

Theory of Concentrated Solutions of Strong Electrolytes

Part 2.—Thermodynamic Properties of Mixed Electrolytes. Theoretical Basis of the Harned Rule

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Received 12th September, 1977

The lattice-like model of electrolyte solutions has been used to interpret the thermodynamic properties of mixtures of strong electrolytes. Activity coefficients and the partial molar enthalpy content of several pairs of electrolytes have been calculated by assuming a cubic lattice of the common ion in which the two sorts of counter ions occupy body-centred positions. Comparison with experiment shows fairly good agreement. The theoretical treatment yields a correlation between Harned rule coefficients and the activity coefficients of the pure components at the total concentration of the mixture. According to this correlation the absolute value of the Harned rule coefficients, $\alpha_{1,2}$ and $\alpha_{2,1}$, must be the same, which is in agreement with measured values in case of acid mixtures, while the difference in their absolute value points to local hydrolysis in salt solutions.

In Part 1¹ a model has been suggested for concentrated solutions of strong electrolytes which has the following main features: (i) the ions are distributed in a lattice-like arrangement (body-centred cubic for z - z -type electrolytes and fluorite-like for z - $2z$ -type ones); (ii) ions are immersed in a structureless continuous dielectric, but this medium has a dielectric gradient in the vicinity of ions due to the polarizing effect of their electric field; (iii) coulombic interactions are calculated with respect to an average dielectric constant, lowered due to the above polarization effect and depending on the interionic separation distance and (iv) the dielectric gradient region around the ions acts as a repulsive force between them because work is required to remove the solvent from the dielectric gradient region when lowering the interionic separation distance.

The excess free energy calculated on the basis of these interactions is in rather good agreement with measured values of mean activity coefficients even in fairly high (2.5 mol kg⁻¹) concentrations. The relative partial molar enthalpy content of the solutes (excess enthalpy) has been also deduced with some further approximations. These data are in satisfactory agreement with experimental ones up to 0.5-3 mol kg⁻¹ concentrations. In general, the smaller the ions of the salt, the lower the concentration above which the theory fails to predict correct values.

In the present paper this model is applied to the case of aqueous electrolyte mixtures with the aim of interpreting the thermodynamic quantities of a solute component in the presence of others and as a function of the composition of the solution. Such an extension of the lattice model, if successful, would be an additional support to its reliability in revealing the structure of electrolyte solutions.

EQUATIONS

The excess free enthalpy, ΔG_e , of the solute in a binary electrolyte solution can be calculated as follows:¹

$$\Delta G_e = -A(c^{\frac{1}{2}} - Bc^{\frac{3}{2}} + Fc) \quad (1)$$

where c is the concentration in mol dm^{-3} and the meaning of A , B , and F is given in eqn (2)-(7):

$$A = \frac{2Nz^2e^2}{v\epsilon_0r^0}M \quad (2)$$

$$B = \frac{2}{3\pi\sqrt{3}z^2hf_a^5r^0}\left(\frac{\epsilon_0}{\hat{\epsilon}_d}-1\right) - \frac{1}{hf_ar^0}\ln\frac{\epsilon_0}{\hat{\epsilon}_d} \quad (3)$$

$$F = \frac{2}{3\pi\sqrt{3}z^2h^2f_a^6r^{02}}\ln\frac{\epsilon_0}{\hat{\epsilon}_b} \quad (4)$$

$$r^0 = \begin{cases} \frac{\sqrt{3}\left(\frac{1000}{N}\right)^{\frac{1}{3}}}{2}, & \text{for } z\text{-}z\text{-type electrolytes} \\ \frac{\sqrt{3}\left(\frac{500}{N}\right)^{\frac{1}{3}}}{2}, & \text{for } z\text{-}2z\text{-type electrolytes} \end{cases} \quad (5)$$

$$\hat{\epsilon}_d = \epsilon_0(1 - g e^{-hf_ar^0}) \quad (6)$$

$$f_a^2 = \frac{\frac{2}{9}\left[1 - \frac{\pi(a_a^3 + a_c^3)}{r^{03}}c\right]}{\left[\frac{\pi}{2}\ln\frac{2+\sqrt{2}}{2-\sqrt{2}} + \frac{3\sqrt{2}}{16}\left(1 - \frac{\sqrt{2}}{2}\right) - \frac{\pi\sqrt{2}(a_a + a_c)}{2r^0}c^{\frac{1}{3}}\right]z} \quad (7)$$

where the denotations are: N = Avagadro number, v = the number of ions in the formula of the solute, M = Madelung constant (1.762 67 and 5.038 78 for z - z and z - $2z$ -type electrolytes, respectively), z = the highest common factor of the charge of the cation and anion (in atomic units), e = electron charge, ϵ_0 = static dielectric constant of the solvent, $\hat{\epsilon}_d$ = volume average relative permittivity of the solvent, r^0 = the shortest cation-to-anion distance in the lattice-like arrangement of a 1 mol dm^{-3} solution, $g = 6.52$ and $h = 0.939$ (for water at 25°C), numerical values used in the approximation of the average relative permittivity of the solvent, f_a = function including the effect of the only individual parameters of the solute, the ionic radii, considered in this theory, a_a = radius of the anion and a_c = radius of the cation.

