The constituent velocity is proportional to $\bar{r}/\sigma$, and the ratio $(\bar{r}/\sigma)_{\text{behind}}/(\bar{r}/\sigma)_{\text{ahead}}$ will be referred to as the sharpening ratio. If this ratio is greater than one, the net effect is to sharpen the boundary; if the ratio is equal to one, there will be no sharpening or spreading effect, and if the ratio is less than one, the net effect is to spread the boundary. The calculated sharpening ratios for the aspartate and glutamate boundaries in both the ascending and descending channels are shown in the right hand columns of Tables IV and V. These calculations are in agreement with the fact that the ascending moving boundaries appear to move in a steady state and the descending boundaries continue to spread.

Since proteins are such complicated weak electrolytes, it is not possible to apply directly the equations derived here. However, these calculations and experiments indicate some of the problems in determining the true composition of a protein mixture by electrophoresis. If the components of a mixture can be isolated, it is always possible to obtain the true analysis of a mixture by an empirical method. This was done by Bock and Alberty[22] for mixtures of adenosine phosphates. Apparent analyses for mixtures of known composition were obtained by moving boundary experiments, and calibration curves showing the relationship between the actual composition and apparent analysis for a given set of conditions were constructed.

Acknowledgments.—The authors are indebted to Prof. Louis J. Gosting for helpful discussions and to Prof. Robert M. Bock for making available the Spinco Model H electrophoresis apparatus. The authors are also indebted to Prof. P. C. Hammer, Mrs. Hildegard Frazier and Mr. Werner Schanzenbach of the Numerical Analysis Laboratory of the University of Wisconsin for assistance with the numerical computations. This research was supported by the Research Committee of the Graduate School of the University of Wisconsin from funds supplied by the Wisconsin Alumni Research Foundation and by a Grant-in-Aid from the du Pont Company.

(22) R. M. Bock and R. A. Alberty, *J. Biol. Chem.*, **193**, 435 (1951).

MADISON, WISCONSIN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

Semiempirical Potential Energy Functions. III. Generalization for Ionic Molecules and the Inclusion of London Forces[1]

BY ARTHUR A. FROST AND JOHN H. WOODSON

RECEIVED NOVEMBER 16, 1957

This semi-empirical potential energy function previously proposed for covalent diatomic molecules has been extended to apply to ionic molecules and to interaction of inert gas atoms. It is shown that this leads to a useful prediction of the dissociation energy and internuclear equilibrium distance of ionic molecules using as the only experimental information the known interaction of the corresponding inert gas atoms.

In previous papers[2,3] there has been proposed a semi-empirical function V for covalent diatomic molecules of the form

$$V = e^{-aR}\left(\frac{c}{R} - b\right) \qquad (1)$$

where R is the internuclear distance and a, b and c are parameters determined by fitting experimental data. c is interpreted as the product of the effective charges on the kernels of the two atoms.

This function was devised in order to provide a proper dependence of V on R as R goes to zero. The same idea is here extended to ionic molecules and to inert gas atom interaction.

Inert Gas Atom Interaction.—The usual empirical function for this case is the exp-six or Buckingham potential[4]

$$V = be^{-aR} - \frac{d}{R^6} \qquad (2)$$

where the first term is a repulsion due to non-bonded interaction of closed shells and the second term is a London attraction. It is obvious that as R goes to zero this V goes to minus infinity instead of positive infinity as it should reasonably do owing to internuclear coulomb repulsion. As a result various modified Buckingham potentials have been used. Buckingham and Corner[5] and Rice and Hirschfelder[6] have replaced the exp-six function at small distances by an arbitrary function that does behave more satisfactorily. This has been necessary in particular for virial coefficient calculations.

