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**A Dynamic Partial Order Model  
of Electrolyte Solutions**

by

R.M. Pytkowicz,  
K. Johnson, and  
C. Curtis

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20. Abstract (continued)

displacements from average positions lead to a symmetric increase in energy which is not cancelled out, and a hydration correction for the effect of hydration upon the effective ionic concentrations. Ions are given partial counter-ion character as a function of the degree of order so that the free energy of ionic interactions can be calculated rigorously, as if the lattice were perfect, without resort to cluster integrals in the case of single salt solutions.

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A Dynamic Partial Order Model of Electrolyte Solutions

R. M. Pytkowicz, K. Johnson, and C. Curtis

School of Oceanography  
Oregon State University  
Corvallis, Oregon

To the Creator who, in his infinite wisdom, did not give us infinite knowledge but granted us the challenge and the pleasure to slowly glimmer an understanding of his laws.

To Joyce Pytkowicz to whom he granted nearly infinite patience.

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Foreword

Dear Colleague:

At this point, when we need your critical comments and suggestions on the substance of this work, on other electrolyte chemists who should receive it, and on the format and place where we should publish it, this work has become too long for a journal article and too short for a book. We hesitate in shortening it at present because the novel concepts presented here may lose clarity. We, therefore, decided to issue it for the time being as a technical report.

Should you wish to refer to it, a suggested format is:

Pytkowicz, R.M., Johnson, K. and C. Curtis. 1976. A dynamic partial order model of electrolyte solutions. Oregon State University School of Oceanography Technical Report. October 1976.

We look forward to your thoughts and, should you have the theoretical and experimental tools to improve and pursue this work or, should you already be doing parallel work, we would appreciate word from you at your convenience.

Sincerely,

R.M. Pytkowicz  
K. Johnson  
C. Curtis

Corvallis, October 1976

Abstract

The purpose of this work was to develop a dynamic partial order model of electrolyte solutions which avoids inconsistencies present in the Debye-Hückel<sup>11</sup> and in related theories. It is shown that our results are consistent with activity coefficient data in aqueous electrolyte solutions. The main features of our work are a partial long-range order which increases with concentration due to the increase in the coulombic energy of interaction and decreases with temperature, a contribution from ionic fluctuations because it is shown that displacements from average positions lead to a symmetric increase in energy which is not cancelled out, and a hydration correction for the effect of hydration upon the effective ionic concentrations. Ions are given partial counter-ion character as a function of the degree of order so that the free energy of ionic interactions can be calculated rigorously, as if the lattice were perfect, without resort to cluster integrals in the case of single salt solutions.

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Symbols

$a_D$	Debye distance of closest approach between ion centers
$\bar{a}$	anion sub-lattice
$A_C$ through $E_C$	parameters of Eqn. (1-27)
$A_D, B_D$	Debye-Hückel parameters
$A_M$	Madelung constant
$b$	general distance of closest approach of two ions, not limited to the Debye $a_D$ parameter
$B_b$	Born repulsive constant
$B_l$	constant of lattice theory
$c$	molarity
$\bar{c}$	cation sub-lattice
$\bar{d}$	degree of disorder
$D_e$	dielectric constant
$E_i$	electrical potential energy of ion $i$
$E_l$	configurational energy
$E_{(xtal)}$	lattice energy of an ionic crystal
$f$	molal activity coefficient
$f^{(D-H)}$	activity coefficient calculated from the Debye-Hückel equation
$f_{\pm}$	mean molal activity coefficient
$f_{\pm}^{(G)}$	Guntelberg activity coefficient
$f_{\pm}^{(corr)}$	activity coefficient corrected for hydration
$f_{\pm}^{(exp)}$	experimental value of $f_{\pm}$
$f_{\pm}^{(interp)}$	interpolated value of $f_{\pm}$

$\Delta F_{(\text{corr})}$	value obtained from the integral of $f_{\pm(\text{corr})}$ (see Eqn. (5-20))
$\Delta F_{(\text{exp})}$	value of $\Delta F_{\ell}$ obtained from $f_{\pm(\text{exp})}$ (see Eqn. (3-16))
$\Delta F_{\ell(\text{min})}^*$	value from theory which equals $\Delta F_{(\text{exp})}$
$h$	hydration number
$H_{\ell}$	configurational enthalpy
$I_S$	molal ionic strength
$I_S^{(c)}$	molar ionic strength
$k_B$	Boltzman constant
$\ell$	degree of order
$\ell_{\text{min}}$	value of $\ell$ for which $\Delta F_{\ell}$ has a minimum value
$\ell^*$	value of $\ell$ which yields $\Delta F_{\ell(\text{min})}^*$
$L$	order parameter
$m$	molality
$M_2$	molecular weight of solute
$n_i$	number of moles of ions of type $i$ (also used at times to represent the number of moles in a given volume or weight of solution when so indicated in the text)
$N_A$	Avogadro's number
$\bar{N}_i$	mole fraction of $i$
$N$	number of ions in a given volume or mass
pLRO	partial long-range order
PLRO	perfect long-range order
$P$	pressure
$q$	electrical charge

$r_o$	nearest neighbor ionic distance
$r_{(J)}$	distance from the central ion J
$r_x$	potential distance
$\bar{r}_x$	average value of $r_x$
R	gas constant
$S_\ell$	configurational entropy
T	absolute temperature
v	parameter of the partial order model
v'	defined by Eqn. 4-6
V	volume
w	fraction of ions in the counter-ion lattice
x	displacement
$z_i$	valence of ion of type i
$\epsilon$	electronic charge
$\kappa$	reciprocal of the thickness of the ion atmosphere (distance of the ion atmosphere from $r = a_D$ )
$\mu$	chemical potential
$\mu^o$	standard chemical potential
$\mu_i$	chemical potential of hydrated ions of type i
$\nu_i$	number of moles of ion i formed from one mole of salt
$\phi_{(J)}$	electrical potential due to all ions in solution at a volume element
$\phi$	potential due to the ion atmosphere
$\rho$	density of a solution
$\phi$	practical osmotic coefficient

$\rho_{(J)}$  charge density at a distance  $r_{(J)}$  from the central ion J

$\rho_o$  density of pure water

$\tau(\kappa a_D)$  quantity defined by Eqn. (1-17)

Introduction

Our purpose in developing this partial order theory of activity coefficients in electrolyte solutions was to bypass inconsistencies present in the Debye-Huckel theory and in related ones such as extensions applied to specific ionic interactions. These inconsistencies, some of which have not been pointed out before, arise primarily from the use of the Boltzman distribution to a problem the very essence of which is the interaction of charged particles, and from neglecting the quasi-lattice nature of ionic solutions which precludes net electrical densities from decaying monotonically with distance from a central (reference) ion.

We will start this work with a brief sketch of the derivation of the Debye-Huckel equation, followed by a critique which will bring to light logical impasses not previously revealed.

We will then examine early lattice models in which a fixed and, generally, perfect degree of long range order was assumed causing the resulting equations for activity coefficients to only apply over limited ranges of concentrations.

Finally we will present our model, valid at all concentrations, in which the degree of order increases with concentration because of the increase in the coulombic energy of interaction and decreases with increasing temperature. Our model will be developed step-by-step for greater clarity with the successive addition of relevant factors, namely, partial long-range order, translational energy and hydration. The translational energy is especially important because oscillations of ions around central positions lead to a symmetric energy contribution which is not canceled out.

We will not prove conclusively that our model is the only right one because, as in all other models of activity coefficients, we have an adjustable parameter of suspected physical significance but of unknown a priori analytical form as a function of the concentration, but we will show that the model is plausible and is consistent with experimental data. Thus, our main purpose at this stage is explanatory rather than predictive, a feature common to all models of activity coefficients which require empirical fitting at some stage in their application.

## 1. Debye-Hückel Theory and Critique

It will ease our critical review and refresh the memory of some of our readers if we sketch the derivation of the Debye-Hückel (1923) equation for activity coefficients of electrolytes in solution at the outset of this work.

### a) The Debye-Hückel equation

Consider a central (reference) ion J which is assumed to sense the other ions present in the solution as a smeared continuous distribution of charges with a charge density  $\rho_{(J)}$  in a volume element  $dV$  placed at a distance  $r_{(J)}$  from J. Poisson's equation at  $dV$  is then

$$\nabla^2 \phi_{(J)} = -\frac{4\pi}{D_e} \rho_{(J)} \quad (1-1)$$

in which  $\phi_{(J)}$  is the electrical potential at  $dV$  resulting from the fields produced by all the ions in the solution and  $D_e$  is the dielectric constant.

Assume next that the Boltzmann law is valid for the distribution of ions around J and let  $i$  represent each ionic species present in the solution (e. g.,  $i = \text{Na}^+, \text{Cl}^-$  in a NaCl solution). Then, one may write

$$n_i' = n_i \exp\left(-\frac{z_i \epsilon \phi_{(J)}}{k_B T}\right) \quad (1-2)$$

$n_i'$  is the number of ions of type  $i$  per unit volume at  $dV$ ,  $n_i$  is the bulk value at great distances from J,  $z_i$  is the valence of  $i$ ,  $\epsilon$  is the electronic charge,  $k_B$  is

Boltzman's constant, and T is the absolute temperature.

The net charge density at dV is

$$\rho_{(J)} = \sum_i n_i z_i e = \sum_i n_i z_i e \exp\left(-\frac{z_i e \phi_{(J)}}{k_B T}\right) \quad (1-3)$$

which decays to the bulk value

$$\rho_{(J)} = \sum_i n_i z_i e = 0 \quad (1-4)$$

at large distances from J (and implicitly from other ions so that  $\phi_{(J)}$  may be essentially zero).

The intrinsic concept at this point is that, because of coulombic attraction, there is an excess of counter-ions around J, i. e., of ions of opposite charge, and a deficiency of ions of like charge but that one reaches electrical neutrality when the volume element dV is moved far enough from J.

By introducing Eqn. (1-4) into (1-1) Poisson's equation becomes

$$\nabla^2 \phi_{(J)} = -\frac{4\pi}{D_e} \sum_i n_i z_i e \exp\left(-\frac{z_i e \phi_{(J)}}{k_B T}\right) \quad (1-5)$$

There are two difficulties with this equation; its rigorous solution is to be avoided and it is not compatible with the principle of the superposition of fields. In effect, if the ionic charges were doubled one should expect the potential at

$dV$  to also be doubled but this does not occur due to the exponential nature of Eqn. (1-3).

Debye and Huckel avoided these problems by expanding the exponential term by means of the series

$$e^{-x} = 1 - x + \frac{x^2}{2!} - \frac{x^3}{3!} + \dots \quad (1-6)$$

and obtained

$$\nabla^2 \phi_{(J)} = -\frac{4\pi}{D_e} \sum_i n_i z_i^2 \epsilon \left[ 1 - \frac{z_i \epsilon \phi_{(J)}}{k_B T} + \frac{1}{2!} \left( \frac{z_i \epsilon \phi_{(J)}}{k_B T} \right)^2 - \dots \right] \quad (1-7)$$

The first term in the expansion is zero because of electrical neutrality (see Eqn. (1-4)) and it can be shown that all the terms in even powers vanish for symmetric (but not for asymmetric) electrolytes.

Eqn. (1-7) is then reduced to

$$\nabla^2 \phi_{(J)} = \frac{4\pi \epsilon^2}{D_e k_B T} \sum_i n_i z_i^2 \phi_{(J)} = \kappa^2 \phi_{(J)} \quad (1-8)$$

where

$$\kappa^2 = \frac{4\pi \epsilon^2 \sum_i n_i z_i^2}{D_e k_B T} = \frac{8\pi \epsilon^2 I_S^{(c)} N_A}{1000 D_e k_B T} \quad (1-9)$$

$I_S^{(c)}$  being the molar ionic strength of the solution and  $N_A$  Avogadro's number. Converting Eqn. (1-8) into polar coordinates and integrating, one obtains the solution

$$\phi_{(J)} = k_1 \frac{e^{-\kappa r_{(J)}}}{r_{(J)}} + k_2 \frac{e^{\kappa r_{(J)}}}{r_{(J)}} \quad (1-10)$$

When  $r_{(J)}$  tends to infinity,  $\phi_{(J)}$  must remain finite and, therefore,  $k_2 = 0$ .

Electrical neutrality requires that

$$\int_{a_D}^{\infty} 4\pi\rho_{(J)} dr = -z_J e \quad (1-11)$$

where  $a_D$  is the distance of closest approach of the center of other ions to the center of J.  $k_1$  is calculated by introducing

$$\phi_{(J)} = k_1 \frac{e^{-\kappa r_{(J)}}}{r_{(J)}} \quad (1-12)$$

into the expression (1-3) for the charge density after it is linearized, and integrating by parts. One then obtains

$$\phi_{(J)} = \frac{z_J \epsilon}{D_e} \times \frac{\kappa a_D}{1 + \kappa a_D} \times \frac{e^{-\kappa r_{(J)}}}{r_{(J)}} \quad (1-13)$$

$\kappa$  can be shown to be the reciprocal of the thickness of the ion atmosphere where this thickness is the distance from  $r = a_D$  to a sphere such that all the other ions act upon J as if they were uniformly distributed upon its surface.

Eqn. (1-13) can be split into the contributions to  $\phi_{(J)}$ , the potential at a distance  $r_{(J)}$  from J, of the central ion J and of the ion atmosphere and, at  $r = a_D$ , the potential due to the ion atmosphere is found to be

$$\phi'_{a_D} = -\frac{z_J \epsilon}{D_e} \times \frac{\kappa}{1 + \kappa a_D} \quad (1-14)$$

That part of the electrical work done to charge J which results from the presence of other ions is then, if equated to the electrical free energy,

$$\Delta F_{(el)} = -\frac{1}{D_e} \int_0^{z_J \epsilon} \frac{\kappa q dq}{1 + \kappa a} \quad (1-15)$$

where  $q dq$  represents the differential charge increment. One then obtains, keeping in mind that  $\kappa$  is also a function of the charge (Fowler and Guggenheim, 1939, p. 393; Koryta et al., 1973, p. 22)

$$\Delta F_{(el)} = - \frac{z_J e^2}{3D_e} \kappa \tau (\kappa a_D) \quad (1-16)$$

where

$$\tau(\kappa a_D) = \frac{3}{x} \left[ \ln(1+x) - x + \frac{x^2}{2} \right] \quad \text{with } x = \kappa a_D \quad (1-17)$$

Note that  $\Delta F_{(el)}$  can be calculated for any one ion in solution so that we may replace the subscript J which characterizes a specific central ion by the symbol i. Furthermore, the free energy F rather than the work function is used because the small electrostrictive term is neglected so that there is no PdV work considered.

For a component i in solution one has

$$\mu_i = \mu_i^{\circ} + RT \ln f_i + RT \ln m_i \quad (1-18)$$

where  $\mu_i$  and  $\mu_i^{\circ}$  are the actual and the standard chemical potentials,  $f_i$  is the molal activity coefficient, and  $m_i$  is the molality. Equivalent expressions could have been written in terms of the rational and of the molar activity coefficients.

If the departure from ideality is attributed to coulombic interactions between ions then

$$\Delta\mu_{(cl)i} = \frac{\partial\Delta F_{(cl)i}}{\partial n_i} = RT \ln f_i \quad (1-19)$$

$\partial n_i$  represents the addition of an infinitesimal amount of  $i$  to an amount of solution which contains 1 kg of water and could have been represented by  $\partial m_i$ .

One obtains from (1-16), neglecting the electrostrictive term,

$$\ln f_i^{(D-H)} = -\frac{z_i^2 e^2}{2D e k_B T} \frac{\kappa}{1 + \kappa a} \quad (1-20)$$

which, from the definition of  $\kappa$ , yields

$$\log f_i^{(D-H)} = -\frac{A_D z_i^2 I_S^{0.5}}{1 + B_D a I_S^{0.5}} \quad (1-21)$$

and

$$\log f_{\pm}^{(D-H)} = -\frac{A_D |z_C z_A| I_S^{0.5}}{1 + B_D a I_S^{0.5}} \quad (1-22)$$

where  $f_{\pm}$  is the mean activity coefficient of an electrolyte while  $z_C$  and  $z_A$  are the cationic and anionic valences.  $A_D$  and  $B_D$  are the Debye constants.

In molal units

$$A_D = \left( \frac{2\pi N_A \rho}{1000} \right)^{0.5} \frac{\epsilon^3}{(2.3026 D_e k_B T)^{1.5}} \quad (1-23)$$

$$B_D = \left( \frac{8\pi N_A e^2 \rho}{1000 D_e k_B T} \right)^{0.5} \quad (1-24)$$

$A_D$  is in  $\text{mole}^{-1} \text{kg}^{0.5} (\text{deg K})^{1.5}$  and  $B_D$  in  $\text{cm}^{-1} \text{mole}^{-0.5} \text{kg}^{0.5} (\text{deg K})^{0.5}$ .

The Debye-Hückel limiting law at nearly infinite dilutions can be obtained directly from Eqns. (1-21) and (1-22) by setting  $B_D a_D I_S^{0.5} \ll 1$ , or can be derived as done above but assuming that the ions are far enough apart so that they may be represented by point charges. The law then has the forms

$$\log f_i^{(D-H)} = -A_D z_i^2 I_S^{0.5} \quad (1-25)$$

$$\log f_{\pm}^{(D-H)} = -A_D |z_C z_A| I_S^{0.5} \quad (1-26)$$

It is of interest to students of this field to have available to them the values of  $A_D$ ,  $B_D$  and of  $f_{\pm}^{(D-H)}$  as a function of  $a_D$  for various molalities, which we calculated and present in the next two tables. The values of  $f_{\pm}^{(D-H)}$  will also be useful in what follows.

b) Parameters and activity coefficients from the Debye-Hückel equation

Values for the Debye-Hückel parameters are presented in Table 1-1. Values for  $f_i^{(D-H)}$  calculated from (1-26) are presented in Table 1-2 and 1-3 as functions of the ionic strength and of the Debye distance of closest approach  $a_D^o$ . Note that  $a_D$  is often termed the ion-size parameter, a misnomer as it refers to the distance of closest approach of a cation and an ion for a given electrolyte.

c) Interpolated values of experimental mean activity coefficients of 1-1 electrolytes (Culberson equation)

Experimental results for mean activity coefficients will be needed for comparative purposes with various theoretical equations. As such results are too widely spaced as a function of ionic strength, C.H. Culberson (Pytkowicz, Atlas and Culberson, 1965) applied an empirical interpolation equation of the type

$$\log f_{\pm(\text{interp})} = \frac{A_C I^{0.5}}{1 + B_C I^{0.5}} + C_C I + D_C I^{1.5} + E_C I^2 \quad (1-27)$$

to several 1-1 and 2-1 electrolytes at 25° C.

Values of the parameters are presented in Table 1-3 and of  $f_{\pm(\text{interp})}$  versus  $f_{\pm(\text{exp})}$  (experimental values) in Table 1-4. It can be seen that one may use values of  $f_{\pm(\text{interp})}$  to represent actual values as will be done in the next section. Four decimal places are reported to smooth the data although only the first three are known because  $f_{\pm(\text{interp})}$  was obtained by fitting Eqn. (1-27)

Table 1-1. Molal values of the Debye-Huckel parameters  $A_D$  and  $B_D$  as a function of temperature.

T(°C)	$A_D$ [mole <sup>-1</sup> kg <sup>0.5</sup> (deg K) <sup>1.5</sup> ]	$B_D$ [cm <sup>-1</sup> mole <sup>-0.5</sup> kg <sup>0.5</sup> (deg K) <sup>0.5</sup> ]
0	0.4918	0.3248
5	0.4953	0.3256
10	0.4989	0.3264
15	0.5027	0.3271
20	0.5067	0.3279
25	0.5108	0.3287
30	0.5151	0.3294
35	0.5196	0.3302
40	0.5243	0.3310

\* These values are calculated from Eqns. (1-23) and (1-24) using the density of pure water and pertain, therefore, to dilute solutions.

Table 1-2. Values of  $f_{\pm}^{(D-H)}$ , the molal activity coefficient from the Debye-Huckel equation, calculated in this work for 1-1 electrolytes at 25° C, as a function of the ionic strength  $I_S$  and of  $a_D$ .