The first term in eqn (1) is the lattice energy of the ions in a medium with a dielectric constant ϵ_0 . This term comprises the limiting law of the lattice model. If the volume average of the relative permittivity is appreciably different from ϵ_0 , the terms containing coefficients B and F contribute to the lattice energy by additional attraction terms (F and the second term in B) and by a repulsion term (first term in B). The physical background of these terms is, partly, that the Coulomb law takes a modified form if the dielectric constant depends on the separation distance, partly, that the charge-dielectric medium interaction acts mainly in favour of larger separation distances, since the dipoles of the solvent are attracted by the common field of the ions, and a fraction of the solvent must be disposed of when shortening the separation distance.

From the point of view of their application to electrolyte mixtures, the important feature of the calculations leading to the results above is that charge-charge as well as charge-dielectric medium interactions are to be considered in a single elementary cell of the lattice which contains only one central ion and eight times one eighth of the counter ions at the vertices of the cube, and the total lattice energy, including the interactions with farther neighbours, can be obtained by a simple multiplication

by the Madelung constant. This advantageous simplicity of the treatment gives the clue to the handling of electrolyte mixtures, since they can be modelled by two or more different types of elementary cubes mixed together at random.

TRACE ACTIVITY COEFFICIENTS

First consider the simplest case of the mixtures of z - z -type electrolyte solutions, when the amount of one component is present in an overwhelming excess to the other. Thus any thermodynamic parameter of the component in excess remains practically unaltered, while that of the "trace" component may change significantly. Many precise experimental data have been measured for such systems² that can serve for comparison. They are mainly mean activity coefficients of the trace component, nevertheless there are also some excess enthalpy data available.

To avoid complicated phrases in describing the model of such a mixture, consider one of the classical cases as an example, that of a "trace" amount of HCl in NaCl solution of concentration c_2 ; and assume that the structure of this solution is a body-centred arrangement of Na^+ and Cl^- ions in which a few Na^+ ions are replaced by H^+ . Thus, in a sea of adjacent NaCl-like elementary cubes, there are some HCl-like ones very far apart from one another. Let us further assume that the HCl-type elementary cubes are exactly the same as those in pure HCl solution at the concentration c_2 . In this way, when calculating the mean activity coefficient of HCl in NaCl solution, one has to know the excess free enthalpy fraction of HCl corresponding to interactions between a hydrogen ion and its first chloride neighbours, interactions within a single HCl-like elementary cell, and the other fraction of ΔG_e which originates from interactions between the ions of this HCl-like cell with its environment of NaCl-like cells from adjacent ones to those infinitely far apart. (Each cell contains one "molecule" of HCl or NaCl, since the central ion plus one eighth of eight counter ions belong to it.)

Utilizing the fact that the excess partial molar free enthalpy is a measure of the mean ionic activity coefficient:

$$\Delta G_e = \nu RT \ln \gamma^\circ \quad (8)$$

we can rewrite eqn (1) in the following form:

$$\ln \gamma_1^\circ = Mf(a_a, a_c, c) \quad (9)$$

where γ_1° is the mean ionic activity coefficient of component 1 in its pure solution at concentration c_2 , M is the Madelung constant, and function f contains all the rest of the right hand side of eqn (1) divided by νRT due to eqn (8). As mentioned above, $f\nu RT$ is a measure of the excess partial molar energy of the solute in a single elementary cell of the lattice, and the multiplication by M converts this into the total lattice energy. (One could say that out of the factor of 1.762 67, which is the value of M for a body-centred cubic lattice, the factor 1 accounts for a single elementary cell, and the factor 0.762 67 for all the interactions of this given cell with the second, third, etc. neighbours).³

Thus, if component 1 is the trace component, $(\ln \gamma_1^\circ)/M$ will measure the interactions within the single elementary cube. The effect of the sea of component 2 type cells forming its environment will be proportional to the total lattice energy of component 2 minus the single cell fraction of component 2: $(\ln \gamma_2^\circ)(1 - 1/M)$. Thence, the trace activity coefficient of component 1, γ_1 , can be expressed as follows:

$$\ln \gamma_1 = \frac{1}{M} \ln \gamma_1^\circ + \left(1 - \frac{1}{M}\right) \ln \gamma_2^\circ \quad (\text{for } z\text{-}z\text{-types}) \quad (10)$$

or, after substituting the numerical value of M :

$$\gamma_1 = \gamma_1^{0.56732} \cdot \gamma_2^{0.43268} \quad (\text{for } z\text{-}z\text{-types}). \quad (11)$$

In table 1 the comparison of measured γ_2 and calculated γ_1 values shows excellent agreement in the case of Li, Na and K salts up to very high concentrations. In addition to the assumption already mentioned, *viz.* that the elementary hydrogen halide cell is entirely the same in a salt solution as it were in pure hydrogen halide in concentration c_2 , we have neglected the error caused by the slightly different density of the pure acid and salt solutions at the same *molality*, and made comparisons not at the same c_2 , but at identical m_2 . This error is largest with Cs halides, but negligible for the other salts in question.

