_e (exp.)), the last figure may be in error by 2 or 3 units, as most of the calculations were made by slide rule.

$$a' = (2.0625a^2 + 0.7154M\omega_e x_e)^{\frac{1}{2}} - 1.750a, \quad (3a)$$

$$C' - C = 5.85 \times 10^{-6} M\omega_e^2 / aa', \quad (3b)$$

$$C = (C' - C) / (a/a' - 1), \quad (3c)$$

$$r_{12} - r_e = (2.303/a) \log C. \quad (3d)$$

It was found that, as with molecules containing only first row elements, the same value of a could be used successfully for various different molecules. Thus for all hydrides containing from 6 to 8 valence electrons and other diatomic molecules containing from 8 to 14 valence electrons, the assumption of $a = 6.0$ leads to satisfactory agreement between the calculated r_{12}

TABLE II. Values of a and r_{12} used in calculating r_e (Huggins) for Tables III and IV.

A. Hydrides containing 6 to 8 valence electrons and other molecules containing 8 to 14 valence electrons: $a = 6.0$ and $r_{12} = r_1 + r_2$			
<i>Element</i>	r_1 (or r_2)	<i>Element</i>	r_1 (or r_2)
H	0.38×10^{-8} cm	Br	1.11×10^{-8} cm
Be, B, C, N, O, F	0.73	Te, I	1.26
Al, Si, P, S, Cl	0.96	Pb, Bi	1.25
Ca, Ti	1.00		
B. Hydrides of Zn, Cd, Hg (also Cu, Ag, Au?): $a = 4.5$			
<i>Molecule</i>	(CuH?), ZnH	(AgH?), CdH	(AuH?), HgH
r_{12}	1.55	1.66	1.66
C. Hydrides of Be, Mg, Ca (also Li, Na, K, Al?): $a = 3.5$			
<i>Molecule</i>	(LiH?), BeH	(NaH?), MgH, (AlH?)	(KH?), CaH
r_{12}	1.59	1.81	1.92
D. Li_2 : $a = 2.0$. $r_{Li_2} = 2.54$			
E. Na_2 , (K_2) : $a = 1.65$. $r_{Na_2} = 3.01$, $r_{K_2} = 3.44$ (?)			
F. H_2 : $a = 4.5$, $r_{H_2} = 1.01$ or $a = 5.0$, $r_{H_2} = 0.95$ or $a = 6.0$, $r_{H_2} = 0.90$.			

TABLE III.² Comparisons of calculated and experimental equilibrium distances.

