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Thermodynamics of strong electrolyte solutions: Prediction of osmotic coefficients by pair correlation function method

Rim, One Kwon, Ph.D.

New Jersey Institute of Technology, 1991

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Thermodynamics of Strong Electrolyte Solutions: Prediction of Osmotic Coefficients by Pair Correlation Function Method

By

One Kwon Rim

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ABSTRACT

Title of Dissertation :

Thermodynamics of Strong Electrolyte Solutions: Prediction of Osmotic Coefficients by Pair Correlation Function Method.

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Doctor of Philosophy, 1991

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Thermodynamic properties (osmotic coefficients) of strong electrolyte solutions have been studied by the method of statistical mechanics. First the charged soft sphere potential is developed based on the Pauling type model. Next the charged soft sphere potential is converted to the thermodynamically corresponding charged hard sphere potential by way of the perturbation method developed by Verlet and Weis. Simultaneously, the radial distribution function is developed by modification of the Exponential theory through introduction of the Stillinger-Lovett moment condition. The effective hard sphere diameter values calculated by the perturbation method are combined with the modified Exponential theory, and these quantities are integrated to get the osmotic coefficients. These procedures are applied to 28 single electrolyte solutions. They are 1-1, 1-2, and 2-2 type strong electrolyte solutions. The calculated results are compared with

Pitzer's model. Generally, the new model gives better results than Pitzer's. This model shows excellent results at low concentrations, as well as at higher concentrations up to the limitation of the experimental data in most of the cases.

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Chapter 1. INTRODUCTION

A. Background and History

The practical interest in electrolyte solutions can be attributed to their frequent presence in biological and industrial processes. For example, many of the process problems in the oil, gas, and chemical industries require accurate knowledge of the thermodynamic properties of electrolyte solutions and electrolyte solutions are also involved in clean-up processes such as acid gas removal and sour water stripping. Electrolytes also play an important role in enhanced oil recovery processes. Petroleum sulfonates form a typical class of surfactants being considered for oil recovery.

From a theoretical point of view, electrolyte solutions exhibit appreciable deviations from ideality, even at ambient conditions. This kind of behavior was recognized for the first time by Arrhenius(1) about a hundred years ago. After decades, in 1923, an effort in describing dissolved salts was done by Debye and Hückel.(2) This theory can be regarded as the first successful theory of electrolyte solutions. Briefly, they combined Poisson's equation of electrostatics with the Boltzmann factor of statistical mechanics to derive a nonlinear partial differential equation for the electrostatic potential about a central ion in solution. The partial differential equation is now known as the Poisson-Boltzmann equation. A key step in the Debye-Hückel treatment is the linearization of this nonlinear equation. The linearized partial differential equation is easily solvable and leads to simple expressions for the thermodynamic properties of electrolyte solutions.

Later Fowler(3)and Onsager(4) showed that the Debye-Hückel theory is exact in the dilute concentration range and also showed that the practical region of its applicability is limited to concentrations less than 0.01M(mol/liter) for aqueous 1-1 electrolytes. It is important to realize that the small concentration limit of the Debye-Hückel theory is not simply due to the linearization of the Poission-Boltzmann equation. In fact, it has been clearly demonstrated theoretically by many authors like Kirkwood and Poirier(5) that the Poisson-Boltzmann equation itself is rigorously valid only in the limit in which linearization becomes possible, i.e. in the limit of zero ionic strength. However, Debye-Hückel theory is considered a milestone in the theory of the electrolyte solution.

There was little improvement after the Debye-Hückel theory until 1950, when Mayer(6) reformulated his cluster expansion theory(7-9) of nonideal gases to solutions of electrolytes. The end result of his analysis was a virial type expansion of the thermodynamic properties of ionic solutions. He was able to show that the Debye-Hückel theory results from the lowest order in the concentration and yielded results that compare favorably with experiment up to 0.1M for 1-1 type electrolytes.(10)

The Mayer theory remained the most successful theory of ionic solutions until the late 1960s when several significant advances appeared simultaneously. One of the modern (after Mayer) statistical mechanical theories of ionic solutions was presented by Rasaiah and

Friedman(11) in 1968. Instead of formulating the statistical thermodynamics in terms of a virial type expansion as Mayer had done, Rasaiah and Friedman utilized techniques that had been developed in the theory of liquids. These techniques consist of deriving integral equations for the radial distribution function (pair correlation function), which in the case of ionic solutions represents the distribution of ions about one another. The solution of these integral equations requires a fairly elaborate numerical procedure, but once this is done, the thermodynamic properties of the solution follow by straightforward statistical thermodynamics. They found that one of this class of integral equations, called the hypernetted chain (HNC) equation,(12) gives the best results for ionic solutions up to 1 M for a 1-1 type electrolyte.

The Mayer theory for electrolyte solutions is based on cluster theory, which was developed for nonelectrolyte systems. Similarly, another theory, which would be the basis for a different model of electrolyte solutions, was developed in the late 1950s. In 1958, Percus and Yevick(13) developed a theory of molecular distributions, which can also be expressed as an integral equation, and which provides a more accurate alternative to the simple Boltzmann distribution. Their theory of pair correlation functions is based on the combination of collective coordinate analysis(14) and cluster expansion theory for crystalline structures. It is not limited to dilute solutions, but does reduce to the Boltzmann distribution in the low concentration limit.

In 1970, Waisman and Lebowitz(15) were able to obtain an analytical solution for a special case of the Percus-Yevick (PY) theory for charged hard spheres embedded in a dielectric continuum which was known as the Mean Spherical Approximation (MSA). This PY theory was applied to electrolyte solutions. Although their results were limited to equal-size ions (Restricted Primitive Model), in 1975 Blum(16) solved the MSA for the case of arbitrary ion size (Primitive Model). Later, Blum and Høye(17) presented analytical expressions for the thermodynamic properties of electrolyte solutions as given by MSA theory.

Also in 1970, Card and Valleau(18)undertook a program of using Monte Carlo techniques to evaluate directly the statistical mechanical partition function of a restricted primitive model consisting of several hundred ions. This was a very important advance since it provided numerical data on the restricted primitive model. Since, of course, real experimental systems are only modeled by the restricted primitive model, such Monte Carlo calculations can be considered as the analog of experimental data. These "data" are indispensable in comparing competitive theories since the intermolecular (or interionic) model is completely specified. Thus, discrepancies are due to inadequacies of the theory and can not be dismissed by an adjustment of parameters.

Almost simultaneously (1970-1972) with the previous theories or methods, Andersen and Chandler(19-21) developed a convergent expansion for the Helmholtz free energy by transforming the partition function into the Fourier domain. The first term in this expansion corresponds to the so-called random phase approximation (RPA). A faster converging expansion is obtained when a special optimization of the long-range, Coulombic interaction potential, inside the hard sphere (the ion is considered as a charged hard sphere) is performed. As a result of this optimization, inclusion of only the first term in the expansion, referred to as the optimized random phase approximation (ORPA), is found to be identical to MSA. The approximation obtained by inclusion of the second term in this expansion, called the optimized random phase approximation + the second mode (ORPA+a_2), gives excellent agreement with the Monte Carlo calculations of Card and Valleau.

This successful initial approach was followed by an even more successful approach(22-25) which arises through a somewhat complicated topological reduction of the graphs (cluster diagrams) that occur in the Mayer theory and the same optimization of the long range interaction potential inside the hard sphere. This theory is called the optimized random phase approximation plus "virial correction," ORPA + B_2, the results of which are essentially identical to those obtained by Rasaiah and Friedman for a 1-1 electrolyte, but the applicable range is up to 2 M and the numerical calculations are less complicated. An important result of this work is the so-called exponential approximation for the interionic radial distribution function (pair correlation function), an approximation which Andersen, Chandler show is almost exact if formulated according to their prescription. The limitation of this exponential approximation is that it becomes exact only in the limit of low concentrations (below 2M) and/or weak interactions (1-1 type). Their preliminary calculations on fused salts indicate that the exponential approximation for the pair correlation function at contact (surface) is drastically too large for high densities and/or strong Coulombic interactions. This breakdown of accuracy begins to appear in the 2-2 type.

In 1975, Olivares and McQuarrie(26) proposed a modification of the exponential approximation. Their suggestion was to introduce the moment condition suggested by Stillinger and Lovett.(27-29) There was an improvement in that the 2-2 type electrolyte could be analyzed by this approach. The limiting maximum concentration is still 2M, and only the Restricted Primitive Model (RPM) can be analyzed.

In 1985, Boyle and McQuarrie(30) tried to calculate osmotic coefficients using the perturbation approach. The innovation of this method was the comparison of the various types of interaction potentials for application of the perturbation approach. The potentials used are the charged soft sphere, charged hard sphere, and charged square well potentials. But still only 1-1 electrolytes at less than 1M concentration were treated.

In 1985, Landis(31) correlated about 100 industrial salt solutions for the calculation of osmotic coefficients by the application of MSA. He suggested that the exponential approximation could be used to calculate osmotic coefficients of several salts and salt mixtures up to the limitation of the published experimental data by varying the cation diameter proportional to the concentration at fixed temperature. To reduce the huge computation time, he replaced the modified form of MSA by introducing some additional parameters instead of using the exponential approximation. But with the advent of high speed computers and advanced numerical techniques, the "huge computation time " is no longer a serious problem in this case.

There are some other approaches,(32-34) which are different from the primitive model in that they consider the solvent granularity. But these are still in an early stage of development, and many problems remain to be solved.

All of the discussed theories can be summarized as being built on the viewpoint of statistical mechanics. But the 1970's and early 1980's also produced other types of approaches that though they may include the concept of statistical mechanics, mainly depend on the use of semi-empirical parameters. They were developed by Bromly,(35) Meissner,(36) Pitzer,(37) and Chen.(38) Among these, the Pitzer model is the most widely used one at the time of this writing, and the Chen model is a new method which shows promise. The characteristics of the two models follow.

In 1973, K.S. Pitzer developed an accurate model for electrolyte solutions to concentrations as high as 6 molal (m). His model includes the effect of the finite size of ions, but is still limited to an expansion of the Boltzmann distribution. Therefore, several (between three and six) parameters are introduced which have questionable physical meaning. The reliable concentration range is limited to a maximum 6 m, and for some salts the limitation is even more severe.

In 1979, Chen et al introduced a new approach to the theory of electrolyte solutions. Their model is based on the local composition theory for nonelectrolyte systems of Renon and Prausnitz,(39) and has been applied to solvents and mixtures of solvents other than water. The main difference between the Pitzer and Chen models is that the former dealt mainly with strong electrolytes while the latter began to treat weak electrolytes and non-aqueous solutions. However, the Chen model is subject to the same limitations as the Pitzer model; namely, concentrations below 6 m.

The advantage of these two semi-empirical models relative to the previously discussed theories is that they can be applied at higher concentrations, at the expense of introducing more parameters.

As a summary of this section, the available models or theories have the following limitations. The maximum applicable concentration is limited to around 6 m, and this is possible only at the cost of introducing some empirical parameters. There is still no effective model for the higher concentration, saturated and supersaturated regions. The molecular theory-based models show poor accuracy or have lower applicable concentration ranges, but do avoid the use of empirical parameters. Clearly, there is a need for improvement of this kind of model.

B. Objectives and Strategy

There are two objectives for this work. The first is to approach the study of electrolytes from a rigorous molecular point of view. The second one is to develop a model which is valid in a higher concentration range for strong electrolytes. To achieve these objectives, all the models and theories should first be critically reviewed.

As described in section A, two kinds of approaches have been identified. One is the approach that is based on the rigorous molecular point of view, and the other is the approach that, though also based on the molecular point of view, is less rigorous and uses semi-empirical parameters. The first category includes, Debye-Hückel theory, Mayer theory, HNC , PY, MSA, ORPA, ORPA+B_2, Exponential Approximation theory (EXP theory), Modified Exp (by Olivare & McQuarrie), Perturbation and the work done by Landis. The second includes the models of Bromly, Meissiner, Pitzer and Chen.

Generally the models in the first group are valid at relatively lower concentration ranges than those in the second category. But they are also relatively less empirical- parameter dependent, give analytical or theoretically rigorous solutions and permit most of the thermodynamic properties to be derived from one quantity. The models from the second category have higher accuracy and are valid at higher concentrations. Also, the computation procedure is simpler. Some models are hand calculable or require little computing time. They are therefore very practical, but are strongly parameter-dependent. Thus it is difficult to improve the model theoretically for higher concentration ranges.

The best approach seems to be to adapt the advantages of both cases if possible. Therefore, it was decided to start from the first approach because it allows improvement by manipulation of current methods. In this thesis, the combination of the perturbation approach and the modified exponential approximation (EXP theory) is considered as the basis for further development. The reasons will be detailed in the following chapters.

Chapter 2. BASIC THEORY

A. Activity Coefficients and Osmotic Coefficients in Electrolyte Solutions

The activity coefficient, f, is conveniently defined in the usual way in terms of the chemical potential, μ, of an electrolyte. For a salt of charge-type $Z^+:Z^-$ corresponding to stoichiometry υ_+, υ_-, i.e., $M^{z+}_{\upsilon+}A^{z-}_{\upsilon-}$,

$$\mu = \upsilon_+ \mu^o_{M^{z+}} + \upsilon_- \mu^o_{A^{z-}} + \upsilon_+ RT\, ln\, a_{M^{z+}} + \upsilon_- RT\, ln\, a_{A^{z-}} \qquad (2.1)$$

$$\mu = \upsilon_+ \mu^o_{M^{z+}} + \upsilon_- \mu^o_{A^{z-}} + RT\, ln\, (C_{M^{z+}})^{\upsilon+} (C_{A^{z-}})^{\upsilon-}$$

$$+ RT\, ln\, (f_{M^{z+}})^{\upsilon+} (f_{A^{z-}})^{\upsilon-} \qquad (2.2)$$

where the last term is the nonideal free energy of the system associated with ionic interactions and any other effects giving rise to nonideality. In sufficiently dilute solutions, this latter term is accounted for primarily by long-range coulombic interactions, as treated at various levels of the Debye-Hückel theory, or as in more modern treatments such as those introduced in chapter 1.