TABLE 1.—TRACE ACTIVITY COEFFICIENTS OF HYDROGEN HALIDES IN ALKALI HALIDE SOLUTIONS

m_2	γ_1^1	γ_2^2	$\gamma_{1,calc.}$	$\gamma_{1,obs.}$	γ_2^2	$\gamma_{1,calc.}$	$\gamma_{1,obs.}$	γ_2^2	$\gamma_{1,calc.}$	$\gamma_{1,obs.}$	γ_2^2	$\gamma_{1,calc.}$	$\gamma_{1,obs.}$
HCl			in LiCl			in NaCl			in KCl			in CsCl	
0.1	0.796	0.790	0.793	0.796	0.778	0.778	0.784	0.770	0.785	0.782	0.756	0.778	0.773
0.2	0.767	0.757	0.763	0.766	0.755	0.753	0.752	0.718	0.745	0.747	0.694	0.735	0.730
0.3	0.756	0.744	0.751	—	0.710	0.736	—	0.688	0.726	—	0.656	0.711	—
0.5	0.757	0.739	0.749	0.757	0.681	0.723	0.730	0.649	0.708	0.706	0.606	0.688	0.669
1.0	0.809	0.774	0.794	0.801	0.657	0.739	0.754	0.604	0.713	0.720	0.544	0.681	0.644
2.0	1.009	0.921	0.960	0.986	0.668	0.844	0.878	0.573	0.790	0.781	0.496	0.742	0.641
3.0	1.316	1.156	1.244	1.284	0.714	1.010	1.068	0.569	0.917	0.860	0.479	0.850	0.672
4.0	1.762	1.510	1.648	1.708	0.783	1.241	—	0.577	1.087	—	0.474	0.998	—
HBr			in LiBr			in NaBr			in KBr				
0.1	0.805	0.796	0.801	0.802	0.782	0.795	0.791	0.772	0.791	0.783			
0.2	0.782	0.766	0.775	0.783	0.741	0.764	0.767	0.722	0.755	0.750			
0.5	0.789	0.753	0.773	0.792	0.697	0.748	0.756	0.657	0.729	0.717			
1.0	0.871	0.803	0.841	0.878	0.687	0.786	0.801	0.617	0.750	0.728			
2.0	1.168	1.015	1.099	1.160	0.731	0.954	0.981	0.593	0.871	0.810			
3.0	1.674	1.341	1.521	1.641	0.812	1.224	1.233	0.595	1.070	0.926			

On the other hand, it must be emphasized that the strength of the corresponding alkali metal hydroxides increases from the undoubtedly weak base LiOH to the strong electrolyte CsOH,⁴ while, though to a less pronounced degree, the acid strength of hydrogen halides increases from HCl to HI. Thus, local hydrolysis of the weaker base–stronger acid salts⁵ results in an increase in the proton activity of water molecules in the vicinity of the small cations, making the solution more acidic, *i.e.*, seemingly it behaves as if there were more acid present. This apparent increase of acidity is, however, not a real hydrolysis since, the number of water molecules in the vicinity of the cations being proportional to the concentration, the degree of “hydrolysis” is constant. However, we can handle this local hydrolysis as if the γ_2^2 values corresponded to slightly acidic salts instead of neutral ones. The addition of a trace amount of acid would just slightly increase the original acidity of the salt of a small cation, and eqn (11) would still yield correct values, since γ_2^2 includes the effect of local hydrolysis too. However, if CsCl shows a basic local hydrolysis, as it probably does,⁶ the added amount of acid is partly neutralised by the excess basicity in the hydrolysed salt, and the measured trace activity coefficients will be consequently lower than expected.

If the measured activity coefficients of salts are wrong in the sense that they include the effect of their local hydrolysis, the deviations of the theoretical mean ionic activity coefficients from measured values [*cf.* fig. (12)–(13) in ref. (1)], which were greatest for LiI and MgI₂ but practically nil for Rb and Cs halides, become easily interpretable. The curves shown in fig. 1 also support this explanation. Although the measured trace activity coefficients of alkali metal hydroxides in their chloride salts come from

less precise measurements,² they are in better agreement with calculated ones, if theoretical γ_2° values, obtained by eqn (3) and (18) of ref. (1), rather than experimental ones are inserted in eqn (11).