It is possible to remedy the negative infinity defect in a smooth manner by modifying the London term as follows: Replace $1/R^6$ by

$$\frac{1}{R^6}\left[1 - e^{-aR}\left(1 + aR + \frac{(aR)^2}{2!} + \frac{(aR)^3}{3!} + \frac{(aR)^4}{4!} + \frac{(aR)^5}{5!}\right)\right] \qquad (3)$$

which can also be expressed as

$$\frac{1}{R^6} - \frac{a^6}{5!}A_5\,(aR) \qquad (4)$$

where

$$A_5(\alpha) = \int_1^\infty e^{-\alpha x}\, x^5\, dx$$

---

(1) This research was supported by a grant from the National Science Foundation. This paper was presented at the September, 1957, meeting of the American Chemical Society.

(2) A. A. Frost and B. Musulin, *J. Chem. Phys.*, **22**, 1017 (1954). (Paper I.)

(3) P. S. K. Chen, M. Geller and A. A. Frost, *J. Phys. Chem.*, **61**, 828 (1957). (Paper II.)

(4) E. A. Mason and W. E. Rice, *J. Chem. Phys.*, **22**, 522, 843 (1954).

(5) R. A. Buckingham and J. Corner, *Proc. Roy. Soc. (London)*, **A189**, 118 (1947).

(6) W. E. Rice and J. O. Hirschfelder, *J. Chem. Phys.*, **22**, 187 (1954).

is a Rosen function.[7] The function 3 was arrived at by looking for the simplest exponential-power series function which would behave as $1/R^6$ for large R but which would remain finite at $R = 0$.

To obtain the desired positive infinity at $R = 0$, the same technique as used in equation 1 is applicable, that is, to incorporate a modified coulomb term

$$\frac{c}{R}e^{-aR} \tag{5}$$

where c is the product of effective nuclear charges.

Therefore it is proposed that a suitable function for inert gas atom interaction should be of the form

$$V = \frac{c}{R}e^{-aR} + be^{-aR} - d\left[\frac{1}{R^6} - \frac{a^6}{5!}A_5(aR)\right] \tag{6}$$

Ionic Molecules.—A function similar to the Born–Mayer[8] function for ionic crystals has been used by Rittner[9] and by Varshni[10] for ionic molecules. This function has the same defect as above in giving rise to a negative infinity as R goes to zero.

In this case the coulomb term (5) should be modified to

$$\frac{c'}{R} + e^{-aR}\left(\frac{c - c'}{R}\right) \tag{7}$$

where c' is the product of the charges on the ions while c, as before, is a product of effective nuclear charges.

Then, if one incorporates coulomb, exponential repulsion and London energy terms, the proposed function becomes

$$V = \frac{c'}{R} + e^{-aR}\left(\frac{c - c'}{R}\right) + be^{-aR} - d\left[\frac{1}{R^6} - \frac{a^6}{5!}A_5(aR)\right] \tag{8}$$

For ion interaction there is also, of course, the possibility of ion-dipole inverse fourth power energies. At normal interatomic distance these energies are the same order of magnitude as the London energy and should probably be included. A satisfactory form would be proportional to

$$\frac{1}{R^4} - \frac{a^4}{3!}A_3(aR) \tag{9}$$

Pauling[11] has also treated ionic molecules but with a high inverse power repulsion rather than the more theoretically accepted exponential term.

Covalent Molecules.—As a result of Pitzer's estimates[12] the London attraction appears to be of considerable importance in covalent molecules. Equation 1 should then be modified to include such a term as well as the coulomb repulsion and covalent attraction energy. And it may be necessary to allow for inner shell repulsions.

The General Case.—The preceding considerations can be generalized by requiring the potential energy to be a sum of terms of the types

1. Coulomb energy

$$V_c = \frac{c'}{R} + e^{-aR}\frac{(c - c')}{R} \tag{10}$$

as in equation 7.

2. Exchange energy

$$V_x = \pm be^{-aR} \tag{11}$$

where the plus sign applies for inner shell or non-bonded repulsion and the minus sign for covalent attraction.