From the last term of Equation (2.2), it is also useful to introduce the definition of the mean activity coefficient $f_\pm$:

$$f_{\pm} = \left[(f_{M^{z+}})^{\upsilon+} (f_{A^{z-}})^{\upsilon-} \right]^{1/(\upsilon+ + \upsilon-)} \tag{2.3}$$

normally used in discussing the experimental activity coefficients of electrolytes. While equation (2.1) or (2.2) suffice formally to represent the thermodynamic behavior of electrolytes in solution at any concentration, no account is explicitly given by these equations of the activity behavior of the solvent as a function of the salt concentration. This can be introduced through the Gibbs-Duhem equation

$$n_1\, d\mu_1 + n_2\, d\mu_2 = 0 \tag{2.4}$$

which relates differentially the chemical potential μ_1 of solvent 1 to the chemical potential of μ_2 of solute 2, through the composition defined by n_1 and n_2 where n_1 and n_2 are the number of moles of solvent and solute respectively. Equation (2.4) is important because it implies a reciprocal variation of solvent chemical potential with changing solute chemical potential, i.e., with changing composition: $d\mu_1 = -(n_2/n_1)\, d\mu_2$. Since μ_1 and μ_2 involve the activities in equations (2.1) and (2.2), Equation (2.4) can be written in the form

$$d\, ln\, a_1 = -(n_2 /n_1)\, d\, ln\, a_2 \tag{2.5}$$

Applied to a solution at molality m in a solvent s of molecular weight W_s, Equation (2.5) gives

$$-\frac{1000}{W_s}\, d\, \ln a_s = \upsilon\, m\, d(\ln f_{\pm}\, m) \tag{2.6}$$

where $\upsilon = \upsilon_+ + \upsilon_-$, so that solvent activity, a_s, is related to solute activity, ($f_{\pm}$ m). One thing that should be considered is that the activity of the pure solvent is unity. In dilute solutions of electrolytes, the activity and even the activity coefficient of the solvent vary only slightly from unity, so that the reporting of solvent properties in these terms requires a large number of significant figures. For example,(40) at 298.15 K, a 2 m solution of potassium chloride has a water activity of 0.9364; this results in a water activity coefficient of 1.004 which does not reflect the departure from ideality indicated by the solute activity coefficient. To overcome this problem and to simplify calculations, experimentalists have traditionally defined the so-called osmotic coefficient, ϕ_m :

$$\upsilon\, m\, \phi_m = -\frac{1000}{W_s} \ln a_s \tag{2.7}$$

Equation (2.6) may be transformed to

$$(\phi_m - 1)\frac{dm}{m} + d\phi_m = d\ln f_{\pm} \tag{2.8}$$

which, on integration, gives the well-known relation

$$\ln f_{\pm} = (\phi_m - 1) + \int_0^m [(\phi_m - 1)/\, m\,]\, d\, m \tag{2.9}$$

since $\phi \longrightarrow 1$ as $m \longrightarrow 0$, and $ln\ f_{\pm} \longrightarrow 0$. Alternatively,

$$\upsilon\, m\, \phi_m = \int_0^m \upsilon\, m\, d\, ln\, (f_{\pm}\, m) \tag{2.10}$$

so that

$$\phi_m = 1 + \frac{1}{m} \int_0^m m\, d\, ln\, f_{\pm} \tag{2.11}$$

Thus a relation is established between the activity coefficient of electrolyte solute, $f_{\pm}$, and the solvent activity through ϕ_m. The next step is to define the osmotic coefficient on the molar scale.

Let's consider a volume of pure solvent at a pressure P_o and a volume of solvent plus solute at pressure P. If these volumes are separated by a membrane which is permeable to the solvent but not to the solute, then in order to establish equilibrium, the pressure exerted on the solution must be greater than the pressure exerted on the pure solvent by the value of the osmotic pressure, or $P = P_o + \Pi$ where Π is the osmotic pressure of the solution. The osmotic coefficient on the molar scale is defined :

$$\phi_c = \Pi / (\upsilon\ C\ RT) \tag{2.12}$$

where Π is the osmotic pressure, υ is the sum of υ_+ and υ_-, and C is molarity. By these procedures the activity and osmotic coefficient are defined, and the next step is to establish the relation between the quantities in the different concentration scales.

B. Concentration Scale Conversion

The activity coefficients (or osmotic coefficients) for various concentration scales (mole fraction, molal, and molar) are different, especially at applicable concentrations, and so it may be useful to give the relations between activity coefficients or osmotic coefficients on the various scales. These relations follow from the requirement that the chemical potential, μ, of the "unsolvated " solute in solution must be the same, whatever the concentration scale used. This implies that the μ^o term for each concentration scale differs from one scale to another, but its sum with the respective RT *ln a* term is constant for a given solution.

These requirements lead to the inter-conversion equations:(41)

$$f_{\pm} = \gamma_{\pm} \, (1 + 0.001 \, \upsilon \, W_s m) \tag{2.13}$$

$$f_{\pm} = y_{\pm} \, \frac{d + 0.001C(\upsilon W_s - W_{MA})}{d_o} \tag{2.14}$$

$$\gamma_{\pm} = y_{\pm} \, \frac{d - 0.001C(\upsilon W_s - W_{MA})}{d_o}$$

$$= y_{\pm} \, \frac{C}{m \, d_o} \tag{2.15}$$

$$\phi_m = \phi_c \frac{C}{m\ d_o} \tag{2.16}$$

and

$$y_{\pm} = \gamma_{\pm} \frac{(1 + 0.001m\ W_{MA})\ d_o}{d}$$

$$= \gamma_{\pm} \frac{m\ d_o}{C} \tag{2.17}$$

where υ is the number of moles of ions derived from one mole of salt, MA, of molecular weight W_{MA}, W_s is the solvent molecular weight, d is the density of the solution, d_o is the density of the solvent, m is the molality and C is the molar concentration. The activity coefficients are the mean rational quantity, $f_{\pm}$, the mean molal quantity, $\gamma_{\pm}$. and the mean molar quantity, $y_{\pm}$. The osmotic coefficients are molal quantity, ϕ_m, and the molar quantity, ϕ_c. It is obvious, as is thermodynamically required, that as $m=C \longrightarrow 0$ (i.e., as $d \longrightarrow d_o$), $f_{\pm} = \gamma_{\pm} = y_{\pm} = 1$ and $\phi_m = \phi_c = 1$. Also, at finite concentrations, there is a relation between molality and molarity:

$$C = m\ d/(1+0.001\ m\ W_s) \tag{2.18}$$

$$m = C/(d-0.001C\ W_s) \tag{2.19}$$

Thus the basic relations of quantities between the different concentration scales have been established. But still, information about the solution density (d) and solvent density (d_o) are required. One thing to keep in mind is that d_o is not the value for the pure solvent in itself, it is the density of the solvent part of the solution. By this kind of consideration, d_o can be expressed as

$$d_o = \bar{W}_s / \bar{V}_s \tag{2.20}$$

where $\bar{V}_s$ is the partial molal volume of the solvent. The result is that information about the solution densities and partial molal volumes are required. This will be further discussed in the next section.

C. The relation between solution density and partial molal volume at fixed temperature and pressure

The density and volumetric properties of aqueous electrolyte solutions cover a very wide field of characteristics, such as the following:

(1) Molar(or molal) volume(cm^3mol^{-1})

(2) Partial molar(or molal) volume

A main feature of these properties is that there are rigorous relationships between most of them. Consequently, if one of them is known, then the others can be evaluated through definitions which will be discussed below.

The liquid density of the aqueous electrolyte solution (d) is obtained from the expression

$$d = \frac{\text{total solution mass/1000 g solvent}}{\text{total solution volume/1000 g solvent}}$$

$$= \frac{(m_2\, W_2 + 1000)/1000 \text{ g solvent}}{V_{soln}} \qquad (2.21)$$

where m_2 is the concentration (molality) of the electrolyte and W_2 is the molecular weight of the electrolyte (ex. NaCl=58.5). The volume, V_{soln}, is the volume of an electrolyte solution that contains n_2 moles of electrolyte per 1000 g of solvent. The partial molal volume of the electrolyte ($\bar{V}_2$) in the solution that contains n_1 moles of solvent and n_2 moles of electrolyte can be defined by the equation

$$\bar{V}_2 = \left[\frac{\partial V}{\partial n_2} \right]_{T,P,n_1}$$

$$= \left[\frac{\partial V/1000 \text{ g solvent}}{\partial n_2/1000 \text{ g solvent}} \right]_{T,P,n_1}$$

$$= \left[\frac{\partial V_{soln}}{\partial m_2} \right]_{T,P,m_1} \qquad (2.22)$$

also the partial molal volume of solvent, $\bar{V}_1$, is

$$\bar{V}_1 = \left[\frac{\partial V}{\partial n_1} \right]_{T,P,n_2}$$

$$= \left[\frac{\partial V_{soln}}{\partial m_1} \right]_{T,P,m_2} \qquad (2.23)$$

where V is the total solution volume. By equations (2.21), (2.22), and (2.23), the basic expression for the solution density and partial molal volume can be obtained. Landis[(31)] treated this relationship by a sophisticated method and it is now possible to get these values for aqueous solutions as a function of molality. In his work, the solution density is fitted to the expression

$$d = 0.99707 + A\,m_2 + B\,m_2^{1.5} + C\,m_2^{2.} + D\,m_2^{2.5} + E\,m_2^{3.} \qquad (2.24)$$

where d is the solution density at 298.15 K, and A, B, C, D, and E are parameters. The parameter values for each solution were obtained from experimental data by regression.

The partial molal volume of the solvent may be conveniently calculated from the solution density. The volume of an electrolyte solution per 1000 g of solvent is given from equation (2.21) by

$$V_{soln} = \frac{(\,m_2 W_2 + 1000)/1000 \text{ g solvent}}{d} \qquad (2.25)$$

where component 1 is the solvent (water) and component 2 is the electrolyte. Generally

$$V = n_2 \bar{V}_2 + n_1 \bar{V}_1$$

$$= n_2\bar{V}_2 + (1000/W_1)\ \bar{V}_1 \qquad (2.26)$$

Solving for the partial molal volume of the solvent gives

$$\bar{V}_1 = (V - n_2\bar{V}_2)\ (W_1/1000)$$

$$= 1000\ (V_{\text{soln}} - m_2\bar{V}_2)\ (W_1/1000) \qquad (2.27)$$

By equations (2.22) and (2.25)

$$\bar{V}_2 = \left[\frac{\partial\ V_{\text{soln}}}{\partial\ m_2} \right]_{T,P,m_1}$$

$$= \frac{\dfrac{\partial[m_2W_2 + 1000]}{\partial\ m_2}\ \dfrac{1}{d} + \dfrac{\partial(\frac{1}{d})}{\partial\ m_2}\ \dfrac{[m_2W_2 + 1000]}{1}}{1000 \text{ g of solvent}}$$

$$= \frac{\dfrac{W_2}{d} - \dfrac{1}{d^2}\ [m_2W_2 + 1000]\ \dfrac{\partial\ d}{\partial\ m_2}}{1000 \text{ g of solvent}} \qquad (2.28)$$

Substituting equation (2.25) and (2.28) into equation (2.27) provides the following equation for the partial molal volume of the solvent:

$$\bar{V}_1 = \frac{W_1}{1000}\left\{ V_{soln} - m_2 \left[\frac{W_2}{d} - \frac{1}{d} V_{soln} \frac{\partial d}{\partial m_2} \right] \right\} \qquad (2.29)$$

Since the solution density (d) is expressed as an m_2-dependent polynomial by equation (2.24), it is now possible to calculate the partial molal volume of water ($\bar{V}_1$).

D. Summary of Chapter 2

If osmotic coefficients are calculated on either the molar or molal concentration scale, it is possible to convert from that concentration scale to the other scale, and the conversion between the osmotic coefficient value and activity coefficient value is also possible by the equations (2.9), (2.10), and (2.16).

Chapter 3. MODEL DEVELOPMENT I: BASIC PROCEDURE FOR THE THEORETICAL DERIVATION OF THE OSMOTIC COEFFICIENT

A. The Needs for the Theoretical Approach in the Study of the Fluid.

The most important thing in the study of solution thermodynamics from the theoretical viewpoint is to understand the structure of the solution. The possible methods (tools) developed for this purpose can be divided into three categories. The first includes such experimental methods as X-ray scattering and neutron scattering. This category reflects the real interactions of the molecules, including the many-body interactions, and generates the structural factors and scattering functions. These results are exact for real fluids (within the range of the experimental error), but the detailed information of the molecular motions are difficult to decipher.

The second method involves computer simulations such as the Monte Carlo and molecular dynamics methods. These use idealized molecular interaction potentials and the simulated results generate both the time-dependent and independent properties (e.g., radial distribution functions, virial pressure and energy, mean squared torque, and velocity autocorrelations). The results are exact for the assumed potential, so if the proper potential suitable for the description of the real fluid system is chosen, then the results can be regarded as equivalent to experimental data. These methods require much computation time, so that they can be considered as experiments done by computer.

The third category is the integral equation method. This method also uses an idealized molecular interaction to generate the radial distribution function (pair correlation function). Compared to the two other methods, this is the most valuable for the theoretical understanding of the properties of model fluids. This method is useful in formulating correlations of physical properties and fast solutions which can be obtained on a computer. Thus the third method is the most economical for the calculation of fluid properties.

B. Osmotic Coefficient Calculation by the Pair Correlation Function Method

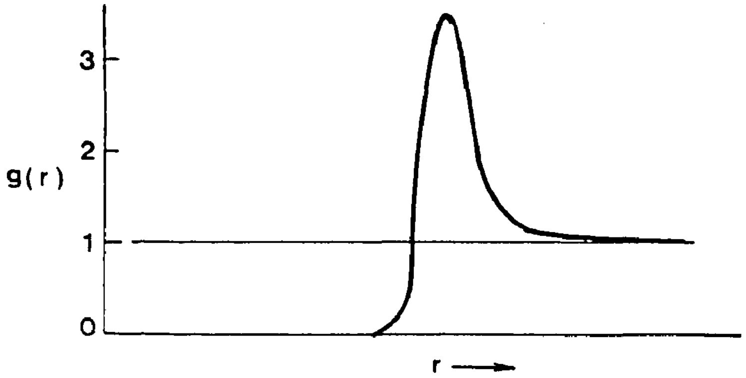
The calculation of osmotic coefficients by the pair correlation function method yields results on a molarity basis which are strongly related with the so-called pressure equation. This is illustrated below. In this section, the three basic steps for the calculation of the osmotic coefficient are introduced. The first step is the introduction of the pair correlation function, though this will be treated systematically in chapter 6. The second is the correlation between the thermodynamic properties and the pair correlation function. The third and final step, is the application of this derivation to the ionic solution.

Pair Correlation Function

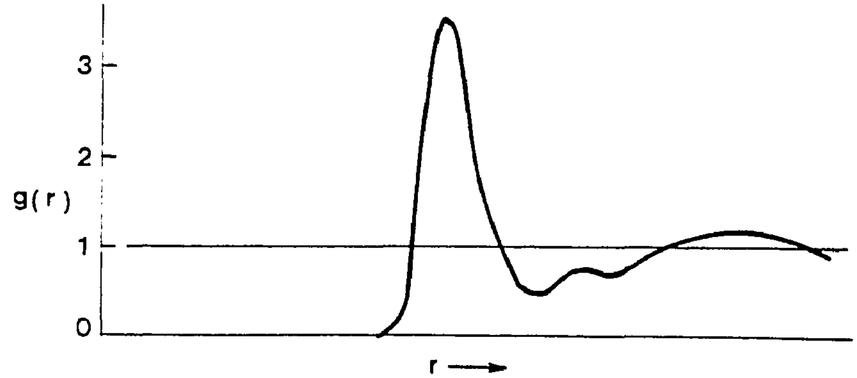
The pair correlation function is defined as follows for an isotropic fluid. Consider a pure liquid which consists of spherical molecules, and a radially symmetric coordinate system whose origin is at the center of one of the molecules. The distribution of the other molecules around this central molecule must be found. As the system is a fluid, the distribution is spherically symmetric so that the probability of the distribution of the particles around the central molecule is only dependent on the distance from the central molecule. This probability is the so-called pair correlation function in an isotropic fluid, also known as the radial distribution function, $g_{ij}(r)$.