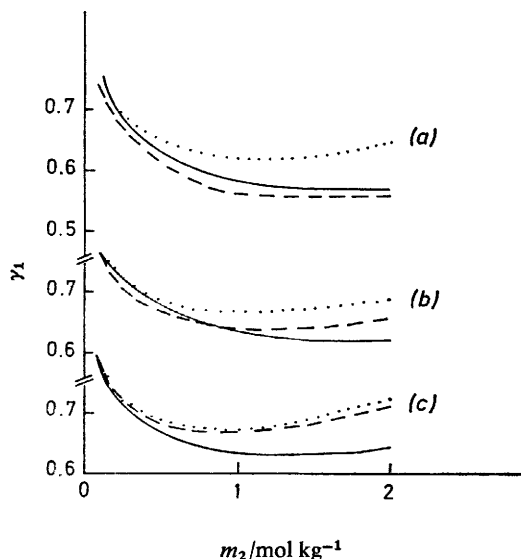


FIG. 1.—Trace activity coefficient of alkali metal hydroxides as a function of the concentration of their chloride salt added: — measured, ... calculated using measured activity coefficients for the salts, --- calculated using theoretical activity coefficients obtained by the lattice theory [see ref. (1)]. (a) LiOH in LiCl, (b) NaOH in NaCl, (c) KOH in KCl.

For the trace activity coefficient of a z - z -type electrolyte in excess z - $2z$ -type electrolyte, we can deduce an equation similar to eqn (11). First one must take into account that the Madelung constant of a fluorite-type lattice includes a factor of 2, because in eqn (2) not the ionic charges themselves but their highest common factor is expressed explicitly. Another factor of 2 included in M arises from the fact that in such a lattice the middle of every other cube of the z -charged ions is occupied by a $2z$ -charged ion, *i.e.*, one molecule of solute is represented by two cubes, one with the $2z$ ion in the middle and one empty. In this way, distinguishing the Madelung constant of the body-centred cubic and that of the fluorite-type lattice by subscripts 1 and 2, respectively, we have analogously to eqn (10):

$$\ln \gamma_1 = \frac{1}{M_1} \ln \gamma_1^\circ + \left(1 - \frac{4}{M_2}\right) \ln \gamma_2^\circ \quad (\text{for } z\text{-}z + z\text{-}2z\text{-types}) \quad (12)$$

or

$$\gamma_1 = \gamma_1^{\circ 0.56732} \cdot \gamma_2^{\circ 0.20616} \quad (\text{for } z\text{-}z + z\text{-}2z\text{-types}) \quad (13)$$

where γ_1° must be now taken at $2c_2$ concentration of the pure z - z -type component, because the z -charged common ion of the two electrolytes, which determines the edge of an elementary cube, is present in $2c_2$ concentration.

A few characteristic data calculated by eqn (13) for hydrogen chloride in alkali earth metal chlorides are collected in table 2. The agreement between calculated and measured data² is again quite satisfactory, the more so since $m_2 = 1 \text{ mol kg}^{-1}$ represents an ionic strength as high as 3.

It has been observed⁷ that the trace activity coefficient of one component in an excess of the other is in many cases identical to the trace activity coefficient of the second component in the solution of the first one provided that the total concentration is not too high. By subtracting from eqn (10) an equation similar to it but with subscripts exchanged, we can deduce :

$$\Delta \ln \gamma = (2/M - 1) \Delta \ln \gamma^\circ \quad (\text{for } z\text{-}z\text{-types}). \quad (14)$$

The numerical value of the term in parentheses is as small as 0.1346. Thus, although this model predicts an inequality for the trace activity coefficients of the two components, the difference is negligible if there is not too great a difference in the activity coefficients of the pure components, which usually holds for not too high a concentration.

TABLE 2.—TRACE ACTIVITY COEFFICIENTS OF HYDROGEN CHLORIDE IN ALKALI EARTH CHLORIDE SOLUTIONS

m_2	γ_1^*	in SrCl_2			in BaCl_2		
		γ_2°	$\gamma_{1,\text{calc.}}$	$\gamma_{1,\text{obs.}}$	γ_2°	$\gamma_{1,\text{calc.}}$	$\gamma_{1,\text{obs.}}$
0.1	0.767	0.515	0.750	0.731	0.508	0.748	0.732
0.2	0.755	0.466	0.728	0.706	0.450	0.723	0.701
0.3	0.763	0.446	0.726	0.711	0.425	0.719	0.698
0.5	0.809	0.433	0.746	0.739	0.403	0.735	0.721
1.0	1.009	0.465	0.858	0.888	0.401	0.833	0.823

* Taken at $2m_2$ (for reason, see text).

Mainly on the grounds of the Debye-Hückel theory it has been deduced⁷ that $2 \log \gamma_1 = \log \gamma_2$, if component 1 is a z - z -type electrolyte and component 2 is a z - $2z$ -type one with a z -charged common ion. In table 3, the difference $\Delta \log \gamma$ for such types of mixtures is compared with the values calculated by the above rule and with the results of the lattice model. In addition to the fact that the trace activity coefficients themselves are in good agreement with those obtained by the lattice model, the observed $\Delta \log \gamma$ values are also closer to the predictions of this theory than to those of the Debye-Hückel approach.