$I_S$	$a_D$ (distance of closest approach)						
	3.80	3.82	3.84	3.86	3.88	3.90	3.92
.0001	.9885	.9885	.9885	.9885	.9885	.9885	.9885
.0005	.9747	.9747	.9747	.9747	.9748	.9748	.9748
.0010	.9649	.9649	.9649	.9649	.9649	.9649	.9649
.0015	.9575	.9575	.9575	.9575	.9575	.9575	.9575
.0020	.9514	.9514	.9514	.9514	.9515	.9515	.9515
.0025	.9462	.9462	.9462	.9462	.9462	.9462	.9462
.0030	.9415	.9415	.9415	.9415	.9416	.9416	.9416
.0035	.9373	.9373	.9373	.9373	.9373	.9374	.9374
.0040	.9334	.9334	.9334	.9335	.9335	.9335	.9335
.0045	.9298	.9298	.9298	.9299	.9299	.9299	.9300
.0050	.9264	.9265	.9265	.9265	.9265	.9266	.9266
.0055	.9233	.9233	.9233	.9234	.9234	.9234	.9235
.0060	.9203	.9203	.9204	.9204	.9204	.9205	.9205
.0065	.9175	.9175	.9175	.9176	.9176	.9176	.9177
.0070	.9148	.9148	.9148	.9149	.9149	.9150	.9150
.0075	.9122	.9122	.9123	.9123	.9124	.9124	.9124
.0080	.9097	.9098	.9098	.9098	.9099	.9099	.9100
.0085	.9073	.9074	.9074	.9075	.9075	.9076	.9076
.0090	.9051	.9051	.9052	.9052	.9053	.9053	.9054
.0095	.9029	.9029	.9030	.9030	.9031	.9031	.9032
.0100	.9007	.9008	.9008	.9009	.9009	.9010	.9011
.0110	.8967	.8967	.8968	.8968	.8969	.8970	.8970
.0120	.8929	.8929	.8930	.8930	.8931	.8932	.8932
.0130	.8892	.8893	.8894	.8894	.8895	.8896	.8897
.0140	.8858	.8859	.8860	.8860	.8861	.8862	.8863
.0150	.8826	.8826	.8827	.8828	.8829	.8829	.8830
.0160	.8794	.8795	.8796	.8797	.8798	.8798	.8799
.0170	.8764	.8765	.8766	.8767	.8768	.8769	.8770
.0180	.8736	.8737	.8738	.8739	.8739	.8740	.8741
.0190	.8708	.8709	.8710	.8711	.8712	.8713	.8714
.0200	.8682	.8683	.8684	.8685	.8686	.8687	.8688
.0300	.8458	.8459	.8461	.8462	.8463	.8465	.8466
.0400	.8284	.8286	.8288	.8289	.8291	.8293	.8294
.0500	.8142	.8144	.8146	.8147	.8149	.8151	.8153

.0600	.8020	.8023	.8025	.8027	.8029	.8031	.8033
.0700	.7914	.7917	.7919	.7922	.7924	.7927	.7929
.0800	.7821	.7823	.7826	.7828	.7831	.7834	.7836
.0900	.7736	.7739	.7742	.7745	.7748	.7750	.7753
.1000	.7660	.7663	.7666	.7669	.7672	.7675	.7678
.2000	.7136	.7140	.7145	.7149	.7154	.7158	.7163
.3000	.6821	.6827	.6833	.6838	.6844	.6849	.6855
.4000	.6600	.6606	.6612	.6619	.6625	.6631	.6637
.5000	.6430	.6437	.6444	.6451	.6458	.6465	.6471
.6000	.6294	.6301	.6309	.6316	.6324	.6331	.6338
.7000	.6180	.6188	.6196	.6204	.6212	.6220	.6228
.8000	.6084	.6093	.6101	.6109	.6118	.6126	.6134
.9000	.6001	.6010	.6018	.6027	.6036	.6044	.6053
1.0000	.5928	.5937	.5946	.5955	.5964	.5972	.5981

 $a_D$ 

$I_S$	3.94	3.96	3.98	4.00	4.20	4.40	4.60
.0001	.9885	.9885	.9885	.9885	.9885	.9885	.9885
.0005	.9748	.9748	.9748	.9748	.9748	.9748	.9749
.0010	.9649	.9649	.9649	.9649	.9650	.9651	.9651
.0015	.9576	.9576	.9576	.9576	.9577	.9578	.9579
.0020	.9515	.9515	.9515	.9515	.9517	.9518	.9519
.0025	.9463	.9463	.9463	.9463	.9465	.9466	.9468
.0030	.9416	.9416	.9417	.9417	.9419	.9421	.9422
.0035	.9374	.9374	.9375	.9375	.9377	.9379	.9381
.0040	.9336	.9336	.9336	.9336	.9339	.9341	.9344
.0045	.9300	.9300	.9300	.9301	.9303	.9306	.9309
.0050	.9266	.9267	.9267	.9267	.9270	.9273	.9276
.0055	.9235	.9235	.9236	.9236	.9239	.9242	.9246
.0060	.9205	.9206	.9206	.9206	.9210	.9213	.9217
.0065	.9177	.9178	.9178	.9178	.9182	.9186	.9190
.0070	.9150	.9151	.9151	.9152	.9156	.9160	.9164
.0075	.9125	.9125	.9126	.9126	.9130	.9135	.9139
.0080	.9100	.9101	.9101	.9102	.9106	.9111	.9115
.0085	.9077	.9077	.9078	.9078	.9083	.9088	.9092
.0090	.9054	.9055	.9055	.9056	.9061	.9065	.9070
.0095	.9032	.9033	.9033	.9034	.9039	.9044	.9049
.0100	.9011	.9012	.9012	.9013	.9018	.9023	.9029
.0110	.8971	.8971	.8972	.8973	.8978	.8984	.8990
.0120	.8933	.8934	.8934	.8935	.8941	.8947	.8954
.0130	.8897	.8898	.8899	.8899	.8906	.8913	.8919
.0140	.8863	.8864	.8865	.8865	.8873	.8880	.8887
.0150	.8831	.8832	.8832	.8833	.8841	.8848	.8856
.0160	.8800	.8801	.8802	.8802	.8810	.8818	.8826

.0170	.8770	.8771	.8772	.8773	.8781	.8790	.8798
.0180	.8742	.8743	.8744	.8745	.8753	.8762	.8771
.0190	.8715	.8716	.8717	.8718	.8727	.8736	.8744
.0200	.8688	.8689	.8690	.8691	.8701	.8710	.8719
.0300	.8467	.8468	.8470	.8471	.8484	.8497	.8509
.0400	.8296	.8297	.8299	.8301	.8317	.8332	.8348
.0500	.8155	.8157	.8159	.8161	.8179	.8198	.8216
.0600	.8035	.8038	.8040	.8042	.8063	.8084	.8104
.0700	.7931	.7934	.7936	.7938	.7962	.7985	.8007
.0800	.7839	.7842	.7844	.7847	.7872	.7897	.7921
.0900	.7756	.7759	.7762	.7764	.7792	.7819	.7845
.1000	.7681	.7684	.7687	.7690	.7719	.7748	.7775
.2000	.7167	.7172	.7176	.7180	.7224	.7266	.7307
.3000	.6860	.6865	.6871	.6876	.6929	.6981	.7030
.4000	.6644	.6650	.6656	.6662	.6722	.6781	.6837
.5000	.6478	.6485	.6492	.6499	.6565	.6629	.6690
.6000	.6346	.6353	.6360	.6368	.6439	.6507	.6573
.7000	.6236	.6243	.6251	.6259	.6334	.6407	.6476
.8000	.6142	.6150	.6158	.6166	.6245	.6321	.6394
.9000	.6061	.6070	.6078	.6087	.6169	.6248	.6323
1.0000	.5990	.5999	.6008	.6016	.6101	.6183	.6261

<sup>a</sup>D

I <sub>S</sub>	4.80	5.00	5.20	5.40	5.60	5.80	6.00
.0001	.9885	.9885	.9885	.9885	.9885	.9885	.9885
.0005	.9749	.9750	.9750	.9750	.9751	.9751	.9751
.0010	.9652	.9653	.9653	.9654	.9655	.9655	.9656
.0015	.9580	.9581	.9582	.9583	.9584	.9585	.9586
.0020	.9521	.9522	.9523	.9524	.9526	.9527	.9528
.0025	.9470	.9471	.9473	.9474	.9476	.9477	.9479
.0030	.9424	.9426	.9428	.9430	.9432	.9433	.9435
.0035	.9383	.9386	.9388	.9390	.9392	.9394	.9396
.0040	.9346	.9348	.9351	.9353	.9355	.9358	.9360
.0045	.9311	.9314	.9317	.9319	.9322	.9324	.9327
.0050	.9279	.9282	.9285	.9288	.9291	.9293	.9296
.0055	.9249	.9252	.9255	.9258	.9261	.9264	.9267
.0060	.9220	.9224	.9227	.9230	.9234	.9237	.9240
.0065	.9193	.9197	.9200	.9204	.9207	.9211	.9214
.0070	.9167	.9171	.9175	.9179	.9183	.9186	.9190
.0075	.9143	.9147	.9151	.9155	.9159	.9163	.9167
.0080	.9119	.9124	.9128	.9132	.9136	.9140	.9145
.0085	.9097	.9101	.9106	.9110	.9115	.9119	.9123
.0090	.9075	.9080	.9085	.9089	.9094	.9098	.9103
.0095	.9054	.9059	.9064	.9069	.9074	.9079	.9083

.0100	.9034	.9039	.9044	.9049	.9054	.9059	.9064
.0110	.8996	.9001	.9007	.9012	.9018	.9023	.9028
.0120	.8960	.8966	.8972	.8977	.8983	.8989	.8995
.0130	.8926	.8932	.8938	.8945	.8951	.8957	.8963
.0140	.8893	.8900	.8907	.8914	.8920	.8927	.8933
.0150	.8863	.8870	.8877	.8884	.8891	.8898	.8905
.0160	.8834	.8841	.8849	.8856	.8863	.8870	.8877
.0170	.8806	.8814	.8821	.8829	.8837	.8844	.8852
.0180	.8779	.8787	.8795	.8803	.8811	.8819	.8827
.0190	.8753	.8762	.8770	.8779	.8787	.8795	.8803
.0200	.8728	.8737	.8746	.8755	.8764	.8772	.8780
.0300	.8521	.8534	.8545	.8557	.8569	.8580	.8591
.0400	.8363	.8377	.8392	.8406	.8420	.8434	.8448
.0500	.8233	.8250	.8267	.8284	.8300	.8316	.8332
.0600	.8124	.8143	.8162	.8181	.8199	.8217	.8234
.0700	.8029	.8050	.8071	.8092	.8112	.8131	.8151
.0800	.7945	.7968	.7991	.8013	.8035	.8056	.8077
.0900	.7870	.7895	.7920	.7943	.7967	.7989	.8012
.1000	.7803	.7829	.7855	.7880	.7905	.7929	.7953
.2000	.7346	.7385	.7422	.7458	.7494	.7528	.7562
.3000	.7078	.7125	.7170	.7213	.7256	.7297	.7337
.4000	.6891	.6944	.6995	.7044	.7091	.7137	.7182
.5000	.6750	.6807	.6862	.6916	.6967	.7017	.7066
.6000	.6637	.6698	.6757	.6814	.6869	.6922	.6974
.7000	.6543	.6608	.6670	.6730	.6788	.6844	.6898
.8000	.6464	.6532	.6597	.6659	.6720	.6778	.6834
.9000	.6396	.6466	.6534	.6598	.6661	.6721	.6780
1.0000	.6336	.6409	.6478	.6545	.6610	.6672	.6732

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Table 1-3. Coefficients for Eqn. (1-27) and the standard deviation of fit relative to measured mean activity coefficients at 25° C.

	KCl	NaCl
$A_C$	-0.5108	-0.5108
$B_C$	1.3070	1.3500
$C_C$	0	0.043663
$D_C$	0	-0.0093698
$E_C$	0.0020748	0
Molality range	0-1.0	0-1.0
Std. deviation of fit	0.08% in $f_{\pm}$	0.09% in $f_{\pm}$

---

Table 1-4. Values of  $f_{\pm(\text{interp})}$  obtained from Eqn. (1-27) and experimental values  $f_{\pm(\text{exp})}$  from the literature. Data on the molal scale at 25° C.

$I_S$	KCl		NaCl	
	$f_{\pm(\text{interp})}$	$f_{\pm(\text{exp})}$	$f_{\pm(\text{interp})}$	$f_{\pm(\text{exp})}$
0.0001			0.9885	
0.0005	0.9748	0.975	0.9748	0.975
0.001	0.9649	0.965	0.9651	0.965
0.002	0.9515	0.952	0.9518	0.952
0.003	0.9417		0.9421	
0.004	0.9336		0.9341	
0.005	0.9267	0.928	0.9273	0.927
0.006	0.9206		0.9214	
0.007	0.9151		0.9160	
0.008	0.9101		0.9111	
0.009	0.9055		0.9066	
0.010	0.9012	0.902	0.9024	0.902
0.020	0.8690		0.8713	
0.030	0.8470		0.8503	
0.040	0.8299		0.8341	
0.050	0.8159		0.8210	
0.060	0.8040		0.8099	
0.070	0.7936		0.8004	
0.080	0.7844		0.7920	
0.090	0.7761		0.7845	
0.10	0.7686	0.770	0.7778	0.778
0.15	0.7391		0.7518	
0.20	0.7177	0.718	0.7336	0.735
0.25	0.7009		0.7199	
0.30	0.6873	0.688	0.7091	0.710
0.35	0.6758		0.7004	
0.40	0.6660	0.666	0.6931	0.693
0.45	0.6574		0.6871	
0.50	0.6498	0.649	0.6819	0.681
0.55	0.6431		0.6775	
0.60	0.6370	0.637	0.6736	0.673
0.65	0.6315		0.6703	
0.70	0.6264	0.626	0.6674	0.667
0.75	0.6218		0.6649	
0.80	0.6176	0.618	0.6626	0.662
0.85	0.6137		0.6606	
0.90	0.6100	0.610	0.6589	0.659
0.95	0.6066		0.6574	
1.0	0.6035	0.604	0.6560	0.657
2.0		0.573		0.668
3.0		0.569		0.714
4.0		0.577		0.783
5.0				0.874
6.0				0.986

to experimental data reported to three decimals.

d) Comparison of Debye-Hückel and experimental results

It is of interest to compare results obtained from Eqn. (1-26) and shown in Table 1-2 with experimental data as represented by Eqn. (1-27). This is done in Table 1-5.

Guntelberg (1926) suggested a simplified form of the Debye-Hückel equation, namely,

$$\log f_{\pm}^{(G)} = - \frac{A_D |z_C z_A| I_S^{0.5}}{1 + I_S^{0.5}} \quad (1-28)$$

which corresponds to  $a_D = 3.04 \text{ \AA}$  at  $25^\circ \text{C}$  to be applied to all electrolytes.

This form was adopted by Guggenheim (1935) and by Davies (1938) among others as the first term, which describes non-specific coulombic interactions, in their equations. Values of  $\log f_{\pm}^{(G)}$  for 1-1 electrolytes are presented in Table 1-6. If one remembers that  $a_D$  is the distance of closest approach of an ion with its counter-ion, a virtue of Eqn. (1-28) is that, for empirical fitting of data by means of additional specific interaction terms in mixed electrolyte solutions, one does avoid the uncertain meaning of  $a_D$ . This quantity is only well defined in the Debye-Hückel equation for a single electrolyte at a time.

The results in Table 1-5 indicate that the Debye-Hückel equation fits KCl data quite well; to within less than 0.1% at  $m = 0.1$  and to within less than 1% at  $m = 1.0$ . The agreement is not as good for NaCl and becomes worse

Table 1-5. A comparison of values calculated from the Debye-Huckel equation with experimental ones as represented by Eqn. (1-27)  $\Delta\%$  represents the percent deviation of  $f_{\pm}^{(D-H)}$  from  $f_{\pm}(\text{interp})$ .

m	KCl ( $a^{\circ} = 3.94 \text{ \AA}$ )			NaCl ( $a^{\circ} = 4.60 \text{ \AA}$ )		
	$f_{\pm}(\text{interp})$	$f_{\pm}^{(D-H)}$	$\Delta\%$	$f_{\pm}(\text{interp})$	$f_{\pm}^{(D-H)}$	$\Delta\%$
0.001	0.9649	0.9649	0.00	0.9651	0.9651	0.00
0.005	0.9267	0.9266	0.01	0.9273	0.9276	0.03
0.01	0.9012	0.9011	0.01	0.9024	0.9029	0.06
0.05	0.9159	0.8155	0.05	0.8210	0.8216	0.07
0.1	0.7686	0.7681	0.07	0.7778	0.7775	0.04
0.2	0.7177	0.7167	0.14	0.7336	0.7307	0.41
0.3	0.6873	0.6860	0.18	0.7091	0.7030	0.86
0.4	0.6660	0.6644	0.24	0.6931	0.6837	1.36
0.5	0.6498	0.6478	0.31	0.6819	0.6690	1.89
1.0	0.6035	0.5990	0.75	0.6560	0.6216	5.24

---

Table 1-6. Values of  $f_{\pm}^{(G)}$  obtained from the Guntelberg equation for 1-1 electrolytes at 25° C.

m	0.001	0.005	0.01	0.05	0.1
$f_{\pm}^{(G)}$	0.9646	0.9253	0.8986	0.8066	0.7538

---

for other electrolytes, especially multivalent ones. The Guntelberg equation, as is to be expected provides a poorer fit.

It is our contention that, as will be discussed in the next section, the Debye-Huckel equation is not theoretically satisfactory and that it, as well as extended forms based upon it, provide activity coefficients that agree with measured ones through empirical curve fitting.

e) Critique of the Debye-Huckel theory

Several conceptual problems of the Debye-Huckel theory arise from the use of the Boltzman distribution for the distribution of ions around a central ion. The Boltzman law is derived for non-interacting particles or for canonical ensembles of systems which may contain interacting particles. And yet the law is applied to individual particles in a problem the very essence of which is, for intermediate concentrations, to calculate activity coefficients resulting from sizeable coulombic interactions. As an example, at  $m = 0.1$  the nearest neighbor energy for a 1-1 electrolyte is  $1.459 \times 10^{14}$  ergs, a significant fraction of  $k_B T = 5.836 \times 10^{14}$  ergs.

Some problems that arise from the Boltzman law are resolved by the linearization of the density. This is especially true when the linearization is used to render the density of charge and the resulting potential compatible with the principle of superposition of charges. This procedure depends, however, upon the condition

$$x = \frac{E_i}{k_B T} = \frac{z_i e \phi}{k_B T} \ll 1 \quad (1-29)$$

especially in the case of asymmetric electrolytes for which terms in even powers do not vanish in principle in Eqn. (1-7).  $E_i$  is the electrical potential energy of an i-ion.

It is easy to show that condition (1-29) is not met even in what is usually considered the range of validity of the extended Debye-Hückel equation. Consider the energy of interaction of a single cation with an anion

$$E = -\frac{e^2}{D_e r_o} \quad (1-30)$$

for a 1-1 electrolyte.  $r_o$  is the nearest neighbor distance. This energy is smaller than that of an ion in an actual solution as will become apparent when we develop the partial order theory in later chapters. We do not use here Eqn. (1-29) because  $\phi_{(J)}$  given by Eqn. (1-13) already presupposes the validity of condition (1-29). Values of  $E$  are compared to  $k_B T$  in Table 1-7 and it can be seen that the neglect of the second power term is not justified for asymmetric electrolytes even at  $m = 0.01$  and the neglect of the third power term for symmetric electrolytes at  $m \geq 0.05$ . The errors would of course be more severe for higher valence salts.