In general, the mean number of molecules observed in the spherical shell at a distance r from the central ion is expressed as $\rho\, g_{ij}(r)\, 4\, \pi\, r^2 dr$, where ρ is the bulk number density of the fluid. All molecules become effectively hard for small r, i.e., no two molecules can occupy precisely the same location. They also do not interact strongly at large separations so that their distribution will follow the average properties of the fluid there. For these reasons the limits of the pair correlation function are $g_{ij}(r) \longrightarrow 0$ as $r \longrightarrow 0$, and $g_{ij}(r) \longrightarrow 1$ as $r \longrightarrow \infty$. Experimentally, this function can be determined by the methods mentioned previously, and the sample results are given in Figure 3.1.(42)

The mathematical treatment of this function will be given in detail in chapter 6. The radial distribution function is of interest



(a) dilute gas



(b) liquid

Fig. 3.1. Typical experimental radial distribution functions for (a) dilute gas and (b) liquid

in statistical mechanics primarily because the thermodynamic functions of the fluid can be expressed in terms of it. We turn to this topic in the next section.

Relation of thermodynamic functions to the pair correlation function

There are several connections between the thermodynamic properties and the pair correlation function. The simplest connection to establish, concerns the internal energy E. It follows immediately from statistical mechanics that

$$E = \frac{3}{2} N k T + \bar{U} \tag{3.1}$$

The first term is the mean kinetic energy, and the second term is the mean potential energy. It is easy to express $\bar{U}$ in terms of $g_{ij}(r)$. Consider any molecule as the central molecule. The total intermolecular potential energy between the central molecule and other molecules in the fluid at distances between r and $r+dr$ can be expressed with the help of the pair correlation function because the presence of the molecule produces the potential energy. The total intermolecular potential energy between the shell around the central molecule and the central molecule is

$$u_{ij}(r) \, \rho \, g_{ij}(r) \, 4\pi^2 r \;\; dr$$

where $u_{ij}(r)$ is the intermolecular potential energy (and will be described in detail in chapter 4). $\bar{U}$ is obtained by integrating over all values of r and multiplying by $N/2$, since any of the N molecules might be "central." The factor of two is inserted so that each pair interaction is counted only once. Thus

$$\frac{E}{N\,k\,T} = \frac{3}{2} + \frac{\rho}{2\,k\,T} \int_0^\infty u_{ij}(r)\; g_{ij}(r)\; 4\;\pi\; r^2\; dr \tag{3.2}$$

The next step in relating the osmotic coefficient to $g_{ij}(r)$ is to derive the pressure equation. There are several ways to do this and one of them is to calculate the pressure as the force per unit area which the molecules on one side of a mathematical surface S (see Fig. 3.2)(42) in the fluid exert on the molecules on the other side. There are two contributions to this force: the first, P_k, is associated with momentum transport and the second, P_u, with intermolecular forces. As indicated in the procedure for the derivation of the Maxwell-Boltzmann velocity distribution,(43) the momentum distribution is independent of the existence of intermolecular forces. Thus, the contribution of momentum transport to the pressure is just the same as in an ideal gas at the same density and temperature, namely, $P_k = \rho\ k\ T$. The second contribution involves P_u. In Figure 3.2, the surface S is the plane X=0. The force which a molecule at P a distance X from S exerts on a molecule at P' on the other side of S is $-u'(r) = -du(r)/dr$. The force normal to S is $-u'(r)h/r$. The mean number of molecules in the ring (radius R) with values of R between R and $R+dR$ and values of h between h and $h+dh$ is $\rho g(r)\ 2\pi R\ dR\ dh$. The normal force exerted by the one molecule at P on the molecules in the ring is then

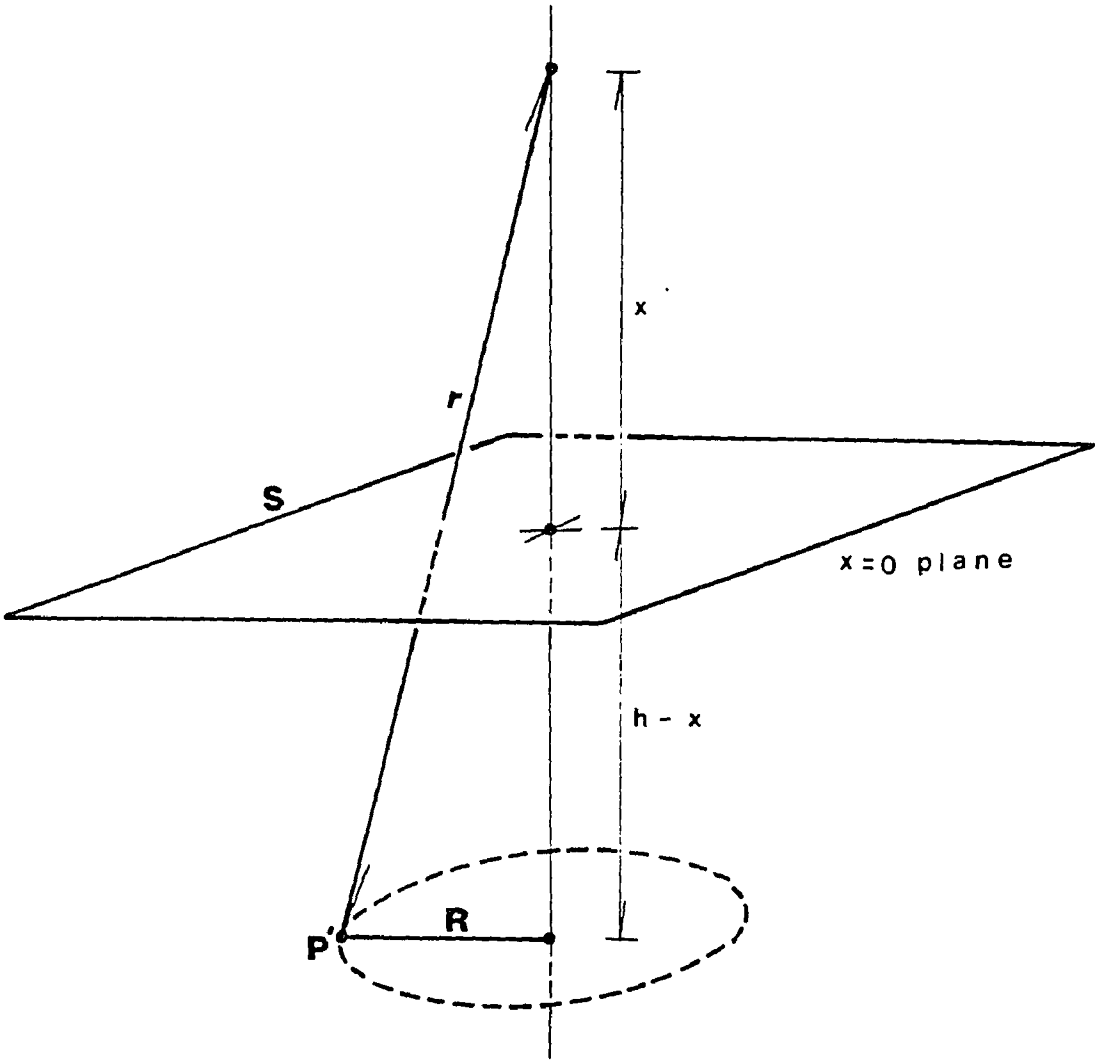


Fig. 3.2. Construction for calculation of pressure in a fluid

$$-u'_{ij}(r)\frac{h}{r}\ \rho\ g_{ij}(r)\ 2\pi R\ dR\ dh \tag{3.3}$$

Since $r^2 = h^2 + R^2$, $r\ dr = R\ dR$. Hence (3.3) becomes

$$-u'_{ij}(r)\ \rho\ g_{ij}(r)\ 2\pi\ dr\ h\ dh. \tag{3.4}$$

Then the normal force exerted by the molecule at P on all molecules on the opposite side of S (X $\leq$ 0) is $-2\pi\rho\ I_1(\mathrm{X})$, where

$$I_1(\mathrm{X}) = \int_{\mathrm{x}}^{\infty} h\ dh \int_{h}^{\infty} u'_{ij}(r)\ g_{ij}(r)\ dr \tag{3.5}$$

Finally, P_u can be obtained if the contributions $-2\pi\rho\ I_1(\mathrm{X})$ of all molecules in a cylinder of unit cross-sectional area and with axis perpendicular to S, extending from X=0 to X=∞ are known. The number of molecules in this cylinder between X and X + dX is $\rho\ d$X. Therefore

$$P_u = -2\pi\rho^2 \int_0^{\infty} I_1(\mathrm{X})\ d\mathrm{X} \tag{3.6}$$

Equation (3.6) can be simplified. An integration by parts reduces $I_1(\mathrm{X})$ in (3.5) to

$$I_1(\mathrm{X}) = -\frac{\mathrm{X}^2}{2}\int_{\mathrm{x}}^{\infty} u'_{ij}(r)\ g_{ij}(r)\ dr + \frac{1}{2}\int_{\mathrm{x}}^{\infty} r^2\ u'_{ij}(r)\ g_{ij}(r) dr \tag{3.7}$$

This result is substituted in Equation (3.6), and two further integrations by parts are carried out. Then, P_u is obtained as

$$P_u = -2\pi\rho^2\left(-\frac{1}{6}+\frac{1}{2}\right)\int_0^{\infty} r^3 u'_{ij}(r)\, g_{ij}(r)\, dr \qquad (3.8)$$

where the two fractions result from the respective terms in (3.7). Finally, $P = P_k + P_u$, and hence

$$\frac{P}{k\ T} = \rho - \frac{\rho^2}{6\ k\ T}\int_0^{\infty} r\ u'_{ij}(r)\ g_{ij}(r)\ 4\pi r^2\ dr \qquad (3.9)$$

Equation (3.9) is the so-called pressure equation and can be generalized to a fluid mixture to give

$$\frac{P}{k\ T} = \sum \rho_i - \frac{1}{6\ k\ T}\sum_i \sum_j \rho_i \rho_j \int_0^{\infty} r\ u'_{ij}(r)\ g_{ij}(r)\ 4\pi r^2 dr \qquad (3.10)$$

This equation can be applied to an ionic solution, for which the cation and anion can be considered as species i and j, the solvent can be considered as a continuous dielectric medium, the pressure calculated would be the osmotic pressure.

Osmotic Coefficient on molar basis

It is not difficult to derive the osmotic coefficient (ϕ_c) by manipulation of equation (3.10). If both sides of equation (3.10) are divided by $\sum \rho_i$, then the osmotic coefficient expression which is based on the molarity can be obtained.

$$\phi_c = \frac{P}{\sum_i \rho_i k\, T} = 1 - \frac{1}{6 \sum_i \rho_i k\, T} \sum_i \sum_j \rho_i \rho_j \int_0^\infty r\, u'_{ij}(r)\, g_{ij}(r)\, 4\pi r^2 dr \qquad (3.11)$$

The following quantities are needed in order to get a numerical value of the osmotic coefficient. They are the temperature (T), number densities of the cation (ρ_1) and anion (ρ_2), interaction potential derivative ($u'_{ij}(r)$) and pair correlation function ($g_{ij}(r)$). The means of determining these last two values has not been addressed. There are many possible choices for the means of obtaining these two values, and it was decided that suitable equations for these quantities should be developed. The development of these equations is the essential feature in the model development.

C. Summary of Chapter 3

A general expression for the osmotic coefficient of the ionic solution system can be derived by an extension of the general fluid case, but suitable models, for the ionic interaction and pair correlation functions must be developed.

Chapter 4. MODEL DEVELOPMENT II: SELECTION OF MOLECULAR INTERACTION POTENTIAL

A. Review of the Molecular Interaction Potential Model

There are several models which describe molecular interaction potentials, for example, the hard sphere potential, the charged hard sphere potential, the charged soft sphere potential, the Lennard-Jones potential etc. Each of the models reflects a different type of interaction and corresponds to a fluid with different properties. The purpose of this review is to select and modify the molecular interaction model for the description of ionic solution behavior.

Hard Sphere Potential

The study of fluids composed of hard spheres represents a first step in correcting ideal-gas behavior. An ideal gas is characterized as molecules without interaction energy. As a consequence, ideal gas molecules have no excluded volume and no cohesive forces. This picture contradicts the behavior of real gases. As an improvement, one surrounds each molecule with an excluded volume, i.e., a hard core. The simplest such molecules are hard spheres. The potential energy of this interaction, $u_{ij}(r)$, is described by

$$u_{ij}(r) = +\infty \qquad r < d$$

$$= 0 \qquad r > d \tag{4.1}$$

where r is the distance between the centers of two hard spheres and d is the hard sphere diameter. To see the consequence of equation (4.1) in terms of interaction forces, the following formula is applied:

$$F_{ij} = - \nabla u_{ij}(r)$$

$$= + \delta(r-d) \tag{4.2}$$

F_{ij} is the force exerted on molecule i by molecule j and $\delta(r-d)$ is the Dirac Delta Function. The physical meaning of equation (4.2) is that the interaction force is zero except at the position where $r=d$. At $r=d$ the value is $+\infty$. Therefore, the force at contact is an infinite force of repulsion. For a collection of hard spheres, the total potential energy $\bar{U}$ is

$$\bar{U} = \sum_{i<j} u_{ij}(r) \tag{4.3}$$

For a canonical ensemble, the partition function can be readily expressed as

$$Z_N = \frac{1}{N!\ \Lambda^{3N}} \int dr^N \exp\left[- \beta \sum_{i<j}^{N} u_{ij}(r) \right] \tag{4.4}$$

Where N is the number of particles, $\beta = 1/(k\ T)$ and $\Lambda = h/\ (2\pi mkT)^{0.5}$

Also, h is Planck's constant, m is the particle mass and the other quantities have been previously defined. Efforts have been made since the 1960s to characterize Z_N and related quantities for hard spheres. Now, the behavior of hard spheres is well understood. Modern liquid state theory started with the elucidation of hard sphere properties. Earlier, liquids had always been thought of as either dense gases or disordered solids. As repulsive forces are dominant in dense liquids, hard core molecules give a realistic description of the liquid structure.

Lennard-Jones Potential(44)

Real molecules possess repulsive forces as well as attractive forces (short-ranged, e.g., hydrogen bonds and longer-ranged for dispersion and polar forces). A simple pair potential that possesses both the repulsive and the inverse sixth power London forces is the Lennard-Jones (LJ) potential.

$$u_{ij}(r) = 4\, \varepsilon_0 \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right] \tag{4.5}$$

where r is the intermolecular separation and σ and ε_0 are force constants characteristic of the molecular species. The meaning of these constants is examined below.