TABLE 3.—TRACE ACTIVITY COEFFICIENTS OF NaCl +ALKALI EARTH METAL HALIDE SOLUTIONS AT $I = 3$

MCl_2	γ_{NaCl}		γ_{MCl_2}		$\Delta \log \gamma$		
	obs.	calc.	obs.	calc.	obs.	calc.	calc.*
MgCl_2	0.767	0.708	0.635	0.624	0.0819	0.0548	0.1152
CaCl_2	0.724	0.689	0.564	0.547	0.1156	0.1002	0.1403
SrCl_2	0.703	0.679	0.525	0.537	0.1275	0.1019	0.1530
BaCl_2	0.650	0.657	0.449	0.442	0.1608	0.1721	0.1871

* Calculated by the rule $2 \log \gamma_1 = \log \gamma_2$, see ref. (7).

In analogy with the above treatment of trace activity coefficients, we can easily obtain the equations for the relative partial molar heat content of a trace component in electrolyte mixtures by considering the fact that, instead of the $\ln \gamma$ terms which are a measure of partial molar excess free enthalpy, we should write the corresponding relative partial molar heat contents, $L_{2,1}$, $L_{2,1}^\circ$, etc. :

$$L_{2,1} = \begin{cases} L_{2,1}^\circ/M_1 + L_{2,2}^\circ(1 - 1/M_1) & (\text{for } z\text{-}z\text{-types}) \\ L_{2,1}^\circ/M_1 + L_{2,2}^\circ(1 - 4/M_2) & (\text{for } z\text{-}z + z\text{-}2z\text{-types}). \end{cases} \quad (15)$$

The measured partial molar heat contents of HCl as the trace component in LiCl and KCl solutions at 25°C² are plotted in fig. 2 as a function of the concentration of the salts together with the $L_{2,1}^0$ and $L_{2,2}^0$ values of the components. Eqn (15) seems to yield correct values for both of the rather different cases, one including a salt with positive, the other a salt with negative, $L_{2,2}^0$ values at higher concentrations.

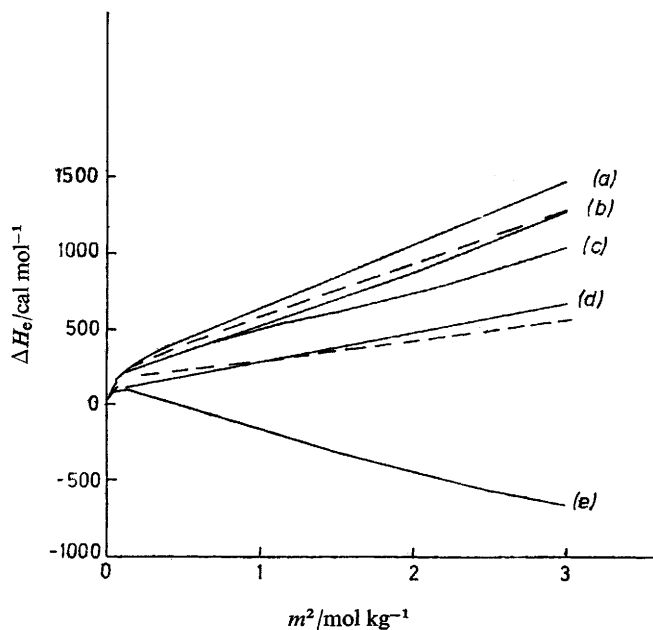


FIG. 2.—Relative partial molar heat content of hydrochloric acid in alkali metal chloride solutions. --- measured, — calculated. (a) HCl, (b) HCl in LiCl, (c) LiCl, (d) HCl in KCl, (e) KCl.

ACTIVITY COEFFICIENTS OF COMPONENTS IN MIXTURES AT CONSTANT IONIC STRENGTH

THEORETICAL BASIS OF THE HARNED RULE

Taking one step further towards more complicated mixtures of electrolytes, consider those at constant ionic strength. On the grounds of many experimental data and some semi-empirical thermodynamic calculations assisted by the Debye-Hückel theory, it has been established² that the partial molar excess free enthalpy, or the logarithm of the mean ionic activity coefficient, of a component varies linearly with the ionic strength contribution of the other components:

$$\log \gamma_1 = \log \gamma_1^0 - \alpha_{1,2} I_2 \quad (16)$$

and

$$\log \gamma_2 = \log \gamma_2^0 - \alpha_{2,1} I_1 \quad (17)$$

where I_1 and I_2 are the fractions of the ionic strength corresponding to components 1 and 2, respectively, and $\alpha_{1,2}$ and $\alpha_{2,1}$ are the so-called Harned rule coefficients having a constant value for a given total ionic strength L .

