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CELL THEORY OF STRONG ELECTROLYTE SOLUTIONS

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CELL THEORY OF STRONG ELECTROLYTE SOLUTIONS

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GLOSSARY OF SYMBOLS

A,	Helmholtz free energy; Madelung constant
a,	(underlined in text) ion size parameter in centimeters (also referred to as "distance of closest approach")
C,	concentration on molar scale
D,	dielectric constant
E,	electromotive force of cell
E^0 ,	standard electromotive force of cell
E' ,	electromotive force of concentration cell with transference
E_R^0 ,	standard electromotive force of concentration cell with transference with reference solution of specified concentration
e,	electronic charge = 4.80223×10^{-10} esu; base of natural logarithms = 2.71828
exp(x),	exponential function = e^x
F,	Faraday = 96493.1 absolute coulomb/equivalent
I(x),	function defined by equation (3-11)
$\bar{J}_2$,	relative partial molar heat capacity
k,	Boltzmann constant = 1.38026×10^{-16} erg/degree-molecule; the quantity $2.3026 RT/F$
$\bar{L}_2$,	relative partial molar enthalpy
ln, log,	logarithms to bases e and 10, respectively
M,	abbreviation for "molar"
m,	abbreviation for "molal"

N,	Avogadro's number = 6.02380×10^{23}
n,	magnitude of valence of the more highly charged ion in an unsymmetrical electrolyte; concentration (molecules/cubic centimeter)
q,	ionic or molecular partition function (described more completely in text by subscripts); mobility function in conductivity equation
R,	gas constant = 1.98719 calorie/degree-mole; radius of cell in cell theory = $7.346 \times 10^{-8} \text{ cm}$
r,	variable representing distance in centimeters
T,	absolute temperature
t° ,	ionic transference number at infinite dilution
V,	volume in cubic centimeters
X,	the quantity $Ze^2/2DkT$
y ,	mean ionic activity coefficient on molar scale
Z,	valence coefficient of electrostatic energy terms
α ,	expansibility or coefficient of thermal expansion = $(\partial \ln V / \partial T)_P$
$\gamma_{\pm}$,	mean ionic activity coefficient on molal scale
ΔH_D ,	integral heat of dilution (heat absorbed per mole of electrolyte upon diluting an electrolyte solution from a specified concentration to infinite dilution)
η ,	viscosity
κ ,	"reciprocal radius of ionic atmosphere" in centimeters
Λ ,	equivalent conductivity of electrolyte
Λ° ,	equivalent conductivity at infinite dilution
ν ,	number of moles of ions formed from one mole of electrolyte
ϕ_J ,	relative apparent molar heat capacity

ϕ_L , relative apparent molar enthalpy = $-\Delta H_D$
 χ , the quantity $4\pi NC/3000 = 1/R^3$

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CELL THEORY OF STRONG ELECTROLYTE SOLUTIONS

CHAPTER I

INTRODUCTION

Some forty years ago, the Debye-Hückel["] formulation of interionic attraction theory was brought forth (1). Although that attempt to explain the properties of electrolyte solutions on the basis of ionic interactions was not the first, it has been the most useful and most durable.

A few years prior to the advent of the theory of Debye and Hückel["], Milner had arrived at essentially the same result (2,3). Milner's approach, although straightforward in principle, entailed much tedious computation. Its prediction of a simple square-root-of-concentration dependence of the equilibrium properties of a mixture of ions was so well-hidden that Milner himself apparently did not realize it immediately. With Milner's work in the background, Debye and Hückel["] produced their simpler treatment which predicted linearity of thermodynamic properties in the square root of concentration at high dilutions.

The Debye-Hückel["] argument is based on the combination of the Poisson equation of electrostatics and the classical

Boltzmann distribution function. The principal feature of the Debye-Hückel["] theory is its implication of complete disorder among the ions around any arbitrary central ion except for the spherically symmetrical orienting forces of electrical interaction with the central ion. Later treatments such as those of Mayer (4), Meeron (5), and Kirkwood and Poirier (6) are apparently quite rigorous, but the complexity of applying or even testing the results puts them at a considerable practical disadvantage. Poirier, however, has applied Mayer's equations for the activity coefficient to a few salts of different valence types (7). Good agreement with experiment up to a concentration of about 0.1 mole per liter was obtained only with sodium chloride.

In general, these later approaches yield the Debye-Hückel["] results when considered at very low concentrations. For convenience then, only the Debye-Hückel["] theory itself need be dealt with in the ensuing discussions.

The Debye-Hückel["] theory was born primarily of a need for a consistently reliable means of extrapolating low-concentration data on strong electrolytes to infinite dilution. Its success in this respect has fostered a tolerant attitude toward shortcomings in others, most notably its inability to cope, except through semi-empirical extensions, with concentrated solutions. Dissatisfaction with this state of affairs has prompted some recent investigators to re-examine the whole problem in terms of a lattice model. This model is successful from only a limited point of view, but is sug-

gestive of the important characteristics that a better model must have.

A lattice model of strong electrolyte solutions is actually not a new approach. Ghosh (8) proposed a lattice theory that predicted cube-root dependence of colligative properties in 1918. His theory unfortunately contained unsatisfactory elements that were independent of the square-root vs. cube-root issue, and it was discredited even before the Debye-Hückel theory captured the attention of scientists by its successful predictions--all carrying with them a limiting square-root dependence of colligative properties. This combination of circumstances tended to suppress further inquiry into the relevance of cube-root dependence.

From 1923 on, a great deal of low-concentration electrolyte data has been turned out in order to test the Debye-Hückel relations. Consistency of the data with limiting square-root equations has been universally deemed adequate proof of the theory. Cube-root plots, however, also show consistency with low-concentration experimental results. The formulation of the cell theory is therefore preceded by discussions of the extrapolation problem and of the lattice model.

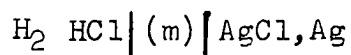
CHAPTER II

EXTRAPOLATION PROBLEMS AND THE LATTICE MODEL OF STRONG ELECTROLYTE SOLUTIONS

Extrapolation Functions in the Treatment of Strong Electrolyte Data

The extrapolation functions generally employed to obtain the value of E^0 from electromotive force and of Λ^0 from conductance data are based on the conventional model of interionic attraction, which requires, at sufficiently low concentration, linearity of appropriately chosen data against the square root of concentration. In practice the square-root relation is frequently modified because it is not strictly valid at experimentally realizable concentrations. It is demonstrated here that (unmodified) cube-root-of-concentration as an extrapolation function in the same concentration region also produces linear plots and that extrapolations made along these plots result in values (such as Λ^0 and E^0) that differ appreciably from those commonly accepted.

The hydrochloric acid data obtained by Harned and Ehlers (9) from the cell without transference



have been examined by several different methods. The electromotive force, E , of a cell of this type is given by the equation

$$E + 2k \log m = E^0 - 2k \log \gamma_{\pm} \quad (2-1)$$

where $k = 2.3026RT/F$. By plotting the left side of this equation against a suitable function of concentration and extrapolating to zero concentration, the intercept E^0 is obtained. A plot against $m^{1/2}$ at low concentrations would be linear if the limiting law of Debye and Huckel were strictly valid there. A curvature still exists at low concentration which, however, can be interpreted in Debye-Huckel theory as an effect of ion size. Harned and Ehlers overcame the difficulty by taking for $\log \gamma_{\pm}$

$$-\log \gamma_{\pm} = 0.5m^{1/2} - bm \quad (2-2)$$

(b an undetermined constant) and substituting into (2-1):

$$E + 2k \log m - km^{1/2} = E^0 - 2kbm \quad (2-3)$$

Plots of the left side of (2-3) against m were linear and resulted in a value of 0.22239 volts for E^0 at 25° . Results of other investigations obtained by similar extrapolation techniques differ by less than one part per thousand.

Extrapolation of the left side of equation (2-1) against m , which implies an Arrhenius incomplete dissociation model, is complicated by still more curvature. Using extrapolation means which utilize only a few of the lowest concentration points leads to $E^0 = 0.22480$. The equation employed for this extrapolation was obtained by converting the logarithms in equation (2-1) to the base e , rearranging,

and taking the exponential of both sides. The resulting equation is

$$\exp(-FE/2RT) = m \gamma_{\pm} \exp(-FE^0/2RT) \quad (2-4)$$

By plotting the left-hand side of the equation against m , E^0 can be found from the limiting slope. Higher concentration points, however, as well as other types of data are inconsistent with m as the extrapolation function. Such is not the case with $m^{1/3}$ as the extrapolation function.

The above data for hydrochloric acid (Figure 1) as well as data in Figure 2 for potassium (10) and sodium chloride (11) from concentration cells with transference, have been plotted against $m^{1/3}$ (or $C^{1/3}$) as would be required by an expanded lattice model of solutions. The left side of (2-1) was plotted on the ordinate in the case of hydrochloric acid, and the quantity $E' + 2k \log C$ for the cell-with-transference data. E' is defined as

$$E' = \int_0^E dE/t_{\pm} \quad (2-5)$$

where $t_{\pm}$ is the transference number of the cation. The value of E' at any concentration is obtained by graphical integration of a plot of $1/t_{\pm}$ against E . The complete equation for concentration on the molar scale is thus

$$E' + 2k \log C = E_R^0 - 2k \log y_{\pm} \quad (2-6)$$

where E_R^0 is the intercept at zero concentration and depends on the concentration of the reference solution. All three plots give straight lines that extend from the lowest con-

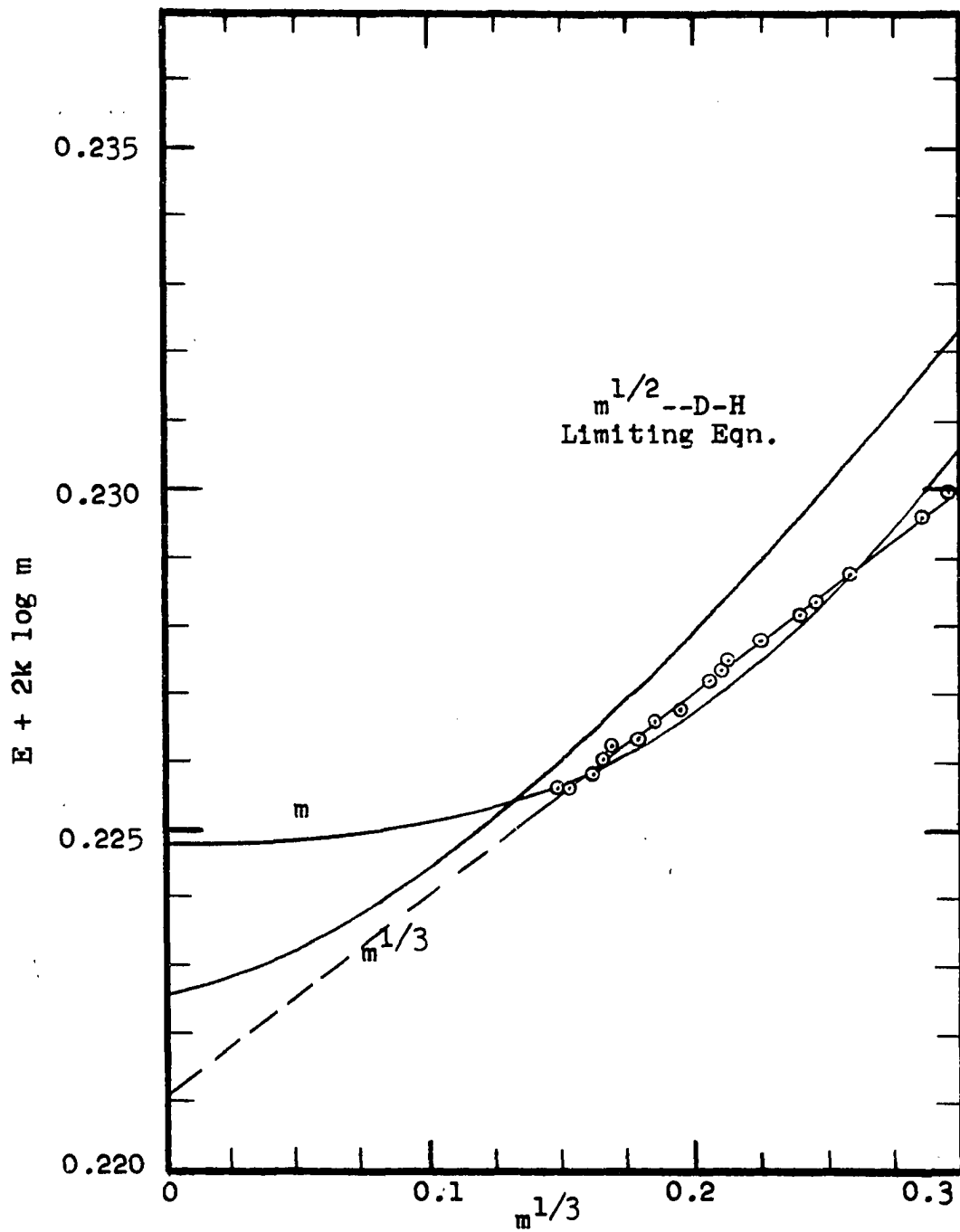


Fig. 1--Hydrochloric acid electromotive force data-- $m^{1/3}$ plot with comparison curves from other extrapolation methods.