An important contradiction of the Debye-Hückel theory which is applicable even to the limiting law arises in the ion atmosphere concept. Let us examine Eqn. (1-2) or, rather, its continuous linearized counterpart. After linearization it can be shown that

Table 1-7. Values of powers of  $x = E/k_B T$  and of their percent ratios to $E/k_B T$  versus the molality for 1-1 electrolytes at 25° C.

m	$r_o \times 10^8$ (cm)	$E \times 10^{14}$ (ergs)	$E/k_B T$	$x^2$	$x^3$	$x^2/x$ (%)	$x^3/x$ (%)
0.01	43.73	0.678	0.165	0.027	0.0045	16.5	2.7
0.05	25.58	1.159	0.282	0.079	0.022	28.2	7.9
0.1	20.31	1.459	0.354	0.125	0.044	35.4	12.5
0.2	16.13	1.837	0.446	0.199	0.089	44.6	19.9
0.5	11.91	2.489	0.605	0.366	0.221	60.5	36.5

$$\rho_{(J)} = -\frac{D \kappa^2 e}{4\pi} \phi_{(J)} \quad (1-31)$$

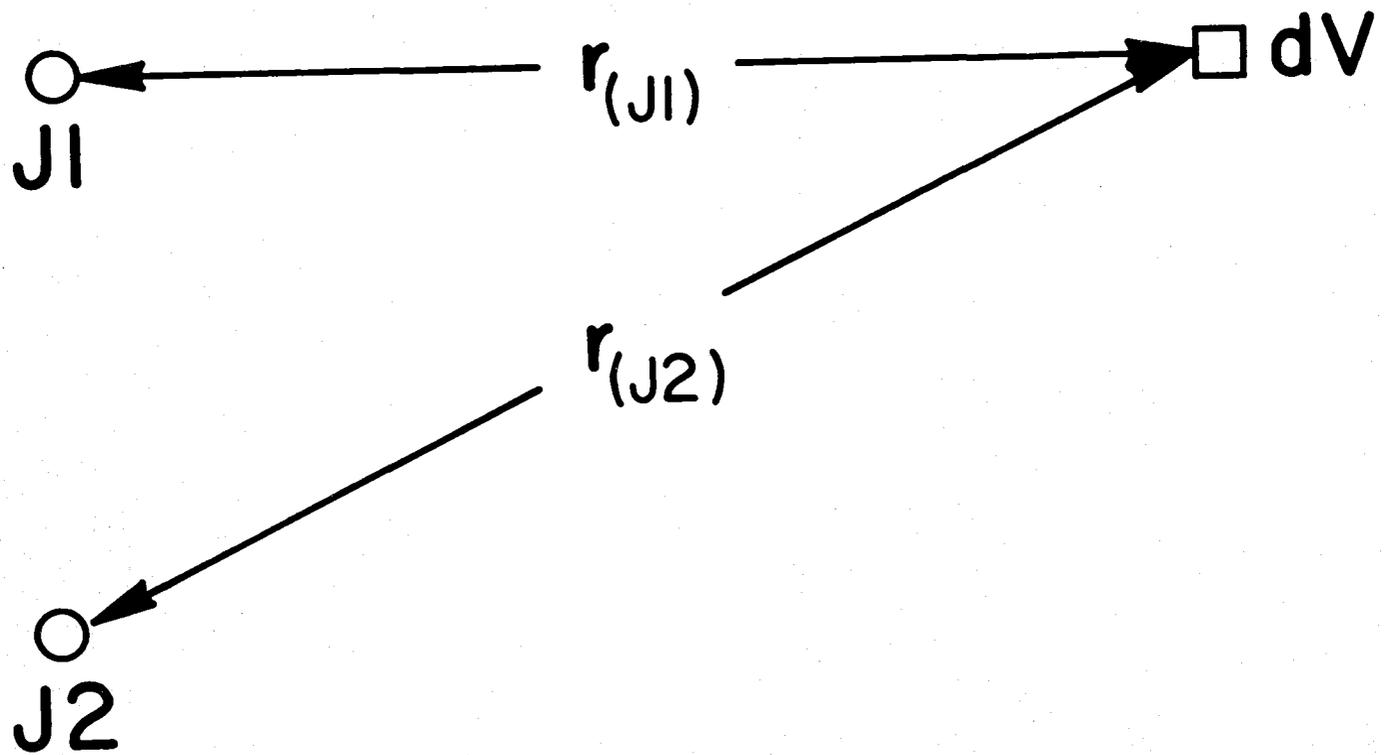
and, introducing Eqn. (1-13),

$$\rho_{(J)} = -\frac{z_J e}{4\pi} \frac{\kappa^2 e}{1 + \kappa a_D} \frac{e^{-\kappa r_{(J)}}}{r_{(J)}} \quad (1-32)$$

One observes that  $\rho_{(J)}$ , the net charge density, decays monotonically from a maximum value at  $r_{(J)} = a_D$  to zero at  $r_{(J)} = \infty$ . This is simply a formal statement of the ion atmosphere concept, namely, that the surroundings of J contain an excess of counter-ions and that this excess decays with distance. This concept leads to a serious contradiction because if now we select one of the counter-ions near the original J as the new central ion J, it is surrounded by an excess of ions like it in contradiction to the basic tenet of the Debye-Hückel theory. Thus, there is undue bunching of like ions.

Another conceptual difficulty is that the Debye-Hückel theory leads to potentials which are not uniquely defined as a function of position in a solution. In effect, let us retain a volume element  $dV$ , at which we calculate by means of Eqn. (1-13) the potential  $\phi_{(J)}$  due to all the ions in solution, but let us take two ions of the same kind as successively the central ion. Let these two ions be  $J_1$  and  $J_2$ , placed at different distances from  $dV$  (Fig. 1-1). The potentials at  $J$  due to the solution will be

Fig. 1-1. The use of alternate central ions.



$$\phi_{J1} = \frac{z_J \epsilon}{D_e} \frac{e^{\kappa a_D}}{1 + \kappa a_D} \frac{e^{-\kappa r_{(J1)}}}{r_{(J1)}} \quad (1-33)$$

and

$$\phi_{J2} = \frac{z_J \epsilon}{D_e} \frac{e^{\kappa a_D}}{1 + \kappa a_D} \frac{e^{-\kappa r_{(J2)}}}{r_{(J2)}} \quad (1-34)$$

so that the potential at  $dV$  due to all the ions present in the solution depends upon the choice of the reference ion.

These problems arise because Debye and Huckel<sup>11</sup> did not take into consideration the quasi-lattice nature of ionic solutions, that is, that there is some degree of regularity in the spacial distribution of ions which precludes excessive bunching of counter-ions in the ionic atmosphere as well as a decay of the net charge density towards zero at large distances from any given ion.

If we look at the essence of the Debye-Huckel<sup>11</sup> theory, it consists in obtaining a quantity

$$\phi'_{a_D} = -\frac{z_J \epsilon}{D_e} \frac{1}{r_{ia}} \quad (1-35)$$

where  $r_{ia}$ , the radius of the ion atmosphere, is  $a_D + 1/\kappa$  and integrating it to obtain  $\Delta F_{(el)}$ . If we consider Eqn. (1-35) alone, where  $r_{ia}$  is the radius of a sphere such that  $-z_J \epsilon$  distributed uniformly over it simulates the effect of the

solution potential upon  $J$ , without concern about how  $r_{ia}$  was obtained, then Eqn. (1-35) is logically sound. The difficulty arises with a proper evaluation of  $r_{ia}$  which takes into account the actual and partially regular distribution of cations and anions in the solution. The apparent success of the Debye-Hückel equation indicates that their choice of  $r_{ia} = a_D + 1/\kappa$  yields, by means of the adjustable parameter  $a_D$ , values of  $\partial\Delta F_{(el)}/\partial m$  which are correct at low concentrations.

Note that the above conclusion does not imply that the values of  $\phi'_{a_D}$  and of  $\Delta F_{(el)}$  are correct but only that the derivative of the latter yields proper values, that is, that the slope of  $\Delta F_{(el)}$  versus  $m$  is the proper one. We will obtain from the partial order theory at  $m = 0.01$  a value  $\Delta F_{(el)} = -3.508 \times 10^7$  ergs while from the Debye-Hückel equations one obtains  $\Delta F_{(el)} = -4.537 \times 10^7$  ergs and yet both approaches yield  $f_{\pm} = 0.902$  (if  $a_D = 4.60 \text{ \AA}$  is used in the Debye-Hückel equation). These results confirm the opening statement of this paragraph, if our value of  $\Delta F_{(el)}$  is accepted as the correct one, a point which the reader will be able to evaluate later on in this work.

In the limiting case the Debye-Hückel theory should be valid because the Boltzmann distribution should be nearly correct for weak interactions and our objections, which result from the use of this distribution, should correspond to slight errors. Furthermore, the static nature of the Debye-Hückel theory is acceptable in the limiting case because the effect of fluctuations, as seen by a central ion, are unimportant at high dilutions (Frank and Thompson, 1959).

## 2. Original Lattice Theory; Perfect Long-Range Order (PLRO)

In the original lattice theory (e. g., Robinson and Stokes, 1959, p. 226) the ions are assumed to form a regular lattice, with perfect long-range order, in the solution. This theory does not work, that is, it does not yield activity coefficients compatible with experimental ones. Still, it will be described because it serves as the basis for our partial long-range order (pLRO) which does work.

Notice that the PLRO theory contains two assumptions; the regular distribution of ions in equidistant sites and the perfect long-range order and, furthermore, that the first assumption is compatible with an intrinsic one made by Debye-Hückel. Indeed, Debye-Hückel assumed stationary charges, which must therefore occupy average regularly spaced positions, because the stationary condition is a necessary one when the Poisson equation is used.

The PLRO theory is based upon that of ionic crystal lattices which will be briefly recapitulated next.

### a) Energy of interaction in an ionic crystal

For an ionic crystal in which cations and anions have the same valences, the energy of interaction for the whole lattice is (e. g. Kittel, 1959; Pauling, 1940, p. 337)

$$E_{(\text{xtal})} = -\frac{Nz^2e^2A_M}{r_o} + \frac{B_B}{r_o^n} \quad (2-1)$$

where  $N$  is the number of ions of each kind in the volume  $V$  under consideration,  $A_M$  is the Madelung constant, and  $B_B$  is the Born constant. The last term is the Born repulsion potential.

Madelung's constant (Madelung, 1918) represents the effects of interactions of nearest neighbors, next nearest neighbors, and so on upon the lattice energy. The general shapes of  $E_{(xtal)}$  is sketched in Fig. 2-1. At  $r = r_0$  the binding energy passes through a minimum and yields a stable lattice.

b) Ionic solution with perfect long-range order

Let us divide a solution into equal cubes, place an ion at the center of each cube, and alternate cations and anions. The resulting ionic lattice is represented by Fig. 2-2. The structure corresponds to a face-centered cubic lattice with anions distributed hexagonally around cations and vice-versa. As the short-range repulsive forces would only be significant at extremely high concentrations, the counterpart of Eqn. (2-1) is now

$$\Delta E_{\ell} = -\frac{N_A z^2 \epsilon^2 A_M}{D_e r_0} c \quad (2-2)$$

where  $\Delta E_{\ell}$  is the lattice (configurational coulombic) energy relative to that at infinite dilution energy and  $c$  is the molarity. Thus,  $N_A c$  represents the number of ions of each kind present per liter of solution. Note that  $\Delta E_{\ell}$  and  $E_{\ell}$  can be used interchangeably because  $E_{\ell}$  at  $c = 0$  is zero.

As  $r_0$  is

Fig. 2-1. The shape of the lattice (binding) energy  $E_{(xtal)}$ .

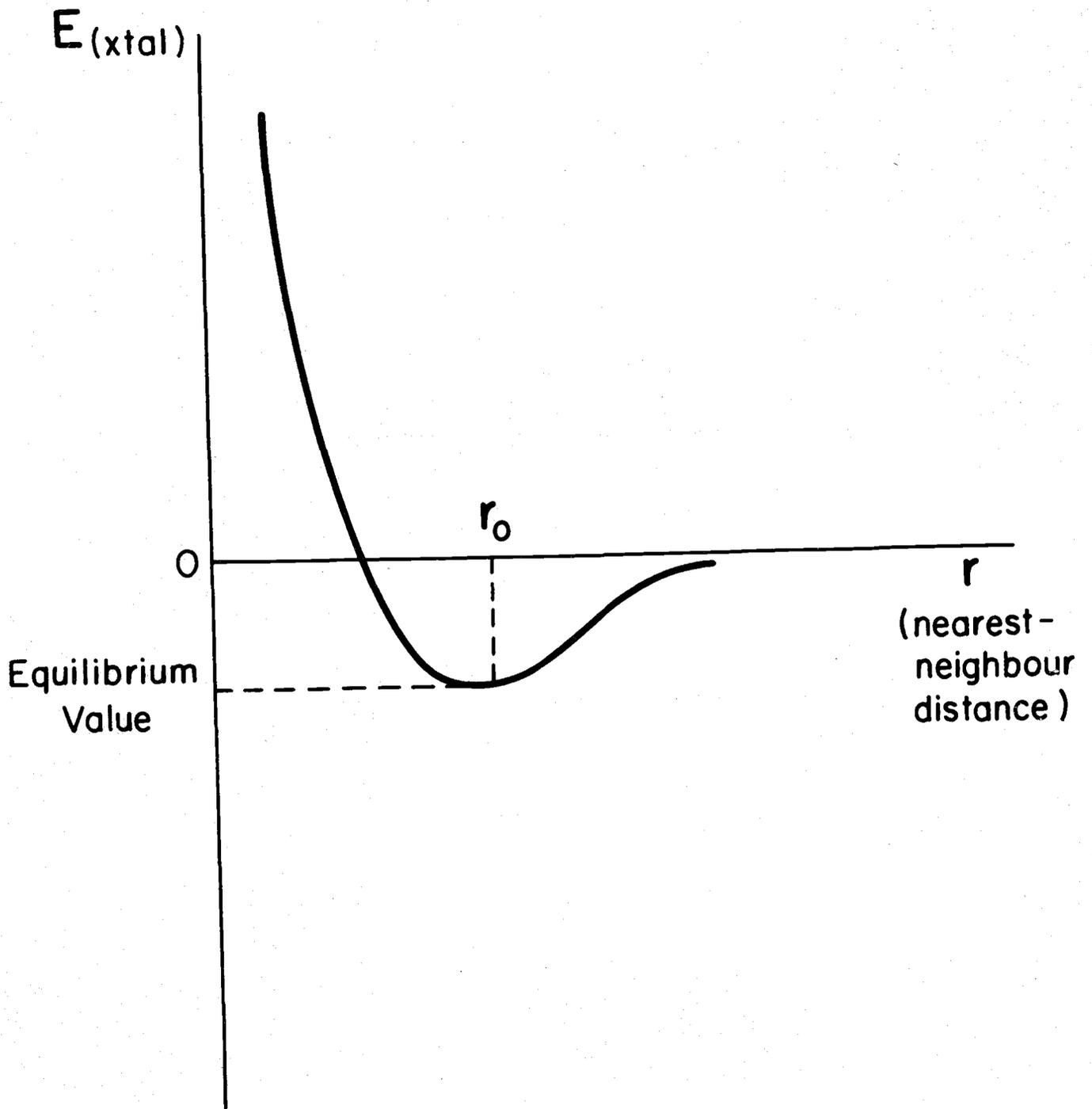
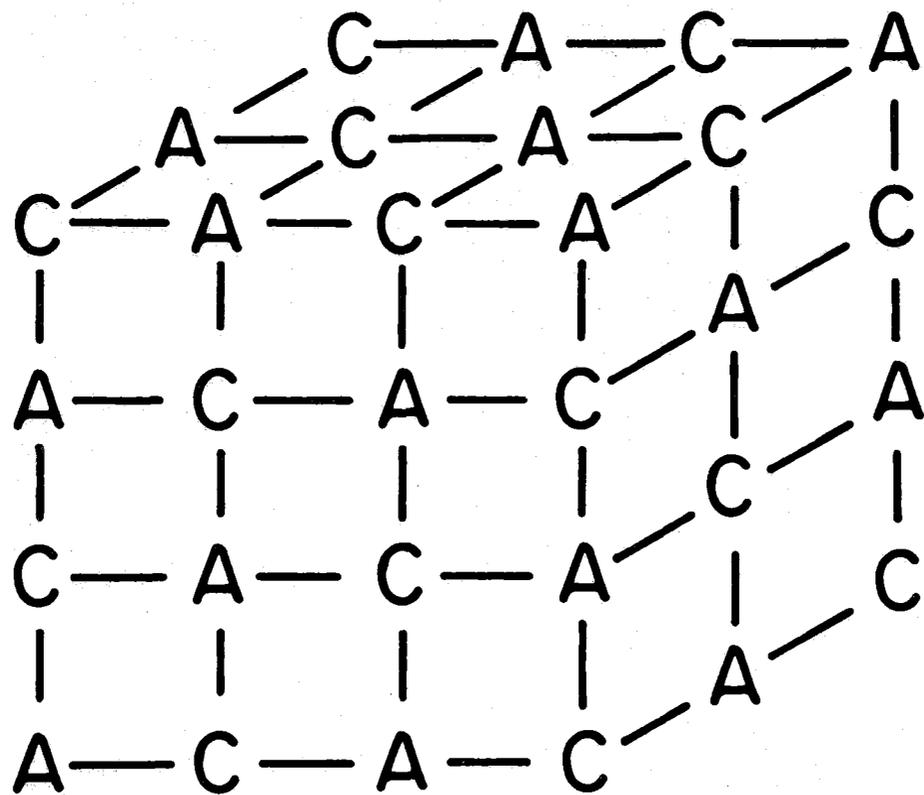


Fig. 2-2. Surface of ionic lattice in solution for a perfectly ordered symmetric (1-1, 2-2, etc.) electrolyte. C and A represent cations and anions.



$$r_o = \left( \frac{1000}{2N_A c} \right)^{1/3} \quad (2-3)$$

Eqn. (2-2) becomes

$$\Delta E_{\ell} = - \frac{2^{1/3} N_A^{4/3} z^2 e^2 A_M}{10 D_e} c^{4/3} = -B_{\ell} A_M z^2 c^{4/3} \quad (2-4)$$

with

$$B_{\ell} = \frac{2^{1/3} N_A^{4/3} e^2}{10 D_e} \quad (2-5)$$

We use molalities throughout this work to avoid changes in concentration due to pressure and temperature effects so let us convert Eqn. (2-4) to a molal base. Then, we start from

$$\Delta E_{\ell} = - \frac{N_A z^2 e^2 A_M}{D_e r_o} m \quad (2-6)$$

As

$$c = \frac{\rho m}{1 + 0.001 m M_2} \quad (2-7)$$

where  $M_2$  is the molecular weight of the solute and  $\rho$  is the density of the solution,  $r_o$  is now

$$r_o = \left( \frac{1000 + mM_2}{2N_A m \rho} \right)^{1/3} \quad (2-8)$$

and

$$\Delta E_\ell = - \frac{10B_\ell z^2 A_M \rho^{1/3}}{(1000 + mM_2)^{1/3}} m^{4/3} \quad (2-9)$$

or

$$\Delta E_\ell = - \frac{B_\ell z^2 A_M \rho^{1/3}}{(1 + 0.001 mM)^{1/3}} m^{4/3} \quad (2-10)$$

In dilute solutions we may write Eqn. (2-8) in the form

$$\Delta E_\ell \cong - \frac{B_\ell z^2 A_M \rho^{1/3}}{1} m^{4/3} \quad (2-11)$$

and calculate

$$\log f_{\pm} = \frac{1}{2.3026 RT} \frac{\partial \Delta E_1}{\partial m} \times 0.5 \quad (2-12)$$

No configurational entropy change is used in this model because, as the degree of order does not change with concentration,  $\Delta S_{\ell} = 0$ .  $\Delta E_{\ell}$  is a potential electrical energy change and is, therefore, the change in internal energy. It can be equated to  $\Delta H_{\ell}$ , the enthalpy change, because electrostrictive effects are neglected.

As  $A_M = 1.7476$  for face-centered cubic lattices, one obtains from Eqns. (2-11) and (2-12)

$$\log f_{\pm} = -\frac{2B_{\ell} z^2 A_M^{\theta} m^{1/3}}{3 \times 2.3026 RT} = -0.3842 m^{1/3} \quad (2-13)$$

for a 1-1 electrolyte. In molar units

$$\log f_{\pm} = -0.3846 c^{1/3} \quad (2-14)$$

These results differ from those reported in the literature, e. g. (Robinson and Stokes, 1959, p. 226)

$$\log f_{\pm} = -0.29c^{1/3} \quad (2-15)$$

because the latter equation is improperly derived. In effect, it is obtained by setting

$$\Delta E_{\ell} = -\frac{N_A z^2 \epsilon^2 A_M}{D_e r_o} = \frac{0.5}{2.3026 RT} \log f_{\pm} \quad (2-16)$$

by stating that  $\Delta E_{\ell}$  represents the configurational energy when one mole ( $N_A$  ions of each kind) of salt is dissolved in an infinite amount of water (i. e.,  $\Delta E_{\ell}$  is the chemical potential  $\Delta \mu_{\ell}$ ). And yet,  $r_o$  is calculated from Eqn. (2-3) for a finite molarity  $c$  so that the derivation of Eqn. (2-15) is not self-consistent.

It is of interest to compare results obtained from Eqns. (2-14) and (2-15) with experimental data noting that, to a first approximation, we do not have to distinguish  $c$  and  $m$  for rough comparisons at high dilutions. This is done in Table 2-1. Neither equation agrees well with experiments as is to be expected because the energy of interaction is small in dilute solutions and should be easily overcome by the thermal energy  $k_B T$ , leading to considerable translational freedom for the ions. This should result into quasi-lattices with at best only partial long-range order.

Table 2-1. A comparison of  $f_{\pm}$  obtained from Eqns. (2-14) and (2-15) with experimental values for NaCl

<u>m</u>	<u>Eqn. (2-14)</u>	<u>Eqn. (2-15)</u>	<u>Experimental</u>
0.0005	0.932	0.948	0.975
0.001	0.915	0.935	0.965
0.002	0.894	0.919	0.952

### 3. Partial Long-Range Order Model (pLRO): A First Approximation

This first approximation to the partial long-range order model will serve as a basis for further developments shown in the following chapter and to illustrate concepts.