FORMULA	ω_e (exp.) (cm ⁻¹)	r_e (exp.) (10 ⁻⁸ cm)	r_e (calc.) - r_e (exp.) (Huggins) (10 ⁻⁸ cm)	r_e (calc.) - r_e (exp.) (Badger) (10 ⁻⁸ cm)	REFER- ENCE
C ₂	1832.45	1.251	-0.201	-0.031	
	1792.55	1.261	-0.060	-0.033	
	1608.31	1.315	-0.031	-0.045	
N ₂ ⁺	1641.55	1.308	-0.028	-0.047	
	2419.84	1.071	-0.059	+0.036	
N ₂	2207.19	1.113	-0.004	+0.020	
	1732.84	1.201	+0.002	+0.011	
	1692.28	1.209	+0.011	+0.012	
	1460.39	1.289	-0.025	-0.013	
	2359.60	1.092	+0.008	+0.022	
O ₂ ⁺	898.9	1.41	-0.02	+0.06	
	1876.4	1.14	-0.02	+0.02	
O ₂	710.14	1.599	-0.112	-0.005	
	1432.615	1.223	+0.009	+0.035	
	1584.91	1.204	+0.016	+0.017	
F ₂	977	1.45	—	-0.095	
	1139.8	1.28	+0.021	+0.036	
CN	2164.15	1.148	-0.042	-0.003	
	1788.66	1.236	-0.010	-0.020	
	2068.79	1.169	+0.007	-0.003	
BeO	1006	> 1.47	> -0.007	< +0.027	
	1370.81	1.358	+0.013	-0.014	
	1127.77	1.468	-0.034	-0.030	
	1486.87	1.327	-0.005	-0.017	
BO	1280.3	1.301	+0.051	+0.046	
	1297.13	1.343	+0.010	-0.002	
	1260.42	1.342	+0.011	+0.013	
	1940.26	1.203	+0.011	-0.017	
	1885.44	1.202	+0.012	-0.006	
CO ⁺	1722.1	1.16	-0.03	+0.06	
	1564.53	1.24	+0.01	+0.01	
	2212	1.11	+0.02	+0.03	
CO	2182	1.118	—	+0.022	
	1516.7	1.232	-0.001	+0.035	
	1739.3	1.202	-0.006	+0.014	
	2169.32	1.127	+0.017	+0.014	
NO	2355	1.07	0.000	+0.034	
	1038.6	1.413	-0.003	+0.001	
	2375.3	1.060	+0.002	+0.043	
	1906.5	1.146	+0.008	+0.023	
BeF	1172.6	1.390	+0.015	+0.012	
	1265.6	1.357	+0.021	+0.010	
HO	3182.5	1.009	-0.015	+0.021	
HF	4123.12	0.915	+0.008	+0.013	4
HCl ⁺	1603	1.528	-0.027	+0.137	
HCl	2989.68	1.272	+0.009	+0.026	
HBI	1716.94	1.784	-0.008	—	
	1678.16	1.804	-0.018	—	
CP	1239.67	1.558	-0.005	-0.017	5
	1061.99	1.667	-0.055	-0.083	5
	836.32	1.685	+0.007	+0.011	5
CS	1072.3	1.56	+0.01	+0.02	6
	1285.1	1.53	+0.01	-0.02	6
SiN	1031.01	1.576	-0.087	+0.005	
	1151.68	1.568	-0.004	-0.032	
PN	1337.24	1.487	+0.015	-0.014	5
	1103.09	1.542	+0.021	+0.003	5
AlO	868.15	1.663	+0.005	-0.021	
	977	1.614	-0.016	-0.026	
SiO	848.1	1.618	+0.037	+0.031	7
	1240.5	1.505	+0.020	-0.014	
SO	628.7	1.769	-0.025	-0.024	
	1123.73	1.489	+0.056	+0.030	

FORMULA	ω_e (exp.) (cm ⁻¹)	r_e (exp.) (10 ⁻⁸ cm)	r_e (calc.) - r_e (exp.) (Huggins) (10 ⁻⁸ cm)	r_e (calc.) - r_e (exp.) (Badger) (10 ⁻⁸ cm)	REFER- ENCE
SiF	716.5	1.595	+0.076	+0.111	8
	865.0	1.595	+0.041	+0.021	8
P ₂	475.22	2.115	-0.092	+0.066	9
	780.43	1.856	-0.001	-0.009	
S ₂	727.4	1.840	+0.030	+0.029	10
Cl ₂	261.1	2.42	-0.27	+0.02	
	564.9	1.983	-0.066	-0.023	
Br ₂	165.39	2.65	-0.15	+0.09	
	323.86	2.28	+0.01	+0.01	
Te ₂	250.9	2.85	-0.24	-0.30	
I ₂	128.0	3.010	-0.197	-0.005	
	214.26	2.660	-0.004	-0.017	
ICl	212.3	2.644	-0.117	+0.046	
	384.6	2.310	-0.015	-0.015	
CaO	705.8	1.82	-0.09	-0.04	11
	718.5	1.74	0.00	+0.03	
TiO	837.86	1.690	-0.016	+0.003	
	1008.12	1.617	-0.004	+0.003	
PbO	530.6	2.042	+0.034	+0.001	
	451.7	2.089	+0.011	+0.042	
	722.3	1.918	+0.020	-0.021	
Li ₂	269.69	2.93	0.00	+0.07	
	253.2	3.11	-0.01	-0.01	
	351.60	2.67	+0.01	-0.04	
Na ₂	123.79	3.404	+0.033	+0.098	
	115.60	3.663	-0.008	-0.058	
	159.23	3.070	-0.001	+0.084	
K ₂	75.00	4.22	-0.09?	-0.02	
	92.64	3.91	0.00?	-0.07	
BeH ⁺	1476.1	1.603	+0.023	-0.089	
	2220.0	1.310	-0.030	-0.077	
BeH	2087.6	1.330	-0.016	-0.059	
	2058.5	1.340	+0.005	-0.060	
MgH ⁺	1138.4	2.008	-0.012	-0.049	
	1702.2	1.649	-0.001	-0.016	
MgH	1603.45	1.68	0.00	0.00	
	1493.45	1.73	-0.01	0.00	
CaH	1448	1.85	+0.03	-0.04	
	1147.5	2.61	-0.62	-0.60	
	1285	1.95	+0.03	-0.04	
	1333	1.99	-0.03	-0.11	
	1316.7	2.02	-0.05	-0.13	
LiH	287.4	2.5	+0.2?	+1.4	
	1406.1	1.6	0.0?	0.0	
NaH	345.20	3.0	-0.3?	+0.6	
AlH	1680.6	1.644	+0.044?	-0.003	
ZnH ⁺	1365	1.71	+0.01	+0.14	
	1916	1.51	0.00	+0.10	
CdH ⁺	1250	1.86	+0.02	—	
	1773	1.66	0.00	—	
CdH	874.1	2.378	-0.37	—	
	1749.8	1.660	+0.01	—	
	1430.7	1.754	-0.02	—	
HgH ⁺	1647	1.69	-0.09	—	
	2016	1.59	0.00	—	
HgH	2063.2	1.580	0.00	—	
	1432.7	1.729	-0.22	—	
CuH	1699.9	1.568	-0.017?	+0.120	
	1939.9	1.460	+0.051?	+0.142	
AgH	1663.6	1.638	-0.095?	—	
	1760.0	1.614	+0.054?	—	
AuH	1690	1.67	-0.08?	—	
	2302	1.52	+0.01?	—	