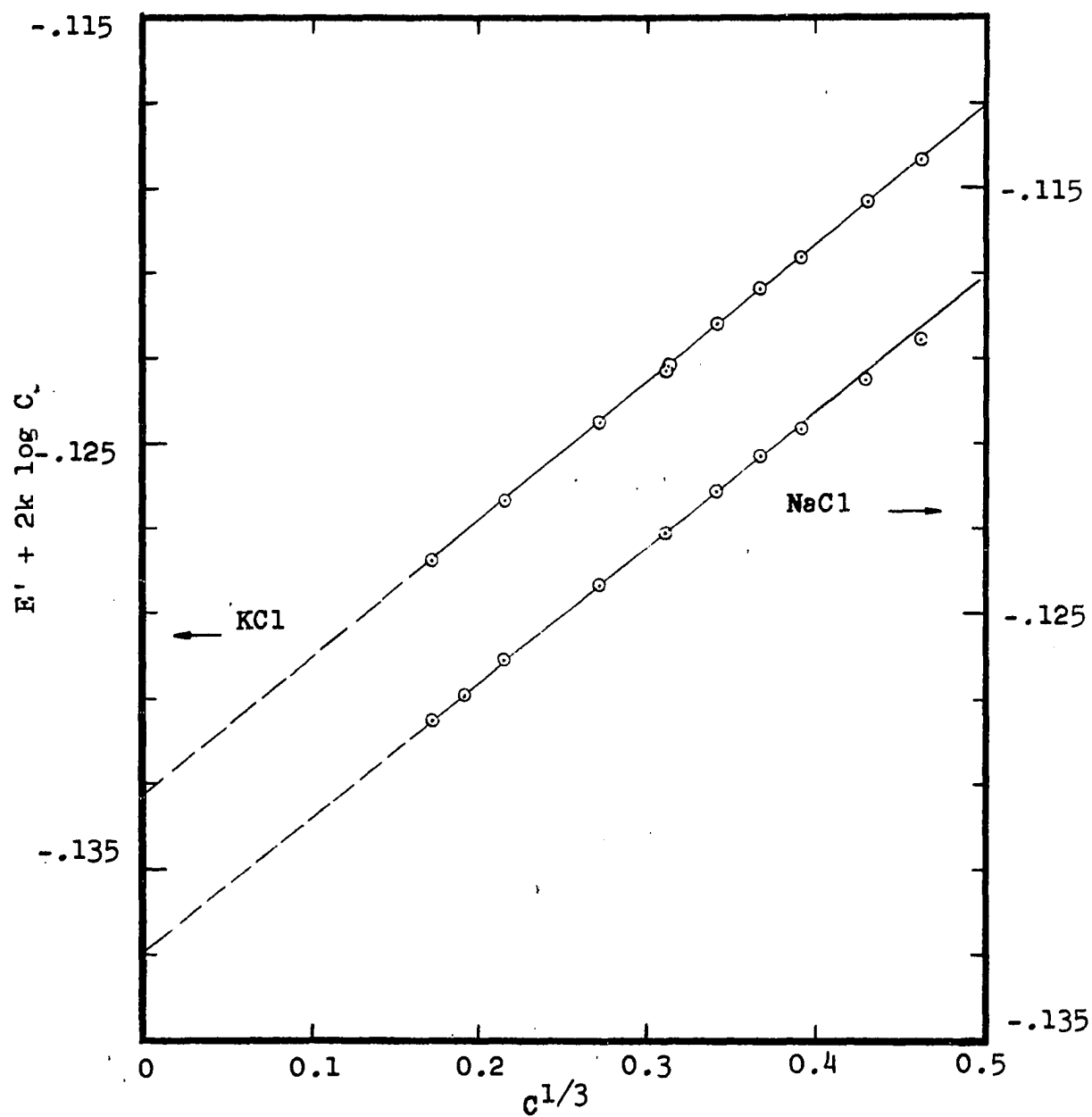


Fig. 2--Concentration cell with transference: sodium and potassium chloride.

centration (about 0.005 M). The linearity persists to almost 0.1 M for potassium chloride, with the upper limit decreasing somewhat for sodium chloride and hydrochloric acid, in that order. E^0 for the hydrochloric acid cell without transference is determined to be 0.22104 volts by means of the $m^{1/3}$ extrapolation function. However, it has been observed that the hydrogen-calomel electrode cell data of Hills and Ives (12) show less data scatter in $E + 2k \log m$ than that of Harned and Ehlers, and that the $m^{1/3}$ plot shows slight but distinct departure from linearity.

In the case of HCl, we thus have three very different values of E^0 :

<u>Extrapolation Function</u>	<u>E^0</u>
$m^{1/3}$	0.22104
$m^{1/2}$	0.22239
m	0.22480

It is obvious that the use of different E^0 's will lead to different values of $\gamma_{\pm}$, a fact not generally appreciated. It is in fact common practice to analyze the concentration dependence of $\gamma_{\pm}$ determined and widely tabulated on the basis of the $m^{1/2}$ extrapolation, as if these values had absolute significance; in the use of such tables the relative nature of $\gamma_{\pm}$ should always be borne in mind. A change in the value of E^0 has the effect of shifting all values of $\log \gamma_{\pm}$ in the table by a constant.

Lattice Model of Strong Electrolyte Solutions

The above findings suggest an expanded crystal lattice as a model for electrolyte solutions. In an ionic crystal the electrical potential energy is directly proportional to the reciprocal of the distance between an ion and its nearest neighbors. Thus in a solution the energy would vary directly with $c^{1/3}$.

Electrostatic Energy and Thermodynamic Properties of the Lattice Model

* The electrostatic energy of a solution containing one mole of a 1-1 electrolyte can be expressed as

$$U - U^0 = -NAe^2/Dr \quad (2-7)$$

where U^0 is the electrostatic energy at infinite dilution, N is Avogadro's number, A is the Madelung constant (for the rock salt lattice, $A = 1.74756$), e is the electronic charge, D is the dielectric constant of the solvent, and r is the distance between an ion and its nearest oppositely charged neighbor. If equation (2-7) is taken to be the electrostatic contribution to the Gibbs free energy, the activity coefficient can be immediately written as

$$\ln y_{\pm} = -(Ae^2/2DkT)(2NC/1000)^{1/3} \quad (2-8)$$

where k is the Boltzmann constant and T the absolute temperature. For an aqueous solution at 25° , equation (2-8) becomes

$$-\log y_{\pm} = 0.2881 c^{1/3}$$

or

$$2k \log y_{\pm} = -0.0341 c^{1/3} \quad (2-9)$$

where again k has the value assigned to it in equation (2-1).

As will be discussed later, this theoretical value of the activity coefficient for a 1-1 electrolyte agrees well with experiment, considering the oversimplification of the model.

Equations for the limiting thermochemical behavior of a 1-1 electrolyte can be obtained by differentiating (2-8) with respect to temperature. (See Chapter III for a fuller account of thermochemical quantities.) The relative partial molar enthalpy $\bar{L}_2$ can be expressed by the equation

$$\bar{L}_2 = -2RT \left[(\partial \ln V / \partial \ln T) / 3 + (\partial \ln D / \partial \ln T) + 1 \right] (\kappa e^2 / 2DkT) \quad (2-10)$$

in which κ , the effective reciprocal radius of the ionic atmosphere is given by the lattice model as

$$\kappa = A/r = A(2NC/1000)^{1/3} \quad (2-11)$$

The relative apparent molar enthalpy ϕ_L in the limiting case comes from the relation

$$\phi_L = (1/C) \int_0^C \bar{L}_2 \, dC = (3/4) \bar{L}_2 \quad (2-12)$$

which gives for a 1-1 electrolyte in water at 25°

$$\phi_L = 194.5 \, C^{1/3} \text{ calories/mole} \quad (2-13)$$

In Figure 3 are plotted the heat-of-dilution data of Gulbransen and Robinson (13) on sodium chloride with comparison curves from the lattice model, the Debye-Hückel limiting equation, and the cell model to be discussed in Chapter III.

Theory of Conductivity Based on the Lattice Model

Data for the equivalent conductivity of hydrochloric acid (14) have been plotted against the cube root of concen-

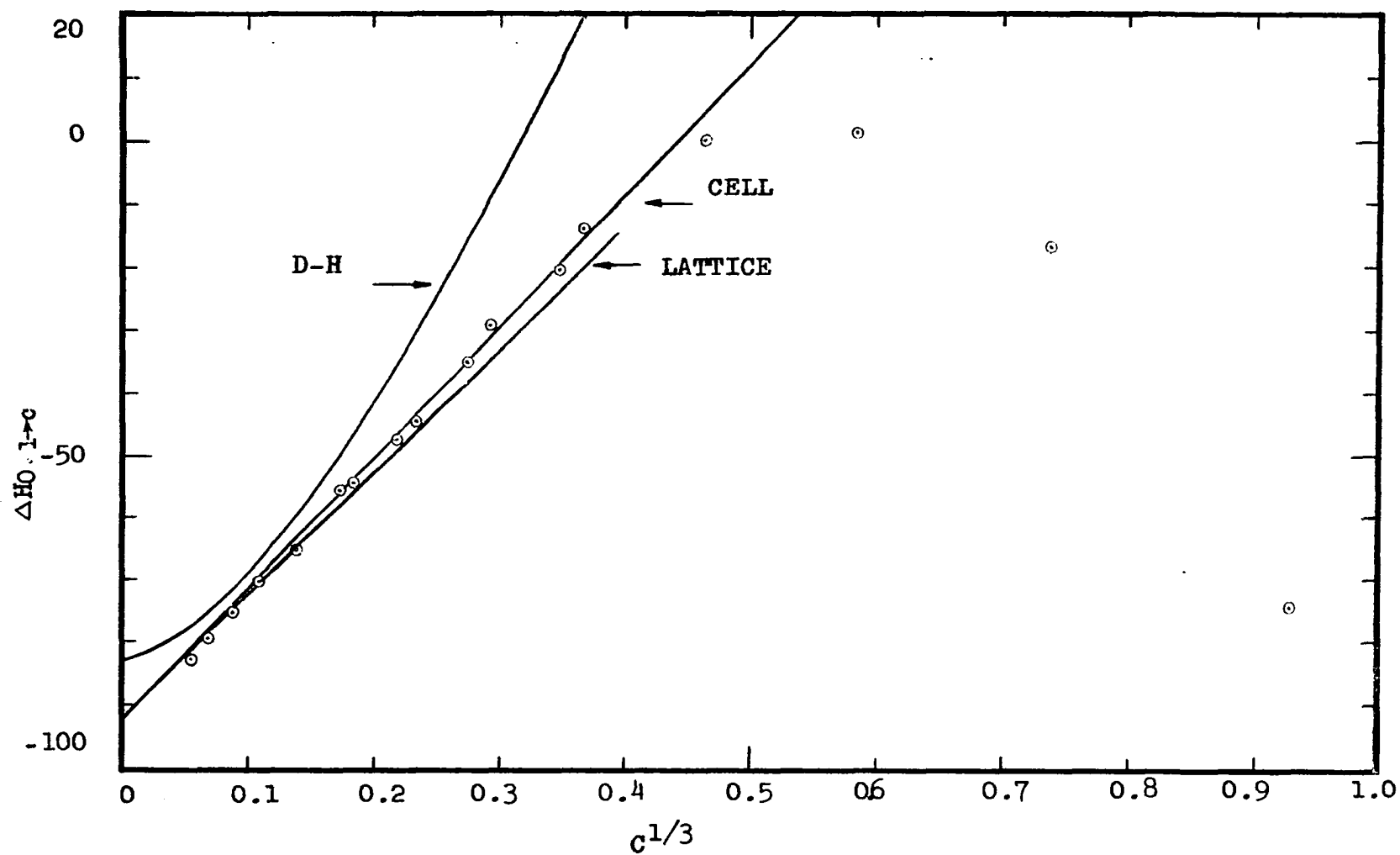


Fig. 3--Heat of dilution of sodium chloride at 25° with theoretical limiting slopes.

tration in Figure 4. A linear relationship is found from below 0.001 to 0.05 M. Sodium and potassium chloride conductivity data (15) (not shown here) are linear in the same range. These facts have been interpreted in terms of the lattice model.

It is assumed that Onsager's limiting equation for the equivalent conductivity in the form

$$\Lambda = (\Lambda^0 - F^2 r / 3\pi\eta N)(1 + \Delta X/X) \quad (2-14)$$

is correct, with r , the reciprocal radius of the ionic atmosphere, dependent on the model. Here

Λ^0 = limiting Λ at infinite dilution.

$F^2 r / 3\pi\eta N$ = correction term for electrophoresis (η is the viscosity of the solvent).

$\Delta X/X = -0.2929e^2 r / 3DkT$ for 1-1 electrolytes, correction for relaxation.

The complete equation for low concentration conductivity therefore becomes, upon dropping the product of electrophoretic and relaxation terms,

$$\Lambda = \Lambda^0 - \left(\frac{0.2929e^2}{DkT} \Lambda^0 + \frac{F^2}{N\pi\eta} \right) \frac{A}{3} \left(\frac{2NC}{1000} \right)^{1/3} \quad (2-15)$$

The slope predicted by (2-11) is plotted in Figure 4 along with other theoretical slopes to be discussed later.