In this model we will retain the assumption, later to be removed, of ions occupying on the average the centers of equal cubes, but will consider a partial degree of long-range order which is a function of temperature and concentration. The temperature dependence is analogous to that of binary alloys (e. g. Kittel, 1959, p. 340). We introduce the concentration dependence because it is conceivable that, as the ions become closer together, their coulombic energy of interaction increases and their translational freedom decreases. This should lead to an increase in the degree of order because  $\Delta E_{\ell}/RTm$  increases.  $m$  is introduced in the denominator because then  $\Delta E_{\ell}/m$  is the energy per mole, the quantity to be compared to  $RT$ .

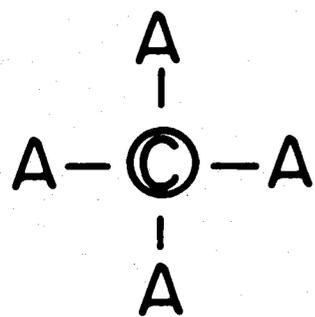
The concept of long-range order is appealing because, on the average, the nature of the ions which surround a given central ion should be the same as that of the ions which surround the ion next to the central one, and so on, leading to a quasi-lattice. In Fig. 8-1 we illustrate this process for the perfect order case.

Let us now define a long-range order parameter defined by each pair ( $T$ ,  $m$ ) and with the range of values

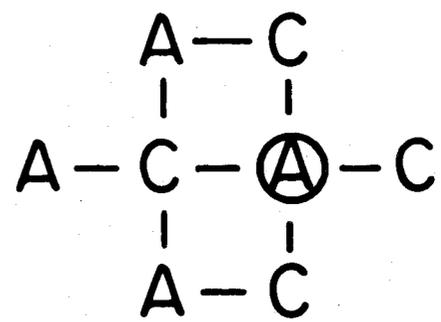
$$0 \leq L \leq 1$$

(3-1)

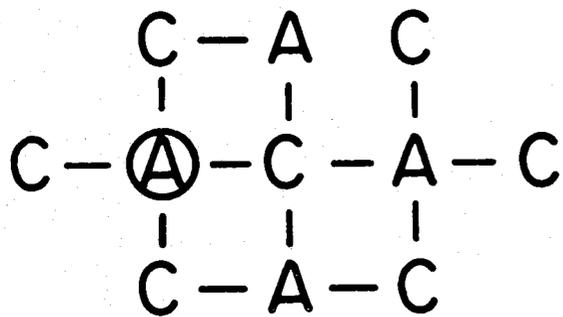
Fig. 3-1. The building-up of a quasi-lattice in two dimensions with the central ion being indicated by a circle.



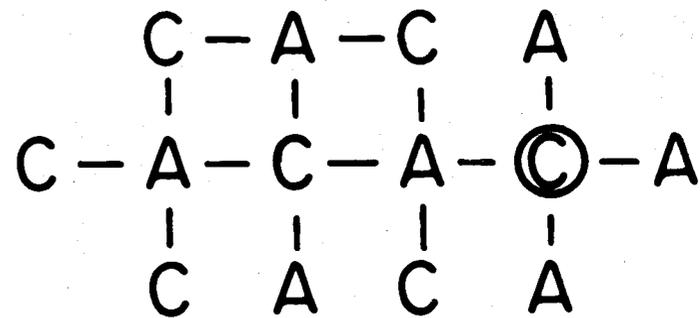
(1)



(2)



(3)



(4)

so that Eqn. (2-10) becomes

$$\Delta E_{\ell} = - \frac{B_{\ell} z^2 A_M \rho^{1/3} L}{(1 + 0.001 mM_2)^{1/3}} m^{4/3} \quad (3-2)$$

$L = 0$  for  $T \rightarrow \infty$  or  $m \rightarrow 0$  and  $L = 1$  for  $T \rightarrow 0$  or  $m \rightarrow \infty$ . It is logical that  $\Delta E_{\ell}$  be zero when  $L = 0$  (perfect randomness) because then there is an equal probability of a cation C or an anion A occupying any given lattice site. Any one ion is, therefore, surrounded by the same numbers of cations and anions in the nearest neighbor and in further layers so that the net potential on the central ion is zero.

Let us next express  $L$  in terms of the degree of order and of related quantities. We will be able, by means of an artifice and of the Madelung constant to obtain a rigorous expression for  $\Delta E_{\ell}$  in contrast to the case on non-ionic binary alloys for which successive approximations for the interactions of nearest neighbors, next nearest neighbors, and so on, are required.

Let us consider two sub-lattices;  $\bar{c}$  for the cations and  $\bar{a}$  for the anions, and let  $w$  be the fraction of 'wrong ions' (C on  $\bar{a}$  and A on  $\bar{c}$ ), that is, the fraction of the ions of a given type which are in the counter-ion lattice. Let us set  $w = 0.25$  for example, in order to clarify our thoughts. Then, on the average, one obtains the pattern shown in Fig. 3-2. This figure represents the average state of what in reality is a flickering series of structures.

Formally we can then represent the partially ordered lattice by a perfectly ordered one in which the ionic charge is  $(0.75 - 0.25)z\epsilon = (1 - 2w)z\epsilon$  and one

Fig. 3-2. Average lattice configuration for the fraction of ions in the counter-ion lattice being  $w = 0.25$ .



 cation

 anion

may construct Table 3-1.  $\bar{d}$  and  $\ell$ , the degrees of disorder and of order, are defined by

$$\bar{d} = 2w \quad \ell = (1 - 2w) \quad (3-3)$$

Randomness occurs when there is an equal probability of any lattice being occupied by an anion or by a cation so that the time-average net charge at any lattice site is zero (Fig. 3-3).

Note that, if the effective charge is  $(1 - 2w)ze$  then Eqn. (2-10) becomes

$$\Delta E_{\ell} = - \frac{Bz^2 A_M \rho^{1/3} (1 - 2w)^2}{(1 + 0.001 mM_2)^{1/3}} m^{4/3} \quad (3-4)$$

or

$$\Delta E_{\ell} = - \frac{Bz^2 A_M \rho^{1/3} \ell^2}{(1 + 0.001 mM_2)^{1/3}} m^{4/3} \quad (3-5)$$

where the order parameter  $L$  is related to the degree of order  $\ell$  by

$$L = \ell^2 \quad (3-6)$$

Let us next obtain the configurational entropy  $\Delta S_{\ell}$  by the traditional

Table 3-1. Values of  $w$ ,  $\bar{d}$  = degree of disorder, and  $\ell$  = degree of order.

$w$	$\bar{d}$	$\ell$	
0.5	1	0	randomness
0.4	0.8	0.2	
0.3	0.6	0.4	
0.25	0.5	0.5	
0.1	0.2	0.8	
0	0	1.0	perfect order

Fig. 3-3. The random lattice.



super-lattice treatment. There are

$N_A m (1 - w)$  cations on lattice  $\bar{c}$  or anions on lattice  $\bar{a}$

$N_A m w$  cations on lattice  $\bar{a}$  or anions on lattice  $\bar{c}$

As, from Eqn. (3-3)

$$w = 0.5 (1 - \ell) \quad 1 - w = 0.5 (1 + \ell) \quad (3-7)$$

there are

$0.5 N_A m (1 + \ell)$  cations on lattice  $\bar{c}$  or anions on lattice  $\bar{a}$

$0.5 N_A m (1 - \ell)$  cations on lattice  $\bar{a}$  or anions on lattice  $\bar{c}$

The number of arrangements of these ions is

$$g(\ell) = \left[ \frac{N_A m!}{[0.5 (1 + \ell) N_A m]! [0.5 (1 - \ell) N_A m]!} \right]^2 \quad (3-8)$$

From Stirling's theorem

$$\ln x! \approx x(\ln x - 1) \quad (3-9)$$

Eqn. (3-8) becomes

$$\ln g(\ell) \approx 2N_A m \ln 2 - N_A m [(1 + \ell) \ln (1 + \ell) + (1 - \ell) \ln (1 - \ell)] \quad (3-10)$$

$$\ln g(0) \approx 2N_A m \ln 2 \quad (3-11)$$

where  $g(0)$  corresponds to complete randomness.

Boltzman's definition of entropy applied here is

$$S_\ell = k_B \ln g(\ell) \quad (3-12)$$

as  $g(\ell)$  is the multiplicity of the state defined by  $\ell$ , i. e., by a pair  $(T, m)$  at a given pressure (the atmospheric one in our case). Therefore,

$$\Delta S_\ell = k[\ln g(\ell) - \ln g(0)] = -Rm [(1 + \ell) \ln (1 + \ell) + (1 - \ell) \ln (1 - \ell)] \quad (3-13)$$

and the configurational free energy  $\Delta F_\ell = \Delta E_\ell - T\Delta S_\ell$  is

$$\begin{aligned} \Delta F_\ell = & -\frac{B_\ell^2 A_M \rho^{1/3} \ell^2}{(1 + 0.001 mM_2)^{1/3}} m^{4/3} + \\ & + RTm [(1 + \ell) \ln (1 + \ell) + (1 - \ell) \ln (1 - \ell)] \end{aligned} \quad (3-14)$$

The value of  $\ell$  at any given  $m$  which yields the most stable configuration is that one for which  $\Delta F_\ell$  is at a minimum. This value, indicated by  $\ell_{\min}$ , can be obtained graphically or by setting  $\partial \Delta F_\ell / \partial \ell = 0$ , which yields

$$\frac{1}{\ell_{\min}} \ln \frac{1 + \ell}{1 - \ell} = \frac{2B_\ell^2 A_M \rho^{1/3} m^{1/3}}{RT (1 + 0.001 mM_2)} \quad (3-15)$$

A graphical presentation of  $\Delta F_\ell$  versus  $\ell$  is shown in Fig. 3-4 and a few selected values of  $\Delta F_\ell$ ,  $\Delta E_\ell$ , and  $\Delta S_\ell$  are shown in Table 3-2. It can be seen that there is a critical concentration (somewhere between  $m = 0.4$  and  $0.5$  according to our numerical results not shown here) below which  $\Delta F_\ell$  is a minimum only at  $\ell = 0$ , that is, below which the interactions among ions are weak enough compared to the thermal energy to cause the long-range order to break down. This is analogous to the critical temperature in alloys, or to a critical temperature in the case under study, above which there is no long-range order because the thermal energy is much larger than the lattice energy. It will be shown in the next section, however, that such a critical concentration may not exist in solution when the translational motions of the ions and other factors are taken into consideration.

It is interesting to observe in Fig. 3-4, as is to be expected, that  $\ell_{\min}$  increases with increasing  $m$ . This occurs because, as the distance between nearest neighbors decreases, the coulombic configurational energy increases in magnitude and tends to induce added order.

Let us next compare the values of  $\Delta F_{\ell(\min)}$  with values of  $\Delta F_{(\exp)}$  based upon experiments.  $\Delta F_{(\exp)}$  can be obtained from

$$\Delta F_{(\exp)} = 2RT \int_0^m \ln f_{\pm(\exp)} dm \quad (3-16)$$

If we use Eqn. (1-27) to represent  $\log f_{\pm(\exp)}$  then

Fig. 3-4.  $\Delta F_{\ell} \times 10^{-9}$  ergs versus  $\ell$  as a function of  $m$  at  $25^{\circ}\text{C}$ .

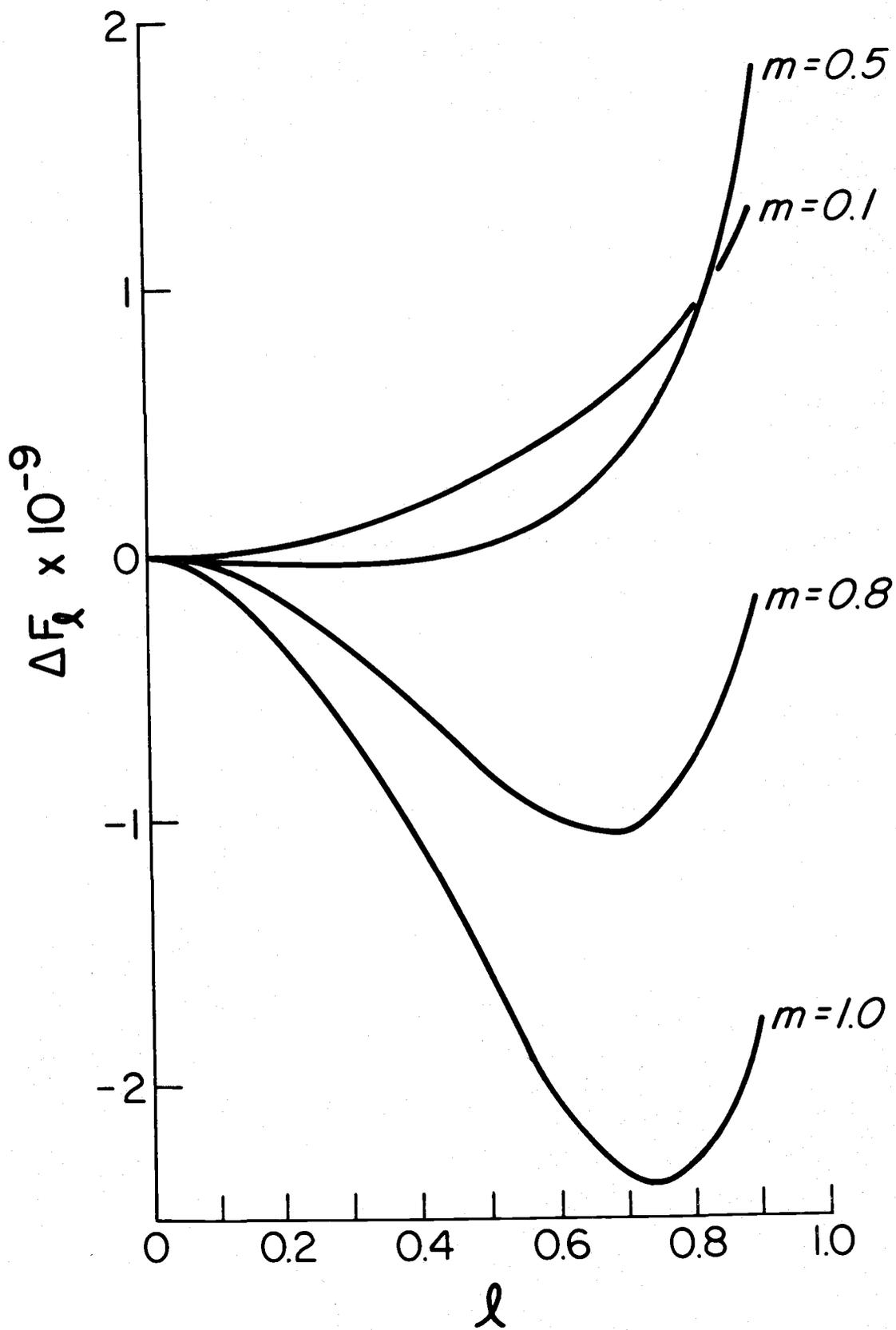


Table 3-2. Examples of the variation of  $\Delta F_\ell$ ,  $\Delta E_\ell$ , and  $\Delta S_\ell$  versus  $\ell$ .

m	$\ell$	$\Delta F_\ell$	$\Delta E_\ell$	$\Delta S_\ell$
0.1	0.1	$9.5720 \times 10^6$	$-1.5260 \times 10^7$	$-8.328 \times 10^4$
	0.2	$3.8794 \times 10^7$	-6.1040	$-3.3483 \times 10^5$
	0.3	8.9248	$-1.3734 \times 10^8$	-7.5995
	0.4	$1.6381 \times 10^8$	-2.4416	$-1.3683 \times 10^6$
	0.5	2.6708	-3.8150	-2.1753
	0.6	4.0629	-5.4936	-3.2052
	0.7	5.9312	-7.4774	-4.4971
	0.8	8.4826	-9.7664	-6.1205
	0.9	$1.2164 \times 10^9$	$-1.2361 \times 10^9$	-8.2252
0.4	0.1	$3.1716 \times 10^6$	$-9.6156 \times 10^7$	$-3.3314 \times 10^5$
	0.2	$1.4710 \times 10^7$	$-3.8463 \times 10^8$	$-1.3393 \times 10^6$
	0.3	4.0944	-8.6541	-3.0398
	0.4	9.3365	$-1.5385 \times 10^9$	-5.4731
	0.5	$1.9041 \times 10^8$	-2.4039	-8.7011
	0.6	3.6096	-3.4616	$-1.2821 \times 10^7$
	0.7	6.5177	-4.7117	-1.7988
	0.8	$1.1456 \times 10^9$	-6.1540	-2.4482
	0.9	2.0211	-7.7887	-3.2901
0.5	0.1	$-4.9906 \times 10^6$	$-1.2915 \times 10^8$	$-4.1642 \times 10^5$
	0.2	$-1.7432 \times 10^7$	-5.1660	$-1.6742 \times 10^6$
	0.3	-2.9415	$-1.1624 \times 10^9$	-3.7998
	0.4	-2.6574	-2.0664	-6.8414
	0.5	1.4134	-3.2288	$-1.0876 \times 10^7$
	0.6	$1.2882 \times 10^8$	-4.6494	-1.6026
	0.7	3.7592	-6.3284	-2.2486
	0.8	8.5887	-8.2656	-3.0603
	0.9	$1.8010 \times 10^9$	$-1.0461 \times 10^{10}$	$-4.1126 \times 10^7$
1.0	0.1	$-7.3091 \times 10^8$	$-3.2141 \times 10^8$	$-8.3284 \times 10^5$
	0.2	-2.8730	$-1.2856 \times 10^9$	$-3.3483 \times 10^6$
	0.3	-6.2682	-2.8927	-7.5995
	0.4	$-1.0629 \times 10^9$	-5.1426	$-1.3683 \times 10^7$
	0.5	-1.5495	-8.0353	-2.1753
	0.6	-2.0143	$-1.1571 \times 10^{10}$	-3.2052
	0.7	-2.3405	-1.5749	-4.4971
	0.8	-2.3213	-2.0570	-6.1205
	0.9	-1.5099	-2.6034	-8.2252

$$\begin{aligned} \Delta F_{(\text{interp})} = & 2 \times 2.3026 RT \left[ \frac{2A_C}{B_C} \left\{ 0.5 B_C^2 m^2 - B_C m^{1/2} + \right. \right. \\ & + 2.3026 \ln (1 + B_C m^{1/2}) \left. \left. \right\} + 0.5 C_C m^2 + \right. \\ & \left. + 0.4 D_C m^{2.5} + 0.333 E_C m^3 \right] \end{aligned} \quad (3-17)$$

As an alternative,  $\Delta F_{(\text{exp})}$  can be calculated from

$$\Delta F_{(\text{exp})} = n_{\text{H}_2\text{O}} \Delta\mu_{\text{H}_2\text{O}} + n_{\text{NaCl}} \Delta\mu_{\ell, \text{NaCl}} \quad (3-18)$$

where  $n_{\text{H}_2\text{O}}$  and  $n_{\text{NaCl}}$  are the numbers of moles in the given amount of solution.

$\Delta\mu_{\text{H}_2\text{O}}$  is the chemical potential of the water and  $\Delta\mu_{\ell, \text{NaCl}}$  is the configurational chemical potential of NaCl. As

$$\Delta\mu_{\ell, \text{NaCl}} = 2 RT \ln f_{\pm\text{NaCl}} \quad (3-19)$$

and

$$1 - \phi_{\text{H}_2\text{O}} = \frac{\Delta\mu_{\text{H}_2\text{O}}}{2 m RT} \frac{1000}{M_{\text{H}_2\text{O}}} \quad (3-20)$$

Eqn. (3-18) becomes

$$\Delta F_{(\text{exp})} = 55.51(1 - \phi_{\text{H}_2\text{O}}) 2 m_{\text{NaCl}} RT \frac{18}{1000} +$$

$$+ 2m RT \ln f_{\pm\text{NaCl}} \quad (3-21)$$

$\phi_{\text{H}_2\text{O}}$  and  $M_{\text{H}_2\text{O}}$  represent the practical osmotic coefficient and the molecular weight of water. Values of  $\Delta F_{(\text{interp})}$  and of  $\Delta F_{(\text{exp})}$  are compared to minimum values obtained from Eqn. (3-14) in Table 3-3. It is obvious that the theory in its present form does not work, as it does not yield correct configurational free energies. This problem will be remedied in the next chapters by considering processes which have been neglected so far.