values. Moreover, these r_{12} values were nearly the same for practically all compounds satisfying these requirements which have the same distribu-

tion of kernel electrons, e.g., for all molecules composed of one first row element and one second row element. In addition there is ap-

⁴ Kirkpatrick and Salant, Phys. Rev. **48**, 945 (1935).

⁵ Bärwald, L. Herzberg and G. Herzberg, Ann. d. Physik **20**, 569 (1934).

⁶ Crawford and Shurcliff, Phys. Rev. **45**, 860 (1934).

⁷ Jevons gives r_0 but not r_e . To obtain the latter, use was made of the rough value of α computed by means of Eq. (21) of the previous paper.

⁸ The r_0 values given for the SiF molecule by Jevons are divided by $\sqrt{2}$ to accord with the conclusions of Badger and Blair, Phys. Rev. **47**, 881 (1935). The equilibrium distance r_e was then calculated from r_0 as outlined in reference 7.

⁹ G. Herzberg, Ann. d. Physik (5) **15**, 677 (1932); Phys. Rev. **40**, 313 (1932).

¹⁰ The value of r_e used is from Badger, Phys. Rev. **46**, 1025 (1934). Van Dijk and Lameris, Physica **2**, 785 (1935), obtain $r_0=1.73\text{Å}$, which is certainly too low, if the values of ω_e and $\omega_e x_e$ are correct. If the data on F₂ and Cl₂ are not in error, calculations of the sort made in this paper lead one to expect a value of about 1.90Å. Maxwell, Hendricks and Mosley, Phys. Rev. **49**, 199 (1936), obtain $1.94\pm 0.03\text{Å}$ for the internuclear distance in S₂ molecules by electron diffraction.

¹¹ Brodersen, Zeits. f. Physik **79**, 613 (1932).

proximate additivity of these r_{12} values. From the set of "basic radii" given in Table II one can, by addition, calculate r_{12} values and from these and the experimental constants ω_e and $\omega_e x_e$ compute equilibrium distances r_e for a large number of molecules. The degree of agreement with the experimental equilibrium distances is shown in Table III.

It should be mentioned that some of the data on which the calculation of the radii in Table II are based are meager and inadequate. In many cases also the data are for highly excited states, for which, in considering only the first row elements, poor agreement was found. Slightly better agreement between calculated and experimental values of r_e could also be obtained if one gave up the assumption of additivity or used different values of a for different molecules. For present purposes at least, with the limited data available, the usefulness of the additivity and constancy of a approximations would seem to make their use advisable.

To obtain reasonable agreement between the r_{12} values calculated for different states of other hydride molecules and of molecules of the alkali metals, smaller values of a have to be assumed. The values chosen and the r_{12} values resulting therefrom are listed in Table II. The equilibrium distances computed from these are compared with the experimentally determined distances in Table III. Again the agreement is satisfactory.