Discussion of Lattice Model

The agreement of the slopes calculated from the lattice model with those observed experimentally is good for all kinds of data--electromotive force, conductivity, and heat

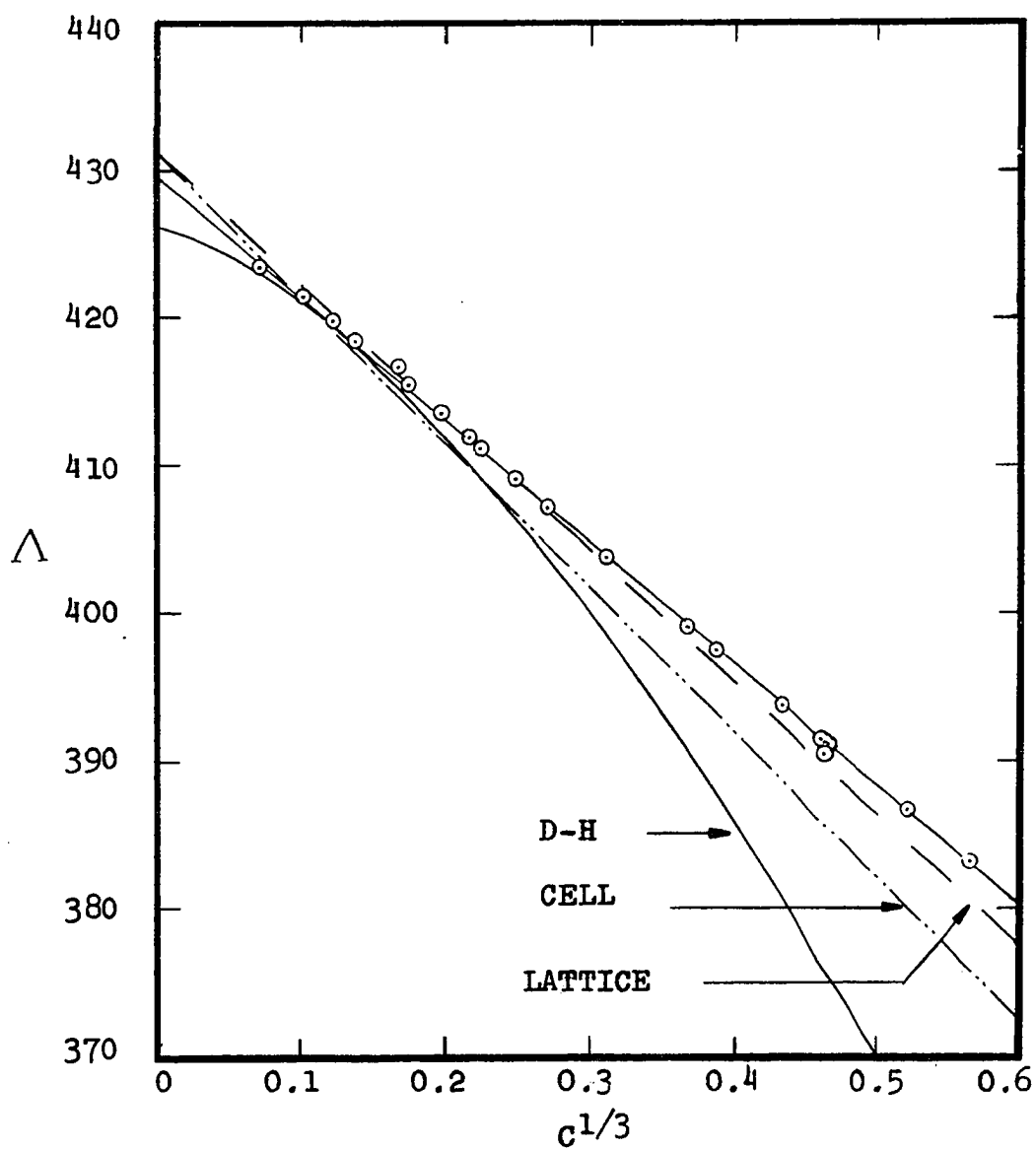


Fig. 4--Equivalent conductance of aqueous hydrochloric acid at 25° with theoretical limiting slopes.

of dilution. The results are all the more striking if one considers that no attempt has been made to blur the lattice structure by introducing temperature-dependent terms into the theory. Thus, from the electromotive force data, values for $2k \log \gamma_{\pm}$ (or $y_{\pm}$) of $-0.0300m^{1/3}$, $-0.0319c^{1/3}$, and $-0.0323c^{1/3}$ were found for hydrochloric acid, sodium chloride, and potassium chloride, respectively, as compared with the predicted value of $-0.0341c^{1/3}$.

Bjerrum (16) was apparently the first to suggest the dependence of the activity coefficient on the cube root of concentration. He does not seem to have based his proposal on other than empirical grounds, however.

More recently, Robinson and Stokes (17) have called attention to the correspondence of low concentration activity coefficient data with the cube-root relation and with the energy of an expanded rock-salt lattice, and Glueckauf (18) and Frank and Thompson (19) have expressed the view that a diffuse lattice structure may account for the observed dependencies of equilibrium properties. Glueckauf sets the lower concentration limit of validity of the Debye-Hückel expression at 0.1 M, but we find, as do Frank and Thompson, that the cube-root dependence is followed at much lower concentrations.

The data for the heat of dilution of sodium chloride are linear in $c^{1/3}$ from the lowest measured concentration to about 0.1 M. The experimental slope is 213, as compared

with the lattice model slope of 194.5.

In the conductance data, the slopes for Λ vs. $c^{1/3}$ calculated on the basis of the lattice model were -89.94, -50.93, and -53.99. The calculated slopes would be changed but little if values of Λ^0 closer to those commonly accepted were used. The observed slopes, in the same order as before, are -83.7, -48.7, and -52.0.

Although in his later years he decided in favor of a limiting square-root dependence, Kohlrausch (20) who pioneered investigations in the field of electrolytic conductance, had long utilized linearity in the cube root of concentration. Thus, both equilibrium and conductivity data can be fitted to a lattice model with almost quantitative prediction of properties into solutions of moderate concentration.

There are two obvious limitations of the lattice model: (1) in the crystal close packing of ions, along with the electrostatic interactions, forces a nearly perfect ordering. The steric factor is removed when the lattice is substantially expanded, thus permitting thermal effects to reduce the order; no account of this is taken in the theory. The facts denoted above suggest, however, that the system rearranges itself to a configuration not greatly different in energy from that of the lattice model. (2) No provision is made for higher concentrations, where the properties will be affected by ion size and other factors. Thus the ability

of the lattice model to predict the limiting slopes of strong electrolyte data as well as it does must be viewed as a remarkable coincidence.

CHAPTER III

CELL THEORY OF STRONG ELECTROLYTE SOLUTIONS

A model of strong electrolyte solutions is needed that will remedy the defects of the lattice model while remaining both conceptually and mathematically simple. It would not have to concern itself with detailed ionic distribution if it would lead to the correct electrostatic energy; many configurations can have the same energy: the crystal lattice is suggestive. After having evaluated the energy of the known distribution of N molecules of electrically interdependent cations and anions, one finds that it can be represented as N times the energy of an electrically independent pair of oppositely charged ions at a distance r/A , where r is the nearest neighbor distance. The distance r/A is less than the radius of a spherical cell of volume V/N , where V is the total volume of solution.

The findings above suggest the consistency of the model with a cube-root-of-concentration dependence of properties such as $\log \gamma_{\pm}$ at sufficiently low concentrations.

The model proposed here will be justified initially by plausibility arguments; its consequences will then be

tested against experimental data. It must be emphasized that this treatment is no attempt to describe a detailed ionic distribution in the solution, only an energetic equivalent of the distribution.

Partition Function for Symmetrical Electrolytes

Consider one of the two types of ions in a binary electrolyte solution--the cation. If the total volume available is divided into n equal volumes, each of the subdivided volumes will be occupied on the average by one cation. Assuming for the moment that both particles were uncharged, there would be on the average one other particle in the same volume. Introduction of the coulomb force requires this to be an anion. The cell concept is therefore based on the average occupancy of a molecular volume element in the solution by one cation and one anion.

With the center of coordinates fixed on the selected ion, its counter ion in the cell is pictured as a spherically symmetrical atmosphere of unit charge. Its electrostatic potential outside the cell is the same as if it were at the center of the cell. It shields electrostatically the central ion. Hence the net potential due to the selected ion and its atmosphere is zero everywhere outside the cell.

The ability to effect such a simplification in transferring from the rigid lattice to the solution is due to the disappearance of steric factors, for in crystalline sodium chloride we have no choice but to consider the interaction of

a selected ion with first six unlike, then twelve like, and so on, neighbors. The movement of the unlike ion causes the smearing out of charge and the resulting cell becomes subject to the aforementioned electrostatic theorem.

A particular ion constituting the atmosphere is not to be regarded as trapped in the cell. Ions can move from cell to cell on an exchange basis. But at any given instant, no ion could be included in the atmosphere of more than one cell.

The assumptions of the cell model for symmetrical electrolytes can be summarized as follows:

1. A selected ion is assumed to be situated in a spherical cell of volume $V = 1000/CN$. The radius of the cell is found to be $7.346 \times 10^{-8} C^{-1/3}$.
2. One oppositely charged ion in the cell constitutes the ionic atmosphere. The radius varies, subject to the coulomb force and thermal agitation, between a , the distance of closest approach, and R , the cell radius, assumed to be the same for all cells.
3. Each cell is electrostatically independent of all other cells. The energy of the solution is thus the sum of the energies of the individual cells.
4. The energy of an ion and its atmosphere, when at a distance r , is $Ze^2/2Dr$, as determined by a reversible charging process starting with charge reservoirs at infinity. (Z is the product of the valences of the two ions.)

5. Except for the electrostatic interactions, each ion is to be treated as ideal gas-like.

6. Dielectric constant and ion size are assumed to be independent of concentration.

Spherical cell size, uniform radius, and assumption 6 will be recognized as approximations whose sole justification is simplification of mathematical treatment.

The partition function for a particular ion is therefore obtained from the product of its translational partition function with the Boltzmann factor averaged over the cell.

$$q = (2\pi mkT/h^2)^{3/2} (V-b) \frac{\int_a^R 4\pi r^2 \exp(Ze^2/2DkTr) dr}{(4\pi/3)(R^3-a^3)}$$

The free volume factor $(V-b)$ is taken equal to $(4\pi/3)(R^3-a^3)$, so that the expression becomes

$$q = q_{tr} \int_a^R 4\pi r^2 \exp(Ze^2/2DkTr) dr \quad (3-1)$$

where q_{tr} is the translational contribution per unit volume to the partition function. The partition function for the ion and its atmosphere is the product of two such terms.

Partition Function for Unsymmetrical Electrolytes

Generalization of the cell concept to unsymmetrically valent types of electrolytes follows immediately from the preceding treatment of symmetrical electrolytes. For any 1-n or n-1 electrolyte (n represents the valence of the

more highly charged ion) a model similar to that of symmetrical electrolytes can be postulated. The same assumptions noted for symmetrical electrolytes also hold in this case, except that more than one ion of the lower valence type can exist together in a cell. The theory has not been extended to encompass 2-3 or higher order unsymmetrical types because it is doubtful that such bona fide strong electrolytes exist free from hydrolysis.

Figure 5 schematically depicts the model for a 2-1 electrolyte. The two anions are assumed equidistant from the central cation. Because of electrostatic repulsion the anions will tend always to remain the maximum distance away from each other. This distance is, for the case in question, $2r$, or twice the cation-anion distance. The partition function for the cation is thus given by

$$q = q_{tr} \int_a^R 4\pi r^2 \exp (4e^2/2DkTr) dr \quad (3-2)$$

The value of the coefficient $Z = 4$ is obtained by considering the electrostatic energy term in the partition function as the sum of the interactions of the bivalent cation with each univalent anion. A similar partition function holds for each anion except that $Z = 3/2$ since each anion interacts with the other as well as with the central cation. This coefficient also arises from the sum of two interactions--one with the cation at a distance of r and the other with the remaining anion at a distance of $2r$. The

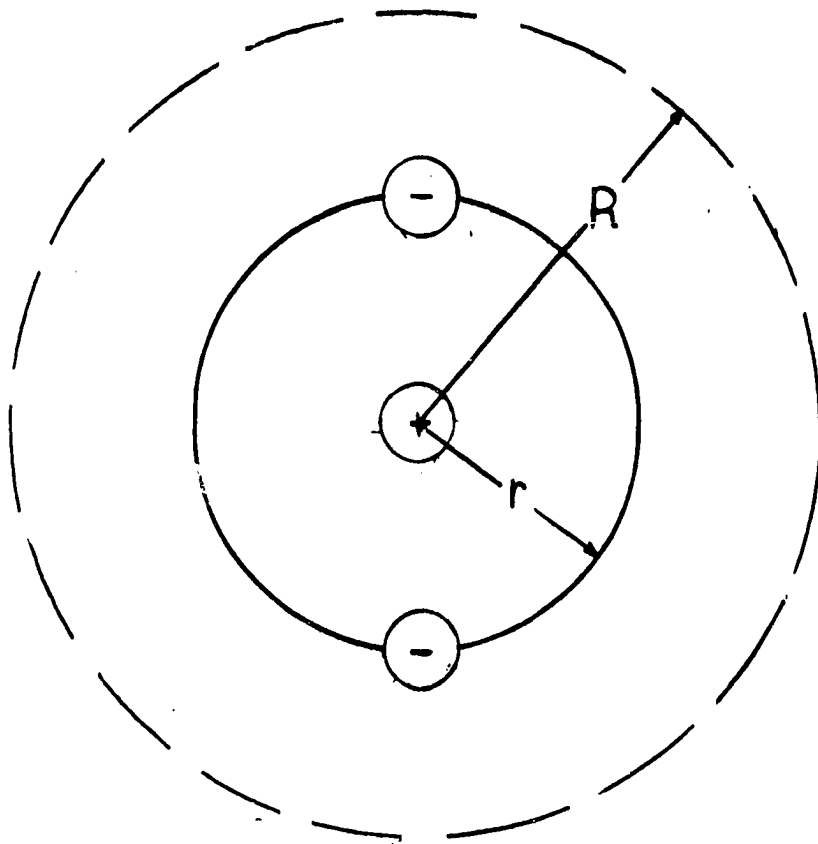


Fig. 5--Model of cell for 2-1 electrolyte.

total molecular partition function exclusive of translational contributions is therefore

$$q = \left[\int_a^R 4\pi r^2 \exp(4e^2/2DkTr) dr \right] \left[\int_a^R 4\pi r^2 \exp(1.5e^2/2DkTr) dr \right]^2 \quad (3-3)$$

An analogous argument is applicable to 3-1 (or 1-3) electrolytes. In this case the condition of maximum separation of like-charged ions constrains the univalent ions to the relative configuration of an equilateral triangle. Likewise, for a 4-1 electrolyte the univalent ions would be at the corners of a regular tetrahedron. The molecular partition function without translational contributions for a 3-1 electrolyte would accordingly be

$$q = \left[\int_a^R 4\pi r^2 \exp(9e^2/2DkTr) dr \right] \left[\int_a^R 4\pi r^2 \exp(1.8453e^2/2DkTr) dr \right]^3 \quad (3-4)$$

The partition function for a 4-1 electrolyte can be obtained similarly.

Thermodynamic Properties

All the useful equilibrium properties of an electrolyte solution can be predicted with the preceding molecular partition function. The statistical thermodynamic relation for the Helmholtz free energy is

$$A = -RT \ln q_t \quad (3-5)$$

where q_t is the total molecular partition function. As is customary, the very good approximation is made here that there is no difference between the Helmholtz and the Gibbs

free energy. From equation (3-5) the mean ionic activity coefficient and all thermochemical properties can ultimately be derived.