3. London energy

$$V_l = -d\left[\frac{1}{R^6} - \frac{a^6}{5!}A_5(aR)\right] \tag{12}$$

as in equation 4.

4. Other energies such as the ion-dipole inverse fourth power term as well as higher inverse power terms than the sixth. Also there can be resonance effects such as are involved in the change over from ionic to covalent bonding of an alkali halide molecule at large distance.

The parameter a that appears in all of the terms is not necessarily uniform for a given molecule. For example, in the Morse function the repulsion term has an a twice as great as in the attraction term. Huggins[13] has generalized this. However, except when two exchange energy terms may be required, the simpler assumption of constant a will at least be tried first.

Calculations.—Because of the increased number of parameters in these more generalized semi-empirical functions, the determination of the best values of the parameters has not been completed. A simpler calculation is involved in the following comparison of the alkali halide ionic diatomic molecules with the corresponding isoelectronic inert gas atom pairs.

Examination of the functions proposed for the inert gas interactions equation 6, and for ionic molecules equation 8, shows that the ionic molecule function is similar to the inert gas atom function except for the extra term c'/R. The c of the inert gas function is equal to $(c - c')$ for the ionic molecule if there are equal numbers of electrons in two outer shells interacting. In this work the atomic kernels for which c is the effective charge product are taken to be the nuclei plus the electrons of all the inner shells. Thus, leaving an outer shell of eight electrons, except of the He atom and the Li ion which are not involved in these calculations. This term c'/R is just the interaction energy of the two ions considered as point charges. In this case c' is equal to minus one atomic unit.

Since the parameters, a, b and d are probably primarily dependent on the electron shells, their values may be nearly the same in ionic molecules and the corresponding inert gas pairs. Therefore, it would be expected that the function for the interaction of two argon atoms, for example, plus the term c'/R (negative), would represent the potential energy curve for the KCl gaseous molecule.

On the basis of this idea the term c'/R was added to the potential energy functions for Ar, Kr and Xe pairs as determined by Whalley and Schneider[14] from virial coefficient data, resulting in the function

$$V = \frac{c'}{R} + be^{-aR} - \frac{d}{R^6} \tag{13}$$

The functions for unlike inert gas atom interactions

---

[7] N. Rosen, *Phys. Rev.*, **38**, 2099 (1931).

[8] M. Born and J. Mayer, *Z. Physik*, **75**, 1 (1932).

[9] E. S. Rittner, *J. Chem. Phys.*, **19**, 1030 (1951).

[10] Y. P. Varshni, *Trans. Faraday Soc.*, **53**, 132 (1957).

[11] L. Pauling, *Proc. Nat. Acad. Sci. India*, **25A**, Pt. 1 (1956).

[12] K. S. Pitzer, *J. Chem. Phys.*, **23**, 1735 (1955).

[13] M. L. Huggins, *ibid.*, **3**, 473 (1935); **4**, 308 (1936).

[14] E. Whalley and W. G. Schneider, *ibid.*, **23**, 1644 (1955).

were obtained by using the rules of Mason[15] for combining the parameters of like atom interactions. The parameters of Mason and Rice[4] do not lead to as satisfactory predictions for the alkali halides as do those of Whalley and Schneider.

The depth and position of the minima in the potential energy curves of the six alkali halide molecules containing the electron structures of Ar, Kr and Xe are given with the observed values in Table I. The zero of energy is taken as that of ions at infinite separation. The dissociation energy, D_e, therefore includes the energy change in going from separated atoms to ions. An example of how the whole curve compares with Rittner's more exact approach to ion–ion attraction is shown in Fig. 1. In Fig. 2 the general trend predicted in the equilibrium internuclear distance is seen to be an oversimplification of a slight average trend in the measured distances, experimental values of which are known quite precisely.[16] Plotting the product of the equilibrium internuclear distance and the minimum depth *versus* the mean atomic number of the nuclei in the alkali halide molecules (Fig. 3) reveals that this simple treatment predicts a softening of the electron shell with heavier nuclei rather than a slight hardening shown by the observed data. The values used for the various parameters are listed in Table II in atomic units.