For the hydrogen molecule the results of calculations of r_{12} assuming three different values of a are given (Table IV). There is really little to

TABLE IV.² Comparison of calculated and experimental equilibrium distances for H_2 .

STATE	$\omega_e(\text{exp.})$ (cm^{-1})	α (cm^{-1})	$r_e(\text{exp.})$ (10^{-8}cm)	$r_e(\text{calc.}) - r_e(\text{exp.})$ (Huggins) (Badger)			
				$a=4.5$ $r_{12}=1.01$ (10^{-8}cm)	$a=5.0$ $r_{12}=0.95$ (10^{-8}cm)	$a=6.0$ $r_{12}=0.90$ (10^{-8}cm)	
$1s\sigma^2 \pi^2 \Pi_u$	2293	1.6*	1.052	+0.013	+0.003	+0.008	+0.037
$1s\sigma^2 \pi^2 \Sigma_u$	2309	1.6*	1.052	+0.009	+0.000	+0.006	+0.033
$1s\sigma^2 \pi^2 \Pi_u$	2336.5	1.6*	1.051	+0.003	-0.005	+0.003	+0.026
$1s\sigma^2 \pi^2 \Sigma_u$	2372.53	2.72	1.035	+0.003	-0.001	+0.009	+0.030
$1s\sigma^2 \pi^2 \Sigma^+$	2197	2.2*	1.103	-0.031	-0.038	-0.033	+0.017
$1s\sigma^2 \pi^2 \Pi_u$	2463	1.9*	0.96	+0.06	+0.06	+0.07	+0.08
$1s\sigma^2 \pi^2 \Sigma^+$	2664.61	1.650	0.986	-0.003	-0.001	+0.018	+0.002
$(3^1M) 1^2 \Sigma^+$	2209	3.2*	1.6	-0.5	-0.5	-0.5	-0.5
$1s\sigma^2 \pi^2 \Sigma^+$	2538	2.1*	1.04	-0.10	-0.08	-0.05	-0.02
$1s\sigma^2 \pi^2 \Pi_u$	2252.90	2.1*	1.07	-0.02	-0.02	-0.01	+0.04
$1s\sigma^2 \pi^2 \Sigma^+$	2455.45	2.1*	1.05	-0.09	-0.07	-0.04	-0.01
$2p\sigma^2 \pi^2 \Sigma^+$	2245.4	3.5*	1.74	-0.60	-0.63	-0.64	-0.63
$1s\sigma^2 \pi^2 \Pi_u$	2446.5	1.2	1.05	-0.03	-0.03	-0.02	-0.01
$1s\sigma^2 \pi^2 \Sigma_u^+$	1357.266	1.94	1.276	+0.06	+0.02	-0.02	+0.259
$1s\sigma^2 1^2 \Sigma_u^+$	(4371)	2.9	0.740	-0.031	+0.010	+0.079	

* The values of α marked with an asterisk were calculated by means of Eq. (24) of the earlier paper in this series.

TABLE V. Summary of deviations of calculated from experimental values of r_e .

	$\pm(r_e(\text{calc.}) - r_e(\text{exp.}))$				Total
	0.025A or less	0.026A to 0.050A	0.051A to 0.150A	>0.150A	
Huggins	87	21	19	14	141
Badger	78	21	15	12	126*
	63	33	24	6	126*

* All those for which Badger gives the necessary constants.

choose between them, the general agreement being about equally good in each case. Whether the large disagreement shown, for any choice of a , by some states is due to experimental errors or is an indication that the assumed potential expression is far from accurate for these cases, it does not seem possible at present to decide.

COMPARISON WITH BADGER'S EQUATION

Badger¹² has shown that the equilibrium distances for most diatomic molecules in most of their electronic states for which the data are known may be calculated approximately by the simple empirical equation

$$r_e = d_{ij} + C_{ij}^{1/3} / k_e^{1/3}, \quad (4)$$

in which k_e is the "bond force constant" and C_{ij} and d_{ij} are constants characteristic of the rows of the periodic table in which the two elements occur. As may be seen from Tables III, IV and V, the agreement obtained by using this equation with the constants he gives is nearly as good as by the method described in this paper. In most of the cases of marked disagreement between the experimental value of the equilibrium distance and that calculated by one of the two methods, there is also a similar disagreement when the calculation is made by the other method.