Activity Coefficients

The Helmholtz free energy of an electrolyte can be expressed in terms of its concentration in solution:

$$A = A^{\circ} + \nu RT \ln C + \nu RT \ln y_{\pm} \quad (3-6)$$

The symbol A° in equation (3-6) is the standard Helmholtz free energy of the electrolyte, R is the gas constant, and $\nu = n + 1$, the number of ions per molecule. By equating the right-hand sides of the latter two equations, one obtains

$$\nu RT \ln y_{\pm} = -A^{\circ} - RT \ln(q_{\pm} C^{\nu}) \quad (3-7)$$

Upon converting the molar concentration C to $3000/4\pi NR^3$, and incorporating all concentration-independent terms into A° , the following expression for the molar activity coefficient results:

$$\nu \ln y_{\pm} = -\ln \left[(3/4\pi R^3)^{\nu} q_{12} \right] \quad (3-8)$$

The quantity q_{12} is the total molecular partition function exclusive of concentration-independent terms. Equation (3-8) can also be expressed for an unsymmetrical $n-1$ or $1-n$ electrolyte as

$$\nu \ln y_{\pm} = -\ln \left[(3/4\pi R^3) q_1 \right] \left[(3/4\pi R^3) q_2 \right]^n \quad (3-9)$$

where q_{12} has been factored into q_1 from the central ion of valence $\pm n$, and q_2 from the univalent ions. Each of these q 's corresponds to the integral in equation (3-1). Evaluation of $\ln y_{\pm}$ for any of the unsymmetrical valence types of elec-

trolytes discussed consists simply in adding the logarithm of one integral to n times the logarithm of the other integral. In the case of a symmetrical electrolyte, equation (3-8) is just

$$2 \ln y_{\pm} = -\ln \left[(3/4\pi R^3) q \right]^2$$

or

$$\ln y_{\pm} = -\ln \left[(3/4\pi R^3) \int_a^R 4\pi r^2 \exp(Ze^2/2DkTr) dr \right]$$

Calculations of $\ln y_{\pm}$ can be performed by either (1) reducing the integrals in the partition functions to the exponential integral function or (2) expanding the exponential in the integrand and integrating directly. The former procedure is carried out by changing the variable and integrating by parts. The result is

$$\begin{aligned} \ln \left[(3/4\pi R^3) \int_a^R 4\pi r^2 \exp(Ze^2/2DkTr) dr \right] \\ = \ln \left\{ 3X^3 \left[I(X/a) - I(X/R) \right] / R^3 \right\} \end{aligned} \quad (3-10)$$

which is $-\ln y_{\pm}$ for a symmetrical electrolyte (X represents the quantity $Ze^2/2DkT$). The function $I(x)$ is defined as

$$6 I(x) = Ei(x) - e^x (1 + 1/x + 2/x^2)/x \quad (3-11)$$

where $Ei(x)$ is the widely tabulated exponential integral:

$$Ei(x) = \int_{-\infty}^x e^v v^{-1} dv$$

The method of evaluating $\ln y_{\pm}$ by expanding the exponential gives for the right-hand side of equation (3-10)

$$\begin{aligned} \ln 3 \left\{ \sum_{k=0}^{k \neq 3} \left[(R^{-k} - a^{3-k} R^{-3}) X^k / k! (3-k) \right] + \right. \\ \left. R^{-3} \ln(R/a) X^3 / 3! \right\} \end{aligned} \quad (3-12)$$

If (3-12) is written term by term, there results for a symmetrical electrolyte

$$\ln y = -\ln\left[1 - a^3\chi + \frac{3X}{2}(\chi^{1/3} - a^2\chi) + \frac{3X^2}{2}(\chi^{2/3} - a\chi) + \dots\right] \quad (3-13)$$

where $\chi = 4\pi NC/3000$. By expansion of the logarithm one observes that the low concentration limiting value of $\ln y_{\pm}$ will be proportional to $C^{1/3}$:

$$\ln y_{\pm} = -(3/4)(Ze^2/DkT)\chi^{1/3} \quad (3-14)$$

Thermochemical Quantities

Equations for the enthalpies and heat capacities of an electrolytic solute are obtained by taking temperature derivatives of the expression for the logarithm of the mean activity coefficient. Rigorously, since the molar concentration varies with temperature, $\ln y_{\pm}$ cannot be differentiated partially with respect to temperature. This complication, however, is not of great consequence below moderately high concentrations. Also, the convenience in employing $\ln y_{\pm}$ rather than converting to the molal activity coefficient would hardly be worth sacrificing for somewhat more accuracy in the calculations. This would be especially true at higher concentrations where the decreasing distance of closest approach of the ions and decreasing dielectric constant have a large effect on the agreement of theory with experiment. Consequently, the expression in (3-12) which is $-\ln y_{\pm}$ for a symmetrical electrolyte or part of a sum of two such expressions leading to $-\nu\ln y_{\pm}$ for an un-

symmetrical electrolyte has been differentiated with respect to temperature on the approximation of constant concentration to obtain the thermochemical quantities.

Relative partial molar enthalpy. This property of the solute is its partial molar enthalpy at a particular concentration relative to that at infinite dilution. It is defined by the relation

$$\bar{L}_2 = -\nu RT^2 (\partial \ln y_{\pm} / \partial T)_P \quad (3-15)$$

The symbol R is taken as the gas constant, and the subscript P as denoting constant pressure. Now for a symmetrical electrolyte, differentiation of (3-12) gives

$$\begin{aligned} -(\partial \ln y_{\pm} / \partial T)_P = y_{\pm} & \left[\alpha \left\{ \sum_{k=0}^{k \neq 3} (-kR^{-k} + 3a^{3-k}R^{-3}) X^k / k!(3-k) \right. \right. \\ & \left. \left. + [R^{-3} - 3R^{-3} \ln(R/a)] X^3 / 3! \right\} - 3(1/T + \partial \ln D / \partial T) \right. \\ & \left. \left[\sum_{k=1}^{k \neq 3} (R^{-k} - a^{3-k}R^{-3}) k X^k / k!(3-k) + 3R^{-3} \ln(R/a) X^3 / 3! \right] \right] \quad (3-16) \end{aligned}$$

where α is $\partial \ln V / \partial T$, the expansibility of the solvent, and X is $Ze^2 / 2DkT$. From equation (3-15) one sees that multiplying the right-hand side of (3-16) by νRT^2 gives $\bar{L}_2$. It should be remembered that this result holds only for a symmetrical electrolyte where $\nu = 2$; otherwise $\bar{L}_2$ comprises two such expressions. From equations (3-9), (3-13) and (3-14) the limiting low-concentration behavior of $\bar{L}_2$ can be expressed for a symmetrical electrolyte as

$$\bar{L}_2 = -2RTZ \left[(\partial \ln V / \partial \ln T) / 3 + \partial \ln D / \partial \ln T + 1 \right] \quad (3/4) (e^2 / DkT) \chi^{1/3} \quad (3-17)$$

or for an unsymmetrical n-1 or 1-n electrolyte as

$$\bar{L}_2 = -RT(Z_1 + nZ_2) \left[(\partial \ln V / \partial \ln T) / 3 + \partial \ln D / \partial \ln T + 1 \right] \\ (3/4) (e^2 / DkT) \chi^{1/3} \quad (3-18)$$

Z_1 and Z_2 are the electrostatic energy coefficients arising from the n-valent ion and the univalent ion, respectively.

Relative apparent molar enthalpy. The integral quantity corresponding to $\bar{L}_2$ is ϕ_L , the enthalpy of the solution per mole of solute at a particular concentration relative to that at infinite dilution. On the molar scale, ϕ_L is defined as

$$\phi_L = (1/C) \int_0^C \bar{L}_2 dC \quad (3-19)$$

Of all the thermochemical quantities, ϕ_L is nearest being the actual calorimetrically obtained quantity. ϕ_L is the negative of ΔH_D , the integral heat of dilution to infinite dilution, which is considered to be positive if the process of dilution is endothermic. The experimentally determined quantity is the heat of dilution from one finite concentration to another. In the limit of low concentration the relative apparent molar enthalpy is given by equations (3-19) and (3-17) or (3-18):

$$\phi_L = (3/4) \bar{L}_2 \quad (3-20)$$

Relative partial molar heat capacity. The partial heat capacity of the solute at an arbitrary concentration relative to infinite dilution is defined as

$$\bar{J}_2 = (\partial \bar{L}_2 / \partial T)_P \quad (3-21)$$

or

$$\bar{J}_2 = 2\bar{L}_2/T + T^2 \left[\partial(\bar{L}_2/T^2) / \partial T \right]_P \quad (3-22)$$

Execution of the operations denoted in (3-22) on the expression for $\bar{L}_2$ obtained from (3-16) gives for a symmetrical electrolyte

$$\begin{aligned} \bar{J}_2 = & 2\bar{L}_2/T - (\bar{L}_2/T)^2/\nu R + \nu R_{Y\pm} \left\{ T^2(\partial\alpha/\partial T) \right. \\ & \left[\sum_{k=0}^{K+3} (-kR^{-k} + 3a^{3-k}R^{-3}) X^k/k!(3-k) + (R^{-3} - 3R^{-3} \ln(R/a)) X^3/3! \right] \\ & + 3(1 - T^2(\partial^2 \ln D/\partial T^2)) \left[\sum_{k=1}^{K+3} (R^{-k} - a^{3-k}R^{-3}) k X^k/k!(3-k) + 3R^{-3} \ln(R/a) X^3/3! \right] \\ & + (T^2\alpha^2/3) \left[\sum_{k=0}^{K+3} (k^2 R^{-k} - 9a^{3-k}R^{-3}) X^k/k!(3-k) + 3(3R^{-3} \ln(R/a) - 2R^{-3}) X^3/3! \right] \\ & - 2T\alpha(1 + T\partial \ln D/\partial T) \left[\sum_{k=0}^{K+3} (-kR^{-k} + 3a^{3-k}R^{-3}) k X^k/k!(3-k) + 3(R^{-3} - 3R^{-3} \ln(R/a)) X^3/3! \right] \\ & \left. + 3(1 + T\partial \ln D/\partial T)^2 \left[\sum_{k=1}^{K+3} (R^{-k} - a^{3-k}R^{-3}) k^2 X^k/k!(3-k) + 9R^{-3} \ln(R/a) X^3/3! \right] \right\} \end{aligned} \quad (3-23)$$

Relative apparent molar heat capacity. The heat capacity of a solution per mole of solute relative to its heat capacity at infinite dilution is denoted by ϕ_J . This quantity is found from $\bar{J}_2$ in a way analogous to that by which ϕ_L is determined from $\bar{L}_2$:

$$\phi_J = (1/c) \int_0^c \bar{J}_2 \, dc \quad (3-24)$$

Computer Program for Calculation of Activity Coefficients

Equation (3-10) was utilized in a program written in Fortran for the I.B.M. 1410 computer. Activity coefficients

were calculated for different valence types of electrolytes by employing as input data the ion size parameter $\underline{a}$, electrostatic energy coefficient Z , dielectric constant D , and absolute temperature T . Calculations were made over a concentration range by iterating the calculations for 0.1 unit increments of $C^{1/3}$. The value taken for D was from the recent data of Malmberg and Maryott (21) which give 78.30_3 for the dielectric constant of water at 25° .

The main chore of the program was the evaluation of $I(x)$ as defined in equation (3-11). The evaluation of the exponential integral function in $I(x)$ was performed by calculating the infinite series

$$E_1(x) = \gamma + \ln x + \sum_{n=1}^{\infty} x^n / n!n \quad (3-25)$$

where $\gamma = 0.577216$ is Euler's constant. (See Appendix.)

Conductivity

In order to test the cell model against low concentration conductivity data, one needs only to insert the appropriate value of κ into Onsager's limiting equation which is (2-14) for 1-1 electrolytes or is as follows for $n-1$ or $1-n$ electrolytes:

$$\Lambda = \Lambda^\circ - \left\{ 7.156 \times 10^{-8} n \left[q / (1 + q^{1/2}) \right] \Lambda^\circ + 2.763 \times 10^{-6} \nu \right\} \kappa / 3 \quad (3-26)$$

Equation (3-26) employs the most recent and reliable values for the dielectric constant (21) and viscosity (22) of water

at 25°. The symbol q denotes the quotient

$$n/\nu(nt_2^0 + t_1^0) \quad (3-27)$$

where t_2^0 is the limiting transference number of the uni-valent ions and t_1^0 is the transference number of the n -valent ion.

For the cell theory, κ can be determined from the low concentration limiting form of (3-9). The cell model equation for κ (n -1 or 1- n electrolyte) is thus

$$\kappa = 3(Z_1 + nZ_2)\chi^{1/3}/4\nu \quad (3-28)$$

or in water at 25°

$$\kappa = 1.021 \times 10^7 (Z_1 + nZ_2)C^{1/3}/\nu \quad (3-29)$$

The subscripts on the Z 's in (3-29) have the same meaning as on the t 's in (3-27). From (3-14) the limiting equation for κ is seen to be in the case of a symmetrical electrolyte

$$\kappa = 3Z\chi^{1/3}/4 \quad (3-30)$$

CHAPTER IV

EXPERIMENTAL TESTS OF THE CELL THEORY

Activity Coefficients

Theoretical activity coefficient curves for aqueous solutions at 25° are shown in Figure 6 for 1-1 and in Figure 7 for 2-2 electrolytes for values of the ion size $\underline{a}$ ranging from 1 to 5 Å. Since $\underline{a}$ is the only adjustable parameter employed in the theory, it must bear the burden of predicting the individualities observed among electrolytes of a given valence type. That it does is amply verified by the examples cited below. (In many of these examples density data from standard sources has been utilized to convert from an experimental molal scale to molar scale of concentration.)