Table 3-3. Comparison of  $\Delta F$  values in ergs derived from experimental activity coefficients of NaCl at 25° C with minimum values of  $\Delta F_{\ell}$  obtained from Eqn. (3-14). See Fig. 3-4.

m	$\Delta F$ (interp) Eqn. (3-17)	$\Delta F$ (exp) Eqn. (3-21)	$\Delta F_{\ell}$ (min) Eqn. (3-14)	$\ell$ min
0.001				
0.005				
0.01	$-3.508 \times 10^7$	$-3.516 \times 10^7$		
0.02	$-9.532 \times 10^7$			
0.03	$-1.700 \times 10^8$			
0.04	$-2.553 \times 10^8$			
0.05	$-3.493 \times 10^8$			
0.06	$-4.505 \times 10^8$			
0.07	$-5.580 \times 10^8$			
0.08	$-6.771 \times 10^8$			
0.09	$-7.891 \times 10^8$			
0.10	$-9.116 \times 10^8$			
0.20	$-2.318 \times 10^9$			
0.30	$-3.945 \times 10^9$			
0.40	$-5.076 \times 10^9$			
0.50	$-7.569 \times 10^9$		$-2.942 \times 10^7$	0.2-0.4
0.60	$-9.498 \times 10^9$		$-1.190 \times 10^8$	0.2-0.4
0.70	$-1.148 \times 10^{10}$		$-5.559 \times 10^8$	0.5-0.7
0.80	$-1.350 \times 10^{10}$		$-1.027 \times 10^9$	0.6-0.8
0.90	$-1.556 \times 10^{10}$		$-1.651 \times 10^9$	0.6-0.8
1.00	$-1.764 \times 10^{10}$	$-1.763 \times 10^{10}$	$-2.341 \times 10^9$	0.6-0.8
2.00		$-3.834 \times 10^{10}$		

(\*) Approximate value as did not interpolate values of  $\ell$  beyond the first decimal.

Thus, for example, found a minimum  $\Delta F$  (theor.) at  $\ell = 0.3$  for  $m = 0.5$  and did not seek a more precise value by adding a second decimal figure to values of  $\ell$  between 0.2 and 0.4.

#### 4. Partial Long-Range Order and the Parameter $v$

##### a) The parameter $v$

Several important factors were not considered when Eqn. (3-14) was derived, namely, the effect of ionic motion, possible changes in dielectric constant with concentration, repulsive forces caused by dielectric constant gradients (Bahe, 1972), the formation of ion-pairs if such do occur in chloride solutions, and the change in effective concentration with hydration.

In this chapter we will consider the effects of the first process mentioned above because it pertains to the term  $\Delta E_\ell$  and will initially lump it into a parameter  $v$  such that Eqn. (3-14) now becomes

$$\Delta F_\ell = -\frac{B_\ell z^2 A_M \rho^{1/3} \ell^2 v}{(1 + 0.001 mM_2)^{1/3}} m^{4/3} +$$

$$+ RTm [(1 + \ell) \ln (1 + \ell) + (1 - \ell) \ln (1 - \ell)] \quad (4-1)$$

In this chapter we will calculate values of  $v$  and  $\ell$  and in the next chapter we will recalculate them after considering hydration corrections. The remaining processes will only be treated indirectly in this work. We will proceed in this manner, by a step-wise development of the theory for two reasons; greater clarity and the ease of backtracking if in the future one of our steps should require revision. After recalculating  $v$  and  $\ell$ , we will attempt to justify the values obtained by considering the contributions of ionic motion and of dielectric constant effects.

It is by no means intuitively clear that ionic motions around central positions (translations in dilute solutions tending towards vibrations in very concentrated solutions), and we will justify next the need to take them into consideration. Imagine if you will the three ions shown in Fig. 4-1, with the central one oscillating between its two nearest neighbor counter-ions.

$1/r$  is the key quantity for energies of interaction and, for a given  $x$  is, as is obvious from Fig. 3-5<sup>(\*)</sup>,

$$\frac{1}{r_x} = 0.5 \left( \frac{1}{r_o - x} + \frac{1}{r_o + x} \right) = \frac{r_o}{r_o^2 - x^2} \quad (4-2)$$

and

$$r_x = \frac{r_o^2 - x^2}{r_o} \quad \frac{r_o}{r_x} = \frac{1}{1 - (x/r_o)^2} \quad (4-3)$$

with

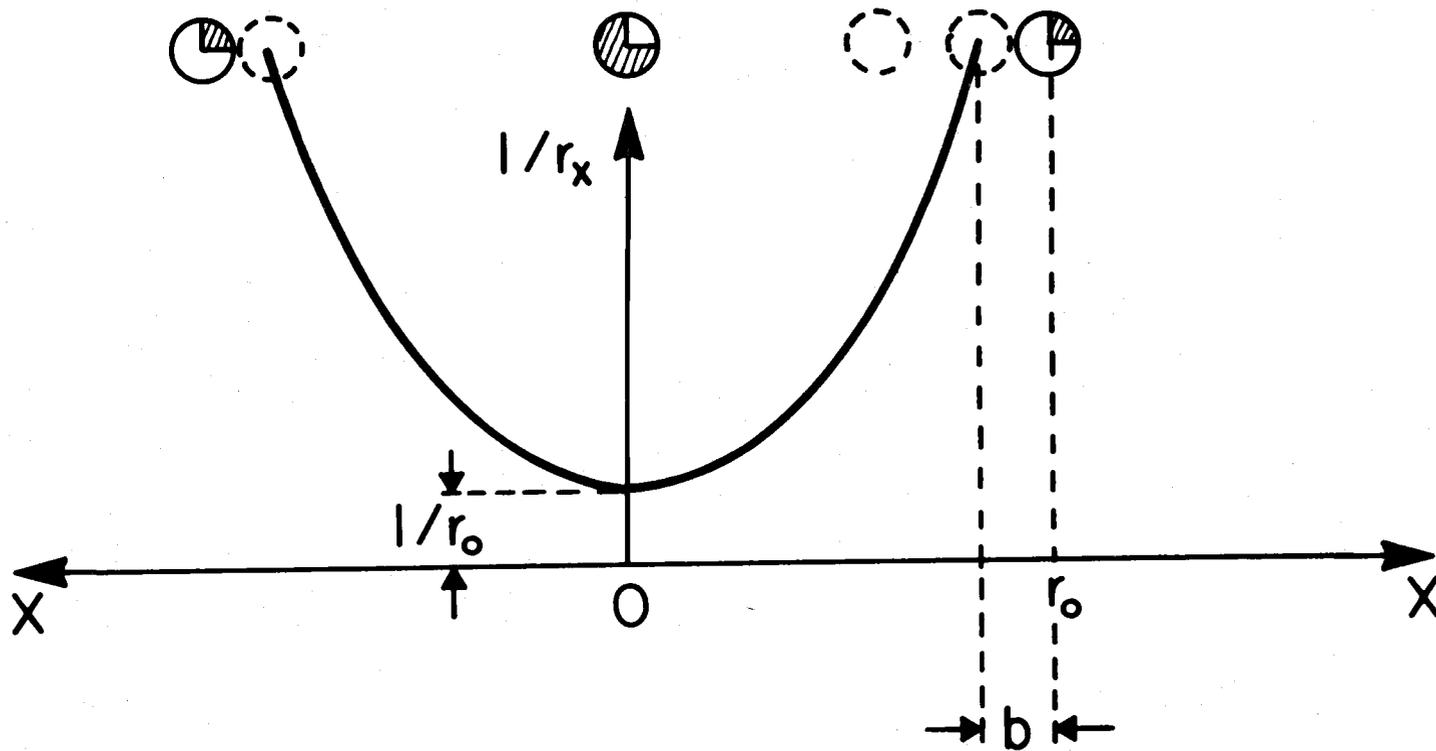
$$r_o \geq r_x \geq \frac{r_o^2 - (r_o - b)^2}{r_o} \quad (4-4)$$

Thus, one observes that  $\Delta E_\ell$  is increased by the motion of ions and should be

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\*The argument that follows is an approximate one as is the calculation of  $\bar{r}_x$  in section 4d because the anions are assumed fixed. This does not detract from the exactness of  $v^*$  calculated from experimental data but only from its quantitative interpretation.

Fig. 4-1. Oscillating ion. The broken arc sphere represents the central cation displaced due to its thermal energy.  $r_0$  is the average nearest neighbor distance,  $b$  is the distance of closest approach, and  $r_x$  is the effective (potential) nearest neighbor distance (see text).  $x$  is the displacement from the central position.



$$\Delta E_{\ell} = - \frac{B_{\ell} z^2 A_M \rho^{1/3} \ell^2}{(1 + 0.001 m M_2)^{1/3}} \left( \frac{r_o}{r_x} v' \right) m^{4/3} \quad (4-5)$$

in order to replace  $r_o$  used in the original derivation of  $\Delta E_{\ell}$  (see Eqn. (2-2)).

$v$  in Eqn. (4-1) is now replaced by

$$v = \frac{r_o}{r_x} v' \quad (4-6)$$

where  $\bar{r}_x$  is the actual average distance between ions and  $v'$  reflects dielectric effects.  $\bar{r}_x$  will be calculated in a latter chapter, after we have considered the effects of hydration. For the time being we will limit ourselves to obtaining values of  $\ell$  and  $v$  from a comparison of Eqn. (4-1) with  $\Delta F_{(exp)}$  (see Eqn. (3-16) and Table 3-3).

b) Procedure for the calculation of  $\ell$  and  $v$

The procedure for the calculation of  $\ell$  and  $v$  was as follows:

1. At each value of the molality  $m$  the values of  $\Delta F$  were calculated for a series of values of  $\ell$  and  $v$  by means of Eqn. (4-1).
2. For each  $(m, v)$  pair there was a non-zero minimum value of  $\Delta F_{\ell}$  provided that  $v$  was equal to or larger than a critical value  $v_c$ . For  $m = 0.1$  as an example, the non-zero minimum value of  $\Delta F_{\ell}$  appeared when  $v \geq 4.0$  and zero was the only minimum value for  $v \leq 3.0$ . We already saw in the preceding chapter that at  $m = 0.1$  and  $v = 1.0$  there was breakdown of long-

range order and now we see that the same is true for  $v = 2.0$  and  $v = 3.0$ . Only one  $(m, v)$  pair and, consequently one value of  $\ell$  yielded a minimum, indicated by  $\Delta F_{\ell(\min)}^*$ , which was in addition equal to  $\Delta F_{(\text{exp})}$ .

3. We found the values of  $\Delta F_{\ell}$  which bracketed  $\Delta F_{\ell(\min)}^*$  and interpolated the corresponding values of  $\ell$  and  $v$  to obtain  $\ell^*$  and  $v^*$  which corresponded to  $\Delta F_{\ell(\min)}^*$ . The results are shown in Table 4-1 for NaCl and in Table 4-2 for KCl.

As is to be expected, the absolute value of  $\Delta E_{\ell}^*$  increases with the concentration because the ions are closer together.  $\Delta S_{\ell}^*$  becomes more negative with increasing  $m$  because it reflects the change of entropy in going from a random configuration to a progressively more ordered one. The absolute value of  $\Delta F_{\ell(\min)}^* = \Delta F_{(\text{exp})}$  increases with concentration and so does the degree of order  $\ell^*$ . The parameter  $v$  decreases partly due to the decrease in  $r_o / \bar{r}_x$  with increasing energy of interaction which tends to dampen the ionic motions. This can be seen from Eqn. (4-3) rewritten in the form

$$\frac{r_o}{\bar{r}_x} = \frac{1}{1 - (\bar{x}/r_o)^2} \quad (4-7)$$

As the energy of interaction increases due to the increasing concentration,  $\bar{x}/r_o$  is expected to decrease from 1 at infinite dilution (i. e.  $r_o/\bar{r}_x \rightarrow \infty$ ) towards 0 ( $r_o/\bar{r}_x \rightarrow 1$ ). The concentration dependences of  $\ell$  and  $v$  are plotted in Figs. 4-2 and 4-3.

c) Equation for the mean activity coefficient

Table 4-1. Values of  $\Delta F_{\ell}$  which bracket  $\Delta F_{(\text{exp})}$ , corresponding values of  $\ell$  and  $v$ , and interpolated values of  $\Delta F_{\ell(\text{min})}^* = \Delta F_{(\text{exp})}$ ,  $\ell^*$  and  $v^*$ .  
 The quantities corresponding to asterisks are shown in parentheses.  
 The results are for NaCl at 25° C.

m	$\Delta E_{\ell}$	$\Delta S_{\ell}$	$\Delta F_{\ell}$	$\ell$	v
0.005	$-9.067 \times 10^7$	$-2.630 \times 10^5$	$-1.224 \times 10^7$	0.750	5.72
	$-9.376 \times 10^7$	$-2.712 \times 10^5$	$-1.288 \times 10^7$	0.760	5.76
	$(-9.366 \times 10^7)$	$(-2.709 \times 10^5)$	$(-1.286 \times 10^7)$	$(0.760)$	$(5.76)$
0.01	$-2.172 \times 10^8$	$-6.121 \times 10^5$	$-3.471 \times 10^7$	0.800	4.78
	$-2.176 \times 10^8$	$-6.121 \times 10^5$	$-3.516 \times 10^7$	0.800	4.79
	$(-2.175 \times 10^8)$	$(-6.121 \times 10^5)$	$(-3.508 \times 10^7)$	$(0.800)$	$(4.79)$
0.02	$-5.001 \times 10^8$	$-1.358 \times 10^6$	$-9.517 \times 10^7$	0.835	4.01
	$-5.073 \times 10^8$	$-1.378 \times 10^6$	$-9.642 \times 10^7$	0.840	4.02
	$(-5.009 \times 10^8)$	$(-1.360 \times 10^6)$	$(-9.532 \times 10^7)$	$(0.836)$	$(4.01)$
0.03	$-8.125 \times 10^8$	$-2.161 \times 10^6$	$-1.683 \times 10^8$	0.855	3.62
	$-8.243 \times 10^8$	$-2.193 \times 10^6$	$-1.706 \times 10^8$	0.860	3.63
	$(-8.212 \times 10^8)$	$(-2.185 \times 10^6)$	$(-1.700 \times 10^8)$	$(0.859)$	$(3.63)$
0.04	$-1.152 \times 10^9$	$-3.011 \times 10^6$	$-2.547 \times 10^8$	0.870	3.38
	$-1.159 \times 10^9$	$-3.011 \times 10^6$	$-2.615 \times 10^8$	0.870	3.40
	$(-1.153 \times 10^9)$	$(-3.011 \times 10^6)$	$(-2.553 \times 10^8)$	$(0.870)$	$(3.38)$
0.05	$-1.503 \times 10^9$	$-3.876 \times 10^6$	$-3.470 \times 10^8$	0.880	3.20
	$-1.512 \times 10^9$	$-3.876 \times 10^6$	$-3.564 \times 10^8$	0.880	3.22
	$(-1.505 \times 10^9)$	$(-3.876 \times 10^6)$	$(-3.493 \times 10^8)$	$(0.880)$	$(3.20)$
0.06	$-1.865 \times 10^9$	$-4.780 \times 10^6$	$-4.453 \times 10^8$	0.889	3.06
	$-1.876 \times 10^9$	$-4.790 \times 10^6$	$-4.514 \times 10^8$	0.890	3.07
	$(-1.874 \times 10^9)$	$(-4.789 \times 10^6)$	$(-4.505 \times 10^8)$	$(0.890)$	$(3.07)$
0.07	$-2.210 \times 10^9$	$-5.539 \times 10^6$	$-5.440 \times 10^8$	0.890	2.94
	$-2.276 \times 10^9$	$-5.758 \times 10^6$	$-5.591 \times 10^8$	0.900	2.96
	$(-2.271 \times 10^9)$	$(-5.746 \times 10^6)$	$(-5.580 \times 10^8)$	$(0.899)$	$(2.96)$
0.08	$-2.865 \times 10^9$	$-6.600 \times 10^6$	$-6.694 \times 10^8$	0.901	2.86
	$-2.870 \times 10^9$	$-6.600 \times 10^6$	$-6.740 \times 10^8$	0.901	2.87
	$(-2.868 \times 10^9)$	$(-6.600 \times 10^6)$	$(-6.717 \times 10^8)$	$(0.901)$	$(2.87)$

m	$\Delta E_\ell$	$\Delta S_\ell$	$\Delta F_\ell$	$\ell$	v
0.09	$-2.987 \times 10^9$	$-7.406 \times 10^6$	$-7.795 \times 10^8$	0.900	2.78
	$-3.075 \times 10^9$	$-7.627 \times 10^6$	$-8.013 \times 10^8$	0.910	2.80
	$(-3.026 \times 10^9)$	$(-7.503 \times 10^6)$	$(-7.891 \times 10^8)$	(0.904)	(2.79)
0.10	$-3.437 \times 10^9$	$-8.475 \times 10^6$	$-9.104 \times 10^8$	0.910	2.72
	$-3.463 \times 10^9$	$-8.475 \times 10^6$	$-9.357 \times 10^8$	0.910	2.74
	$(-3.438 \times 10^9)$	$(-8.475 \times 10^6)$	$(-9.116 \times 10^8)$	(0.910)	(2.72)
0.20	$-7.630 \times 10^9$	$-1.810 \times 10^7$	$-2.261 \times 10^9$	0.930	2.30
	$-7.696 \times 10^9$	$-1.810 \times 10^7$	$-2.327 \times 10^9$	0.930	2.32
	$(-7.687 \times 10^9)$	$(-1.810 \times 10^7)$	$(-2.318 \times 10^9)$	(0.930)	(2.32)
0.30	$-1.219 \times 10^{10}$	$-2.786 \times 10^7$	$-3.883 \times 10^9$	0.940	2.10
	$-1.231 \times 10^{10}$	$-2.786 \times 10^7$	$-3.999 \times 10^9$	0.940	2.12
	$(-1.229 \times 10^{10})$	$(-2.786 \times 10^7)$	$(-3.945 \times 10^9)$	(0.940)	(2.12)
0.40	$-1.614 \times 10^{10}$	$-3.714 \times 10^7$	$-5.069 \times 10^9$	0.940	1.90
	$-1.623 \times 10^{10}$	$-3.714 \times 10^7$	$-5.154 \times 10^9$	0.940	1.91
	$(-1.622 \times 10^{10})$	$(-3.714 \times 10^7)$	$(-5.076 \times 10^9)$	(0.940)	(1.91)
0.50	$-2.177 \times 10^{10}$	$-4.822 \times 10^7$	$-7.395 \times 10^9$	0.950	1.86
	$-2.210 \times 10^{10}$	$-4.853 \times 10^7$	$-7.629 \times 10^9$	0.950	1.86
	$(-2.202 \times 10^{10})$	$(-4.845 \times 10^7)$	$(-7.569 \times 10^9)$	(0.950)	(1.86)
0.60	$-2.639 \times 10^{10}$	$-5.749 \times 10^7$	$-9.248 \times 10^9$	0.950	1.78
	$-2.725 \times 10^{10}$	$-5.938 \times 10^7$	$-9.548 \times 10^9$	0.960	1.80
	$(-2.711 \times 10^{10})$	$(-5.907 \times 10^7)$	$(-9.498 \times 10^9)$	(0.958)	(1.80)
0.70	$-3.190 \times 10^{10}$	$-6.927 \times 10^7$	$-1.125 \times 10^{10}$	0.960	1.72
	$-3.227 \times 10^{10}$	$-6.927 \times 10^7$	$-1.162 \times 10^{10}$	0.960	1.74
	$(-3.213 \times 10^{10})$	$(-6.927 \times 10^7)$	$(-1.148 \times 10^{10})$	(0.960)	(1.73)
0.80	$-3.670 \times 10^{10}$	$-7.917 \times 10^7$	$-1.309 \times 10^{10}$	0.960	1.66
	$-3.714 \times 10^{10}$	$-7.917 \times 10^7$	$-1.354 \times 10^{10}$	0.960	1.68
	$(-3.710 \times 10^{10})$	$(-7.917 \times 10^7)$	$(-1.350 \times 10^{10})$	(0.960)	(1.68)
0.90	$-4.182 \times 10^{10}$	$-8.906 \times 10^7$	$-1.525 \times 10^{10}$	0.960	1.62
	$-4.232 \times 10^{10}$	$-8.906 \times 10^7$	$-1.576 \times 10^{10}$	0.960	1.64
	$(-4.212 \times 10^{10})$	$(-8.906 \times 10^7)$	$(-1.556 \times 10^{10})$	(0.960)	(1.63)
1.00	$-4.680 \times 10^{10}$	$-9.896 \times 10^7$	$-1.730 \times 10^{10}$	0.960	1.58
	$-4.739 \times 10^{10}$	$-9.896 \times 10^7$	$-1.789 \times 10^{10}$	0.960	1.60
	$(-4.714 \times 10^{10})$	$(-9.896 \times 10^7)$	$(-1.764 \times 10^{10})$	(0.960)	(1.59)
2.00	$-9.791 \times 10^{10}$	$-2.012 \times 10^8$	$-3.792 \times 10^{10}$	0.970	1.33
	$-1.004 \times 10^{11}$	$-2.046 \times 10^8$	$-3.940 \times 10^{10}$	0.970	1.35
	$(-9.862 \times 10^{10})$	$(-2.022 \times 10^8)$	$(-3.834 \times 10^{10})$	(0.970)	(1.34)