The relation between the two methods can be shown in the following way. The force constant k_e , in megadynes per centimeter (the unit used by Badger) is related to ω_e , in cm^{-1} , by the equation

$$k_e = 5.85 \times 10^{-8} M \omega_e^2. \quad (5)$$

This may be combined with Eqs. (3a), (3c) and (3d) to give

$$r_e = r_{12} - \frac{2.303}{a} \log \left(\frac{100k_e}{a^2 - aa'} \right), \quad (6a)$$

¹² Badger, J. Chem. Phys. 2, 128 (1934); 3, 710 (1935).

which is equivalent to

$$r_e = \left[r_{12} + \frac{2.303}{a} \log \left(\frac{a^2 - aa'}{100} \right) - K_{ij} \right] + \left[K_{ij} - \frac{2.303}{a} \log k_e \right], \quad (6b)$$

where K_{ij} is any distance. Now we have shown that a is practically a constant (usually 6) for diatomic molecules of the same ij class—composed of elements from the same two rows of the periodic table—provided the sums of the kernel charges are not too different. Also (see column 7 of the table in the previous paper) a' is almost invariably small compared with a ; moreover, for most states of most molecules of the same ij type, a' has *roughly* the same value. Therefore $(a^2 - aa')$ is the difference between a relatively large number (36) and a small, roughly constant number (approximately 6 for 1, 1 type molecules, zero for 1, 2 type molecules, etc.). The quantity in the first set of brackets in Eq. (6b) is thus nearly constant, for a given type, no matter what value K_{ij} has. By choosing a suitable value for K_{ij} the quantity $(K_{ij} - (2.303/a) \log k_e)$ can be made closely equal to $(C_{ij}^{1/2}/k_e^{1/2})$ over quite a range of values of k_e . Making such a choice for the range of k_e values of a given ij type, it is seen that Eq. (6b) is approximately equivalent to Eq. (4).

The relation between Badger's constants d_{ij} and $C_{ij}^{1/2}$ is readily obtained from a comparison of these equations. Equating corresponding portions,

$$K_{ij} = r_{12} + \frac{2.303}{a} \log \left(\frac{a^2 - aa'}{100} \right) - d_{ij} \quad (7)$$

$$\text{and } K_{ij} = \frac{C_{ij}^{1/2}}{k_e^{1/2}} + \frac{2.303}{a} \log k_e. \quad (8)$$

Eliminating K_{ij} we obtain

$$d_{ij} = r_{12} + \frac{2.303}{a} \log \left(\frac{a^2 - aa'}{100k_e} \right) - \frac{C_{ij}^{1/2}}{k_e^{1/2}}. \quad (9)$$

For molecules of first row elements, average values of k_e and a' (neglecting the few high energy states giving poor agreement between experimental equilibrium distances and those

calculated by Eq. (3)) are 1.28 and 1.23, respectively. Substituting these and the values 1.46 for r_{12} and 6.0 for a , we calculate

$$d_{1,1} = 1.214 - 0.92C_{1,1}^{1/2}. \quad (10)$$

This equation is nearly satisfied by Badger's values of 0.68 and 0.571 for $d_{1,1}$ and $C_{1,1}^{1/2}$, respectively. Similar calculations for other ij types lead to similar results.

CONCLUSION

It is evident from the agreement between calculated and experimental equilibrium distances that the type of potential expression used is not a bad approximation for values of r not too far from r_e . The approximate equivalence of the constants a and r_{12} in the repulsive term for different molecules composed of atoms of the same two rows of the periodic table (having not too different a sum of kernel charges) makes this type of potential equation especially useful. In this paper application has been made only to the calculation of r_e values, but other molecular constants can also be roughly calculated by the methods described in the previous paper. The approximate additivity of r_{12} values is useful in extending the calculations to other types of molecule.

Undoubtedly in many of the molecules dealt with in this paper the true variation of potential energy with distance is more accurately approximated by a function of the chosen type with somewhat different values of a and r_{12} than those used here, but with the present data one cannot easily (if at all) determine the best values; also the usefulness of the function for purposes of prediction is greatest if the same values of these constants can be used successfully with large groups of molecules and states.

If the prediction of r_e were the only useful result of the potential energy expression employed in this paper, little advantage could be claimed over the empirical equation proposed by Badger. From the author's relation however, various other unknown or doubtful molecular constants can also be calculated. In addition, the whole potential energy curve can be obtained with reasonable accuracy from a minimum of data.