In Figure 8 the electromotive force data for potassium chloride, sodium chloride, and hydrochloric acid referred to previously, along with higher concentration data obtained from cells without transference (23,24,25) are compared graphically with theoretical predictions. The derived ion size parameters are reasonable: HCl, 5.30; NaCl, 4.00; and KCl, 3.50 Å. The intercepts are respectively,

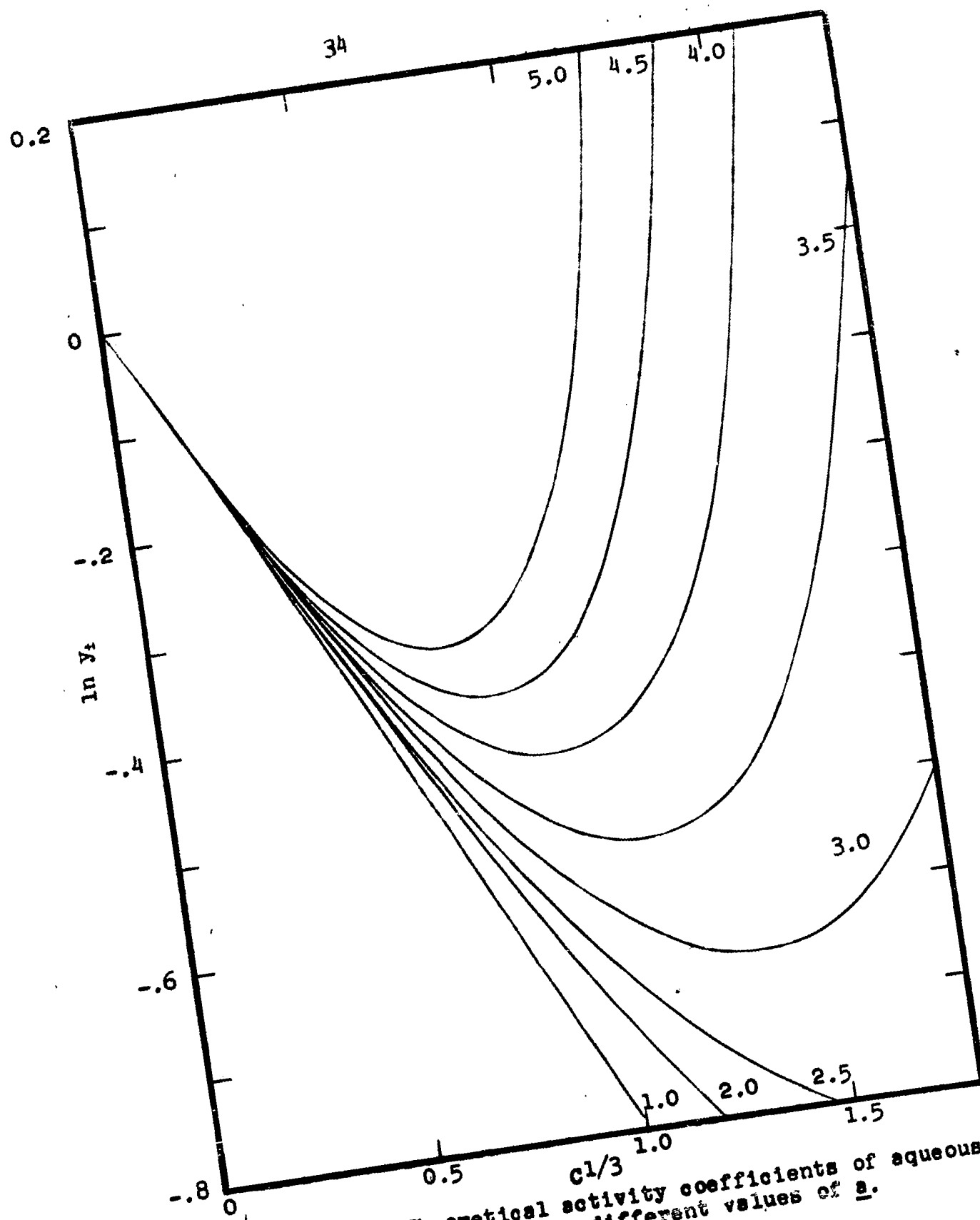


Fig. 6--Theoretical activity coefficients of aqueous 1-1 electrolytes at 25° for different values of a .

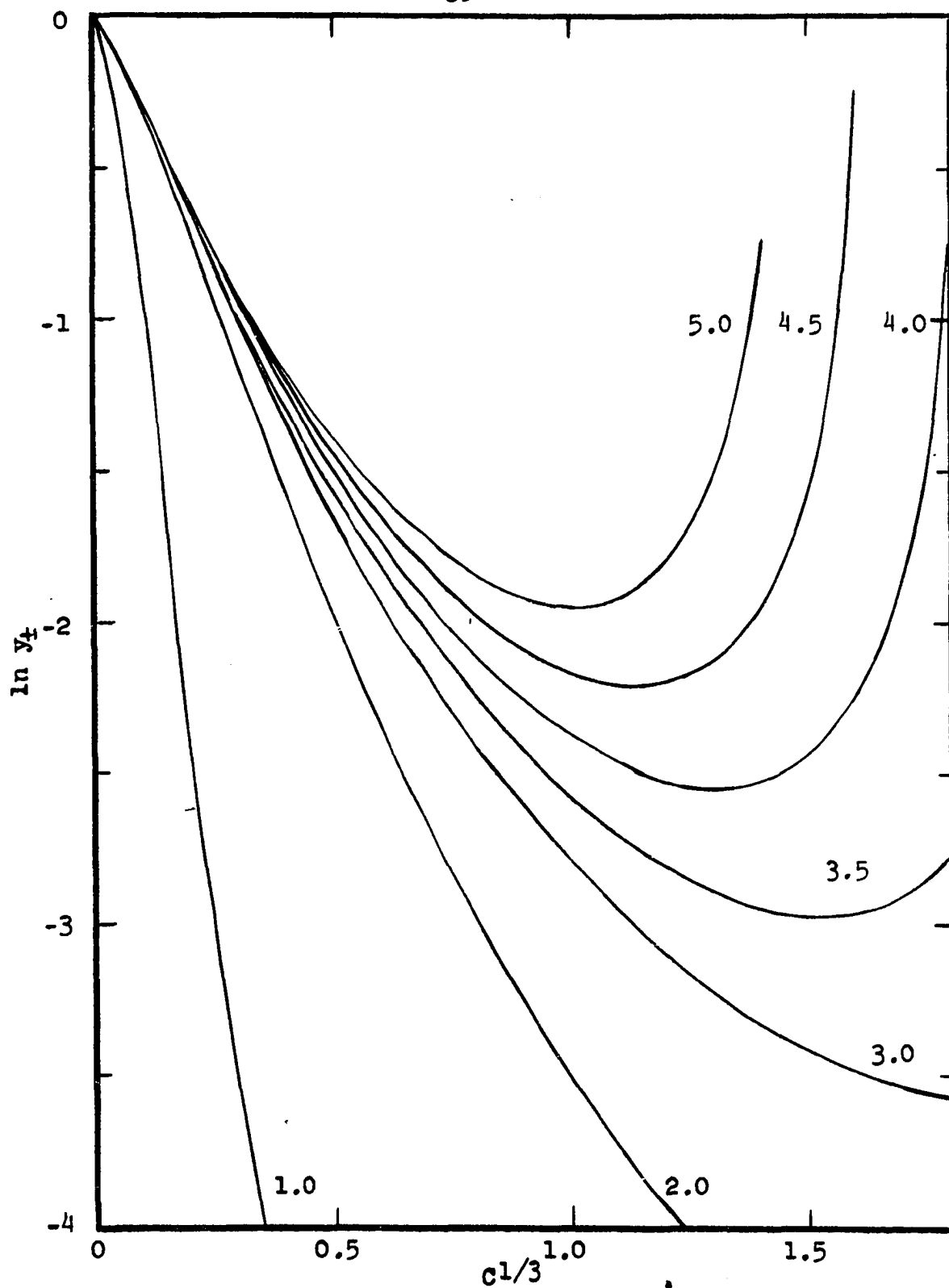


Fig. 7--Theoretical activity coefficients of aqueous 2-2 electrolytes at 25° for different values of a .

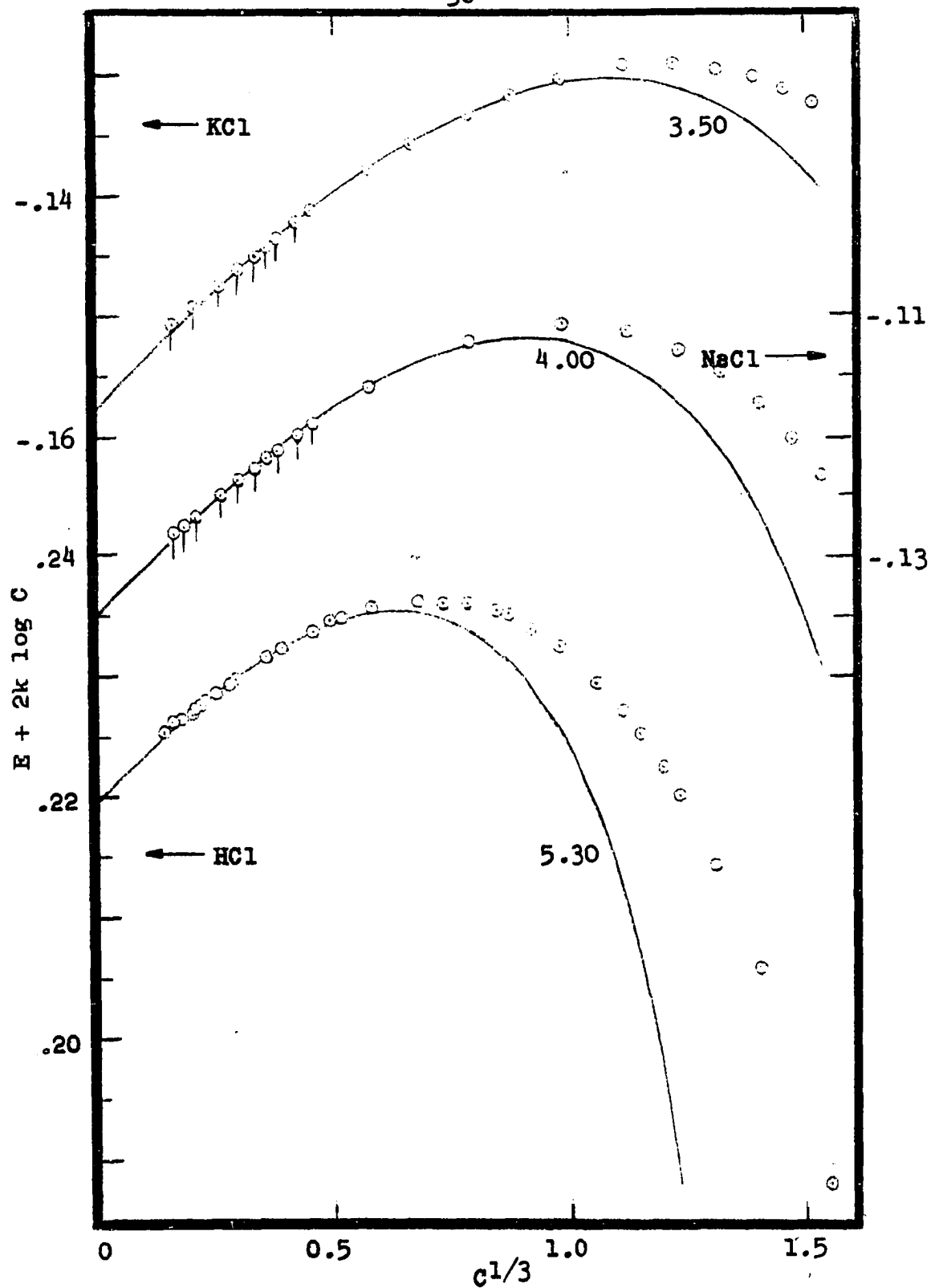


Fig. 8--Experimental electromotive force data for aqueous 1-1 electrolytes at 25° compared with curves calculated for appropriate values of α , transference cell.

0.21956, -0.13475, and -0.16798 volts.

In figure 9, the cell-without-transference data of Bray (26) and of LaMer and Cowperthwaite (27) on zinc sulfate are compared with several theoretical curves. The data cannot be fitted to any of the theoretical curves, but the limiting slope is not greatly in error. The discrepancy is readily explained, for zinc sulfate is known to hydrolyze (28). In fact, it is unlikely that useful data can be obtained for any electrolyte all of whose ions are multiply charged. Even if hydrolysis does not occur, interference may be expected from ionic association due to the high ionic charges.

Families of cell theory curves calculated for the activity coefficients of 2-1 and 3-1 electrolytes are shown in Figures 10 and 11, respectively. Calculated activity coefficients have been compared with experimental data for a 2-1 and 3-1 electrolyte. The data of Robinson (29) and Shedlovsky and MacInnes (30) obtained by isopiestic and electromotive force measurements on calcium chloride solutions at 25° are plotted in Figure 12. The theoretical curve employs an ion size of 5.70 Å. In Figure 13 the electromotive force and isopiestic data on lanthanum chloride of Shedlovsky and MacInnes (31), Shedlovsky (32), and Robinson (33) are presented with the accompanying cell model curve which is based on an ion size of 6.30 Å.