It is quite simple to generalize the application of the lattice model for trace components discussed above to higher and variable non-trace concentrations of the component in question. Take again the example of HCl+NaCl mixtures. The

activity coefficient of hydrochloric acid would depend again on the interactions within the HCl-like elementary cube and on the interactions of this cube with all the others building up the solution lattice. Whereas for trace amounts of HCl the complete environment of a HCl cell is NaCl-like, this environment is a mixture of HCl-like and NaCl-like cells when HCl is present in a concentration commensurable with that of NaCl. The arrangement of the two types of elementary cells can be supposed to be random. Thus the magnitude of the interactions of a given cell with its environment can be taken as a concentration-weighted average of the effect of HCl-like and NaCl-like cells. In this way, only the second term in eqn (10) is to be altered with respect to such weights, and we have :

$$\ln \gamma_1 = \frac{1}{M} \ln \gamma_1^\circ + \left(1 - \frac{1}{M}\right) \left(\frac{c_1}{c_t} \ln \gamma_1^\circ + \frac{c_2}{c_t} \ln \gamma_2^\circ\right) \quad (\text{for } z\text{-}z\text{-types}) \quad (18)$$

where $c_t = c_1 + c_2$ is the total concentration of the two components (and equal to the constant ionic strength in the case of uni-univalent electrolytes). After simple transformations, we get :

$$\ln \gamma_1 = \ln \gamma_1^\circ - \frac{\ln \gamma_1^\circ - \ln \gamma_2^\circ}{c_t} \left(1 - \frac{1}{M}\right) c_2 \quad (\text{for } z\text{-}z\text{-types}). \quad (19)$$

Comparing this equation with eqn (16), the Harned rule coefficient can be given as follows :

$$\alpha_{1,2} = \frac{\log \gamma_1^\circ - \log \gamma_2^\circ}{c_t} \left(1 - \frac{1}{M}\right) \quad (\text{for } z\text{-}z\text{-types}). \quad (20)$$

Performing the same calculation for component 2, one can show that the result is the same as in eqn (19) with the subscripts exchanged. Thus :

$$\alpha_{1,2} = -\alpha_{2,1}. \quad (21)$$

From eqn (20) it can be concluded that the Harned rule coefficients are indeed constant at constant ionic strength for $z\text{-}z\text{-type}$ electrolytes.

TABLE 4.—HARNED RULE COEFFICIENTS IN HYDROCHLORIC AND HYDROBROMIC ACID MIXTURES

$t/^\circ\text{C}$	m_t	γ_1°	γ_2°	$\alpha_{1,2}$	$-\alpha_{2,1}$	$ \alpha_{\text{obs.}} $
0	0.5	0.806	0.7761	0.018	0.008	0.014
15	0.5	0.797	0.7658	0.017	0.013	0.015
25	0.5	0.790	0.7571	0.016	0.017	0.016
35	0.5	0.781	0.7477	0.016	0.017	0.016
45	0.5	0.772	0.7387	0.015	0.018	0.017
25	1.0	0.871	0.8090	0.016	0.013	0.014

$$\text{error} = \pm 0.002 \quad \pm 0.006$$

In table 4 the measured Harned rule coefficients ⁸ appear to support every aspect of the above results, *viz.* the numerical values calculated by eqn (20) are within experimental errors identical with those observed, and eqn (21) holds also for most temperatures.

Agreement between calculated and observed data is less unanimous in the cases listed in table 5. Although the absolute values of the calculated Harned rule coefficients are in good agreement with the average of measured $\alpha_{1,2}$ and $-\alpha_{2,1}$ values, eqn (21) is not valid. One source of the disagreement may be the approximation utilized in the calculations that the elementary cube of, say, HCl remains unaltered

when putting it into a non-HCl-like environment. In reality it may contract or expand depending on the difference between the attractive/repulsive forces of an HCl lattice and those of the salt lattice it is immersed in. However, if so, the largest deviation should occur for caesium salts and the smallest for lithium salts, since the corresponding activity coefficients (and thus the forces within an elementary cube)¹ of HCl are closer to those of LiCl. The other, and apparently more likely, explanation may be the effect of local hydrolysis.

TABLE 5.—HARNED RULE COEFFICIENTS OF MIXTURES OF HYDROCHLORIC ACID AND ALKALI HALIDES AT 25°C

m_t	$\alpha_{1,2}$	$-\alpha_{2,1}$	$ \alpha_{\text{calc.}} $	$\frac{\alpha_{1,2}-\alpha_{2,1}}{2}$	$\alpha_{1,2}$	$-\alpha_{2,1}$	$ \alpha_{\text{calc.}} $	$\frac{\alpha_{1,2}-\alpha_{2,1}}{2}$	$\alpha_{1,2}$	$-\alpha_{2,1}$	$ \alpha_{\text{calc.}} $	$\frac{\alpha_{1,2}-\alpha_{2,1}}{2}$
	LiCl				KCl				CsCl			
0.1	0.0013	—	0.014	—	0.077	—	0.063	—	0.143	—	0.097	—
0.5	0.006	0.011	0.009	0.009	0.062	0.074	0.059	0.068	0.105	0.070	0.085	0.088
1.0	0.005	0.012	0.008	0.009	0.056	0.072	0.056	0.064	0.100	0.060	0.077	0.080
1.5	0.005	0.011	0.008	0.008	0.055	0.069	0.057	0.062	0.099	0.053	0.075	0.076
2.0	0.005	0.012	0.009	0.009	0.057	0.067	0.057	0.061	0.099	0.046	0.073	0.072
3.0	0.004	0.013	0.009	0.008	0.062	0.054	0.057	0.058	0.098	0.041	0.073	0.070
4.0	0.003	—	0.007	—	0.066	0.050	0.058	0.058	—	—	0.072	—