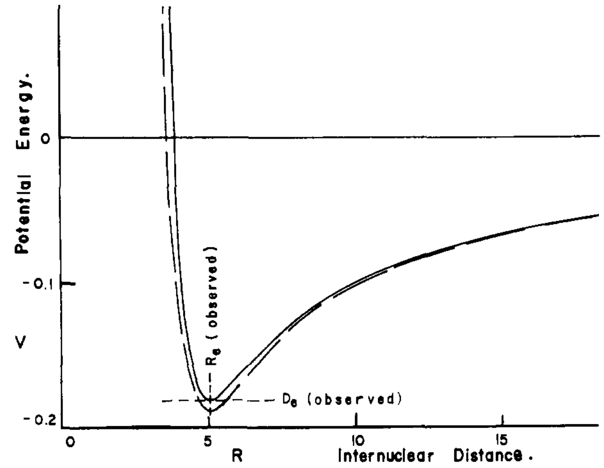

Fig. 1.—Potential energy curve for KCl: V and R in atomic units. Full curve, this calculation; broken curve, Varshni.

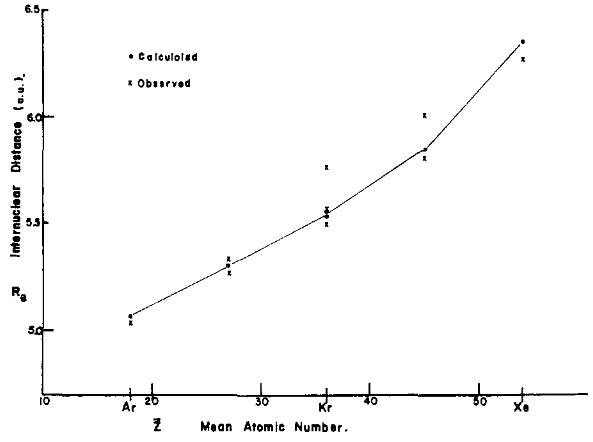

Fig. 2.—Internuclear distance as a function of mean atomic number.

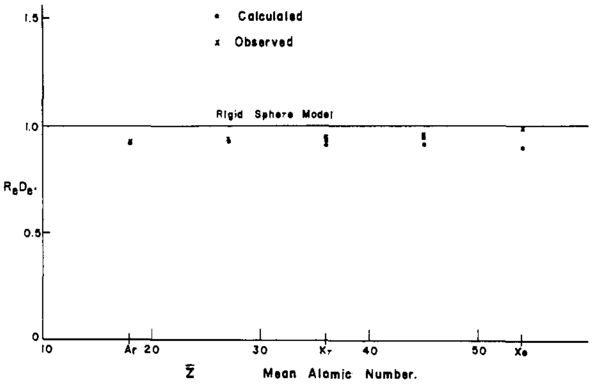

Fig. 3.—Product of the equilibrium internuclear distance and the equilibrium energy as a function of mean atomic number.

TABLE I

COMPARISON OF CALCULATIONS WITH OBSERVED DATA FOR SOME ALKALI HALIDE GAS MOLECULES

Di-atom	R_e(calcd.)	R(obsd.)[a]	D_e(calcd.)	D_e-(obsd.)[b]
KCl	5.075	5.0392	0.1808	0.1814
KBr	5.300	5.3304	.1739	.1735
RbCl		5.2664		.1763
RbBr	5.531	5.5649	.1672	.1681
KI	5.555	5.7596	.1633	.1622
CsCl		5.4920		.1683
RbI	5.846	6.0035	.1556	.1568
CsBr		5.8053		.1616
CsI	6.354	6.2645	.1402	.1561

$$\left(\frac{dV}{dR}\right)_{R=R_e} = 0;\ D_e = -V(R_e)$$

[a] See reference 16. [b] Calculated from data of ref. 9.