In all the above cases, except that of zinc sulfate, the cell theory correctly predicts the value of the activity

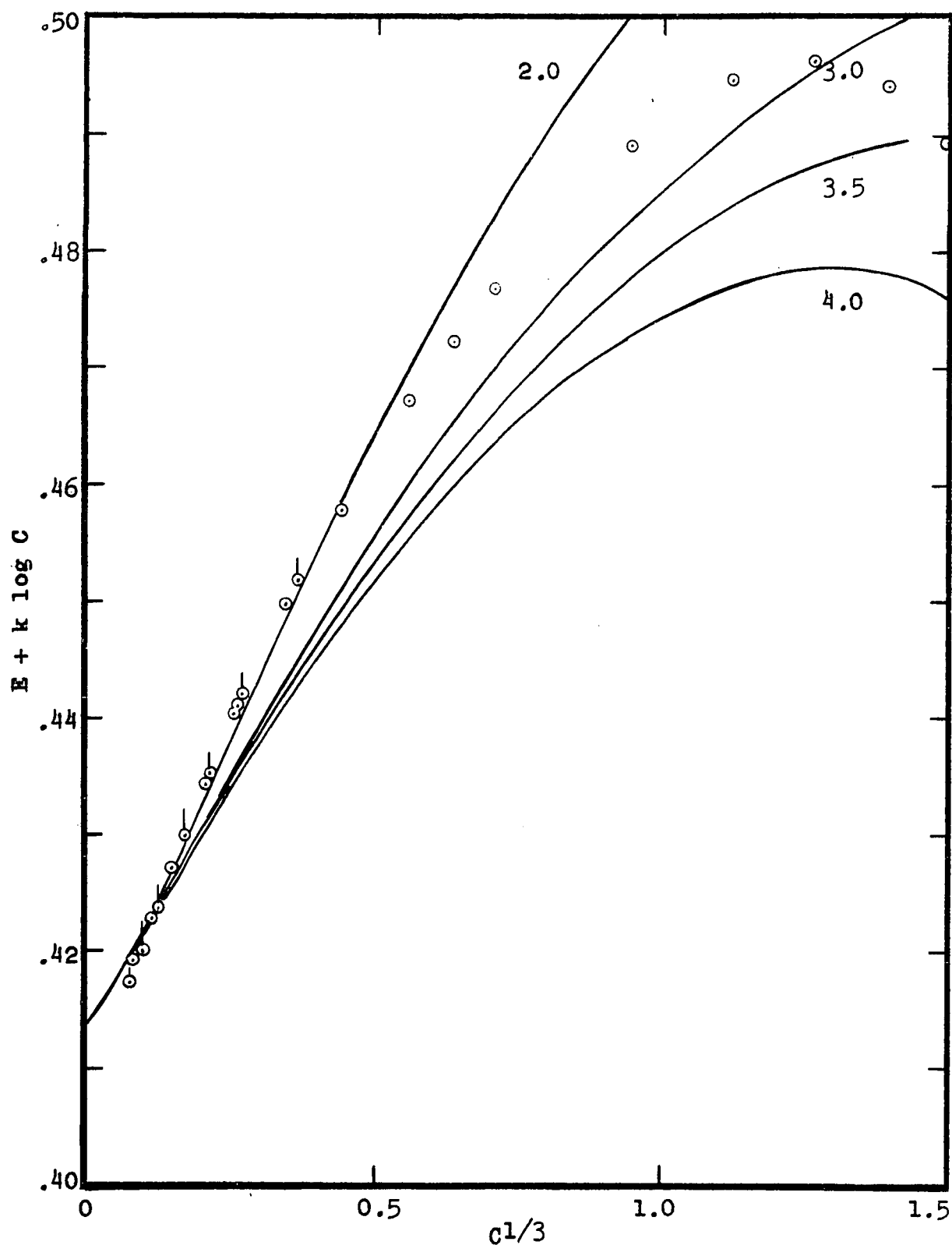


Fig. 9--Experimental electromotive force data for zinc sulfate compared with curves for denoted values of a . o, Cowperthwaite and LaMer; o, Bray.

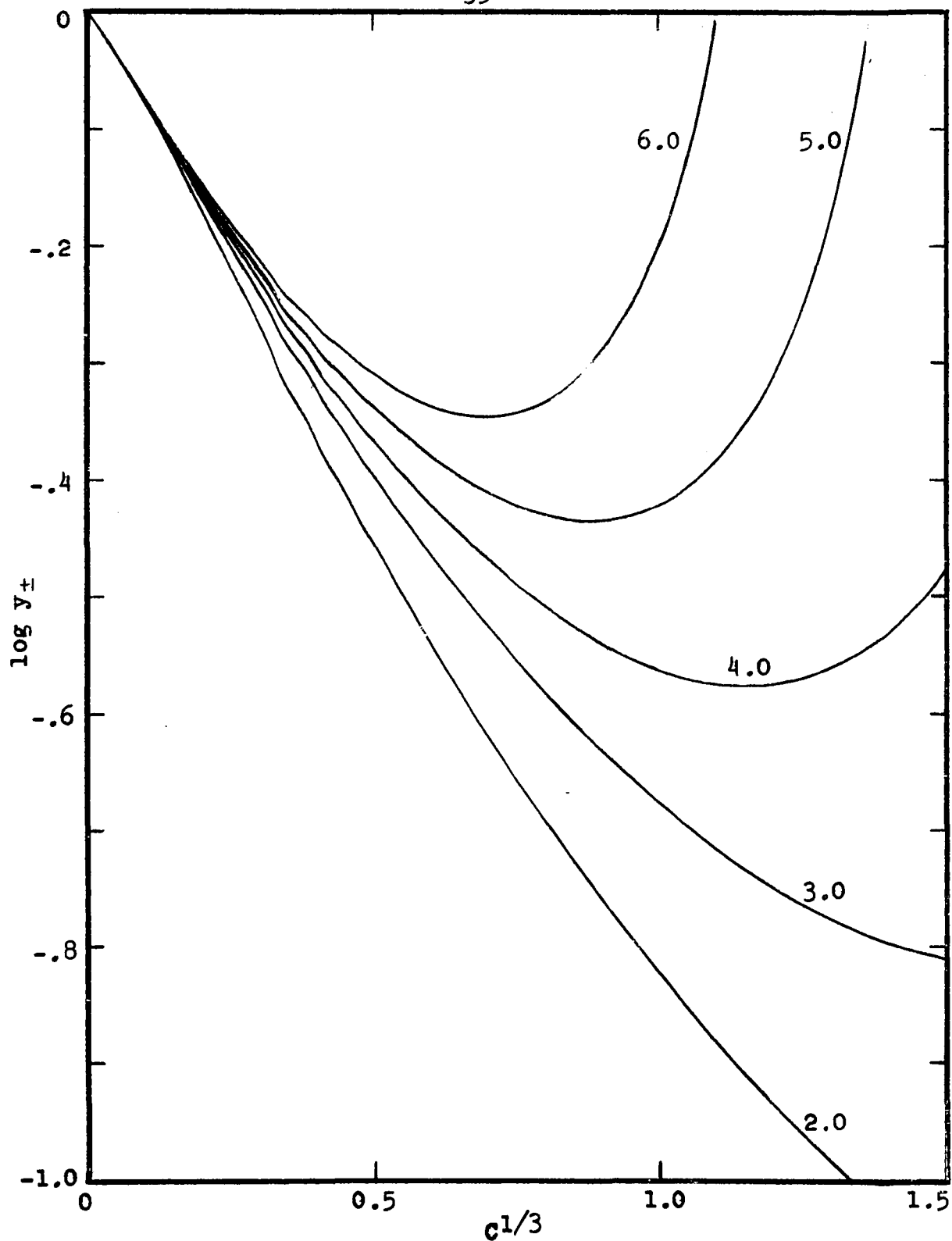


Fig. 10--Theoretical activity coefficients for 2-1 or 1-2 electrolytes in aqueous solution at 25° for different values of a .

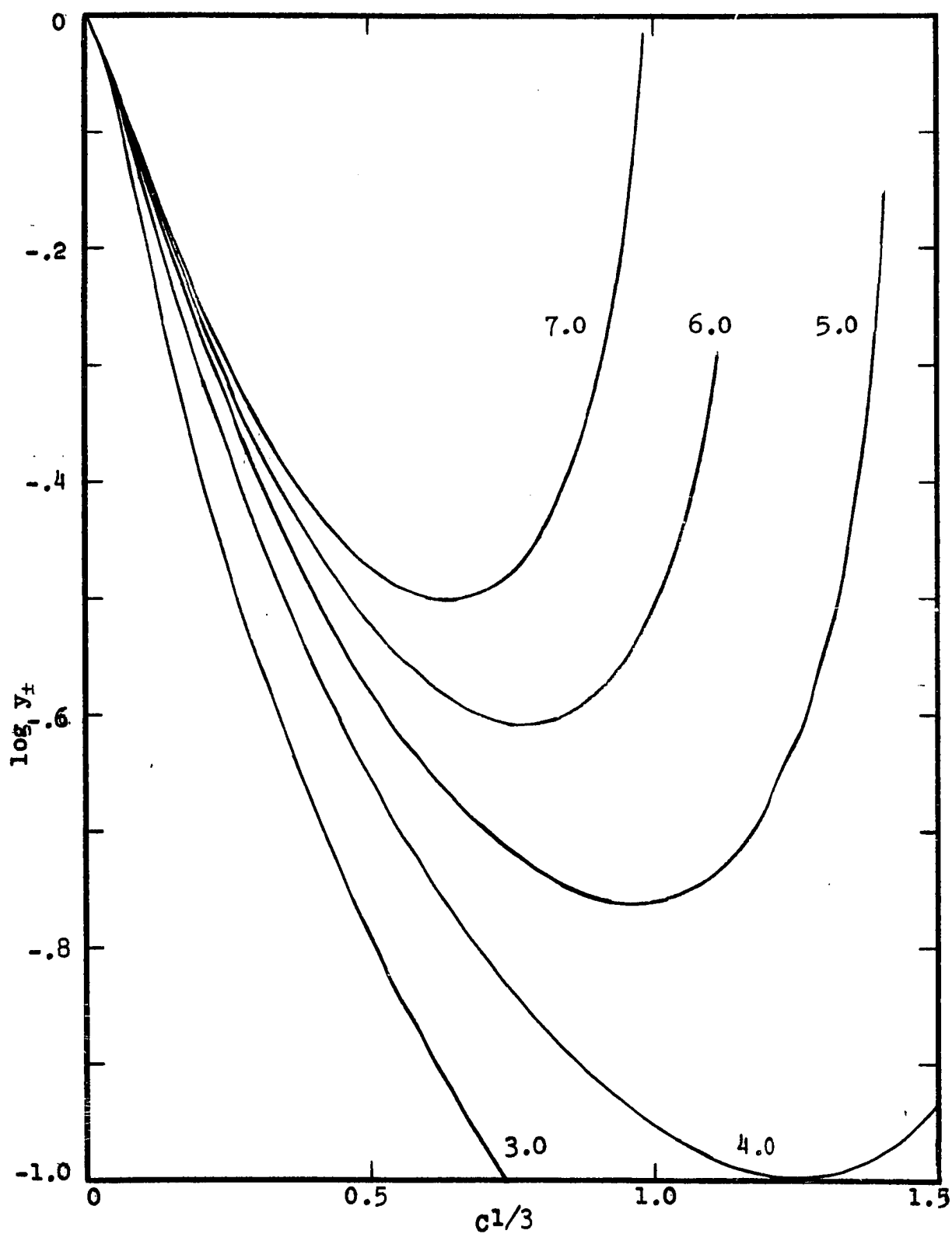


Fig. 11--Theoretical activity coefficients for 3-1 or 1-3 electrolytes in aqueous solution at 25° for different values of a .

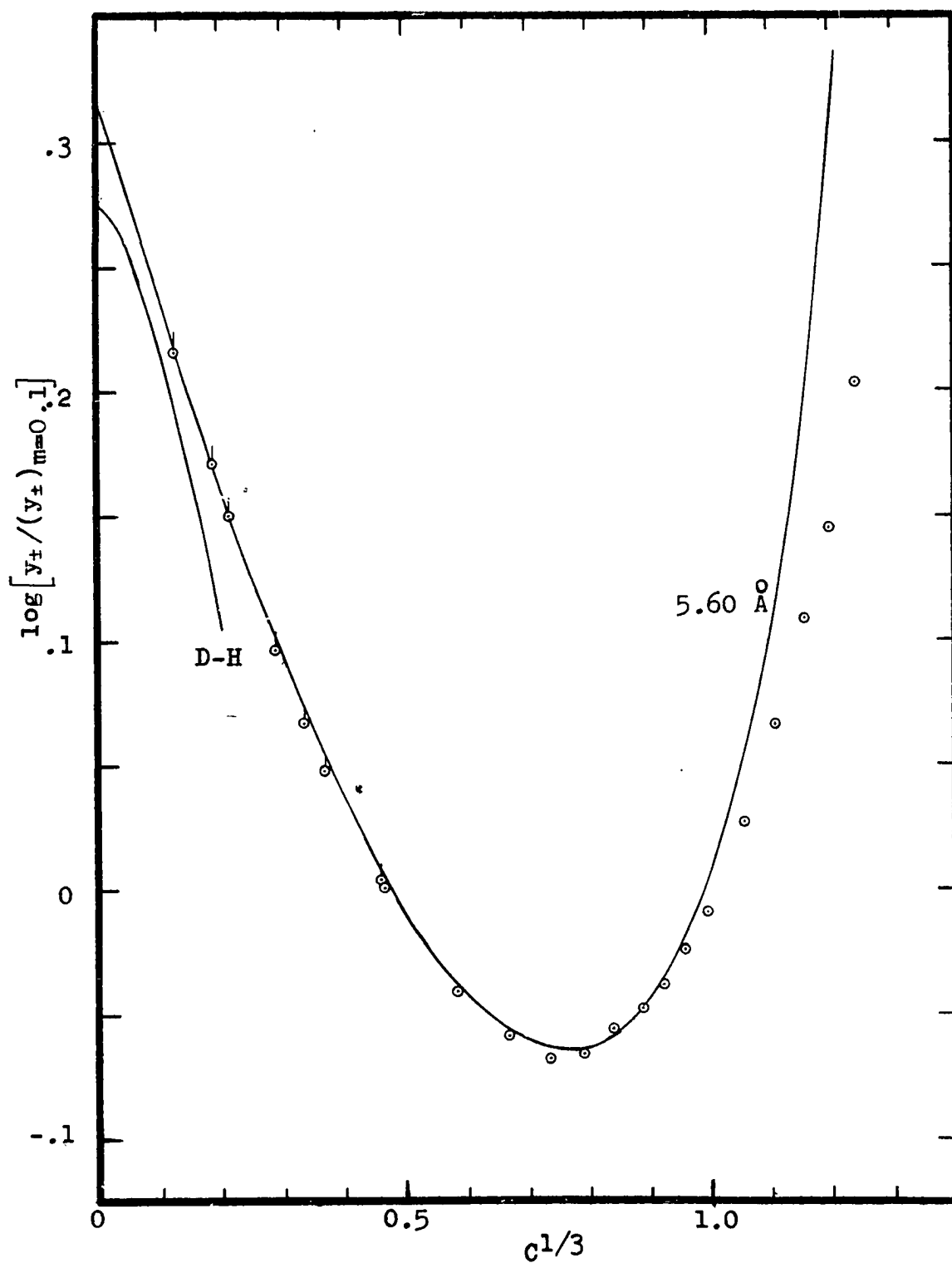


Fig. 12--Activity coefficients of aqueous calcium chloride at 25° with theoretical curve calculated for the denoted value of a and Debye-Huckel limiting equation. $\odot$, Shedlovsky and MacInnes; $\circ$, Robinson.