In this latter case, slightly acidic solution is expected for pure LiCl, very close to neutral for KCl, and slightly basic for CsCl. We are inclined to believe that the activity coefficient of HCl in LiCl is less sensitive to the change in LiCl concentration, because this salt is more acidic in itself due to local hydrolysis. On the other hand, the activity coefficient of HCl shows a more pronounced change as a result of CsCl addition, because CsCl is slightly basic. Qualitatively, this conclusion is in agreement with what has been written in connection with the data in table 1; this may also be the reason why the Harned rule coefficients are not even constant for mixtures of alkali metal hydroxides and the corresponding halides.²

TABLE 6.—ACTIVITY COEFFICIENTS OF HCl IN HCl+SrCl₂ MIXTURES AT VARIOUS CONSTANT IONIC STRENGTHS

m_1	m_t	$\gamma_{1,\text{calc.}}$	$\gamma_{1,\text{obs.}}$	m_1	m_t	$\gamma_{1,\text{calc.}}$	$\gamma_{1,\text{obs.}}$	m_1	m_t	$\gamma_{1,\text{calc.}}$	$\gamma_{1,\text{obs.}}$
$I = 1$				$I = 3$				$I = 5$			
1.0	1.0	(0.809)	0.8111	3.0	3.0	(1.316)	1.318	(lack of data on strontium chloride activity coefficients above 4 mol dm ⁻³)			
0.9	0.967	0.800	0.7985	2.7	2.9	1.273	1.267				
0.8	0.933	0.793	0.7903	2.4	2.8	1.232	1.216				
0.7	0.900	0.784	0.7794	2.1	2.7	1.191	—				
0.6	0.867	0.781	0.7708	1.8	2.6	1.149	1.123				
0.5	0.833	0.768	0.7596	1.5	2.5	1.106	1.079				
0.4	0.800	0.759	0.7495	1.2	2.4	1.071	1.038				
0.3	0.767	0.751	0.7401	0.9	2.3	1.035	0.9955	2.0	4.0	1.674	1.592
0.2	0.733	0.743	0.7281	0.6	2.2	0.999	0.9557	1.5	3.833	1.582	1.489
0.1	0.700	0.734	0.7197	0.3	2.1	0.964	0.9175	1.0	3.667	1.489	1.391

The equation analogous to eqn (18) but valid for mixtures of z - z -type electrolytes with z - $2z$ -type electrolytes can be deduced similarly, taking into account the alterations mentioned in the deduction of eqn (12):

$$\ln \gamma_1 = \frac{1}{M_1} \ln \gamma_1^\circ + \left(1 - \frac{1}{M_1}\right) \frac{c_1}{c_t} \ln \gamma_1^\circ + \left(1 - \frac{4}{M_2}\right) \frac{2c_2}{c_t} \ln \gamma_2^\circ$$

(for z - z + z - $2z$ -types) (22)

where c_t is now the sum $c_1 + 2c_2$ and component 1 is the z - z -type one. Harned rule coefficients for such cases can be also deduced, but the expression for the α values will be constant only if constant *equivalence* is maintained in the measurements and *not* constant ionic *strength*. The inconstancy of Harned rule coefficients for z - z + z - $2z$ -mixtures has long been known,² but unfortunately no measurements are available in the literature that have been performed at constant equivalence.

The applicability of eqn (22) is tested in table 6, again with the rather rough approximation that molarities are taken equal to molalities. It is interesting to note that at $I = 5$ both HCl and SrCl_2 activity coefficients are higher than their "resultant" γ_1 value, and eqn (22) still yields satisfactory agreement.

EFFECT OF LOCAL HYDROLYSIS ON RELATIVE PARTIAL MOLAR HEAT CONTENT DATA

In both of the previous sections local hydrolysis was suspected to be a source of the discrepancies between theoretical and experimental thermodynamic quantities. With a theoretical "mixing rule" at hand, we can attempt to treat a likely hydrolysing salt in a rough approximation as if it were a mixture of the salt and the corresponding acid, and use the difference between theoretical and experimental data to calculate the degree of hydrolysis at several concentrations. Then, knowing the "composition" of the hydrolysed solution, another thermodynamic quantity can be calculated and compared with independently measured ones. Since theoretical values may be erroneous for other reasons, for a test of such a treatment it is