Table 4-2. Counterpart of Table 4-1 but for KCl solutions at 25° C.

m	$\Delta F_{\ell}$	$\ell$	v
0.0001	$-3.609 \times 10^4$	0.510	17.900
	$-4.019 \times 10^4$	0.520	18.000
	$(-3.850 \times 10^4)$	(0.516)	(17.959)
0.0005	$-4.012 \times 10^5$	0.600	11.000
	$-5.028 \times 10^5$	0.640	11.200
	$(-4.253 \times 10^5)$	(0.609)	(11.047)
0.001	$-1.020 \times 10^6$	0.640	8.900
	$-1.302 \times 10^6$	0.670	9.100
	$(-1.193 \times 10^6)$	(0.658)	(9.023)
0.005	$-1.191 \times 10^7$	0.750	5.700
	$-1.353 \times 10^7$	0.770	5.800
	$(-1.286 \times 10^7)$	(0.762)	(5.759)
0.01	$-3.517 \times 10^7$	0.800	4.790
	$-3.562 \times 10^7$	0.805	4.800
	$(-3.543 \times 10^7)$	(0.803)	(4.796)
0.02	$-9.653 \times 10^7$	0.839	4.020
	$-9.779 \times 10^7$	0.840	4.030
	$(-9.667 \times 10^7)$	(0.839)	(4.021)
0.03	$-1.709 \times 10^8$	0.859	3.630
	$-1.731 \times 10^8$	0.860	3.640
	$(-1.729 \times 10^8)$	(0.860)	(3.639)
0.04	$-2.553 \times 10^8$	0.871	3.380
	$-2.622 \times 10^8$	0.873	3.400
	$(-2.605 \times 10^8)$	(0.873)	(3.395)
0.05	$-3.528 \times 10^8$	0.885	3.210
	$-3.575 \times 10^8$	0.885	3.220
	$(-3.573 \times 10^8)$	(0.885)	(3.220)
0.06	$-4.592 \times 10^8$	0.891	3.080
	$-4.654 \times 10^8$	0.893	3.090
	$(-4.620 \times 10^8)$	(0.892)	(3.085)

m	$\Delta F_{\ell}$	$\ell$	v
0.07	$-5.692 \times 10^8$	0.899	2.980
	$-5.769 \times 10^8$	0.900	2.990
	$(-5.734 \times 10^8)$	(0.899)	(2.985)
0.08	$-6.865 \times 10^8$	0.903	2.880
	$-6.958 \times 10^8$	0.905	2.890
	$(-6.910 \times 10^8)$	(0.904)	(2.885)
0.09	$-8.056 \times 10^8$	0.907	2.800
	$-8.166 \times 10^8$	0.909	2.810
	$(-8.141 \times 10^8)$	(0.908)	(2.805)
0.10	$-9.411 \times 10^8$	0.915	2.740
	$-9.539 \times 10^8$	0.915	2.750
	$(-9.422 \times 10^8)$	(0.915)	(2.741)
0.20	$-2.419 \times 10^9$	0.935	2.340
	$-2.453 \times 10^9$	0.936	2.350
	$(-2.434 \times 10^9)$	(0.935)	(2.344)
0.30	$-4.178 \times 10^9$	0.947	2.140
	$-4.237 \times 10^9$	0.948	2.150
	$(-4.194 \times 10^9)$	(0.947)	(2.143)
0.40	$(-6.138 \times 10^9)$		
0.50	$-8.165 \times 10^9$	0.960	1.910
	$-8.285 \times 10^9$	0.960	1.920
	$(-8.221 \times 10^9)$	(0.960)	(1.915)
0.60	$-1.043 \times 10^{10}$	0.962	1.840
	$(-1.042 \times 10^{10})$	(0.962)	(1.840)
0.70	$-1.255 \times 10^{10}$	0.964	1.770
	$-1.274 \times 10^{10}$	0.965	1.780
	$(-1.271 \times 10^{10})$	(0.965)	(1.778)
0.80	$-1.492 \times 10^{10}$	0.966	1.720
	$-1.537 \times 10^{10}$	0.968	1.740
	$(-1.507 \times 10^{10})$	(0.966)	(1.721)

m	$\Delta F_{\ell}$	$\ell$	v
0.90	$-1.718 \times 10^{10}$	0.967	1.670
	$-1.771 \times 10^{10}$	0.971	1.690
	$(-1.751 \times 10^{10})$	(0.970)	(1.686)
1.0	$-1.866 \times 10^{10}$	0.965	1.600
	$-2.019 \times 10^{10}$	0.970	1.650
	$(-1.992 \times 10^{10})$	(0.969)	(1.641)
2.0	$-4.642 \times 10^{10}$	0.978	1.400
	$-4.798 \times 10^{10}$	0.980	1.420
	$(-4.657 \times 10^{10})$	(0.978)	(1.402)

One may next fit the curves in Figs. (4-2) and (4-3) with empirical equations which are then introduced into (4-1). An equation for  $\log f_{\pm}$  can then be obtained from the relation

$$\log f_{\pm} = \frac{1}{2 \times 2.3026RT} \frac{\partial F_{\ell}^*}{\partial m} \quad (4-8)$$

We did not attempt a fit over the whole range of concentrations as the main purpose of this work so far is to illustrate concepts and to provide a model rather than to predict activity coefficients. We found that for  $m > 0.03$

$$\ell^* = \frac{0.9683m}{(0.00580 + m)} \quad (4-9)$$

provided an excellent fit with an  $R^2 = 0.99999$ . For  $m > 0.1$

$$v^* = 1.592/m^{0.2356} \quad (4-10)$$

had an  $R^2 = 0.9999$ . The equation for  $\log f_{\pm}$  then became

$$\log f_{\pm} = \frac{1}{2.3026 RT} \left[ \Delta E \left[ \frac{4}{3m} - \frac{2.356}{m} - \frac{0.183}{3\rho} + \left( \frac{2}{m} - \frac{2\ell^*}{0.9682m} - \frac{0.001M_2}{3(1+0.001mM_2)} \right) \right] - \frac{T\Delta S}{m} + RTm \left[ \ln(1 + \ell^*) - \ln(1 - \ell^*) \right] \left( \frac{\ell^*}{m} - \frac{\ell^{*2}}{0.9682m} \right) \right] \quad (4-11)$$

Resulting values of  $f_{\pm}$  are compared to experimental ones in Table 4-3.

Fig. 4-2. Concentration dependence of  $\ell^*$ .

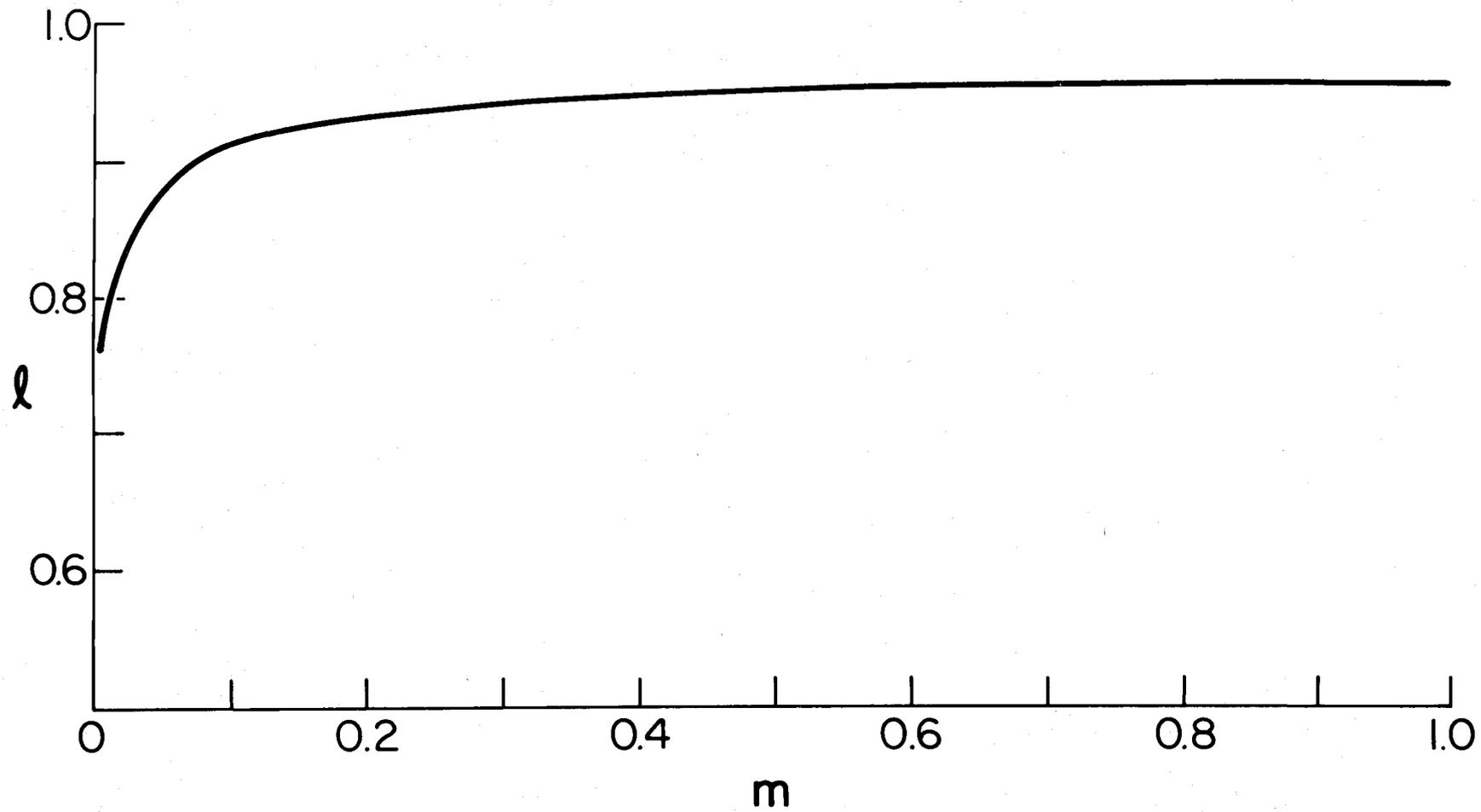


Fig. 4-3. Concentration dependence of  $v^*$ .

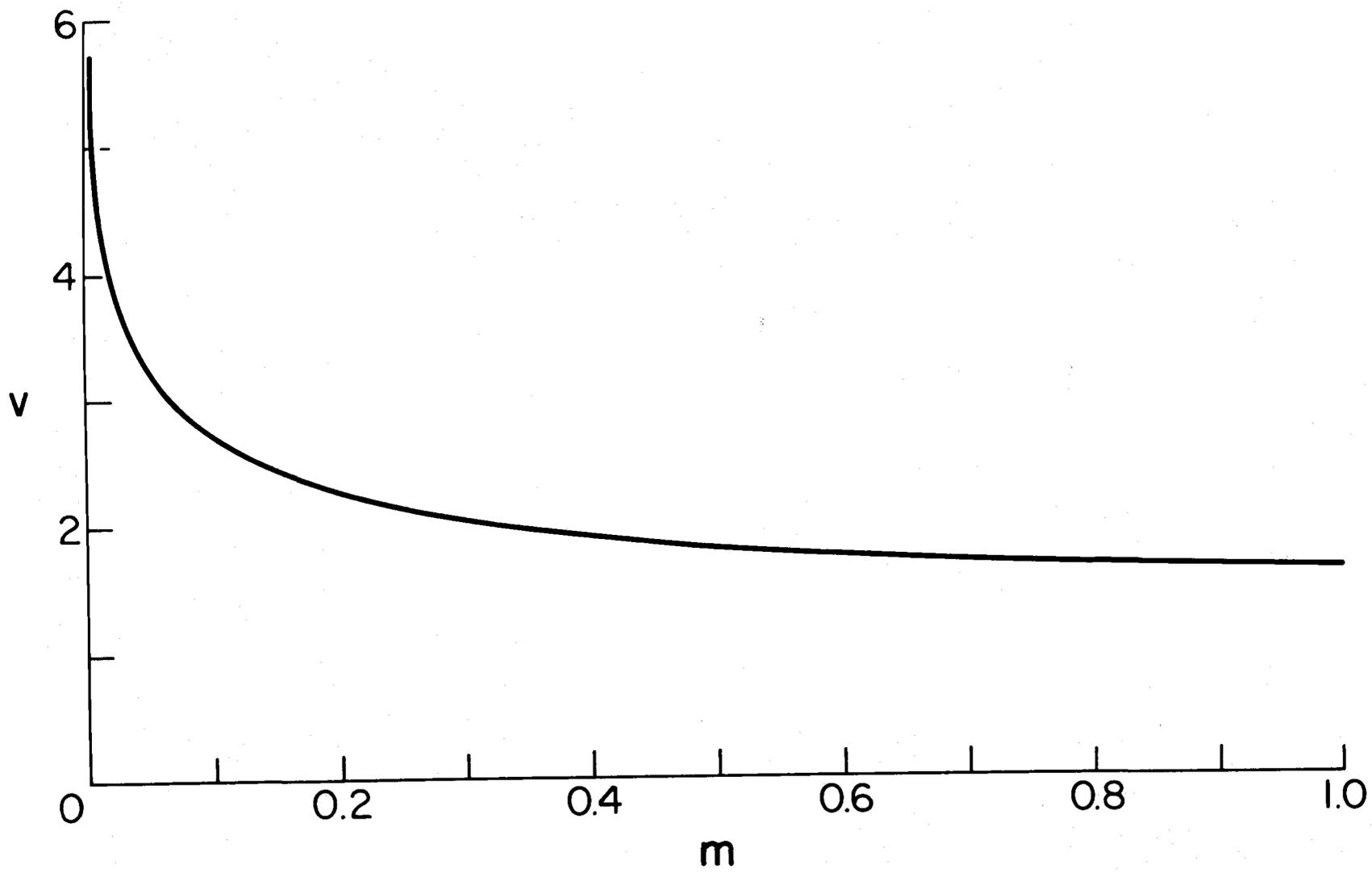


Table 4-3. A comparison of  $f_{\pm}$  obtained from Eqn. (4-11) with experimental values  $f_{\pm(\text{exp})}$  for NaCl at 25° C

m	$f_{\pm}$	$f_{\pm(\text{exp})}$	m	$f_{\pm}$	$f_{\pm(\text{exp})}$
0.1	0.776	0.778	0.6	0.674	0.673
0.2	0.734	0.735	0.7	0.667	0.667
0.3	0.710	0.710	0.8	0.662	0.662
0.4	0.695	0.693	0.9	0.657	0.659
0.5	0.683	0.681	1.0	0.653	0.657

A similar procedure can of course be used for  $m < 0.1$  down to any values by finding the proper fitting equations for  $\ell^*$  and  $v^*$ . Table 4-3 is presented for the sake of completeness but does not prove anything as we obtained  $\ell^*$  and  $v^*$  by a curve fitting procedure in the first place.

Rather, our contention is that the overall logical framework of the model is superior to that of the Debye-Hückel theory and that  $\ell^*$  and  $v^*$  follow expected trends and fall within expected ranges, thus providing credibility for the model.

In the approach to infinite dilution we would of course obtain the same numerical results for  $f_{\pm}$  as those provided by the Debye-Hückel. This would occur because our starting point to obtain  $f_{\pm}$  at high dilutions would be the empirical equation (1-27) which assumes the limiting form

$$\log f_{\pm(\text{interp})} = A I^{0.5} \quad (4-12)$$

with  $A = -0.5108$  (see Table 1-3). However, in our case the equation corresponding to Eqn. (4-11) would be a more complicated function of  $m$  than Eqn. (4-12) and would depend upon the equations used to fit empirically  $\ell^*$  and  $v^*$  as functions of  $m$ . Note that Eqn. (4-12) was obtained under the false premise that  $n_1'$  decays to the bulk value  $n_1$  at large distances from the central ion  $J$  (see Eqn. (1-2) and its critique in section 6-e).

The reason for the use of an empirical equation for  $\ell^*$  is that an explicit rigorous value of  $\ell_{\text{min}}$  versus  $m$  cannot be obtained. Rather, in analogy to Eqn. (3-15), one obtains, by setting  $\partial\Delta F/\partial\ell = 0$ ,

$$\frac{1}{v_{\min} \ell_{\min}} \ln \frac{1 + \ell_{\min}}{1 - \ell_{\min}} = \frac{2 B_{\ell} z^2 A_M \rho^{1/3} m^{1/3}}{RT (1 + 0.001 mM_2)^{1/3}} \quad (4-13)$$

The subscript "min" refers to values of  $\ell$  and  $v$  which yield minimum values of  $\Delta F_{\ell(\min)}$  which do not necessarily equal  $\Delta F_{(\exp)}$ . If they do then the symbols  $\ell^*$ ,  $v^*$  and  $\Delta F_{\ell(\min)}^*$  are used. Furthermore, the symbols  $\Delta F_{(\exp)}$  and  $\Delta F_{(\text{interp})}$  are equivalent as Eqn. (1-27) is used to obtain the values of  $f_{\pm(\text{interp})} = f_{\pm(\text{exp})}$  which are integrated to get  $\Delta F_{(\exp)}$ . It is straightforward to show that the values of  $\ell^*$  and  $v^*$  presented in parentheses in Tables 4-1 and 4-2 obey Eqn. (4-13) quite closely with slight deviations due to the interpolation procedure used in the Tables. Thus, at  $m = 0.01$  the left term of Eqn. (4-13) is 0.573 while the right one is 0.572 and at  $m = 1$  the values are 2.55 and 2.58 respectively.

Another reason for seeking empirical fits at this point is that the term  $r_o / \bar{r}_x$  in  $v = (r_o / \bar{r}_x) v'$  is quite complicated, as will be shown in the next section, and  $v'$  is not yet known as a function of  $m$ .

d) Determination of  $r_o / \bar{r}_x$  and  $v^{(*)}$

The concept of potential distance  $r_x$  was introduced in section 4-a. It is the interionic nearest neighbor distance to be used in the coulombic energy of interaction when an ion is displaced by  $x$  from its equilibrium position, at which the nearest neighbor distance is  $r_o$ .

The average nearest neighbor distance  $\bar{r}_x$  resulting from the balance between the energy of interaction which, combined with the energy of hydration, tends to maintain a regular distance between ions and the thermal energy which

\*See footnote on page 4-2.

produces translation (or vibration at very high concentrations) is given by

$$\bar{r}_x = \frac{\int_{r_{\min}}^{r_o} r_x \exp(-\Delta E_\ell / RT_m) dr_x}{\int_{r_{\min}}^{r_o} \exp(-\Delta E_\ell / RT_m) dr_x} \quad (4-14)$$

where (see Eqn. (4-4))

$$r_{\min} = r_o \left( 1 - \frac{(r_o - b)^2}{r_o^2} \right) \quad (4-15)$$

The exponential term can be written in the form

$$-\frac{\Delta E_\ell^*}{v} \times \frac{1}{RT_m} \times \frac{v}{r_x} = K v' \frac{1}{r_x} \quad (4-16)$$

where

$$K = -\frac{\Delta E_\ell^*}{v} \times \frac{1}{RT_m} \quad (4-17)$$

is a constant at each  $m$ . The values of  $\Delta E_{\ell(\min)}^*$  and  $v^*$  can be obtained for NaCl at 25°C from Table 4-1. The distance of closest approach  $b$  in Eqn. (4-15) can be selected as a reasonable value for hydrated ions. The term  $m$  appears in the denominator of Eqn. (4-17) to convert  $\Delta E_{\ell}$  to a molal basis as  $RT$  refers to the thermal energy per mole.

Note that in Eqn. (4-14) we are applying the Boltzman distribution to a series of systems, each with a given energy of interaction  $\Delta E_{\ell(\min)}^*$  which is a function of  $m$ , rather than to individual interacting particles as was done by Debye-Huckel and successors.