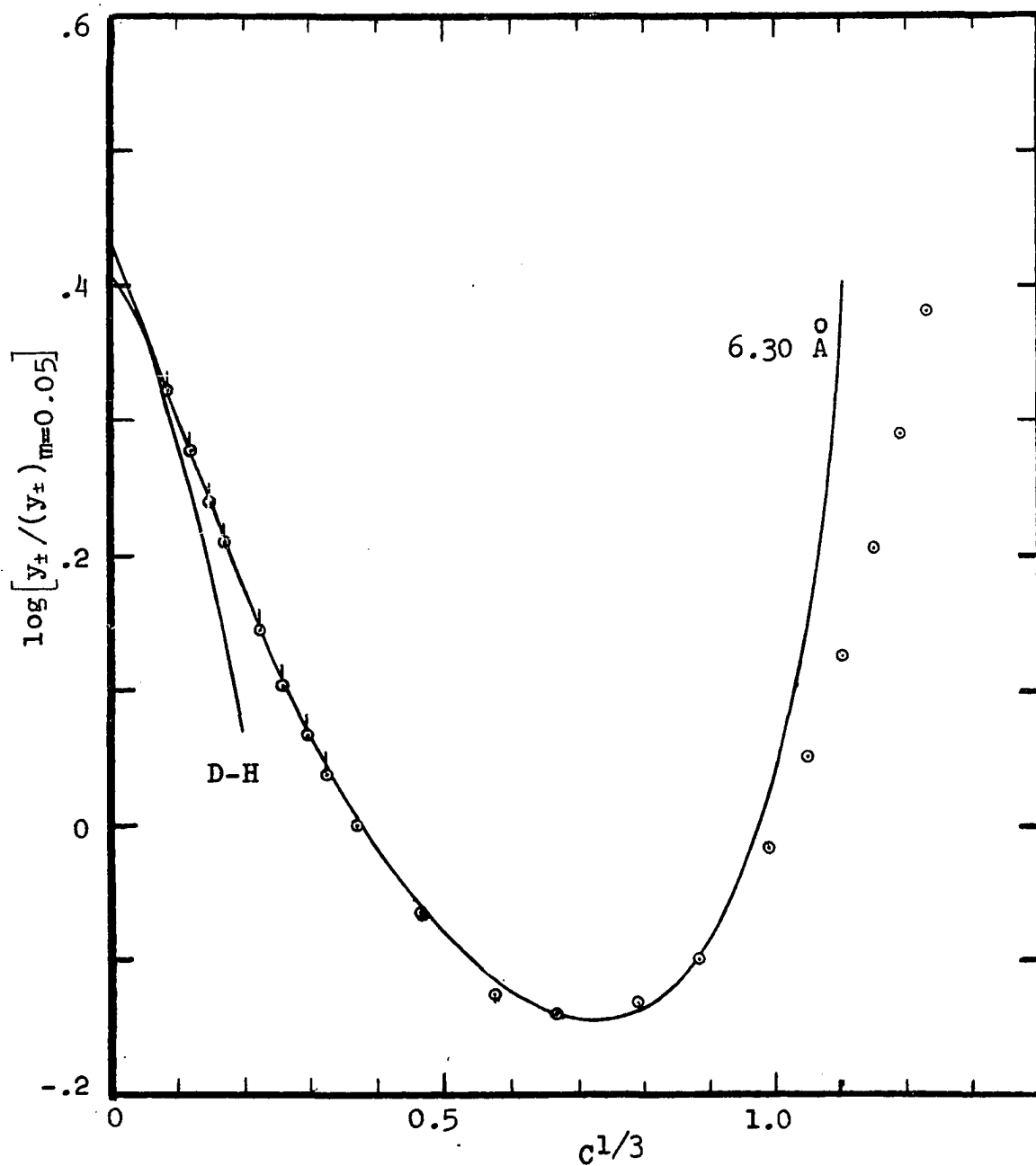


Fig. 13--Activity coefficients of aqueous lanthanum chloride at 25° with theoretical curve calculated for denoted value of a and Debye-Huckel limiting equation. $\odot$, Shedlovsky and MacInnes; $\circ$, Robinson.

coefficients up to moderately high concentrations. Furthermore, it describes qualitatively the correct shape and magnitude of the activity coefficient curves to much higher concentrations.

Thermochemical Quantities

Only low concentration limiting cases of thermochemical properties are presently interpretable on the basis of the cell theory. Preliminary calculations with the complete equations given in Chapter III show the right order of magnitude for the various properties and in many cases predict the correct shapes of the curves. But because of the highly individual thermochemical characteristics displayed even among electrolytes of the same valence type, the good general agreement of theory with experiment obtained for activity coefficients is not observed for these properties. This lack of correspondence is directly traceable to the ion size parameter $\underline{a}$. An assumption involved in the thermochemical equations of Chapter III is the constancy of $\underline{a}$ with concentration and temperature. If either or both of these assumptions fail to hold, however, the thermochemical behavior of the electrolyte may be profoundly affected. This may be the case even though the temperature dependence of $\underline{a}$ has no effect on the activity coefficient at a given temperature, and the concentration dependence an observable effect only at rather high concentrations.

The following comparisons of heat-of-dilution data

with the limiting cell theory equations typify the results obtained for thermochemical quantities in general. The equations employ for the dielectric constant of water the value of Malmberg and Maryott (21) and the density data of Chapuis as formulated by Tilton and Taylor (34). The limiting equation for the relative partial molar heat content for a water solution of a 1-1 electrolyte at 25° is seen from equation (3-17) to be

$$\bar{L}_2 = 284.8C^{1/3} \text{ cal/mole} \quad (4-1)$$

Equation (3-20) then gives the limiting relation for ϕ_L :

$$\phi_L = 213.6C^{1/3} \text{ cal/mole} \quad (4-2)$$

Figure 3 shows that (4-2) predicts exactly the limiting slope for the integral heat of dilution of sodium chloride (35). Agreement over such an extended concentration range is probably fortuitous, but the concordance is nonetheless striking. The Debye-Hückel limiting equation is also plotted. In the neighborhood of 0.001 M it predicts the correct slope, but veers upward beyond this point. The intercept for the square root curve comes from Harned and Owen (36). Equation (3-20) predicts a slope for ϕ_L of $747.6C^{1/3}$ for 2-1 electrolytes and $1552C^{1/3}$ for 3-1 electrolytes. Data for calcium chloride (37) and lanthanum nitrate (38) are plotted along with the limiting cell model slopes in Figure 14. The D-H limiting curves are also shown--the intercept for calcium chloride being taken from Harned and Owen (39); and for lanthanum nitrate from the plot of ϕ_L of Lange and Miederer

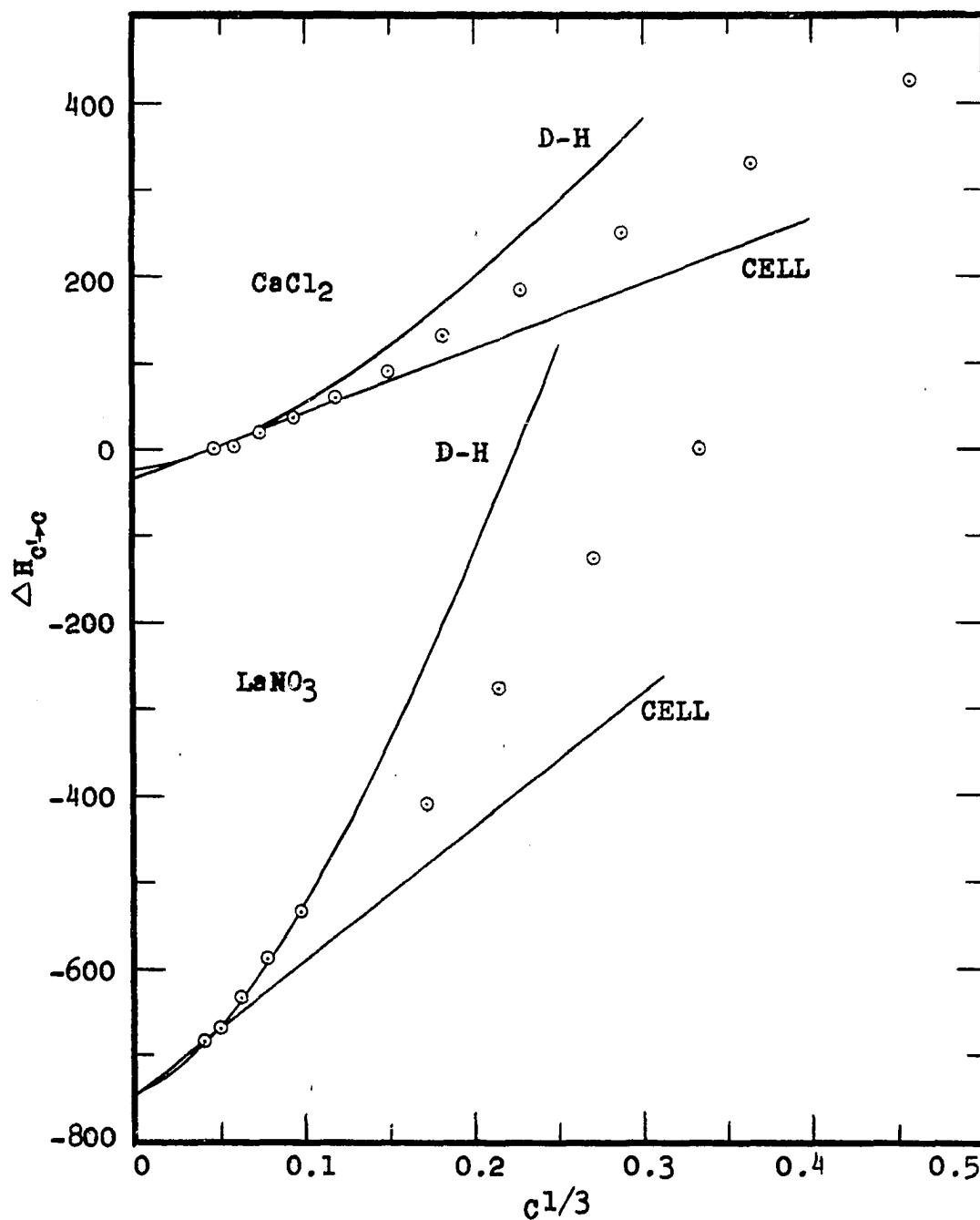


Fig. 14--Heat of dilution of aqueous calcium chloride ($C' = 0.0001059$) and lanthanum nitrate ($C' = 0.0384$) at 25° with theoretical limiting slopes.

(38). The cell model theoretical limiting slopes of ϕ_L are not inconsistent with the lowest concentration experimental slopes for calcium chloride and lanthanum nitrate, but the data do not reach low enough concentrations for unambiguous verification.

Conductivity

The equations for conductivity based on Onsager's limiting expression, assuming κ to be dependent on the particular model, are plotted for hydrochloric acid at 25° in Figure 4. Included are the cell model, lattice model, and Debye-Huckel slopes. Plots of potassium and sodium chloride conductivity data compare similarly with the theoretical slopes.

Data for the equivalent conductance of calcium chloride (40) and lanthanum chloride (41) are compared with the limiting Debye-Huckel and cell model equations in Figure 15. The limiting cell model slope is in almost perfect agreement with experiment for calcium chloride, but the theoretical slope is several per cent higher than the experimental in the case of lanthanum chloride.