1. The energy parameter ε_0 has units of energy and is the well depth of the LJ $u_{ij}(r)$:

$$\min\ u_{ij}(r) = -\varepsilon_0 \tag{4.6}$$

2. The size parameter σ has the units of length and is the location where $u_{ij}(r) = 0$; i.e.,

$$u_{ij}(\sigma) = 0 \tag{4.7}$$

3. The distance r_{min} for the minimum of $u_{ij}(r) = -\varepsilon_0$ can be obtained by setting $du/dr = 0$ and, for the LJ potentials, is related to σ by

$$r_{min} = 2^{1/6}\,\sigma \tag{4.8}$$

This potential has been extensively studied due to its simplicity combined with realism. A Lennard-Jones fluid exhibits two first-order (liquid-vapor, and fluid-solid) phase transitions and one second-order phase transition (a critical point).(45) At moderate densities, it simulates noble gas behavior quite well. Characterization of the LJ fluid represented a major advance in statistical mechanics in understanding real fluid behavior.

Morse potential(46)

The so-called Morse potential

$$u_{ij}(r) = \varepsilon_0[\exp\{-(2c/\sigma)(r-r_{min})\}\ -2\exp\{-c/\sigma)(r-r_{min})\}] \tag{4.9}$$

was introduced by Morse to interpret the vibrational spectra of diatomic molecules and was used by Mayer & Careri(47) as a pair potential to study intermolcular forces in liquids. The parameters ε_0, r_{min}, and σ have their usual meaning and c is related to the curvature of $u_{ij}(r)$ at r_{min},

$$2c^2 = (\sigma^2/\varepsilon_0)\left(\frac{d^2u}{dr^2}\right)_{r=r_{min}}$$

so that $r_{min}/\sigma = 1 + ln(2/c)$. Thus, for the Morse potential σ is not an independent parameter, but depends on r_{min} and c. A small value for c yields a potential with a small curvature at the minimum and, hence, with a wide potential well and a gentle rise in the repulsive portion. A large value for c gives a large curvature at r_{min} and therefore a relatively narrow potential well and and a steep rise in the repulsive limb of the potential. The Morse potential has a finite value at $r=0$, $u_{ij}(0) = 4\ \varepsilon_0 \exp[c\{\exp(c)-1\}]$, and does not fall off as r^{-6} for large r. By several tests(48-50) it was found that the Mose potential gives a better fit at low temperatures than either the LJ 12-6 or the exp-6 potentials.

Guggenheim-McGlashan Potential(51)

Guggenheim and McGlashan have departed from the customary procedure of choosing a simple analytical form for pair potentials and instead have used the following form to apply specifically for argon;

$$
\begin{aligned}
u_{ij}(r) &= \infty , && r < \sigma \\
&= -\varepsilon_0 + \kappa\left[\frac{r - r_{\min}}{r_{\min}}\right]^2 - \alpha\left[\frac{r - r_{\min}}{r_{\min}}\right]^3 + \beta_0\left[\frac{r - r_{\min}}{r_{\min}}\right]^4 , && 3.6\ \text{Å} \le r \le 4.15\ \text{Å} \\
&= -\lambda\left[\frac{r_{\min}}{r}\right]^6 , && r \ge 5.4\ \text{Å} \qquad (4.10)
\end{aligned}
$$

The pair potential in the vicinity of the minimum has been expanded in a power series about $r_{\min}$. For the regions $\sigma \le r \le 3.6$ Å and 4.15 Å $\le r \le 5.4$ Å, a free-hand curve was drawn.

Guggenheim and McGlashan chose λ so as to agree with theoretical dispersion-force calculations. Values for the parameters ε_0, κ, α, and r_m were selected to optimize the agreement with experiment. The parameter σ was determined by fitting the potential to second virial coefficient data. The coefficient β_0 of the anharmonic term in the expansion of $u_{ij}(r)$ about $r_{\min}$ is more difficult to determine. Guggenheim and McGlashan tried several values and concluded that $\beta_0 = \alpha$ is suitable and used this potential to calculate liquid properties at the triple point. The results(52) show good agreement with the experimental energy, but poor agreement with the experimental entropy.

Kihara potential

Kihara(53) replaced the point center model for a molecule by a model with an impenetrable core. For the pair potential he retained the mathematical form of the LJ 12-6 potential, but wrote the potential not as a function of distance between molecular centers but rather as a function of the minimum distance γ between molecular cores,

$$u_{ij}(r) = \infty , \qquad r < \gamma$$

$$= \frac{n\ \varepsilon_0}{n-m}\left(\frac{n}{m}\right)^{m/(n-m)}\left[\left(\frac{\sigma-\gamma}{r-\gamma}\right)^{12} - \left(\frac{\sigma-\gamma}{r-\gamma}\right)^{6}\right], \quad r \geq \gamma \qquad (4.11)$$

Usually. n is taken as 12 and m as 6. When the collision diameter γ is zero, the Kihara potential reduces to the LJ potential. The Kihara potential fits the virial data and viscosities of Ar better than any other potential which has been proposed by choosing a suitable parameter set. These parameters are very close to those found by Myers & Prausnitz(54) in fitting second virial coefficients only.

Charged Hard Sphere Potential(55)

This potential describes the interaction of the molecules of the charged hard sphere system. The equation can be

$$u_{ij}(r) = +\infty \qquad r \leq d_{ij}$$

$$u_{ij}(r) = \frac{q_i\ q_j}{\varepsilon\ r} \qquad r \geq d_{ij} \qquad (4.12)$$

where q_i is a positive and q_j is a negative charge, ε is the dielectric constant and its value is 1, $d_{ij} = (d_{ii} + d_{jj})/2.0$ and d_{ii} is the diameter of the positively charged hard sphere type molecule and d_{jj} is the diameter of the negative one. If $d_{ii} = d_{jj}$ and ε has the value of the solvent then, this corresponds to the Restricted Primitive Model that is discussed earlier; otherwise, it is the Primitive Model. This kind of model has been applied to the description of ionic interactions in a solvent. As an example, EXP theory and MSA adopted this kind of interaction model.

Charged Soft Sphere Potential

The Charged Soft Sphere Potential Model was suggested by Born.(56) The expression of the equation is

$$u_{ij}(r) = \frac{z_i z_j e^2}{r} + \frac{B e^2}{r^n} \tag{4.13}$$

where z_i and z_j are the valences of ion charge, e is the charge of an electron (thus $z_i e = q_i$), and B and n are constants. This potential was modified by Pauling(57) by introducing the Madelung constant(58) and applied to the description of the ionic interaction potential of a crystal. The result was used for the calculation of the Pauling radius, which is the hypothetical ion size in a crystal.

Square Well Potential(59)

The square well potential can be considered as an extension of the hard sphere potential which includes an attractive term and is simple enough to handle analytically :

$$u_{ij}(r) = \infty \qquad r < d$$
$$= -\varepsilon_0 \qquad d < r < \lambda d$$
$$= 0 \qquad \lambda d < r \qquad (4.14)$$

λ, the range of the attractive well, is usually taken to be between 1.5 and 2.0. This potential shows good ability to correlate experimental data for the second virial coefficient, at least at ordinary temperatures.

B. Choice of the Molecular Interaction Potential Model

In the above review of molecular interaction models , we find that some models have been developed for ionic interactions and others have been developed for neutral molecule interactions. The former are the charged hard sphere potential and the charged soft sphere potential, the latter are all the others. It is possible that a model that was developed for the purpose of neutral- molecule interactions can be considered a general case which includes ionic interactions as a special case. The reason for this approach will be discussed later; we here introduce the ionic interaction potential model chosen for this work.

The charged hard sphere model can be used for the description of ionic interactions in a solvent on the condition that the solvent can be considered a dielectric medium, i.e., the solvent granularity is ignored. This is a drastic assumption, but is approximately valid for a strong electrolyte solution. The other theoretical problem of this model is that it treats the ion as a charged hard sphere. In actuality, the ion is not a charged hard sphere, but instead has the property of softness. Softness means that the core repulsion does not produce a discontinuity in the interaction potential. Thus, the charged hard sphere model is not sufficiently realistic.

The other model for ionic interactions is the charged soft sphere model. This also includes the same assumption that the solvent is a dielectric medium, but the softness of the ion is included. It would seem to be easy to choose this model as the ionic interaction model, but the problem is how to fix the constant in the equation, i.e., it is not easy to decide the softness of the ion. Thus, there are many approaches to this kind of model. The equations given by Born and Pauling and introduced earlier are examples.

Ramanathan and Friedman$^{(11)}$ also suggested one model, where the ion-ion pair potential for the 1-1 type is

$$u_{ij}(r) = -\frac{e^2}{\varepsilon r} + \frac{F e^2}{n} \frac{(r_i^* + r_j^*)^{n-1}}{r^n} + \mathrm{CAV}_{ij} + \mathrm{GUR}_{ij} \tag{4.15}$$

where r_i^* is the Pauling radius of an ion of species i and F is the ratio of the Madelung constant to the coordination number for the crystal. The other notations have the same meaning as earlier. The second term is the core repulsion term, where the repulsive exponent n=9 has been taken empirically. The term CAV_{ij} represents a particular known dielectric effect: a cavity in a dielectric medium is polarized by an electric field in a sense opposite to the familiar picture of the polarization of a dielectric in an electric field. That is, the polarization results in a force pushing the cavity toward a region of lower field. The fourth term is the so-called Gurney potential,(60) which represents the effect yielded by the formation of the cosphere (the phenomenon whereby an isolated ion is surrounded by the solvent and the attached solvent behaves as a cosphere of the ion sphere). This equation can be considered as a change in the Pauling model from a description of the ionic interaction of the lattice structure to a model of the interactions in the solution by the introduction of the solvent structure effect.

Here, we make a different suggestion, but for the same purpose as the model suggested by Ramanathan and Friedman. The cavity and cosphere effect (third and fourth terms of equation (4.15)) in the total potential is shown in Figure 4.1. As shown in Figure 4.1, the contribution of these two terms can be neglected, especially the cavity term. Instead, these neglected effects (mainly the Gurney potential effect) are considered in the repulsion term. In addition, the Madelung constant is removed because it is introduced for the expression of the total crystal energy. As a consequence, the equation is reduced to only two terms (attractive and repulsive terms). In the

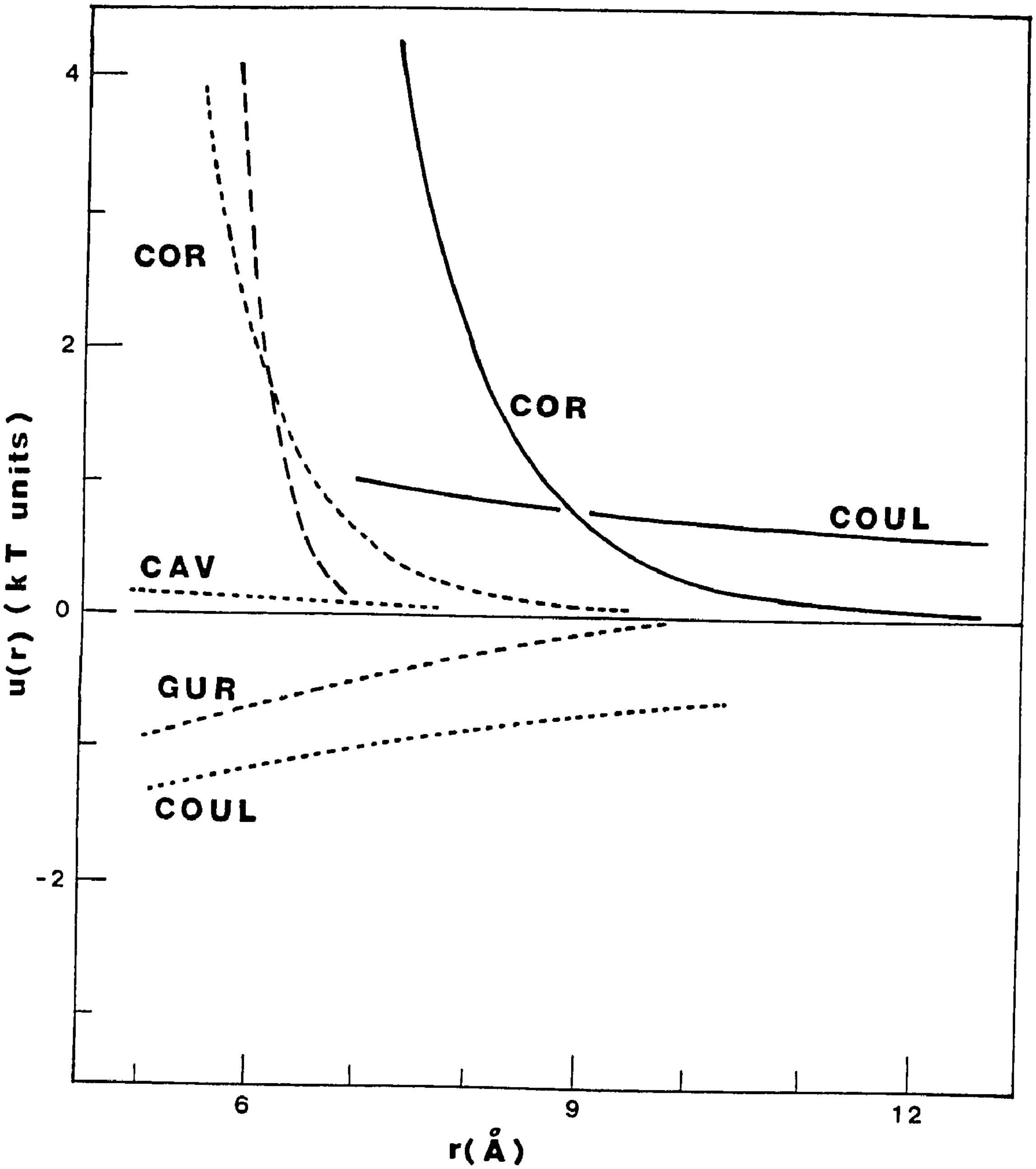


Fig. 4.1. Typical terms of interaction potential energy in equation (4.15)

case of positive and negative ion pair interactions, the potential is

$$u_{ij}(r) = \frac{z_i\ z_j\ e^2}{\varepsilon\ r} + \frac{|z_i\ z_j|e^2}{\varepsilon\ n}\ \frac{[\ r_{\min}\ ]^{n-1}}{r^n} \qquad (4.16)$$

where $r_{\min} = r_i^* + r_j^* + \lambda\ d_w$, r_i^* is the Pauling radius, λ is the range of the hydration, and d_w is the water diameter (2.76 Å). And the minimum energy (potential well depth) is

$$u_{ij}(r_{\min}) = -\varepsilon_0 = -\ \frac{|\ z_i z_j\ |\ e^{\ 2}}{\varepsilon\ (r_i^* + r_j^* + \lambda\ d_w)}\ \frac{n\ -1}{n} \qquad (4.17)$$

Equation (4.15) implies that the hydration effect, i.e., cosphere formation by the solvent (water), is considered. Geometrically, the ion sphere is surrounded by water molecules and they behave as a single particle. The determination of $r_{\min}$ is somewhat cumbersome. Generally, for the cation case λ is 1 or 2 but for the anion it is larger. In either case, the $r_{\min}$ values are determined empirically. One of the differences from the previous charged soft sphere potential is that the n value, which reflects the hardness of the particle, can be changed depending upon the temperature and concentration. This assumption is based on the idea that the hardness of the ion sphere and the cosphere may be different from each other and that the ion itself may have a variable hardness depending on the conditions. Thus we have introduced a simple ionic interaction model, but one which is of different style in terms of physical significance.