TABLE II

PARAMETERS USED IN CALCULATIONS

$c = 63,\ c' = -1$

All values in atomic units.

Di-atom	a	b	d
KCl	2.098	907.0	92.76
KBr RbCl	2 050	1071.9	125.9
RbBr	2.003	1266.7	170.7
KI CsCl	1.709	302.7	178.5
RbI CsBr	1.664	357.7	242.2
CsI	1.324	101 0	343 6

In this crude approximation the same curve is predicted for two alkali halide molecules, such as KBr and RbCl, regardless of which inert gas structure is contained in which ion. However, the predicted values always fall between the observed values of the two molecules. This approach also neglects any added attraction between the ions because of polarization as might be represented by an inverse 4th power term.[9] The success of this

---

(15) E. A. Mason, *J. Chem. Phys.*, **23**, 49 (1955).

(16) A. Honig, M. Mandel, M. L. Stitch and C. H. Townes, *Phys. Rev.*, **96**, 629 (1954).

approach and other formulations that neglect polarization[8,11] seems to bear out Varshni's[10] contention that the added attraction is offset by added repulsion due to the distortion of the electron clouds in the direction of the bond.

EVANSTON, ILLINOIS

[CONTRIBUTION NO. 1477 FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY]

The Diffusion and Activity Coefficient of Sodium Nitrate in Dilute Aqueous Solutions at 25°

BY HERBERT S. HARNED AND JOSEPH A. SHROPSHIRE

RECEIVED DECEMBER 23, 1957

The diffusion coefficient of sodium nitrate has been determined by the conductance method in the concentration range between 0.001 and 0.011 molar at 25°. From these data, its activity coefficient in very dilute solutions has been computed.

It has been shown that activity coefficients of univalent electrolytes at low concentrations can be evaluated with high accuracy in dilute solutions from diffusion coefficients.[1] The method is very favorable numerically and affords a means of obtaining activity coefficients at low concentrations of many electrolytes for which no other methods are available. In this contribution, this method has been applied to solutions of sodium nitrate at 25°.

The diffusion coefficient in dilute solutions may be computed by the equation[2]

$$\mathfrak{D} = 1000\nu\, RT(\bar{\mathfrak{M}}/c)\left(1 + c\,\frac{\partial \ln y_{\pm}}{\partial c}\right) \qquad (1)$$

where $\mathfrak{D}$ is the diffusion coefficient, ν is the number of ions into which the electrolyte dissociates, R is the gas constant in ergs moles deg.$^{-1}$ and T the absolute temperature. $(\bar{\mathfrak{M}}/c)$ is the concentration dependent mobility term and $(1 + c\partial \ln y_{\pm}/\partial c)$ is the thermodynamic term. The equations for computing $(\bar{\mathfrak{M}}/c)$ are given in detail elsewhere[3] and will not be reproduced here. Upon rearrangement, equation 1 becomes

$$\frac{\mathfrak{D}}{1000\,\nu\, RT\,(\bar{\mathfrak{M}}/c)} - 1 \equiv \mathfrak{D}' = c\,\frac{\partial \ln y_{\pm}}{\partial c} \qquad (2)$$

which defines the function $\mathfrak{D}'$. It is observed that c is the molar concentration and $y_{\pm}$ is the activity coefficient on the molar concentration scale. From this equation, we obtain

$$\log y_{\pm} = \frac{\ln y_{\pm}}{2.3026} = 0.8686 \int_0^c \frac{\mathfrak{D}'}{c^{1/2}}\, dc^{1/2} \qquad (3)$$