By setting  $y = 1/r_x$ , Eqn. (4-14) becomes

$$\bar{r}_x = \frac{\int_{1/r_{\min}}^{1/r_0} y^{-3} \exp(\kappa v' y) dy}{\int_{1/r_{\min}}^{1/r_0} y^{-2} \exp(\kappa v' y) dy} \quad (4-18)$$

which integrates to

$$\bar{r}_x = \frac{\left\{ -\frac{e^{\kappa v' y}}{2y^2} - \frac{\kappa v' e^{\kappa v' y}}{2y} + \frac{(\kappa v')^2}{2} \left[ \ln y + \sum_{i=1}^{\infty} \frac{(\kappa v' y)^i}{ixi!} \right] \right\} \Big|_{1/r_{\min}}^{1/r_0}}{\left\{ -\frac{e^{\kappa v' y}}{y} + \kappa v' \left[ \ln y + \sum_{i=1}^{\infty} \frac{(\kappa v' y)^i}{ixi!} \right] \right\} \Big|_{1/r_{\min}}^{1/r_0}} \quad (4-19)$$

The problem consists in finding at each molality  $m$  a value of  $v'$  such that  $\bar{r}_x$  calculated from (4-19) and  $v'$  obey the relationship

$$v^* = \frac{r_0}{r_x} v' \quad (4-20)$$

where  $v^*$  for NaCl is found in Table 4-1. This value for  $v'$  is not unity because for  $v' = 1$ , Eqn. (4-20) yields the data shown in Table 4-4.

We will not seek the correct values of  $v'$  and  $\bar{r}_x$  at this point because first we wish to apply hydration corrections in the next chapter to render  $v'$ ,  $\bar{r}_x$  and the general model more realistic.

Table 4-4. Values of  $r_o$ ,  $\bar{r}_x$  from Eqn. (4-19) with  $v' = 1$ ,  $(r_o/\bar{r}_x)$ , and  $v^*$  from Table 4-1 at different molalities and distances of closest approach  $b$  for NaCl at 25°C. Values of  $r$  and  $b$  in Å.

$m$	$r_o$	$\bar{r}_x$	$(r_o/\bar{r}_x)$	$v^*$	$b$
0.1	20.31	11.07	1.83	2.72	2.76
0.1	20.31	12.69	1.50	2.72	3.80
1.0	9.479	7.73	1.23	1.60	3.80

## 5. The Hydration Correction

In this chapter we will derive a hydration correction in a manner similar to that derived in Robinson and Stokes (1958), with a small change as we will use molal quantities throughout, and will apply the correction to our lattice theory.

### a) Derivation of the hydration equation

The free energy  $F$  of a given amount of solution with  $n_w$  moles of water and one mole of solute which dissociates into  $\nu_C$  moles of cations and  $\nu_A$  moles of anions can be expressed in two equivalent ways:

$$F = n_w \mu_w + \nu_C \mu_C + \nu_A \mu_A \quad (5-1)$$

and

$$F = (n_w - h) \mu_w + \nu_C \mu_C' + \nu_A \mu_A' \quad (5-2)$$

where  $h$  is the hydration number (number of moles of water which solvate one mole of salt) and  $\mu_i'$  is the chemical potential of the hydrated form of ion  $i$ . Eqns. (5-1) and (5-2) are identical because  $F$  is independent of where the water of hydration is assigned. Thus; setting these equations equal to each other and developing the chemical potentials by means of

$$\mu_i = \mu_i^{\circ} + RT \ln f_i m_i \quad (5-3)$$

one obtains the expression

$$\begin{aligned}
 & \left( \frac{h\mu_w^{\circ}}{RT} + h \ln a_w \right) + \frac{\nu_C}{RT} (\mu_C^{\circ} - \mu_C^{\circ'}) + \frac{\nu_A}{RT} (\mu_A^{\circ} - \mu_A^{\circ'}) + \\
 & + \nu_C \ln \frac{m_C}{m_C'} + \nu_A \ln \frac{m_A}{m_A'} = \nu_C \ln f_C' - \nu_C \ln f_C + \\
 & + \nu_A \ln f_A' - \nu_A \ln f_A \quad (5-4)
 \end{aligned}$$

As  $m = 1000/18 n_w$  and  $m' = 1000/18 (n_w - h)$ ,

$$\frac{m}{m'} = \frac{m_C}{m_C'} = \frac{m_A}{m_A'} = \frac{n_w - h}{n_w} \quad (5-5)$$

if one remembers that there are  $n_w$  moles of water per mole of salt in the solution.

Introducing Eqn. (5-5) into (5-4) one obtains

$$\begin{aligned}
 & \left( \frac{h\mu_w^{\circ}}{RT} + h \ln a_w \right) + \frac{\nu_C}{RT} (\mu_C^{\circ} - \mu_C^{\circ'}) + \frac{\nu_A}{RT} (\mu_A^{\circ} - \mu_A^{\circ'}) + \nu \ln \frac{n_w - h}{n_w} = \\
 & = \nu_C \ln f_C' - \nu_C \ln f_C + \nu_A \ln f_A' - \nu_A \ln f_A \quad (5-6)
 \end{aligned}$$

with  $\nu = \nu_C + \nu_A$ . As  $n_w \rightarrow \infty$  all activity coefficients and  $a_w$  tend to unity, their logarithms tend to zero, and

$$\nu \ln \frac{n_w - h}{n_w} = \nu \ln \frac{1 - h/n_w}{1} \rightarrow 0 \quad (5-7)$$

Therefore, all the terms with standard chemical potentials, which do not depend upon  $n_w$ , must add up to zero and Eqn. (5-6) is reduced to

$$\begin{aligned} \nu_C \ln f'_C - \nu_C \ln f_C + \nu_A \ln f'_A - \nu_A \ln f_A &= \\ = \nu \ln \frac{n_w - h}{n_w} + h \ln a_w & \quad (5-8) \end{aligned}$$

Then, remembering that

$$f_{\pm} = (f_C^{\nu_C} f_A^{\nu_A})^{1/\nu} \quad (5-9)$$

one obtains

$$\ln f'_{\pm} = \ln f_{\pm} + \frac{h}{\nu} \ln a_w + \ln(1 - 0.018 h m) \quad (5-10)$$

as  $n_w = 1000/18 m$  leads to  $(n_w - h)/n_w = (1 - 0.018 h m)$ .

In terms of the practical osmotic coefficient

$$\phi = -\frac{1000}{18 \nu m} \ln a_w \quad (5-11)$$

Eqn. (6-10) becomes

$$\ln f_{\pm}' = \ln f_{\pm} - 0.018 h m \phi + \ln (1 - 0.018 h m) \quad (5-12)$$

When one deals with mole fractions

$$\bar{N}_2 = \frac{\nu}{n_w + \nu} \quad \bar{N}_2' = \frac{\nu}{n_w - h + \nu} \quad (5-13)$$

and the counterpart of Eqn. (5-5) is

$$\frac{\bar{N}_2}{\bar{N}_2'} = \frac{n_w - h + \nu}{n_w + \nu} \quad (5-14)$$

Hence the difference between our results and those presented in Robinson and Stokes (1958).

The activity coefficient that corresponds to  $\Delta F_{\ell(\min)}^*$  in our theory is  $f_{\pm}$  in Eqn. (5-12) because we did not make an allowance for the change in effective

m resulting from the removal of water of hydration in going from infinite dilution to molality m. The experimental mean activity coefficient does include this effect and corresponds, therefore, to  $f_{\pm}'$ .

b) Procedure for the calculation of  $\ell$  and  $v$

The counterpart of the procedure in section 4-b is now as follows:

Firstly one calculates  $f_{\pm(\text{corr})}'$ , the mean activity coefficient corrected for hydration, by means of Eqn. (5-12) in the form

$$\ln f_{\pm(\text{corr})}' = \ln f_{\pm(\text{interp})}' + 0.018 h m \phi - \ln (1 - 0.018 h m) \quad (5-15)$$

where  $f_{\pm(\text{interp})}'$  is obtained from Eqn. (1-27).

For  $m \leq 0.1$ ,  $f_{\pm(\text{interp})}'$  can be obtained from the empirical equation

$$\log f_{\pm}' = \frac{A_D I_S^{0.5}}{1 + B_D I_S^{0.5}} \quad (5-16)$$

where  $A_D = -0.5108$ . In the case of NaCl we saw that the best fit between Eqn. (5-16) and the experimental data is obtained for  $a_D^{\circ} = 4.60\text{\AA}$ . As  $B_D = 0.3287$  (see Table 1-1),  $B^{\circ} = B_D \times a_D = 1.512$ .

In the range in which an equation of the type (5-16) is valid, the practical osmotic coefficient can be calculated from (Robinson and Stokes, 1958, p. 34)

$$\phi = 1 - \frac{2.3026 A_D m^{0.5}}{3} \sigma(x) \quad (5-17)$$

with

$$\sigma(x) = \frac{3}{x} \left[ (1+x) - 2 \ln(1+x) - \frac{1}{1+x} \right] \quad (5-18)$$

and

$$x = B m^{0.5} \quad (5-19)$$

At values of  $m \geq 0.1$  there are tabulations of  $\phi$  versus  $m$ .

One then fits  $f_{\pm(\text{corr})}$  by means of an empirical equation and calculates

$$\Delta F_{(\text{corr})} = 2RT \int_0^m \ln f_{\pm(\text{corr})} dm \quad (5-20)$$

Values of  $\Delta F_{\ell(\text{min})}$  as functions of  $v$  and  $\ell$  at each molality are obtained as before either by using printouts of  $\Delta F_1$  given by Eqn. (4-1) for arbitrarily selected  $(\ell, v)$  pairs or by selecting values of  $v$  arbitrarily and calculating  $\ell$  from Eqn. (4-13). One then selects that  $\Delta F_{\ell(\text{min})}$ , labeled  $\Delta F_{\ell(\text{min})}^*$  which equals  $\Delta F_{(\text{corr})}$  and thus obtains the values of  $\ell^*$  and  $v^*$ .

In contrast to chapter 4 in which there was only one pair  $(\ell^*, v^*)$  for each molality  $m$ , there will now be one  $(\ell^*, v^*)$  pair for each  $(m, h)$  pair, where  $h$  is the hydration number, that is, the number of moles of water which solvate

each mole of salt. Our method will only tell us which value of  $h$  is the correct one when we manage to derive the term  $v'$  (see Eqn. (4-6)) from first principles and, at present we must select values of  $h$  based on literature data.

c) Calculation of  $\ell$  and  $v$

We will illustrate this procedure for NaCl solutions at 25°C. The first step is to obtain values of the osmotic coefficient  $\phi$  by means of Eqn. (5-17) for  $m \leq 0.09$  and from the literature (Robinson and Stokes, 1958) for higher concentrations. The values of  $A_D$  and  $B'$  are -0.5108 and 1.512 as was shown in the previous section. The resulting values of  $\phi$  are presented in Table 5-1. Next, by means of Eqn. (5-15) we calculated the values of  $f_{\pm(\text{corr})}$  as a function of  $m$  and of assumed values of  $h$  between 1 and 10. The results are shown in Table 5-2.

Tables 5-3 and 5-4 contain the values of  $\phi$  used to calculate  $f_{\pm(\text{corr})}$  for KCl and the resulting values of  $f_{\pm(\text{corr})}$ . Tables 5-5 and 5-6 contain similar results for LiCl.

The activity coefficients in Table 5-2 can be expressed by equations such as (1-27). The constants from such equations determined at each value of  $h$  were then used to calculate the free energy corrected for hydration  $\Delta F_{(\text{corr})}^*$ . Values of  $\ell^*$ ,  $v^*$  and  $\Delta F_{\ell(\text{min})}^*$  were then calculated as discussed previously for each  $m$  and  $h$ . A summary of the results for NaCl is shown in Table 5-7.

Tables 5-8 and 5-9 contain the results for KCl and LiCl.

Table 5-1. Values of the practical osmotic coefficient  $\phi$  for NaCl at 25° C versus the molality  $m$ .

$m$	$\phi$	$m$	$\phi$	$m$	$\phi$
0.0001	0.9962	0.05	0.9437	0.40	0.9203
0.0005	0.9917	0.06	0.9406	0.50	0.9209
0.001	0.9884	0.07	0.9379	0.60	0.9230
0.005	0.9762	0.08	0.9356	0.70	0.9257
0.01	0.9683	0.09	0.9336	0.80	0.9288
0.02	0.9587	0.10	0.9324	0.90	0.9320
0.03	0.9523	0.20	0.9245	1.0	0.9355
0.04	0.9475	0.30	0.9215	2.0	0.9833

Table 5-2. Values of  $f_{\pm(\text{corr})}$ , the mean activity coefficient corrected for hydration, as a function of  $m$  and  $h$  for NaCl at 25° C.

m	Values of $f_{\pm(\text{corr})}$ for h shown below										
	0	1	2	3	4	5	6	7	8	9	10
.0001	.9885	.9885	.9885	.9885	.9885	.9885	.9885	.9885	.9885	.9885	.9885
.0005	.9749	.9749	.9749	.9749	.9750	.9750	.9750	.9750	.9750	.9750	.9751
.0010	.9651	.9652	.9652	.9652	.9653	.9653	.9653	.9654	.9654	.9654	.9655
.0020	.9519	.9520	.9521	.9521	.9522	.9523	.9523	.9524	.9525	.9525	.9526
.0030	.9422	.9423	.9424	.9425	.9426	.9427	.9428	.9429	.9430	.9431	.9432
.0040	.9344	.9345	.9346	.9348	.9349	.9350	.9352	.9353	.9354	.9356	.9357
.0050	.9276	.9278	.9279	.9281	.9283	.9284	.9286	.9288	.9289	.9291	.9293
.0060	.9217	.9219	.9221	.9223	.9225	.9227	.9229	.9231	.9233	.9235	.9237
.0070	.9164	.9166	.9168	.9170	.9173	.9175	.9177	.9179	.9182	.9184	.9186
.0080	.9115	.9118	.9120	.9123	.9125	.9128	.9131	.9133	.9136	.9138	.9141
.0090	.9070	.9073	.9076	.9079	.9082	.9085	.9088	.9091	.9093	.9096	.9099
.0100	.9029	.9032	.9035	.9038	.9042	.9045	.9048	.9051	.9054	.9058	.9061
.0200	.8719	.8726	.8732	.8738	.8744	.8750	.8756	.8763	.8769	.8775	.8781
.0300	.8509	.8518	.8527	.8536	.8545	.8554	.8563	.8572	.8581	.8590	.8599
.0400	.8348	.8359	.8371	.8383	.8395	.8406	.8418	.8430	.8442	.8454	.8466
.0500	.8216	.8230	.8244	.8259	.8273	.8288	.8302	.8317	.8332	.8346	.8361
.0600	.8104	.8121	.8138	.8155	.8172	.8189	.8207	.8224	.8241	.8259	.8276
.0700	.8007	.8027	.8046	.8066	.8086	.8106	.8125	.8145	.8165	.8185	.8206
.0800	.7921	.7944	.7966	.7988	.8010	.8033	.8055	.8078	.8101	.8123	.8146
.0900	.7845	.7869	.7894	.7919	.7944	.7969	.7994	.8019	.8044	.8070	.8095
.1000	.7778	.7805	.7832	.7860	.7887	.7915	.7942	.7970	.7998	.8026	.8055
.2000	.7336	.7387	.7438	.7490	.7543	.7596	.7649	.7703	.7757	.7812	.7867
.3000	.7091	.7165	.7240	.7316	.7393	.7471	.7551	.7631	.7712	.7795	.7878
.4000	.6931	.7028	.7127	.7227	.7329	.7433	.7538	.7646	.7756	.7867	.7981
.5000	.6819	.6938	.7060	.7185	.7312	.7443	.7576	.7712	.7852	.7995	.8141
.6000	.6736	.6878	.7024	.7173	.7327	.7485	.7647	.7814	.7986	.8162	.8344

m	0	1	2	3	4	5	6	7	8	9	10
.7000	.6674	.6838	.7008	.7183	.7364	.7550	.7743	.7942	.8148	.8361	.8581
.8000	.6626	.6813	.7008	.7209	.7417	.7634	.7859	.8092	.8335	.8587	.8849
.9000	.6589	.6799	.7018	.7247	.7484	.7732	.7991	.8260	.8542	.8836	.9144
1.0000	.6560	.6794	.7038	.7294	.7562	.7842	.8137	.8445	.8769	.9110	.9468
1.2000	.6543	.6826	.7123	.7438	.7770	.8122	.8495	.8890	.9310	.9756	1.0231
1.4000	.6548	.6888	.7234	.7612	.8015	.8446	.8908	.9403	.9935	1.0588	1.1125
1.6000	.6574	.6959	.7373	.7819	.8300	.8820	.9384	.9995	1.0661	1.1386	1.2179
1.8000	.6619	.7059	.7537	.8058	.8625	.9245	.9925	1.0672	1.1495	1.2406	1.3416
2.0000	.6680	.7180	.7727	.8328	.8991	.9724	1.0537	1.1442	1.2454	1.3590	1.4872

Table 5-3. Values of the practical osmotic coefficient  $\phi$  for KCl at 25° C  
versus the molality  $m$ .

$m$	$\phi$	$m$	$\phi$	$m$	$\phi$
0.0001	0.9962	0.05	0.9407	0.40	0.9017
0.0005	0.9916	0.06	0.9372	0.50	0.8989
0.001	0.9883	0.07	0.9342	0.60	0.8976
0.005	0.9758	0.08	0.9315	0.70	0.8970
0.01	0.9675	0.09	0.9292	0.80	0.8970
0.02	0.9572	0.10	0.9266	0.90	0.8971
0.03	0.9502	0.20	0.9130	1.00	0.8974
0.04	0.9450	0.30	0.9063	2.00	0.9124

Table 5-4. Values of  $f_{\pm(\text{corr})}$ , the mean activity coefficient corrected for hydration, as a function of m and h for KCl at 25° C.

m	Values of $f_{\pm(\text{corr})}$ for h shown below											
	0	1	2	3	4	5	6	7	8	9	10	
.0001	.9885	.9885	.9885	.9885	.9885	.9885	.9885	.9885	.9885	.9885	.9885	.9885
.0005	.9748	.9748	.9748	.9748	.9748	.9749	.9749	.9749	.9749	.9749	.9749	.9749
.0010	.9649	.9650	.9650	.9650	.9651	.9651	.9651	.9652	.9652	.9652	.9653	.9653
.0020	.9515	.9516	.9517	.9517	.9518	.9519	.9519	.9520	.9521	.9521	.9521	.9522
.0030	.9417	.9418	.9419	.9420	.9421	.9422	.9423	.9424	.9425	.9426	.9427	.9427
.0040	.9336	.9338	.9339	.9340	.9342	.9343	.9344	.9346	.9347	.9348	.9350	.9350
.0050	.9267	.9269	.9271	.9272	.9274	.9276	.9277	.9279	.9281	.9282	.9284	.9284
.0060	.9206	.9208	.9210	.9212	.9214	.9216	.9218	.9220	.9222	.9224	.9226	.9226
.0070	.9152	.9154	.9156	.9158	.9161	.9163	.9165	.9168	.9170	.9172	.9174	.9174
.0080	.9102	.9104	.9107	.9109	.9112	.9115	.9117	.9120	.9122	.9125	.9128	.9128
.0090	.9056	.9058	.9061	.9064	.9067	.9070	.9073	.9076	.9079	.9082	.9085	.9085
.0100	.9013	.9016	.9019	.9022	.9026	.9029	.9032	.9035	.9038	.9042	.9045	.9045
.0200	.8691	.8698	.8704	.8710	.8716	.8722	.8728	.8734	.8741	.8747	.8753	.8753
.0300	.8471	.8480	.8489	.8498	.8507	.8516	.8525	.8534	.8543	.8552	.8561	.8561
.0400	.8301	.8312	.8324	.8336	.8347	.8359	.8371	.8383	.8394	.8406	.8418	.8418
.0500	.8161	.8175	.8189	.8204	.8218	.8233	.8247	.8261	.8276	.8290	.8305	.8305
.0600	.8042	.8059	.8076	.8093	.8110	.8127	.8144	.8161	.8178	.8195	.8212	.8212
.0700	.7938	.7958	.7977	.7997	.8016	.8036	.8056	.8075	.8095	.8115	.8135	.8135
.0800	.7847	.7869	.7891	.7913	.7935	.7957	.7979	.8001	.8024	.8046	.8069	.8069
.0900	.7764	.7789	.7813	.7838	.7862	.7887	.7912	.7937	.7962	.7987	.8012	.8012
.1000	.7686	.7713	.7740	.7767	.7794	.7821	.7849	.7876	.7904	.7931	.7959	.7959
.2000	.7177	.7226	.7276	.7327	.7378	.7429	.7481	.7533	.7586	.7639	.7693	.7693
.3000	.6873	.6944	.7016	.7089	.7163	.7238	.7315	.7392	.7470	.7549	.7630	.7630
.4000	.6660	.6752	.6846	.6941	.7038	.7137	.7237	.7339	.7444	.7550	.7658	.7658
.5000	.6498	.6611	.6725	.6843	.6963	.7086	.7211	.7339	.7471	.7605	.7743	.7743
.6000	.6370	.6502	.6638	.6777	.6921	.7068	.7219	.7375	.7535	.7699	.7868	.7868

m	0	1	2	3	4	5	6	7	8	9	10
.7000	.6264	.6416	.6573	.6735	.6902	.7074	.7252	.7436	.7626	.7822	.8025
.8000	.6176	.6347	.6525	.6710	.6901	.7099	.7305	.7518	.7740	.7970	.8209
.9000	.6100	.6291	.6490	.6697	.6913	.7138	.7373	.7617	.7873	.8139	.8418
1.0000	.6035	.6245	.6466	.6696	.6937	.7189	.7454	.7731	.8022	.8328	.8650
1.2000	.5928	.6177	.6441	.6718	.7012	.7323	.7651	.8000	.8370	.8763	.9180
1.4000	.5844	.6133	.6440	.6768	.7117	.7491	.7890	.8318	.8778	.9272	.9805
1.6000	.5778	.6106	.6459	.6839	.7247	.7689	.8167	.8684	.9247	.9860	1.0529
1.8000	.5726	.6094	.6494	.6928	.7400	.7916	.8480	.9099	.9780	1.0533	1.1368
2.0000	.5684	.6094	.6541	.7033	.7573	.8170	.8830	.9564	1.0383	1.1301	1.2335

Table 5-5. Values of the practical osmotic coefficient  $\phi$  or LiCl at 25° C versus the molality  $m$ .