C. Summary of Chapter 4.

In this chapter an interaction potential model of the charged soft sphere type, equation (4.15) and (4.16), has been introduced. This model implies the following basic assumptions.

1) Most of the solvent (water) (that which does not participate in ion hydration) is treated as a dielectric medium.
2) A small portion of the solvent is conjugated with the ions and contributes to the formation of ion cospheres which are treated as part of the ion spheres.
3) The hardness of the total ion sphere can change depending on the bulk solution conditions.

Chapter 5. MODEL DEVELOPMENT III: CORRELATION BETWEEN CHARGED SOFT SPHERE POTENTIAL AND CHARGED HARD SPHERE POTENTIAL

A. Intermolecular Interaction Potential and Pair Correlation Function

At the end of chapter 3, the general expression for the osmotic coefficient was introduced. Two things were given as being required for the numerical calculation of the osmotic coefficient. The first was the molecular interaction potential function, and the second was the pair correlation function (radial distribution function). The former has been discussed in the previous chapter. There remains the problem of the pair correlation function. But in reality, the pair correlation function is not independent of the molecular interaction potential, but rather is strongly related to it. In this thesis they are treated separately only for convenience so that their relationship may be understood.

In the earlier description of ionic interactions, we concluded that the charged soft sphere interaction potential is the most reasonable one at the current time. Unfortunately, the pair correlation function corresponding to this potential is not well developed, while the pair correlation function for the hard sphere potential is well known because of its relative simplicity. But as indicated earlier, the hard sphere potential model does not describe the softness of the actual ion sphere. This is a dilemma in attempting the numerical calculation of osmotic coefficients.

To solve this problem, a correlation between the charged soft sphere potential and a related hard sphere potential needs to be developed. For the development of this correlation, the following assumptions are required.

1) Each charged soft sphere potential has a thermodynamically corresponding charged hard sphere potential at specified temperature and concentration.
2) The charged soft sphere potential (equation 4.20) can be treated as a special case of the m-n Lennard Jones potential.

The tool that can convert the charged soft sphere potential to the equivalent charged hard sphere potential should be developed on the basis of these assumptions. The main function of the tool should be to find the corresponding effective hard sphere diameter from the charged soft sphere potential at a given temperature and concentration. This is a task suitable to perturbation theory. The next section is devoted to an introduction of perturbation theory.

B. Review of Perturbation Theory

In chapter 4 several molecular interaction potential models were introduced: hard spheres, soft spheres, LJ molecules, etc. These are all idealized models for real gases. The interaction forces in real gases are more complicated. For example, most real gases are polar or multipolar: carbon dioxide is quadrupolar, and hydrogen chloride is both dipolar and quadrupolar. In addition, polyatomic molecules are nonspherical. The simple potential models can not adequately describe all of these cases. However, the simpler models can serve as reference potentials, and the additional effects, such as quadrupolar forces, can be treated as perturbations on the reference systems. In principle, when the reference system chosen is close to the final system, one would also expect the properties produced by adding the perturbation terms to be close to the full system. This is the basis of the perturbation approach and it can be hoped that a charged soft sphere can be related to a charged hard sphere by the help of this kind of manipulation. Here, three kinds of perturbation methods are introduced. The common feature of these methods is that success would depend on both the choice of the molecular interaction potential and the way that the full potential is separated into the reference and perturbing parts.

The λ Expansion(61)

The perturbation technique can be applied to the equilibrium properties of the fluid or to the structure of the fluid, the latter being a more stringent test of the perturbation theory used. For thermodynamic properties, the perturbation is applied to the Helmholtz free energy, and a series, the λ expansion is formed.

For a fluid whose molecular interaction potential $u_{ij}(r)$ can be separated into $u_0(r)$, the reference part, and $u_p(r)$, the perturbing part:

$$u_{ij}(r;\lambda) = u_0(r) + \lambda\, u_p(r) \tag{5.1}$$

where λ is a parameter varying between 0 and 1 ($0 \leq 1$). When $\lambda=0$, it is reduced to the reference system and when $\lambda=1$, the full system is recovered. The partition function is

$$Z_N(\lambda) = \frac{1}{N!\Lambda^{3N}} \int dr^N \exp\left[-\beta\, \Sigma\, [u_0(r) + \lambda\, u_p(r)]\right] \tag{5.2}$$

where all the notations are same as for equation (4.4).

Since the Helmholtz free energy is related to $Z_N(\lambda)$ by $A(\lambda) = -kT\ ln\ Z_N(\lambda)$, we can expand $A(\lambda)$ in terms of λ in a Taylor series around the value $\lambda=0$:

$$A(\lambda) = A(0) + \lambda\frac{\partial A(0)}{\partial\lambda} + \frac{\lambda^2}{2!}\ \frac{\partial^2 A(0)}{\partial\lambda^2} + \frac{\lambda^3}{3!}\ \frac{\partial^3 A(0)}{\partial\lambda^3} + \ldots.$$

$$= A_0 + A_1 + A_2 + A_3 + \ldots. \tag{5.3}$$

the first term, $A_0=A(0)$ is the free energy of the reference system. The terms A_1, A_2, A_3 may be obtained after lengthy algebra.

Barker-Henderson Theory

Barker and Henderson$^{(62-63)}$ have applied their perturbation theory to a square-well potential and to a LJ potential. Here, the LJ potential case is introduced. They develop the Helmholtz free energy as a double perturbation series. One variable, γ, is a measure of the depth of the attractive well, and the other variable, α, is a measure of the inverse steepness of the repulsive part of potential, i.e., the smaller α, the steeper the repulsive part. They do this by defining a modified function $\mathcal{V}(\alpha, \gamma, d; r)$ corresponding to $u_{\mathrm{ij}}(r)$ by

$$\begin{aligned} \mathcal{V}(\alpha, \gamma, d; r) &= u_{\mathrm{ij}}\left(d + \frac{r-d}{\alpha}\right) && d + \frac{r-d}{\alpha} < \sigma \\ &= 0 && \sigma < d + \frac{r-d}{\alpha} < d + \frac{\sigma - d}{\alpha} \\ &= \gamma\, u_{\mathrm{ij}}(r) && \sigma < r \end{aligned} \tag{5.4}$$

The quantity d is a distance parameter which is as yet unspecified, and σ is customarily taken to be that point at which the potential $u_{\mathrm{ij}}(r)$ passes through zero. $\mathcal{V}(\alpha, \gamma, d; r)$ is independent of d and reduces to $u_{\mathrm{ij}}(r)$ when $\alpha = \gamma = 1$. When $\alpha = \gamma = 0$, on the other hand, $\mathcal{V}$ becomes a hard sphere potential of diameter d. Thus by varying γ and α, we can go from our original potential $u_{\mathrm{ij}}(r)$ to a hard sphere potential. The idea is to express the Helmholtz free energy A in terms of this modified potential as a double power series about $\alpha = \gamma = 0$ according to

$$A = A_0 + \alpha \left[\frac{\partial A}{\partial \alpha}\right]_{\alpha=\gamma=0} + \gamma \left[\frac{\partial A}{\partial \gamma}\right]_{\alpha=\gamma=0} + \frac{\alpha^2}{2}\left[\frac{\partial^2 A}{\partial \alpha^2}\right]_{\alpha=\gamma=0} + \dots \tag{5.5}$$

After some complicated algebra,(59) the following results:

$$A = A_0 + \alpha\ 2\pi\ N\ k\ T\ \rho d^2\ g_{ij}(d)\left[\ d + \int_0^{\sigma} f(z)\ dz\ \right]$$

$$+ \gamma\ 2\pi\ N\ \rho\int_0^{\infty} g_{ij}(r)\ u_{ij}(r)\ r^2 dr$$

$$- \gamma^2\ \pi\ N\ \rho\ \ (\frac{\partial\rho}{\partial p})_0 \frac{\partial}{\partial\rho}\left[\ \rho\int_0^{\infty} g_{ij}(r)\ u^2_{ij}(r)\ r^2\ dr\right]$$

$$+ O(\alpha^2) + O(\alpha\gamma) + \ldots\ldots \qquad (5.6)$$

Here, A_0, $g_{ij}(r)$, and $(\partial\rho/\partial p)_0$ are the free energy, radial distribution function, and compressibility of a system of hard spheres of diameter d. The function $f(z)$ is a special function and it will be treated in the next section in detail. The first order terms in equation (5.6) are exact, but the γ^2 term is an approximation. The value d is not determined. If the value of d is chosen as

$$d = - \int_0^{\sigma} f(z)\ dz \qquad (5.7)$$

then the linear term in α vanishes. This diameter is the so-called Barker-Henderson diameter and gives d as a well-defined temperature-dependent effective hard-sphere diameter. This will be mentioned again in the next section in detail. Barker and Henderson argue that with this choice of d, the terms in α^2 and $\alpha\gamma$ in equation (5.6) are diminished.

For $\alpha = \gamma = 1$, Equation (5.6) is just the Helmholtz free energy for a system with potential $u_{ij}(r)$ and Helmholtz free energy is

$$A = A_0 + 2\pi N \rho \int_0^{\sigma} g_{ij}(r)\, u_{ij}(r)\, r^2 dr$$

$$- \pi N \beta \rho \left(\frac{\partial}{\partial \rho}\right)_0 \left[\rho \int_0^{\sigma} g_{ij}(r)\, u_{ij}^2(r)\, r^2\, dr\right] \tag{5.8}$$

where all notations are the same as the earlier ones. With this approach, thermodynamic properties have been calculated.(64-66) The results are generally excellent and this perturbation theory is one of the most appealing approaches to the liquid state. In this thesis, the concept of Barker-Henderson diameter, equation (5.7), will be used in a later section.

Weeks-Chandler-Andersen theory(67-69)

This perturbation theory has a fundamentally different approach from either Barker-Henderson theory or the λ expansion introduced earlier. The difference with the λ expansion lies in the choice of the expansion functions. The λ expansion expands in terms of the difference of the pair potentials while the Weeks- Chandler-Andersen(WCA) approach expands in terms of Boltzmann factors. There is also a significant difference between the WCA and Barker-Henderson perturbation methods. WCA divides the intermolecular forces into perturbed and unperturbed parts, while there is no separation in Barker-Henderson theory. It was reported in the same paper(69) that for low as well as high temperatures this equation is approximately valid, i.e., errors about 10 % when the density is low, but becomes much more accurate as the density increases. Later, Verlet and Weis(70) adopted this WCA theory and treated the more sophisticated LJ potential. Their method is introduced next.

The procedure adopted by Verlet and Weis is a two-step perturbation scheme. The first step is a perturbation from the HS reference to the WCA-type soft sphere potential. The second step is to perturb the WCA potential by adding on the attractive part of the LJ potential. The usual LJ potential is separated in the WCA formulation into

$$u_{\mathrm{LJ}} = u_{\mathrm{WCA}} + u_{\mathrm{ATT}} \tag{5.9}$$

where

$$u_{\mathrm{WCA}}(r) = \varepsilon_0 \left[4 \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right] + 1 \right] \qquad \text{at } r \le r_{\mathrm{min}}$$

$$= 0 \qquad \text{at } r > r_{\mathrm{min}}$$

and

$$u_{\mathrm{ATT}}(r) = -\varepsilon_0 \qquad \text{at } r \le r_{\mathrm{min}}$$

$$= \varepsilon_0 \, 4 \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right] \qquad \text{at } r > r_{\mathrm{min}}$$

and $\sigma = (r_{\min})\ 2^{-1/6}$, all the other notation is the same as for the LJ potential. Figure 5.1 shows the two potentials as a continuous function. The potential $u_{\text{WCA}}(r)$ is purely repulsive, whereas $u_{\text{ATT}}(r)$ is purely attractive. To get the Helmholtz free energy of the full LJ system, at first the λ expansion was chosen

$$\frac{A_{\text{LJ}}}{N\ k\,T} = \frac{A_{\text{WCA}}}{N\ k\ T} + \frac{\rho}{2\ k\ T} \int_0^\infty dr\ 4\pi\ r^2\ u_{\text{ATT}}(r)\ g_{\text{WCA}}(r)\ + \ \ldots \quad (5.10)$$

To obtain the reference A_{WCA} and $g_{\text{WCA}}(r)$, they made a second expansion with respect to the HS quantities. This time the expansion is by the WCA formula, i.e., expansion in terms of Boltzmann factors.

$$\frac{A_{\text{WCA}}}{N\ k\ T} = \frac{A_{\text{HS}}}{N\ k\ T} - \frac{\rho}{2\ k\ T} \int_0^\infty dr\ 4\pi\ r^2 y_{\text{HS}}(r) \left[e^{-\beta u_{\text{WCA}}} - e^{-\beta u_{\text{HS}}} \right] + \ \ldots \quad (5.11)$$

where the subscript HS refers to hard-sphere quantities and $y_{\text{HS}}(r)$ is a background correlation function that will be described in detail in chapter 6. If a suitable hard sphere diameter, d_e, is chosen, then the second term will be canceled. The procedure to get this d_e (effective diameter) value is the essential feature of Verlet and Weis method. The details will be introduced in the next section. By this manipulation, A_{WCA} is obtained with the high accuracy.