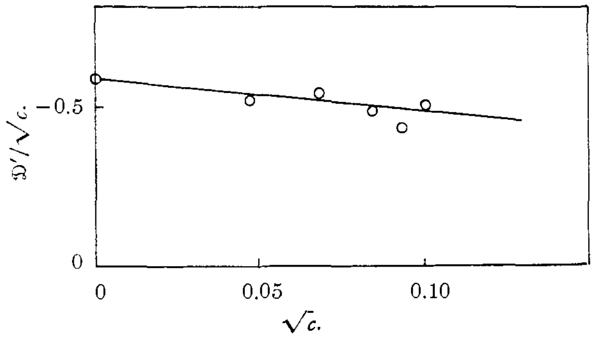

Fig. 1.—Plot for the computation of the activity coefficient of sodium nitrate at 25°.

An important feature of this method is that the limiting value of $\mathfrak{D}'/c^{1/2}$ is fixed and is not dependent upon the diffusion coefficient. Thus

$$\lim_{c=0}\left[\frac{\mathfrak{D}'}{c^{1/2}} = \frac{\partial \ln y_{\pm}}{2\partial c^{1/2}}\right] = -\frac{2.3026}{2}\,\mathcal{S}_{(f)} \qquad (4)$$

where $\mathcal{S}_{(f)}$ is the theoretical slope of the logarithm of the activity coefficient. By plotting $\mathfrak{D}'/c^{1/2}$ against $c^{1/2}$ to this limiting value, the activity coefficient may be obtained by equation 3 by graphical integration.

Table I contains the observed values of the diffusion coefficient of sodium nitrate at the concentrations indicated. It also includes all the data necessary for computing the mobility term $(\bar{\mathfrak{M}}/c)$ according to the equations referred to in reference 3.

TABLE I

COMPUTATION OF $\mathfrak{D}'/c^{1/2}$ USED FOR DETERMINING THE ACTIVITY COEFFICIENT OF SODIUM NITRATE[a]

c	$A'\sqrt{c}$	$\phi(A'\sqrt{c})$	$\Delta\bar{\mathfrak{M}}'/c \times 10^{20}$	$\Delta\bar{\mathfrak{M}}''/c \times 10^{20}$
0.00223	0.0543	1.756	0.022	0.074
.00479	.0788	1.438	.032	.128
.00710	.0969	1.260	.036	.170
.00872	.1074	1.176	.042	.194
.01009	.1155	1.119	.045	.214

$c^{1/2}$	$\mathfrak{D}$(obs.) $\times 10^5$	$(\bar{\mathfrak{M}}/c) \times 10^{20}$	$-\mathfrak{D}'$	$-\mathfrak{D}'/c^{1/2}$
0.0472	1.534	31.707	0.02439	0.5167
.0686	1.516	31.751	.03707	.5408
.0843	1.512	31.786	.04073	.4834
.0934	1.514	31.807	.03997	.4280
.1005	1.498	31.824	.05056	.5033

[a] $\lambda^0_+ = 50.11$; $\lambda^0_- = 71.44$; $\Lambda^0 = 121.55$; $10^3\,\eta = 8.849$; $D = 78.54$; $a = 3.5$ Ångströms; $A' = 1.150$; $\mathcal{S}_{(f)} = 0.5091$.

Figure 1 shows a plot of $\mathfrak{D}'/c^{1/2}$ *versus* $c^{1/2}$ from which the activity coefficients of sodium nitrate at round concentrations recorded in Table II were calculated.

Certain features of this calculation deserve notice. Numerically, the method is very favorable since the limiting value of $\mathfrak{D}'/c^{1/2}$ is known and since the deviation of the activity coefficient from

---

[1] H. S. Harned, *Proc. Nat. Acad. Sci.*, **40**, 551 (1954).

[2] L. Onsager and R. M. Fuoss, *J. Phys. Chem.*, **36**, 2689 (1932).

[3] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd Ed., Reinhold Publ. Corp., New York, N. Y., 1958, p. 121–2, equations (4-4-19), (4-4-20) and (4-4-21).