Comparison of Results of Lattice Model and Cell Model

The limiting slopes of $\log y_{\pm}$ curves are about 10% more negative for the cell model than for the lattice model, corresponding to a 10% more negative electrostatic energy. The concentration dependence of the lattice model slope is the same as that of the limiting cell model slope, but in

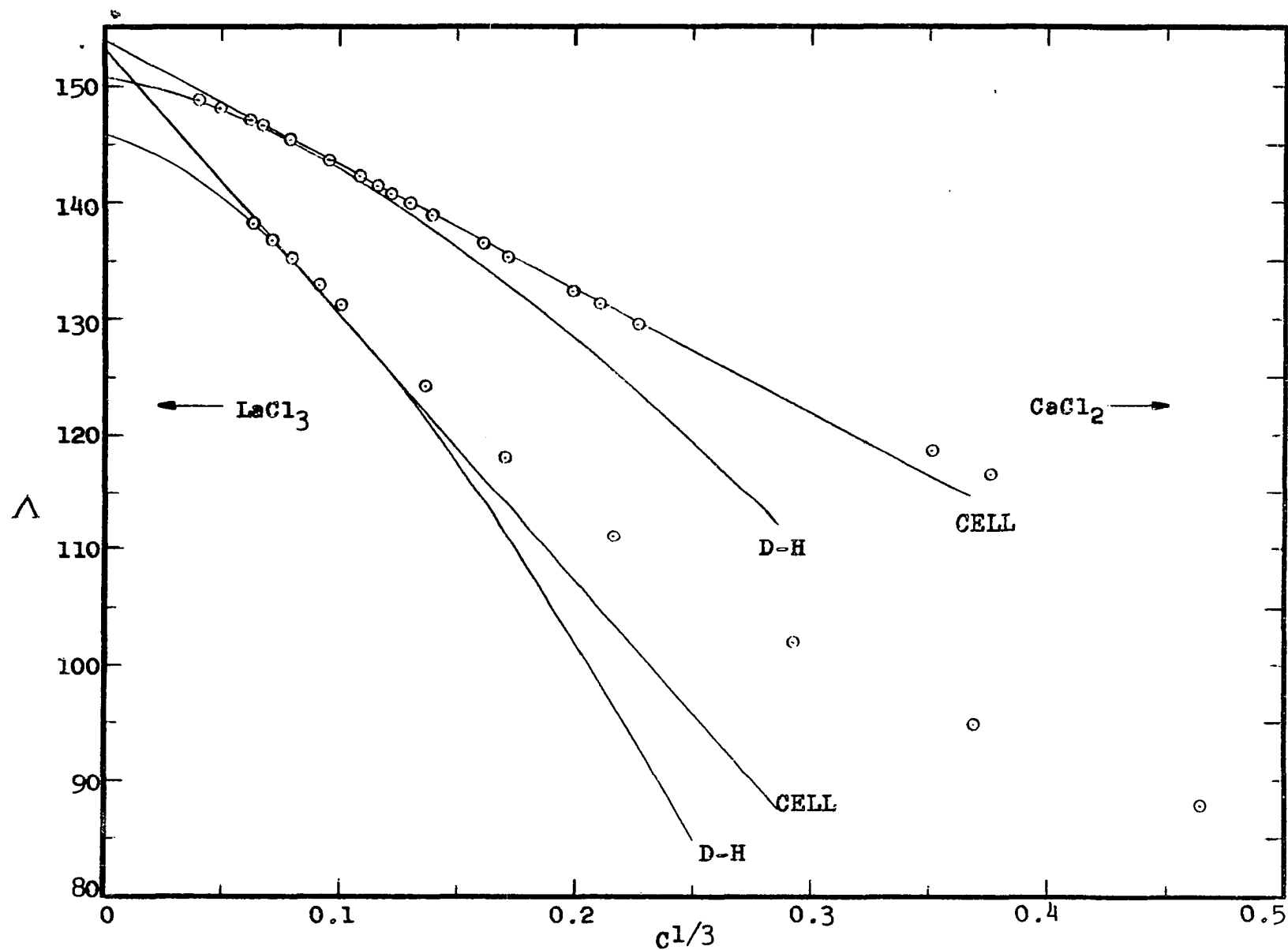


Fig. 15--Equivalent conductance of aqueous calcium chloride and lanthanum chloride at 25° with theoretical limiting slopes.

the cell model the dependence is more complicated at observed low concentration owing to the importance of higher order terms. The significance of the latter terms and of the ion size parameter in the cell model brings slopes at low concentration into even closer correspondence with those actually observed than the lattice model.

The approximately 10% difference between the limiting cell model slope and lattice model slope also appears in comparing predicted heats of dilution and conductivity.

CHAPTER V

EXTENSION OF CELL THEORY TO HIGHER CONCENTRATIONS

The problem of interpreting the behavior of concentrated solutions is one that faces any theory of solutions. Modifications of the Debye-Hückel theory, all of a completely empirical or semiempirical nature, have met with varying degrees of success. These approaches have in general treated the question in terms of decreasing dielectric constant with increasing concentration (41,42), decreasing volume of "free" solvent with increasing concentration due to ionic hydration (43,44), or excluded volume effects on the ions (45).

In the cell theory explicit consideration of the hydration aspect is unnecessary. The molar scale employed throughout is based on the overall solution volume which is independent of whether or not the ions are hydrated. Of course hydration cannot be disregarded, for it is the extent of hydration that determines the distance of closest approach of the ions. Furthermore, the effect of changing dielectric constant is always present no matter what the concentration scale may be. The effect of a smaller di-

electric constant on the ionic activity coefficient is to decrease its value. Qualitatively, the same effect is to be expected with increasing concentration as a result of decreasing distance of closest approach of the ions. As the ionic concentration increases, the average degree of hydration will decrease owing to competition for the water of hydration by a larger number of ions, and the apparent value of a will decrease.

It would obviously be an advantage to incorporate the dielectric constant and ion size effects rather than treating each separately. Since the ion size parameter a must be adjustable in order to fit experimental data, the advantage of incorporation would be enhanced by letting the value of a reflect both effects. That this is a reasonable approach is pointed out by Robinson and Stokes (46). It has been shown that nearly all of the lowering of the observed bulk dielectric constant occurs in the first layer of water molecules surrounding an ion. If this primary hydration sheath is considered to be part of the solute particle, then the bulk dielectric constant of the solvent may be appropriately used.

It has been found that plots of the apparent values of a required to achieve complete agreement with experimental activity coefficient data are linear in the inverse cube root of concentration over a wide range. Such a plot is shown for potassium chloride electromotive force data (23) in Fig-

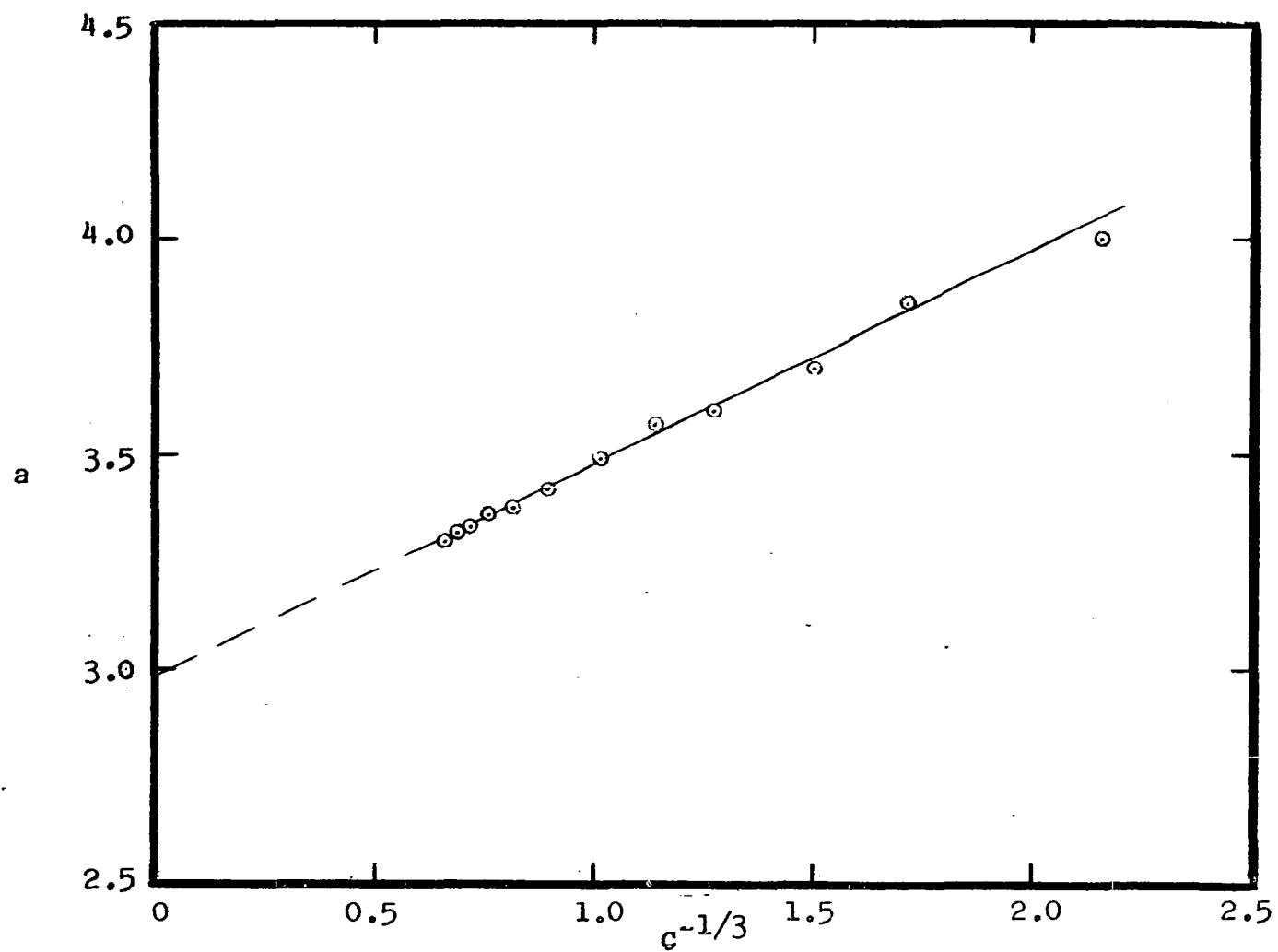


Fig. 16--Apparent value of ion size parameter a required to exactly reproduce activity coefficients.

ure 16. One way of interpreting this relation is by means of an excluded volume approach. Referring back to Chapter III, it is seen that the first equation for the ionic partition function prior to (3-1) contains a free volume factor. The free volume was at that point set equal to the total cell volume minus the spherical volume described by the mean distance of closest approach, or $4\pi(R^3 - a^3)/3$. A better procedure consists in utilizing the effective excluded volume encountered by a pair of colliding bodies. A treatment along these lines leads to a relation for the effective exclusion volume for potassium chloride whose slope is close to that observed in Figure 16.*

*The author is indebted to Dr. G.W. Murphy for this information.

CHAPTER VI

SUMMARY AND CONCLUSIONS

An analysis of the extrapolation problem with low-concentration data of three typical strong 1-1 electrolytes leads to the following conclusions: (1) Intercepts, such as E^0 in the analysis of electromotive force data, and activity coefficients derived therefrom, are not unique but depend upon the model chosen to represent thermodynamic non-ideality; (2) at low concentration, the cube root of concentration yields a better fit of equilibrium data than does the square root, and is not inconsistent with conductivity data; (3) slopes of such plots are in good agreement with the predictions of an expanded rock-salt lattice model.

The fact that an arrangement of ions as well-ordered as that in a rigid lattice cannot possibly exist in a fluid solution gives rise to the cell approach. The cell model serves as a bridge between the rigid lattice and conventional interionic attraction theory.

At vanishingly small concentrations the Debye-Hückel theory predicts square-root dependence of properties; the cell theory cube-root. But with the possible exception of

conductivity and heat of dilution, it is doubtful that data on single electrolytes are available which will permit a direct test of limiting equations. Available low-concentration data are consistent with both theories. Ion size effects and higher-order terms are important in this concentration region.

Extrapolations based on the two theories will yield two mutually exclusive sets of intercepts. The cell theory goes beyond this in its ability to interpret concentrated solutions.

Of course a square-root and a cube-root limiting relation cannot both be right in a finite concentration range. Only a future extension of reliable experimental techniques into the presently inaccessible region can settle the issue. The question of what theory is correct in this region is actually less important than it may appear. If a model on which a limiting equation is based is consistent with data obtained at experimentally realizable concentrations, it becomes, by extrapolation to infinite dilution, an arbitrary reference state which may be convenient to use even if it is incorrect on theoretical grounds at finite concentrations below those experimentally realizable. Hypothetical reference states are common choices in thermodynamic analyses. This is the only thermodynamic meaning of the ambiguity in activity coefficients referred to earlier. Intercepts from extrapolations depend on the chosen

reference state, and, these in turn, determine a set of activity coefficients.

The work that remains to increase the usefulness of the cell theory is indicated in Chapters IV and V. The first step is to provide better agreement of theory with thermochemical measurements, and the second is to extend the theory to higher concentrations. Hopefully, both of these objectives may be accomplished through the free volume approach mentioned in Chapter V. A treatment of this type appears to be feasible, and if so, the cell theory can still be utilized with only the single adjustable parameter a.

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APPENDIX

FORTTRAN PROGRAM FOR COMPUTING ACTIVITY COEFFICIENTS ACCORDING TO CELL THEORY

```
1  READ 35, A, Z, D, T, MAX
40  IF (A) 41, 41, 2
41  STOP 13
2   X1 = Z*8.3540 E-4/(D*T)
3   A = A*1.0 E-8
39  X = X1/A
4   P = 0.0
5   DO 33 N = 0, MAX
6   H = 1.0
7   F = 1.0
8   EIX = 0.577216 + LOGF(X)
9   T = X**H/(F*H)
10  EIX = EIX + T
11  H = H + 1.0
12  F = H*F
13  IF(T - 1.0 E-6) 14, 14, 9
14  RECIP = 1.0/X
15  TERM = EXPF(X)*(RECIP*(1.0 + RECIP*(1.0 + 2.0*RECIP)))
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```

16 IF (P) 17, 17, 20
17 S1 = (EIX - TERM)/6.0
18 PRINT 35, A, Z, D, T, MAX
38 PRINT 36
19 GO TO 28
20 S2 = (EIX - TERM)/6.0
21 DIFF = S1 - S2
22 IF (DIFF) 1, 1, 23
23 B = 3.0*X*X*X*DIFF
24 YLOGE = -LOGF(B)
25 YLOG = 0.43429*YLOGE
26 CLY2K = 0.051386*YLOGE
27 PRINT 37, CUBRC, C, YLOGE, YLOG, CLY2K
28 P = P + 1.0
29 CUBRC = 0.1*P
30 C = CUBRC*CUBRC*CUBRC
31 R = 7.346 E-8/CUBRC
32 X = X1/R
33 CONTINUE
34 GO TO 1
35 FORMAT (4F10.5, I10)
36 FORMAT (6H CUBRC, 6X, 5H C , 4X, 6H YLOGE, 5X, 5H YLOG,
5X, 6H CLY2K)
37 FORMAT (1X, F4.1, 4X, 4F10.5)

```

Input data: A, ion size parameter a in Angstrom units;
 Z, electrostatic energy valence coefficient; D, dielectric
 constant; T, absolute temperature; MAX, maximum number of

concentration points desired in computation.

Output data: C, molar concentration; CUBRC, $C^{1/3}$;
YLOGE, $\ln y_{\pm}$, YLOG, $\log y_{\pm}$; CLY2K, $2k \log y_{\pm}$.