The next step is to calculate the LJ fluid properties from the reference WCA potential. Due the difference between the repulsive

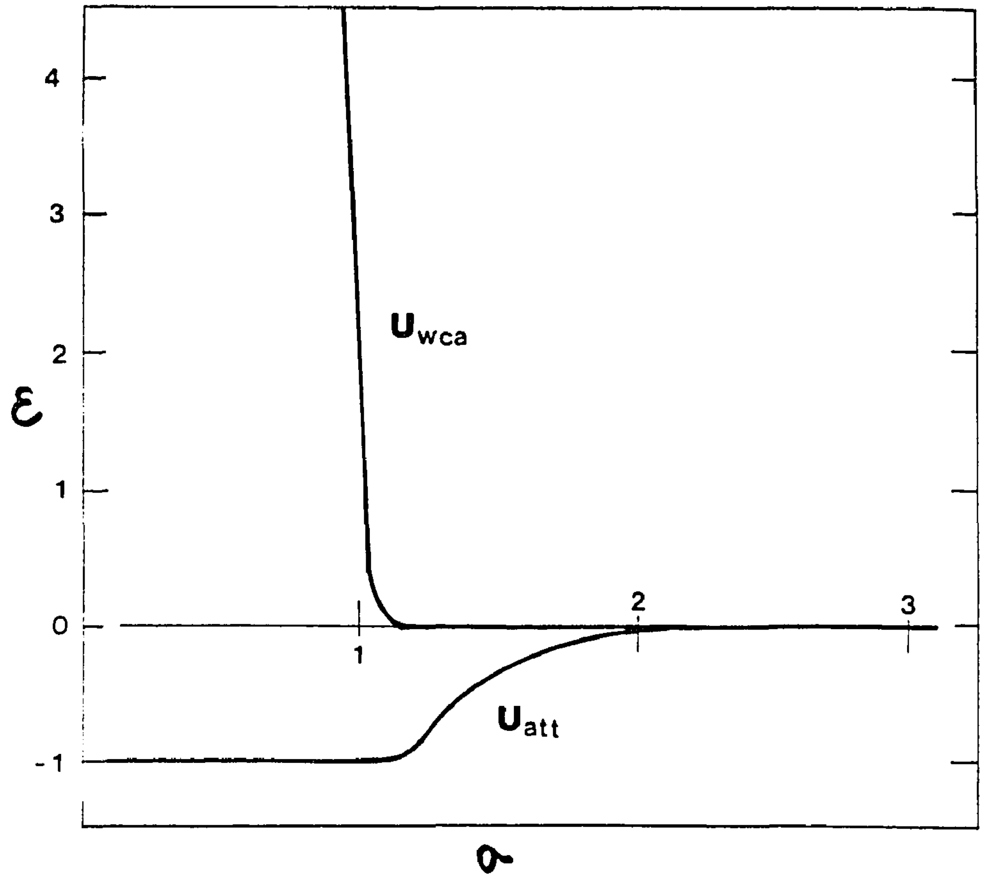


Fig. 5.1. The WCA separation of the Lennard - Jones potential

potentials and those with the attractive terms, at least the first two terms are required for the description of the LJ behavior in equation (5.10). For the calculation of the second term, information on the pair correlation of the WCA fluid, $g_{\mathrm{WCA}}(r)$, is required. But as mentioned previously, the only well-known radial distribution function is for the hard sphere fluid. This is the disadvantage of the WCA theory. To avoid this problem one approximation was made

$$g_{\mathrm{WCA}}(r) \approx y_{\mathrm{HS}}(\frac{r}{d_e}) \exp\,[-\beta\, u_{\mathrm{WCA}}(r)] \tag{5.12}$$

This assumption is possible on the condition that $y_{\mathrm{HS}}(r)$ is not sensitive to the intermolecular potential. Thus the final expression of the equation (5.10) is

$$\frac{A_{\mathrm{LJ}}}{N\ k\,T} = \frac{A_{\mathrm{HS}}}{N\ k\ T} + \frac{\rho}{2\ k\ T_e} \int_{\mathrm{d}}^{\infty} dr\ 4\pi\ r^2\ u_{\mathrm{ATT}}(r)\ y_{\mathrm{HS}}\ (r/d_e)\ \exp\ [-\beta$$

$$u_{\mathrm{WCA}}(r)\ ] + \ \ldots\ldots \tag{5.13}$$

This result was compared with the Monte Carlo simulation of the WCA system and compared. Good agreement was obtained for densities from $\rho^* = \rho\ \sigma^3 = 0.40$ to 1.1 and temperatures from $T^* = kT/\varepsilon_0 = 0.75$ to 3.5.

C. Selection of Perturbation Method.

The purpose of the previous review was to find a suitable means to convert the charged soft sphere potential to a charged hard sphere potential. From such a point of view, the most suitable perturbation scheme is that of Verlet and Weis. In the Verlet and Weis approach, the applied potential is the LJ potential, while here the analogous potential is the charged soft sphere potential. The possibility whether or not the charged soft sphere potential can be subject to the Verlet and Weis perturbation method should be investigated. The common point between the LJ potential and the charged soft sphere potential is that they each consist of only two terms, of which one is an attractive and the other is a repulsive term. The difference is that in the case of an LJ fluid the particles are homogeneous, i.e., each particle has the same size and the same hardness, while in the case of ions the sizes are not all the same and the hardness of the cation and anion may be different. In the real situation, even the the properties of a single cation may vary dependent upon the counterpart anion. To overcome this problem, the following statement is made.

There is a hypothetical state for the cation, M^{+a}, *and the anion,* X^{-a} *such that ions are considered as restricted charged soft spheres, the terminology " restricted " meaning that the cation and anion have the same size and the same hardness with the same magnitude but opposite sign of charge. This hypothetical state for each positive and negative ion represents the average properties of all the cases when* *each ion encounters different kinds of counterpart ion.*

With this assumption the charged soft sphere potential can be regarded as a special case of the m-n LJ potential. The application procedures are introduced below. The mathematical expression of the potential separation is

$$u_{ij} = u_1 + u_2 \tag{5.14}$$

where

$$u_1 = u_{ij}(r_{min}) \left[\frac{n^{\frac{n}{n-1}}}{n-1} \left[\left(\frac{\sigma}{r}\right)^n - \left(\frac{\sigma}{r}\right)^1 \right] + 1 \right] \qquad \text{at } r \le r_{min}$$

$$= 0 \qquad \text{at } r > r_{min}$$

and

$$u_2 = -u_{ij}(r_{min}) \qquad \text{at } r \le r_{min}$$

$$u_2 = u_{ij}(r_{min}) \left[\frac{n^{\frac{n}{n-1}}}{n-1} \left[\left(\frac{\sigma}{r}\right)^n - \left(\frac{\sigma}{r}\right)^1 \right] \right] \qquad \text{at } r > r_{min}$$

where $\sigma = (r_i^* + r_j^* + \lambda\ d)\ n^{\frac{-1}{n-1}}$, and other notation is the same as uesd in equations (4.20-21).

The next step is to apply this separated potential in equations (5.10) and (5.11). Here, u_1 corresponds to u_{WCA} and u_2 to u_{ATT}. As with the LJ potential case in equation (5.11), the second term should be zero:

$$\int_0^\infty dr \quad r^2\, y_{HS}(r)\left[\ e^{-\beta U_1} - e^{-\beta U_{HS}}\ \right] \ = \ 0 \tag{5.15}$$

This equation can be written :

$$\int_0^\infty dr \quad r^2\, y_{HS}(r)\left[\ \frac{e^{-\beta U_1} - e^{-\beta U_{HS}}}{dr}\ \right] dr \ = \ 0 \tag{5.16}$$

As r varies from 0 to near the Pauling radius, a very short range, the difference can be regarded as a differential, so that the equation becomes

$$\int_0^\infty dr \quad r^2\, y_{HS}(r)\ \frac{d\ e^{-\beta U_1}}{d\ r}\ dr = 0 \tag{5.17}$$

Let

$$\psi\ (r) \ = \ \sigma_0(r/d_e - 1) \ + \ (1/2)\ \sigma_1(r/d_e - 1)^2 \ + \ \ldots\ldots \tag{5.18}$$

and

$$d_e(d\psi\ /dr) \ = (r^2/d_e^2\ )\ y_{HS}(r) \tag{5.19}$$

Then the equation becomes

$$\int_0^\infty d\psi \quad \frac{d\ e^{-\beta u_1}}{dr} \quad dr = 0 \tag{5.20}$$

Next consider that

$$d\psi\ (r+\Delta r) = \psi(r+\Delta r)\ - \psi(r) \tag{5.21}$$

All the r values are around d_e, so that it is possible to let $r \approx d_e$, then

$$d\psi(d_e+\Delta r) = \psi(d_e+\Delta r) - \psi(d_e) = \psi(d_e+ \Delta r) \tag{5.22}$$

Finally, if r is around d_e, then

$$d\psi(r) = \psi(r) \tag{5.23}$$

Thus the original equation becomes

$$\int_0^\infty \psi(r)\ \frac{d\ e^{-\beta u_1}}{dr} \ dr = 0 \tag{5.24}$$

Letting $\delta(r) = \dfrac{d\ e^{-\beta u_1}}{dr}$ gives :

$$\int_0^\infty [\sigma_0(r/d_e-1) + (1/2)\sigma_1(r/d_e- 1)^2 + \ldots]\delta(r)\ dr=0 \tag{5.25}$$

which is equivalent to

$$\int_0^\infty [\sigma_0(r/d_e) + (1/2)\sigma_1(r/d_e - 1)^2 + \ldots]\, \delta(r)\, dr$$

$$= \int_0^\infty \sigma_0 \delta(r)\, dr$$

$$= \sigma_0 \int_0^\infty \delta(r)\, dr$$

$$= \sigma_0 \tag{5.26}$$

Multiplying both sides by d_e/σ_0 gives

$$d_e = \int_0^\infty r\, \delta(r)\, dr + d_e \int_0^\infty \frac{1}{2} \frac{\sigma_1}{\sigma_0} \left(\frac{r}{d_e} - 1\right)^2 \delta(r)\, dr \tag{5.27}$$

Defining : $$d_B = \int_0^\infty r\, \delta(r)\, dr$$

The expression d_B is equivalent to equation (5.7). This is the so-called Barker-Hendersen diameter. Here this expression is used for the expression of d_e. Consequently, d_e can be expressed as

$$d_e = d_B + d_B \frac{d_e}{d_B} \; \frac{\sigma_1}{2\sigma_0} \int_0^\infty \left(\frac{r}{d_e} - 1\right)^2 \delta(r)dr \qquad (5.28)$$

Here $d_e \approx d_B$ and the final expression of d_e can be expressed as

$$d_e = d_B \left[1 + \frac{\sigma_1}{2\sigma_0} \int_0^\infty \left(\frac{r}{d_B} - 1\right)^2 \delta(r)dr \right] \qquad (5.29)$$

After this effective diameter has been calculated, the Verlet and Weis perturbation method proceeds until equation (5.13) is reached. Since the purpose here is to convert the charged soft sphere potential into the charged hard sphere potential, there is no need to proceed any further since equation (5.29) solves this problem. It is important to remember that this procedure must be done for both the cation and anion separately.

D. Summary of Chapter 5.

With the help of the assumption that there exists a hypothetical restricted charged soft sphere potential, and the Verlet Weis perturbation technique, it is possible to set up an algorithm to convert a charged soft sphere potential into an equivalent charged hard sphere potential that has the equivalent Helmholtz free energy.

Chapter 6. MODEL DEVELOPMENT IV: DETERMINATION OF PAIR CORRELATION FUNCTION

A. Definition of the Correlation Function

In the previous chapter, the conversion algorithm between the charged soft sphere and charged hard sphere has been established. The necessity for this work is that the analytical expression of the pair correlation function is generally possible only for a hard sphere related fluid model. Pair correlation function theory is not well developed for other than the hard sphere type fluid. The main goal in this chapter is to find or develop the pair correlation function for the ionic solution. To achieve this the first step is to review the definition of the correlation functions that are used for the description of systems governed by a hard sphere potential function.

Mathematical Definition of Pair Correlation Function

In chapter 3 the basic concept of the pair correlation function was introduced but there was no introduction of the mathematical definition of the pair correlation function. Consider a system of N particles in a volume V and at a temperature T. The probability that molecule 1 is in $d\mathbf{r}_1$ at $\mathbf{r}_1$, molecule 2 in $d\mathbf{r}_2$ at $\mathbf{r}_2$, etc., is given by

$$P^{(N)}(\mathbf{r}_1,\ldots\ldots,\mathbf{r}_N)\, d\mathbf{r}_1 \;\ldots.d\mathbf{r}_N = \frac{\exp(-\beta U_N)\; d\mathbf{r}_1\ldots d\mathbf{r}_N}{Z_N} \tag{6.1}$$

where Z_N is the configuration integral and $\mathbf{r}_i$ is a vector notation. The probability that molecule 1 is in $d\mathbf{r}_1$ at $\mathbf{r}_1$,..., $\mathbf{r}_n$, and molecule n is in $d\mathbf{r}_n$ at $\mathbf{r}_n$, irrespective of the configuration of the remaining N-n molecules, is obtained by integrating equation (6.1) over the coordinates of molecules $n+1$ through N:

$$P^{(n)}(\mathbf{r}_1,\ldots\ldots,\mathbf{r}_N) = \frac{\int\ldots\int \;\exp(-\beta U_N)\; d\mathbf{r}_{n+1}\ldots d\mathbf{r}_N}{Z_N} \tag{6.2}$$

Now the probability that any molecule is in $d\mathbf{r}_1$ at $\mathbf{r}_1$, .., $\mathbf{r}_n$, and any molecule is in $d\mathbf{r}_n$ at $\mathbf{r}_n$, irrespective of the configuration of the rest of the molecules, is

$$\rho^{(n)}(\mathbf{r}_1,\ldots\ldots,\mathbf{r}_N) = \frac{N\,!}{(N\,-\,n)\,!}\, P^{(n)}(\mathbf{r}_1,\ldots\ldots,\mathbf{r}_N) \tag{6.3}$$

This comes about since we have N choices for the first molecule, N - 1 for the second, etc.

The simplest distribution function is $\rho^{(1)}(\mathbf{r}_1)$. The quantity $\rho^{(1)}(\mathbf{r}_1)d\mathbf{r}_1$ is the probability that any one molecule will be found in $d\mathbf{r}_1$. For a crystal this is a periodic function of $\mathbf{r}_1$ with sharp maxima at the lattice sites, but in a fluid all points within V are equivalent and so $\rho^{(1)}(\mathbf{r}_1)$ is independent of $\mathbf{r}_1$. For a fluid therefore it can be written

$$\frac{1}{V} \int \rho^{(1)}(\mathbf{r}_1)d\mathbf{r}_1 = \rho^{(1)} = \frac{N}{V} = \rho \tag{6.4}$$

The correlation function is now defined

$$g^{(n)}(\mathbf{r}_1,\ldots\ldots,\mathbf{r}_n) = \frac{\rho^{(n)}(\mathbf{r}_1,\ldots\ldots,\mathbf{r}_N)}{\rho^n} \tag{6.5}$$

If $n=2$, this is the so-called pair correlation function, $g_{ij}(r)$. It is important since it can be determined by experiment.

There are other correlation functions besides the pair correlation function. They include the total correlation function, the background correlation function, and the direct correlation function.

Total Correlation Function

The total correlation function is defined for an isotropic fluid as

$$h_{ij}(r) = g_{ij}(r) - 1 \tag{6.6}$$

Background Correlation Function

This is another function that appears in applications, as in chapter 5 in the discussion of perturbation theories in fluids. This function has many names, such as y correlation function, cavity distribution function, indirect correlation function, or background correlation function. Its mathematical expression for an isotropic fluid is

$$y_{ij}(r) = g_{ij}(r) \exp[\beta \, u_{ij}(r)] \tag{6.7}$$

This function is continuous for all r values, even for hard core fluids. Therefore, it is much used in numerical work where discontinuities are avoided at all costs.

Direct Correlation Function

The direct correlation function, $C_{ij}(r)$, for an isotropic fluid is defined in terms of the total correlation function $h_{ij}(r)$ through a convolution integral known as the Ornstein-Zernike(71)(OZ) relation.

$$C_{ij}(r) = h_{ij}(r) - \rho \sum_{l} \int C_{lj}(s) \, h_{il}(|\mathbf{r}-\mathbf{s}|) \, ds \tag{6.8}$$

where **r** and s are vector notation; thus, this equation contains a triple integration.

B. Review of Pair Correlation Function Theory

The previous section shows that each type of correlation function is related.If one kind of correlation function expression is obtained, then another one, i.e., the pair correlation function, can be also acquired. In this section, the basic theories developed for the expression of the pair correlation function will be reviewed.

Percus Yevick Approximation for Hard Sphere Fluid

Percus and Yevick(13) made an important approximation for the expression of the correlation function relationship in a general fluid:

$$C_{ij}(r) = g_{ij}(r) - y_{ij}(r) \tag{6.9}$$

Especially for hard sphere fluids, this can be transformed by

$$C_{ij}(r) = 0 \qquad \text{if } \sigma > r$$

$$g_{ij}(r) = 0 \qquad \text{if } r < \sigma \tag{6.10}$$

Later Thiele(72) and Wertheim(73) gave the analytical solution for this case, and Lebowitz(74) also gave the analytical solution for a mixture. The results are as follows.