$m$	$\phi$	$m$	$\phi$	$m$	$\phi$
0.0001	0.9962	0.05	0.9473	0.40	0.9540
0.0005	0.9917	0.06	0.9447	0.50	0.9630
0.001	0.9886	0.07	0.9424	0.60	0.9730
0.005	0.9768	0.08	0.9405	0.70	0.9840
0.01	0.9694	0.09	0.9388	0.80	0.9950
0.02	0.9605	0.10	0.9390	0.90	1.0060
0.03	0.9548	0.20	0.9390	1.00	1.0180
0.04	0.9506	0.30	0.9450	2.00	1.1420

Table 5-6. Values of  $f_{\pm(\text{corr})}$ , the mean activity coefficient corrected for hydration, as a function of  $m$  and  $h$  for LiCl at 25° C.

m	Values of $f_{\pm(\text{corr})}$ for h shown below										
	0	1	2	3	4	5	6	7	8	9	10
.0001	.9885	.9885	.9885	.9885	.9885	.9885	.9885	.9885	.9885	.9885	.9885
.0005	.9750	.9750	.9751	.9751	.9751	.9751	.9751	.9751	.9752	.9752	.9752
.0010	.9654	.9654	.9655	.9655	.9655	.9656	.9656	.9656	.9657	.9657	.9657
.0020	.9524	.9525	.9526	.9526	.9527	.9528	.9528	.9529	.9530	.9530	.9531
.0030	.9430	.9431	.9432	.9433	.9434	.9435	.9436	.9437	.9438	.9439	.9440
.0040	.9353	.9354	.9356	.9357	.9358	.9360	.9361	.9362	.9364	.9365	.9366
.0050	.9288	.9289	.9291	.9293	.9294	.9296	.9298	.9299	.9301	.9303	.9304
.0060	.9230	.9232	.9234	.9236	.9238	.9240	.9242	.9244	.9246	.9248	.9250
.0070	.9179	.9181	.9183	.9186	.9188	.9190	.9193	.9195	.9197	.9199	.9202
.0080	.9132	.9135	.9137	.9140	.9143	.9145	.9148	.9150	.9153	.9156	.9158
.0090	.9089	.9092	.9095	.9098	.9101	.9104	.9107	.9110	.9112	.9115	.9118
.0100	.9049	.9053	.9056	.9059	.9062	.9065	.9069	.9072	.9075	.9078	.9082
.0200	.8755	.8761	.8767	.8774	.8780	.8786	.8792	.8798	.8805	.8811	.8817
.0300	.8557	.8566	.8575	.8584	.8593	.8602	.8612	.8621	.8630	.8639	.8648
.0400	.8406	.8418	.8430	.8442	.8454	.8466	.8478	.8489	.8501	.8513	.8525
.0500	.8284	.8298	.8313	.8328	.8342	.8357	.8372	.8386	.8401	.8416	.8431
.0600	.8181	.8198	.8215	.8233	.8250	.8267	.8285	.8302	.8320	.8337	.8355
.0700	.8092	.8112	.8131	.8151	.8171	.8192	.8212	.8232	.8252	.8272	.8293
.0800	.8013	.8036	.8058	.8081	.8104	.8126	.8149	.8172	.8195	.8218	.8241
.0900	.7943	.7968	.7993	.8019	.8044	.8069	.8095	.8120	.8146	.8172	.8198
.1000	.7897	.7924	.7952	.7980	.8008	.8036	.8064	.8093	.8121	.8150	.8179
.2000	.7570	.7623	.7677	.7731	.7785	.7840	.7896	.7952	.8008	.8065	.8123
.3000	.7439	.7518	.7597	.7678	.7760	.7843	.7927	.8012	.8099	.8187	.8275
.4000	.7393	.7498	.7604	.7713	.7824	.7937	.8052	.8168	.8288	.8409	.8533
.5000	.7394	.7526	.7661	.7800	.7941	.8086	.8234	.8385	.8540	.8699	.8861
.6000	.7427	.7587	.7752	.7922	.8096	.8275	.8459	.8648	.8842	.9043	.9249

m	0	1	2	3	4	5	6	7	8	9	10
.7000	.7482	.7672	.7868	.8071	.8280	.8496	.8719	.8950	.9189	.9435	.9691
.8000	.7555	.7776	.8005	.8242	.8489	.8745	.9011	.9288	.9575	.9874	1.0185
.9000	.7641	.7894	.8158	.8434	.8721	.9020	.9333	.9660	1.0001	1.0358	1.0732
1.0000	.7739	.8027	.8328	.8643	.8974	.9320	.9684	1.0067	1.0468	1.0891	1.1336
1.2000	.7966	.8327	.8708	.9112	.9540	.9993	1.0474	1.0984	1.1528	1.2106	1.2722
1.4000	.8228	.8671	.9143	.9648	1.0189	1.0768	1.1390	1.2058	1.2777	1.3552	1.4391
1.6000	.8524	.9057	.9632	1.0252	1.0924	1.1652	1.2442	1.3303	1.4241	1.5267	1.6392
1.8000	.8852	.9485	1.0175	1.0928	1.1753	1.2657	1.3650	1.4746	1.5958	1.7302	1.8799
2.0000	.9213	.9958	1.0779	1.1684	1.2687	1.3799	1.5039	1.6424	1.7979	1.9731	2.1715

Table 5-7. The values of  $\ell^*$ ,  $v^*$  and  $\Delta F_{\ell}^*$  for NaCl at a range of molalities and various h.

m	h	$\ell^*$	$v^*$	$\Delta F_{\ell}^*$
.0001	0	.5203	17.95	$-3.840 \times 10^4$
	2	.5203	17.95	$-3.840 \times 10^4$
	4	.5203	17.95	$-3.840 \times 10^4$
	6	.5203	17.95	$-3.840 \times 10^4$
	8	.5203	17.95	$-3.840 \times 10^4$
	10	.5203	17.95	$-3.840 \times 10^4$
.001	0	.6585	9.020	$-1.190 \times 10^6$
	2	.6580	9.017	$-1.185 \times 10^6$
	4	.6580	9.017	$-1.185 \times 10^6$
	6	.6580	9.017	$-1.185 \times 10^6$
	8	.6575	9.014	$-1.180 \times 10^6$
	10	.6575	9.014	$-1.180 \times 10^6$
.01	0	.7990	4.786	$-3.504 \times 10^7$
	2	.7985	4.783	$-3.490 \times 10^7$
	4	.7978	4.779	$-3.469 \times 10^7$
	6	.7970	4.774	$-3.449 \times 10^7$
	8	.7965	4.771	$-3.435 \times 10^7$
	10	.7960	4.768	$-3.422 \times 10^7$
.1	0	.9093	2.715	$-9.110 \times 10^8$
	2	.9073	2.701	$-8.929 \times 10^8$
	4	.9053	2.837	$-8.752 \times 10^8$
	6	.9033	2.673	$-8.580 \times 10^8$
	8	.9013	2.660	$-8.413 \times 10^8$
	10	.8993	2.653	$-8.251 \times 10^8$
.5	0	.9530	1.858	$-7.582 \times 10^9$
	2	.9485	1.820	$-7.133 \times 10^9$
	4	.9435	1.782	$-6.686 \times 10^9$
	6	.9383	1.745	$-6.266 \times 10^9$
	8	.9320	1.706	$-5.820 \times 10^9$
	10	.9250	1.667	$-5.378 \times 10^9$
1.0	0	.9633	1.562	$-1.766 \times 10^{10}$
	2	.9565	1.505	$-1.594 \times 10^{10}$
	4	.9480	1.446	$-1.417 \times 10^{10}$
	6	.9373	1.386	$-1.238 \times 10^{10}$
	8	.9235	1.321	$-1.058 \times 10^9$
	10	.9050	1.253	$-8.730 \times 10^9$

Table 5-8. The values of  $\ell^*$ ,  $v^*$  and  $\Delta F_{\ell}^*$  for KCl at a range of molalities and various h.

m	h	$\ell^*$	$v^*$	$\Delta F_{\ell}^*$
0.0001	0	.5205	17.95	$-3.848 \times 10^4$
	2	.5205	17.95	$-3.848 \times 10^4$
	4	.5205	17.95	$-3.848 \times 10^4$
	6	.5205	17.95	$-3.848 \times 10^4$
	8	.5205	17.95	$-3.848 \times 10^4$
	10	.5205	17.95	$-3.848 \times 10^4$
0.001	0	.6585	9.022	$-1.192 \times 10^6$
	2	.6585	9.021	$-1.190 \times 10^6$
	4	.6585	9.021	$-1.190 \times 10^6$
	6	.6580	9.018	$-1.185 \times 10^6$
	8	.6580	9.018	$-1.185 \times 10^6$
	10	.6580	9.018	$-1.185 \times 10^6$
0.01	0	.8005	4.796	$-3.545 \times 10^7$
	2	.7995	4.789	$-3.518 \times 10^7$
	4	.7990	4.786	$-3.504 \times 10^7$
	6	.7985	4.784	$-3.490 \times 10^7$
	8	.7980	4.780	$-3.476 \times 10^7$
	10	.7970	4.774	$-3.449 \times 10^7$
0.1	0	.9128	2.742	$-9.443 \times 10^8$
	2	.9108	2.727	$-9.252 \times 10^8$
	4	.9088	2.713	$-9.066 \times 10^8$
	6	.9068	2.698	$-8.885 \times 10^8$
	8	.9048	2.684	$-8.710 \times 10^8$
	10	.9028	2.671	$-8.539 \times 10^8$
0.5	0	.9595	1.924	$-8.335 \times 10^9$
	2	.9550	1.880	$-7.803 \times 10^9$
	4	.9505	1.840	$-7.330 \times 10^9$
	6	.9460	1.803	$-6.907 \times 10^9$
	8	.9410	1.767	$-6.484 \times 10^9$
	10	.9353	1.729	$-6.049 \times 10^9$
1.0	0	.9723	1.665	$-2.064 \times 10^{10}$
	2	.9653	1.587	$-1.825 \times 10^{10}$
	4	.9588	1.528	$-1.649 \times 10^{10}$
	6	.9510	1.471	$-1.477 \times 10^{10}$
	8	.9410	1.409	$-1.297 \times 10^{10}$
	10	.9283	1.346	$-1.117 \times 10^{10}$

Table 5-9. The values of  $\ell^*$ ,  $v^*$  and  $\Delta F_\ell^*$  for LiCl at a range of molalities and various h.

m	h	$\ell^*$	$v^*$	$\Delta F_\ell^*$
0.0001	0	.5203	17.95	$-3.840 \times 10^4$
	2	.5203	17.95	$-3.840 \times 10^4$
	4	.5203	17.95	$-3.840 \times 10^4$
	6	.5203	17.95	$-3.840 \times 10^4$
	8	.5200	17.95	$-3.831 \times 10^4$
	10	.5200	17.95	$-3.831 \times 10^4$
0.001	0	.6580	9.017	$-1.185 \times 10^6$
	2	.6580	9.017	$-1.185 \times 10^6$
	4	.6575	9.014	$-1.180 \times 10^6$
	6	.6575	9.014	$-1.180 \times 10^6$
	8	.6573	9.013	$-1.178 \times 10^6$
	10	.6570	9.011	$-1.176 \times 10^6$
0.01	0	.7975	4.777	$-3.463 \times 10^7$
	2	.7970	4.774	$-3.449 \times 10^7$
	4	.7965	4.771	$-3.435 \times 10^7$
	6	.7958	4.767	$-3.415 \times 10^7$
	8	.7950	4.762	$-3.395 \times 10^7$
	10	.7945	4.759	$-3.382 \times 10^7$
0.1	0	.9048	2.683	$-8.709 \times 10^8$
	2	.9028	2.670	$-8.538 \times 10^8$
	4	.9008	2.656	$-8.372 \times 10^8$
	6	.8988	2.643	$-8.211 \times 10^8$
	8	.8963	2.627	$-8.016 \times 10^8$
	10	.8940	2.614	$-7.846 \times 10^8$
0.5	0	.9420	1.771	$-6.561 \times 10^9$
	2	.9365	1.734	$-6.135 \times 10^9$
	4	.9303	1.696	$-5.704 \times 10^9$
	6	.9228	1.655	$-5.248 \times 10^9$
	8	.9148	1.616	$-4.820 \times 10^9$
	10	.9043	1.571	$-4.333 \times 10^9$
1.0	0	.9455	1.427	$-1.363 \times 10^{10}$
	2	.9335	1.366	$-1.184 \times 10^{10}$
	4	.9185	1.301	$-1.003 \times 10^{10}$
	6	.8988	1.234	$-8.211 \times 10^9$
	8	.8710	1.162	$-6.355 \times 10^9$
	10	.8215	1.070	$-4.191 \times 10^9$

## 6. Discussion

It is interesting to observe that  $f_{\pm(\text{corr})}$  is larger than  $f_{\pm(\text{exp})}$  and increases with  $h$ . This is to be expected when the hydration correction is properly applied because the effective concentration is larger for  $f_{\pm(\text{exp})}$  than for  $f_{\pm(\text{corr})}$  leading to greater interactions which depress  $f_{\pm(\text{exp})}$ . The corresponding free energies decrease in absolute value with increasing  $h$  reflecting the greater stability (salting-in) for lower values of  $h$ . Note that we are referring to the configurational free energy alone and not to the total one, that is, to that part of the free energy that corresponds to activity coefficients rather than to activities.

The lattice theory yields free energies that undergo inflexions when the mean activity coefficients reach their minimum values and reflects, therefore, the salting-out process. The salting-out terms arise in the derivative of the configurational free energy in relation to  $m$  from the derivatives of  $v$  and of the configurational entropy.

$v$ , in addition to the effect of  $\bar{r}_x$ , reflects hard-core effects (Pitzer, 1973), ionic field-dielectric gradient interactions (Bahe, 1972) and ion-cavity interactions (Desnoyers and Conway, 1964). The relative contributions of these terms cannot be assessed at present because the above authors, after demonstrating the theoretical validity of the effects, treated them individually and obtained the relevant coefficients by curve-fitting. Furthermore, Pitzer used a Debye-Huckel type term for non-specific interactions and Bahe as well as Desnoyers and Conway introduced a fixed partial degree of order rather than a

variable one as in our case.

The degree of order increases and  $v^*$  decreases with  $m$  as is expected from the theory but we have no first-principle explanation for the increase in order in going from LiCl to KCl at a given  $m$ . It corresponds, however, to the salting-out trend observed, for example, by Bahe (1972).

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Appendix 1Alternative derivations of the equation for  $\ell$ a) Equilibrium model

Let us represent by  $C-\bar{a}$  a cation on the anion sub-lattice (the reciprocal lattice) and so on. At equilibrium



and

$$K = \frac{f_w^2 (C-\bar{a})(A-\bar{c})}{f_r^2 (C-\bar{c})(A-\bar{a})} \quad (\text{A1-2})$$

where  $f_w$  and  $f_r$  are the activity coefficients of ions in the reciprocal and in the right lattice and  $K$  is the equilibrium constant.

When an ion is added to the right lattice ( $C$  in  $\bar{c}$  or  $A$  in  $\bar{a}$ ) the energy increment is

$$\Delta E_r = -\frac{(ze)^2 A_M \ell^* v^*}{D_e r_o} \quad (\text{A1-3})$$

where asterisks are used because the system is assumed at equilibrium. For a wrong ion ( $C$  in  $\bar{a}$  or  $A$  in  $\bar{c}$ )

$$\Delta E_r = + \frac{(z\epsilon)^2 A_M \ell^{*v*}}{D_{e r o}} \quad (\text{A1-4})$$

For reaction (A1-1) then

$$\Delta E_{r \rightarrow w} = 2(\Delta E_w - \Delta E_r) = \frac{4(z\epsilon)^2 A_M \ell^{*v*}}{D_{e r o}} \quad (\text{A1-5})$$

where  $\Delta E_{r \rightarrow w}$  is the replacement energy.

Setting  $\Delta E = \Delta F$  as  $\Delta S = 0$  at equilibrium,

$$\Delta E^o = -k_B T \ln K = -k_B T \ln \frac{f_w^2}{f_r^2} \frac{w^{*2}}{(1-w)^2} \quad (\text{A1-6})$$

At the standard state there is no interaction energy as the standard state has the properties of an infinitely dilute solution and also  $f_w = f_r = 1$ . Thus

$$\frac{w_o^2}{(1-w_o)^2} = 1 \quad (\text{A1-7})$$

and  $w_o = 0.5$ , the definition of the random state.  $w_o$  represents the fraction of ions in their reciprocal lattices.

As  $K = 1$  at any concentration, from Eqn. (A1-2)

$$\frac{f_r}{f_w} = \frac{w^*}{1 - w^*} \quad (\text{A1-8})$$

In addition,

$$\Delta E_r = RT \ln f_r \text{ and } \Delta E_w = RT \ln f_w \quad (\text{A1-9})$$

and, therefore,

$$RT \ln \frac{f_r}{f_w} = \Delta E_r - \Delta E_w = - \frac{2(z\epsilon)^2 A_M \ell^* v^*}{D_e r_o} = RT \ln \frac{w^*}{1 - w^*} \quad (\text{A1-10})$$

As  $\ell^* = (1 - 2w^*)$ ,  $w^* = 0.5(1 - \ell^*)$  and

$$\ln \frac{w^*}{1 - w^*} = \ln \frac{1 - \ell^*}{1 + \ell^*} \quad (\text{A1-11})$$

Thus

$$\ln \frac{1 - \ell^*}{1 + \ell^*} = - \frac{2(z\epsilon)^2 A_M \ell^* v^*}{D_e r_o k_B T} = - \frac{2 N_A (z\epsilon)^2 A_M \ell^* v^*}{D_e r_o RT} m \quad (\text{A1-12})$$

which yields Eqn. (4-16) when  $r_o$  is replaced by its value shown in Eqn. (2-8).

b) Boltzman law model

Here we use the Boltzman law in the form

$$\text{probability} = \text{constant} \times e^{-E/kT} \quad (\text{A1-13})$$

$w^*$ , the fraction of wrong ions at equilibrium is also the probability of their occurrence. Thus,

$$\frac{w^*}{1 - w^*} = e^{(-\Delta E_w + \Delta E_r)/kT} \quad (\text{A1-14})$$

and

$$\ln \frac{w^*}{1 - w^*} = \ln \frac{1 - \ell^*}{1 + \ell^*} = -\frac{\Delta E_w - \Delta E_r}{kT} = -\frac{2(z\epsilon)^2 A_M \ell^* v^*}{D_e r_o k_B T} \quad (\text{A1-15})$$

which is identical to Eqn. (A1-12).

Thus, Eqn. (3-16) is a necessary condition for equilibrium as  $\ell$  and  $v$  must yield minimum values of  $\Delta F_\ell$ , that is, must be  $\ell_{\min}$  and  $v_{\min}$ . It is not sufficient because only when  $\Delta F_{\ell(\min)} = \Delta F_{(\text{exp})}$  equilibrium is achieved. Eqn. (A1-12), on the other hand, is necessary as well as sufficient for equilibrium.