TABLE 7.—TEST OF ASSUMPTION OF LOCAL METAL ION HYDROLYSIS IN THE CALCULATION OF RELATIVE PARTIAL MOLAR HEAT CONTENT OF LiCl SOLUTIONS

m_1^a	γ_1^b	γ_2^c	γ'^d	m_2^a	L_2^a, b	L_2^c	$L_2^{\text{calc.}}$	$L_2^{\text{obs.}}$
0.1	0.758	0.776	0.772	0.078	77	202	175	173
0.2	0.709	0.748	0.742	0.170	48	273	239	234
0.3	0.680	0.737	0.729	0.259	0	332	286	279
0.5	0.644	0.738	0.723	0.425	-128	430	346	352
1.0	0.615	0.789	0.761	0.855	-574	645	468	491
2.0	0.667	0.984	0.908	1.587	-1973	1055	430	744

^a Calculated with no correction for the difference in density of LiCl and HCl solutions.

^b Calculated values using equations deduced in ref. (1). ^c Measured values for HCl solutions at 25°C. Activity coefficients have been corrected due to the difference in the extrapolation to the infinitely dilute state by the square-root and the cube-root law [see ref. (1)]. ^d Measured values for LiCl solutions. Activity coefficients were corrected in the same way as those of HCl. All L_2 values are given in cal mol⁻¹ units.

reasonable to choose an example for which the disagreement is the largest. In fig. 12 of ref. (1), the lithium halides represent such cases with respect to their activity coefficients, and the relative partial molar heat content of lithium salts was one of the cases when the lattice theory failed even in predicting the correct sign of the excess enthalpy.

Assume that the measured activity coefficient of pure LiCl solutions is indeed an average activity coefficient of HCl and LiCl in the "hydrolysed" solution. On the basis of a Gibbs-Duhem equation applied for the excess (non-partial-molar) free energy we can write:

$$m_1 \ln \gamma' = m_1 \ln \gamma_1 + m_2 \ln \gamma_2 \quad (23)$$

where γ' is the activity coefficient calculated from, say, vapour pressure data for the overall activity coefficient of the electrolyte solution, while γ_1 and γ_2 are the true

activity coefficients corresponding to the fraction of salt that remained unchanged and to the acid formed in the hydrolysis of the salt, respectively. Using eqn (16) and (17) and the theoretical result in eqn (21), we have :

$$m_2 = m_t \frac{\ln \gamma' - \ln \gamma_1^\circ}{\ln \gamma_2^\circ - \ln \gamma_1^\circ} \quad (24)$$

Assuming that, for LiCl, γ_1° can be correctly calculated by eqn (3) and (18) in ref. (1), and taking γ' and γ_2° from experimental data on LiCl and HCl, respectively, m_2 can be obtained.

If, on the other hand, our assumption on hydrolysis is correct, the partial molar heat content of the solute, L'_2 , measured for LiCl solutions is a resultant of that of HCl in a concentration m_2 , and that of LiCl in m_1 . Thus :

$$L'_2 = m_1 L_{2,1}^\circ + m_2 L_{2,2}^\circ \quad (25)$$

where $L_{2,1}^\circ$ is the partial molar heat content of LiCl in its pure solution [calculated from eqn (25) in ref. (1)] and $L_{2,2}^\circ$ is that measurable for pure HCl.

The comparison of L'_2 data shown in table 7 indicates a satisfactory self-consistency of the lattice theory up to 1 mol dm⁻³ solutions, and the apparent degree of hydrolysis (the ratio m_2/m_1) is constant, as can be expected. In this way, table 7 supports our previous assumption that a considerable part of the discrepancies between experiments and the results of the lattice theory can be accounted for by the local hydrolysis of salts in aqueous solution. Thus we conclude that the lattice theory can predict correctly the thermodynamic parameters of *strong* electrolytes and their mixtures up to rather high concentrations, and its eventual errors are, to a great extent, due to the non-strong behaviour of some electrolytes.

¹ I. Ruff, *J.C.S. Faraday II*, 1977, **73**, 1858.

² H. S. Harned and B. B. Owen, *The Physical Chemistry of Electrolyte Solutions* (Reinhold, Princeton, 3rd edn, 1958), chap. 14 and Appendices.

³ See e.g. C. Kittel, *Introduction to Solid State Physics* (John Wiley and Sons, New York, 1966), Appendix.

⁴ C. F. Baes, Jr. and R. E. Mesmer, *The Hydrolysis of Cations* (John Wiley and Sons, New York, 1976), chap. 4.

⁵ R. M. Diamond, *J. Amer. Chem. Soc.*, 1958, **80**, 4808.

⁶ H. Kelm and K. Schwabe, *Z. phys. Chem. (Leipzig)*, 1974, **255**, 475 (fig. 10).

⁷ H. S. Harned and R. A. Robinson, *Multicomponent Electrolyte Solutions* (Pergamon, Oxford, 1968).

⁸ B. B. Owen and T. F. Cooke, Jr., *J. Amer. Chem. Soc.*, 1937, **59**, 2277.