There are two formulas for calculating the pressure: the virial equation and the compressibility equation. Two different pressure values are obtained from a single PY approximation due to its inexactness. The compressibility equation is

$$\beta P^{c} = \rho \frac{1+\eta+\eta^{2}}{(1-\eta)^{3}} - \frac{18}{\Pi} \frac{\eta_{ii}\eta_{jj}}{(1-\eta)^{3}} \frac{(d_{jj}-d_{ii})^{2}}{d_{ii}^{3}d_{jj}^{3}} \left[d_{ii}+d_{jj}+d_{ii}d_{jj}\left(\frac{\eta_{i}}{d_{ii}}+\frac{\eta_{j}}{d_{jj}}\right)\right] \tag{6.11}$$

where d_{ii} and d_{jj} are the diameters of species i and j, the packing fraction of species i is $\eta_i=(\pi/6)\rho_i d_{ii}^3$, and $\eta = \eta_i + \eta_j$. And $\rho_i$is the number density of species i, and $\rho = \rho_i + \rho_j$.

The contact values (values at the hard sphere surface) of the pair correlation function are

$$g_{ii}^{v}(d_{ii}) = (1-\eta)^{-2}\left[1+\frac{\eta}{2}+\frac{3}{2}\frac{\eta_j}{d_{jj}}(d_{ii}-d_{jj})\right]$$

$$g_{jj}^{v}(d_{jj}) = (1-\eta)^{-2}\left[1+\frac{\eta}{2}+\frac{3}{2}\frac{\eta_i}{d_{ii}}(d_{jj}-d_{ii})\right]$$

$$g_{ij}^{v}(d_{ij}) = \frac{d_{jj}\, g_{ii}(d_{ii}) + d_{ii} g_{jj}(d_{jj})}{d_{ii}+d_{jj}} \tag{6.12}$$

where $d_{ij}=(d_{ii}+d_{jj})/2$, The superscript V is to indicate that these contact values yield the virial pressure. Here, the virial pressure will not be used, but these contact values will be used in next section

The direct correlation function is assumed by Lebowitz to have a polynomial form:

$$C_{ii}(r) = -a_1 - b_1 r - d_* r^3 , \qquad r < d_{ii}$$

$$= 0 , \qquad r > d_{ii}$$

$$C_{jj}(r) = -a_2 - b_2 r - d_* r^3 , \qquad r < d_{jj}$$

$$= 0 , \qquad r > d_{jj}$$

$$C_{ij}(r) = -a_1 , \qquad r < \frac{d_{jj} - d_{ii}}{2}$$

$$= -a_1 - [bX^2 + 4 \lambda d_* X^3 + d_* X^4]/r , \qquad \frac{d_{jj} - d_{ii}}{2} \leq r \leq d_{ij}$$

$$= 0 , \qquad r > d_{ij} \qquad (6.13)$$

where $\lambda = \frac{d_{jj} - d_{ii}}{2}$ and $X = r - \lambda$. The constants are

$$a_i = \frac{\partial}{\partial \rho_i} [\beta P^c(\rho_i, \rho_j)]$$

$$b_i = -6 \left[\frac{\eta_i}{d_{ii}} g_{ii}(d_{ii})^2 + \frac{\eta_j}{d_{jj}^3} g_{ij}(d_{ij})^2 d_{ij}^2 \right]$$

$$b_j = -6 \left[\frac{\eta_j}{d_{jj}} g_{jj}(d_{jj})^2 + \frac{\eta_i}{d_{ii}^3} g_{ij}(d_{ij})^2 d_{ij}^2 \right]$$

$$b = -6 \left[\frac{\eta_i}{d_{ii}^2} g_{ii}(d_{ii}) + \frac{\eta_j}{d_{jj}^2} g_{jj}(d_{jj}) \right] d_{ij}\ g_{ij}(d_{ij})$$

$$d_* = \frac{1}{2} \left[\frac{\eta_i}{d_{ii}^3} a_i + \frac{\eta_j}{d_{jj}^3} a_j \right] \tag{6.14}$$

The pair correlation function, $g_{ij}(r)$, of the hard sphere system can be obtained by the following procedure. The 3 Dimensional Fourier transform of the Ornstein-Zernike Relation can be expressed as follows(75):

$$\mathcal{H}(k) = \mathcal{C}(k) + \mathcal{C}(k).\mathcal{H}(k) \tag{6.15}$$

where $\mathcal{H}(k)$ and $\mathcal{C}(k)$ are L by L matrices whose elements (i,j) are the 3 Dimensional Fourier transforms of $(\rho_i \rho_j)^{0.5} h_{ij}(r)$ and $(\rho_i \rho_j)^{0.5} C_{ij}(r)$ respectively. Generally, if the function $f(r)$ is a spherical function, then the 3 Dimensional Fourier Transform can be expressed as

$$\hat{f}(y) = 4\ \pi \int_0^{\infty} dr\ r^2\ \frac{\sin(y\ r)}{y\ r} f(r) \tag{6.16}$$

The inverse 3 D Fourier Transform is

$$f(r) = (2\pi^2)^{-1} \int_0^\infty dy\ y^2\ \frac{\sin(y\ r)}{y\ r}\ \hat{f}(y) \tag{6.17}$$

The $\hat{C}_{ij}(y)$, the direct correlation function of the Percus-Yevick approximation in the Fourier domain, can be expressed as follows from equation (6.13) and (6.16) (in this case i=1 and j=2).

$$\begin{aligned}
&\hat{C}_{11}(y) = - \frac{24}{\alpha^3 y^3 \rho_1} \eta_1 a_1 [\sin(\alpha y) - (\alpha y)\cos(\alpha y)] - \frac{24}{\alpha^3 y^3 \rho_1} \eta_1 \frac{b_1}{\alpha y} [2\alpha y \ \sin(\\
&\alpha y) - (\alpha^2 y^2 - 2) \ \cos(\alpha y) - 2\ ] - \frac{24}{\alpha^3 y^3 \rho_1} \eta_1 \frac{d}{\alpha^3 y^3} \ [\sin(\alpha y)(4\ \alpha^3 y^3 - 24\alpha y) \\
&-\cos(\alpha y)\ (\alpha^4 y^4 - 12\alpha^2 y^2 + 24) + 24\ ]
\end{aligned}$$

$$\begin{aligned}
&\hat{C}_{22}(y) = - \frac{24}{y^3 \rho_2} \eta_2 a_2 [\sin\ y - y\ \cos\ y\ ] - \frac{24}{y^3 \rho_2} \eta_2 \frac{b_2}{y} [2\ y\ \sin\ y - \\
&(y^2 - 2)\ \cos\ y - 2\ ] - \frac{24}{y^3 \rho_2} \eta_2 \frac{d}{\alpha^3 y^3} \ [\sin\ y\ (4\ y^3 - 24\ y\ ) \\
&-\cos\ y\ (y^4 - 12\ y^2 + 24) + 24\ ]
\end{aligned}$$

$$\hat{C}_{12}(y) = -24\eta_2 \left(\frac{a_1}{y^3\rho_2}\right) \Big[\sin\left(\frac{1+\alpha}{2} y\right) - y \left(\frac{1+\alpha}{2}\right) \cos\left(\frac{1+\alpha}{2} y\right)\Big]$$

$$-24\eta_2 \left(\frac{b}{y^4 \rho_2}\right) \Big[(2-(y\alpha)^2 \cos\left(y \frac{1+\alpha}{2}\right) + 2y\alpha \sin\left(\frac{1+\alpha}{2}\right)$$

$$-2 \cos \left(\frac{1-\alpha}{2} y\right)\Big] -24\eta_2 \Big[\frac{d}{y^5\rho_2} 2 (1-\alpha)\Big]\Big[y\alpha \, [6-(y\alpha)^2] \cos\Big($$

$$\frac{1+\alpha}{2} y\Big) + 3 \, [(y\alpha)^2-2 \,] \sin\left(\frac{1+\alpha}{2} y\right) + 6 \sin \left(y \frac{1-\alpha}{2}\right)\Big]$$

$$-24\eta_2\left(\frac{d}{y^6 \rho_2}\right) \Big[-\cos\left(y \frac{1+\alpha}{2}\right) [(y\alpha)^4-12(y\alpha)^2+24 \,] +$$

$$4 y\alpha \sin\left(y \frac{1+\alpha}{2}\right) [(y\alpha)^2-6] + 24 \cos\left(y \frac{1-\alpha}{2}\right) \Big] \qquad (6.18)$$

where $\alpha = d_{11}/d_{22}$, and from the OZ relation, the $\hat{h}_{ij}(y)$ value can be calculated, and then the inverse Fourier transform, by equation (6.17) , can be performed to get $h_{ij}(r)$ in the real domain. Finally, $g_{ij}(r)$ can be obtained by equation (6.6).

Carnahan and Starling rule

Carnahan and Starling$^{(76)}$ introduced their own equation of state and applied it to obtain the contact values of hard sphere systems. The result is

$$g^{CS}_{ij}(d_{ij}) = \frac{1}{3}\, g^{v}_{ij}(d_{ij}) + \frac{2}{3}\, g^{C}_{ij}(d_{ij}) \tag{6.19}$$

where $g^{v}_{ij}(d_{ij})$ can be obtained from equation (6.12) and the compressibility values, $g^{C}_{ij}(d_{ij})$, can be obtained from the scaled particle theory$^{(77)}$:

$$g^{C}_{ij}(d_{ij}) = \frac{1}{(1-\eta)} + \frac{6\ Z}{(1-\eta)^2}\, \frac{d_{ii}\ d_{jj}}{2(d_{ii} + d_{jj})} + 12\frac{Z^2}{(1-\eta)^3}\left[\frac{d_{ii}d_{jj}}{2(d_{ii} + d_{jj})}\right]^2 \tag{6.20}$$

where $Z = \sum \frac{\pi}{6}\, \rho_i d^2_{ii}$. This equation gives an improvement over the Percus-Yevick theory.

Correction of the PY correlation function (Hard Sphere)

Verlet and Weis$^{(70)}$ proposed a slight modification of the pair correlation function given by the PY approximation because of its limitation at high densities, It thus becomes possible to predict the pair correlation function at higher densities with some accuracy.

Generally it is found that the PY correlation function has the following deficiencies:

1. At large r, the PY pair correlation function, $g(r)$, oscillates out of phase with respect to the exact value.
2. The contact values of the PY pair correlation functions are too low.

To solve the first problem, the equivalent packing fraction η_w, which was used in the Wertheim solution, was adjusted in relation to the actual packing fraction (η). Thus a new packing fraction, η_w, is used.

$$\eta_w = \eta - \frac{\eta}{16} \tag{6.21}$$

The diameter in the PY $g(r/d_w)$ is related to the exact diameter, d by

$$d_w^3 / \eta_w = d^3 / \eta \tag{6.22}$$

Additionally, the correction term was added to express the actual pair correlation value.

$$g\ (r/d\ ;\ \eta) = g_w(r/d_w;\eta_w) + \Delta g(r) \tag{6.23}$$

where $\Delta g(r)$ is

$$\Delta g(r) = \frac{A}{r} \exp[-\mu(r-d\ )] \cos \mu(r-d\ ) \tag{6.24}$$

and A and μ are

$$A = d\,(0.75)\,\frac{\eta_w^2\,(1-0.7117\eta_w\ -0.114\ \eta_w^2\ )}{(1-\eta_w^4)}$$

$$\mu = \frac{24A\ /\ d^2}{\eta_w\ g_w(1;\ \eta_w)}$$

Later Lee and Levesque$^{(78)}$ extended this work to mixtures. Their method is almost the same as that of Verlet and Weis. They used η_e instead of η_w , and used the solution of the Lebowitz. But they used the same η_w consistent with the pure value to avoid complexity although they are mixtures. At first the equivalent packing fraction is

$$\eta_e = \eta - \frac{\eta}{16} \tag{6.25}$$

The equivalent diameter d_{iie} is calculated from

$$\frac{d_{iie}^3}{\eta_e} = \frac{d_{ii}^3}{\eta} \tag{6.26}$$

For the other diameters, j ,

$$\frac{d_{jje}}{d_{iie}} = -\ \frac{d_{jj}}{d_{ii}} \tag{6.27}$$

The correction term is

$$g_{ij}(r/d_{ii};\ \eta) = g^{PY}_{ij}(r/d_{iie};\eta_e) + \Delta g_{ij}(r) \tag{6.28}$$

$$\Delta g_{ij}(r) = \frac{A_{ij}}{r} \exp[-\mu_{ij}(r-d_{ij})] \cos \mu_{ij}(r-d_{ij}) \tag{6.29}$$

All the d_{ij}- related notation is the same as previously and A_{ij} and μ_{ij} are given by:

$$A_{ij} = d_{ij} \left[g^{CS}_{ij}(d_{ij}) - g^{PY}_{ij}(d_{ij}/d_{iie};\eta_e) \right]$$

$$\mu_{ij} = \frac{24A_{ij} \ / \ d^2_{ij}}{\eta_e \ g^{PY}_{ij}(d_{ije} \ /d_{iie};\ \eta_e)}$$

Mean Spherical Approximation(15-17)

The mean spherical approximation (MSA) is applicable to model potentials with charged hard spheres. The correlation function expression is

$$g_{ij}(r) = 0 \qquad r < d_{ij} \tag{6.30.a}$$

$$C_{ij}(r) = -\beta\, u_{ij}(r) \qquad r > d_{ij} \qquad (6.30.b)$$

These conditions seem reasonable. Equation (6.30.a) is exact, i.e., there is no particle distribution inside the hard sphere. Equation (6.30.b) is an approximation that can be rationalized by the support of Mayer cluster theory(9,79) which was developed for the convenience of the thermodynamic property calculation by the introduction of topological methods. In the case of hard spheres, i.e., if the potential, $u_{ij}(r)$, is equation (4.1), then MSA is the same as the PY approximation for the hard sphere case. For the case of charged hard spheres with equal ion size and charge (restricted primitive model), Waisman and Lebowitz(15) solved MSA analytically, and the solution is

$$C_{ij}(r) = C^{PY}_{ij}(r) - \beta \frac{q_i\, q_j}{\varepsilon\, r}\, B \left[2 - \frac{B\, r}{d_{ij}} \right], \qquad r < d_{ij}$$

$$= -\beta \frac{q_i\, q_j}{\varepsilon\, r}, \qquad r > d_{ij} \qquad (6.31)$$

Here $C^{PY}_{ij}(r)$ is the direct correlation function of the PY approximation where $B = X^{-2}\, [X^2 + X - X(1+2X)^{0.5}]$, $X = \kappa^2 d^2_{ij}$ and κ is the Debye kappa(2):

$$\kappa^2 = \frac{4\, \pi\, e^2}{\varepsilon\, k\, T} \quad \Sigma\ \rho_i\, z_i^2$$

For different ion size, charge and mixed electrolytes (primitive model) cases, the solution was obtained by Blum.(16-17)

Exponential Approximation(22-25)

This theory is sometimes called the optimized cluster perturbation theory. The main procedures can be described as below.

(1) Express the interactions between the molecules by the graphic method and perturbation. Here all possible combinations are replaced by the topological treatment. This expression has similarity with the vector notation that enables description of the multicomponent system behavior with simple expressions.

(2) Describe the excess Helmholtz free energy and pair correlation function with this graphical expression.

(3) Reduce the graphical expression by compensating with each other and some reasonable truncation. This procedure is very complicated but logical. The graph theory developed by Morita and Hiroike(80) and Stell and Lebowitz,(81) which supplies the lemma for the topological reduction, is used as a tool to execute this procedure.

By the procedures described above, the final expression for the pair correlation function is

$$g_{ij}(\mathbf{r}) \simeq g_{dij}(\mathbf{r}) \exp\,[\mathscr{C}_{ij}(\mathbf{r})] \qquad (6.32)$$

where $g_{dij}(\mathbf{r})$ is the pair correlation function of the hard sphere and the renormalized potential, $\mathscr{C}_{ij}(\mathbf{r})$, is

$$\mathscr{C}_{ij}(r) = -[z_i z_j e^2/(k\, T\, \varepsilon\, r)] \exp(-\kappa\, r) \tag{6.33}$$

This is the so-called EXP theory, and the method to obtain the excess Helmholtz free energy is the ORPA $+B_2$ method. Here we need only the EXP theory, and so ORPA $+B_2$ is not introduced. But basically, EXP theory and ORPA $+B_2$ can be considered equivalent. The important feature of EXP theory is that it is derived on the basis of symmetric (in charge or size) particles.

The Stillinger-Lovett Moment Condition(27-29)

This theory can be considered as a type of ion-pair theory (which was first suggested by Bjerrum(82)) used to describe the physical interactions of the ion pair by separation of the long range and short range parts. In their theory, each anion is formally paired to a cation in a sequential way, so that all the ions can be looked upon as a collection of dipoles. The behavior of the resulting fluid of dipoles may conveniently be described by a wave-length, dependent dielectric constant, $\varepsilon(\lambda)$. The ion-atmosphere mean charge densities may be obtained from $\varepsilon(\lambda)$. This dielectric function is utilized in construction of 2 moment conditions. One is the so-called zeroth moment condition or local electroneutrality condition that states that the amount of charge of the central ion and its surroundings should be the same. The other is the so-called second moment condition. Here, the first one is important. The mathematical description of these two moment conditions will be treated in detail in the next section.

C. Selection of the Pair Correlation Function

In the previous section, several kinds of hard sphere correlation functions and their relationship with the pair correlation function have been reviewed. The most prominent theories that were introduced are PY approximation, MSA, and EXP theory. Apparently their approaches are quite different, but they are interrelated with each other.

As an example, the MSA is the same as the PY approximation when the interaction potential model is changed from the charged hard sphere type to the uncharged hard sphere type. Andersen and Chandler(22)also have pointed out the relation between the MSA and ORPA + B_2. They showed that the MSA, when solved for the restricted primitive model, can be considered as a part of the ORPA + B_2. Also, the ORPA + B_2 is essentially the same as the EXP, as the only difference is that the former is used for the expression of the excess Helmholtz free energy and the latter for the pair correlation function. As a consequence, the EXP theory is considered the most suitable for the expression of the pair correlation function of the theories that were reviewed in the previous chapter.

The remaining problem is the modification of the EXP theory because of its limitations:

1) The EXP theory is developed for the case of symmetric particles.

2) The effective maximum concentration is 2 M.

One of the possible suggestions is the slight modification of the renormalized potential because equation (6.33) is used generally for ionic solutions and this equation is the famous Debye-Hückel Pair Correlation Function, $h_{ij}(r)$. Here, this was defined as a total correlation function. Olivares and McQuarrie(26) have suggested the following modification and have applied it to the symmetrically charged case (restricted primitive model). Their suggestion is

$$g_{ij}(r) = g_{dij}(r) \exp \left[- \frac{z_i z_j \; e^2}{\varepsilon \, k \, T(1 + k \, d_{ij})} \; \frac{\exp[-\kappa \, (r - d_{ij})]}{r} \right] \tag{6.34}$$

where $d_{ii} = d_{jj}$, $z_i e = q_i$ and the other notation is the same as previously. This can be applied to the unsymmetrically charged case, or primitive model, because the value d_{ij} is determined not by the symmetrical treatment of the particle but by the boundary condition of the differential equation.

Another manipulation to this equation is to introduce the Stillinger-Lovett moment condition. In the previous section, two moment conditions were introduced. The first one was the zeroth moment condition (local electroneutrality condition) and the second one was the second moment condition. Olivares and McQuarrie also tried this in the same paper and applied it to the restricted primitive model but the subsequent papers of Stillinger-Lovett(28,29) enable the extension from the restricted primitive model to the primitive model or arbitrary mixtures of electrolytes of unrestricted charge species. Here, the zeroth moment condition is applied to the EXP theory and this modified EXP theory can be extended to the primitive model. By introducing the zeroth moment condition to the EXP theory the accuracy can also be improved up to the higher valence ion systems because of the characteristics of the zeroth moment condition, i.e., electroneutrality condition. Generally, EXP theory and the HNC equation satisfy the electroneutrality condition but the modified form of the EXP theory, equation (6.34), does not satisfy this condition and consequently the accuracy deteriorates as the valence of the ion increases.

The adoption of the second moment condition is not considered here, though it may contribute to a further enhancement of accuracy, because of its complexity. If two conditions are introduced to the modified EXP theory, two parameters will be needed to satisfy this condition and it is not easy to find the two parameters in the nonlinear equation systems. Alternatively, an improvement in the accuracy can be achieved by using the flexibility of the ion size mentioned in the previous chapter instead of introducing the second moment condition. By this procedure, the modified form of the EXP theory introduces one parameter, P, to satisfy the zeroth moment condition of the Stillinger-Lovett moment condition. The expression is

$$g_{ij}(r) = g_{dij}(r) \exp\left[- \frac{z_i z_j \ e^2}{\varepsilon \ k \ T \ (1 + \kappa \ P \ d_{ij})} \frac{\exp[-\kappa \ P(r-d_{ij})]}{r}\right] \qquad (6.35)$$

The remaining task is to evaluate the P by applying the electroneutrality condition. Here the general moment conditions, though only the zeroth moment condition is considered, are shown including not only zeroth moment condition but also second moment condition. The zeroth moment condition for an ionic system, if the cation is 1 and the anion is 2, is

$$-\sum_{i=1}^{2} z_i^2 \rho_i = \sum_{i=1}^{2} z_i^2 \rho_i \int_v [\sum_{j=1}^{2} z_j \rho_j g_{ij}(\mathbf{r})] \, d\mathbf{r} \tag{6.36}$$

The second moment condition is

$$\frac{-6}{\kappa^2} = \frac{\int_v \left[\sum_{j=1}^{2} \sum_{k=1}^{2} z_j \rho_j z_k \rho_k g_{jk}(\mathbf{r}) \right] d\mathbf{r}}{\sum_{i=1}^{2} z_i^2 \rho_i} \tag{6.37}$$

where $\mathbf{r}$ is a vector, $d\mathbf{r} = 4 \pi r^2 dr$, and $\int_v$ is a volume integral.

The P value of the equation (6.35) can be obtained by satisfying the equation (6.36). If the second moment condition is considered also, though it is not considered here, then equation (6.37) should be satisfied by introducing another parameter besides P. After the P value is calculated, the pair correlation for the charged hard sphere is obtained in the form of equation (6.35). The hard sphere pair correlation function, $g_{dij}(r)$, can be calculated by the method of Lee and Levesque that is suggested in equation (6.28).

D. Summary of Chapter 6

In chapter 6, the pair correlation function is determined by way of a complicated procedure. All the theoretical quantities that are used for the calculation of the osmotic coefficient, equation (3.12), are obtained.

Chapter 7. CALCULATION OF OSMOTIC COEFFICIENT

A. Numerical Work

In Chapter 2 to 6 the entire procedure for the calculation of the osmotic coefficient was developed. In this chapter, the numerical evaluation of the osmotic coefficient is executed with the help of the equations and functions developed earlier. A total of 28 single salt solutions are treated at room temperature and pressure. The detailed procedure is as follows.

Preparation of the conversion factor

The object of this step is to calculate the conversion factor between the osmotic coefficients based on molarity and molality. The equations used are (2.16), (2.18-20), and all the equations in section C of Chapter 2. The program used is included in Appendix 1.A, and the parameters that are used in equation (2.24) are obtained from Landis(31) and listed in Table 7.1.

Calculation of the cation diameter

The object of this step is to calculate the hypothetical cation diameter of the charged hard sphere following Chapters 4 and 5. In Chapter 4, the charged soft sphere potential, equations (4.17) and

Table 7.1. Density Parameters Used to Calculate the Solution Density in g/cm^3 from equation (2.24).

Solution	A	B	C	D	E
$KBrO_3$	0.1417E+00	0.5408E-01	0.6203E-02	-0.4838E+00	0.1310E+00
NaF	0.4124E-01	0.9906E-02	-0.1000E-01	-0.8516E-02	0.9904E-02
CsOH	0.1275E+00	0.3902E-02	-0.4170E-02	-0.8682E-03	0.1301E-03
$CsNO_3$	-0.3146E-02	-0.1144E-02	-0.3108E-03	-0.1623E-03	0.1430E-02
KH_2PO_4	-0.2259E-01	-0.6854E-02	-0.3237E-02	-0.1183E-03	0.1333E-02
LiI	0.9695E-01	0.1288E-02	-0.4139E-02	-0.5445E-03	0.3496E-03
$LiClO_4$	0.6407E-01	-0.3611E-02	-0.6984E-03	-0.4178E-03	0.5096E-04
KI	0.1215E+00	-0.4078E-02	-0.3595E-02	-0.4510E-03	0.2006E-03
KCl	0.5522E-01	-0.1004E-01	-0.2448E-03	0.1569E-02	-0.4573E-03
KBr	0.9237E-01	-0.9726E-02	-0.9696E-03	0.7082E-03	-0.1893E-03
NaCl	0.4793E-01	-0.7546E-02	-0.1109E-03	0.8108E-03	-0.2063E-03
HBr	0.5760E-01	-0.2897E-02	-0.6851E-03	0.3405E-03	-0.9543E-04
HI	0.9155E-01	-0.2614E-02	-0.1749E-02	-0.1294E-03	0.5470E-04
NaBr	0.8504E-01	-0.6748E-02	-0.1037E-02	0.3927E-03	-0.7864E-04
HCl	0.2115E-01	-0.2783E-02	-0.7469E-04	0.1470E-03	-0.2703E-04
$NaNO_3$	-0.1143E-01	-0.2899E-02	-0.9346E-03	0.4949E-03	0.9919E-06
NaI	0.1152E+00	-0.2564E-02	-0.2973E-02	-0.3626E-03	0.1430E-03
LiBr	0.6237E-01	-0.1256E-02	-0.1142E-02	-0.1232E-03	0.4302E-04
LiCl	0.2554E-01	-0.2151E-02	-0.1896E-03	0.3851E-04	-0.1422E-05
$LiNO_3$	0.3999E-01	-0.1526E-02	-0.6983E-03	-0.2599E-04	0.1321E-04

Table 7.1. (continuation)

Solution	A	B	C	D	E
Na_2HPO_4	0.4562E-01	-0.1481E-02	-0.1422E-02	-0.1649E-03	0.6472E-04
Na_2SO_4	0.1458E+00	-0.3929E-01	-0.2612E-03	0.2251E-01	-0.1153E-01
Na_2CO_3	0.1220E+00	-0.1870E-01	-0.6075E-02	0.3957E-02	0.4872E-04
$Na_2S_2O_3$	0.1156E+00	0.8659E-02	-0.8971E-02	-0.3420E-02	0.1359E-02
$CuSO_4$	0.1640E+00	-0.7687E-02	-0.1232E-01	-0.3683E-03	0.1043E-02
$MgSO_4$	0.9310E-01	0.3406E-01	-0.1251E-01	-0.9660E-02	0.3942E-02
$ZnSO_4$	0.3897E-01	-0.1433E-01	-0.1362E-01	-0.2756E-02	0.6126E-02
$MnSO_4$	0.1464E+00	0.1005E-01	-0.1656E-01	-0.7548E-02	0.7006E-02

(4.18), was selected. Two values were chosen arbitrarily: the r_{min} value and the n value, which is a variable depending on the concentration at fixed temperature. Once r_{min} is specified, the n value is controlled depending on the concentration. The determined intermolecular potential value is used with the perturbation method, equation (5.29), to calculate the hypothetical cation diameter of the corresponding charged hard sphere. One of the difficulties in determining the cation size is that not only the cation size but also the anion size affects the osmotic coefficient value. The anion and cation diameter values, have mutual interactions and the determination of the cation and anion diameters should be done simultaneously. However, this is not an easy job. To solve this problem, the cation size is determined first based on the following assumption.

> *The cation is hydrated in most cases and the hypothetical diameter decreases proportional to the concentration.*

On the basis of this assumption, the variable range of the cation size is confined to a range around the r_{min} value. This is also consistent with the results suggested by Landis.(31) The table 7.2 shows r_{min} values and the regression results for the n value, which depends on the concentration. The λ values that are used to determine the r_{min} (see equation (4.17)) are between 0 and 2. It is known that the Cs^+ ion is not hydrated.(83) For the case of the hydrogen ion, since there is no Pauling radius available, it is arbitrarily chosen as 0.5 Å. With the size given by the assumption, the value r_{min} is determined

Table 7.2. Regression Coefficient for the n value with concentration change and r_{min} values (Cation).

Cation	Coefficient			equation	r_{min}
	A	B	C	type	value(Å)
Na^+	6.2062	-0.3121	-0.0050	1	4.66
K^+	2.0924	-0.0587	-0.0008	1	5.42
Li^+	3.8124	-0.0974	-0.0046	1	6.72
H^+	2.4956	-0.1574	0.0046	1	6.52
Cs^+	1.411	-0.01199	-0.007348	1	3.38
Cu^{++}	1.2494	-2.2040	5.9885	2	7.44
Mg^{++}	1.1922	-4.6446	18.2297	2	6.82
Zn^{++}	3.3100	-3.7022	14.4042	2	7.0
Mn^{++}	1.0797	-4.5572	19.2001	2	6.44

* There are two types of equations. Here M is molarity.

Type 1 : $n = A + B M + C M^2$, Type 2 : $n = A \exp[(M + B)^2/C]$

as r_{min} = 2(0.5 + 2.76)=6.52. In Table 7.2, the regression coefficients have no physical meaning. They are used only for the regression of the n values; thus, if a better regression scheme is used, then the number of coefficients may decrease. A more appealing approach would be to develop a new perturbation technique for ionic solutions which can predict ion sizes as a function of concentration with a fixed n value, but currently no such perturbation method is available. The sample results for the calculated cation diameter are illustrated in Figures 7.1, 7.2, 7.3 and 7.4 together with results for the anion diameter, which will be introduced in the next section. The sample program used for this calculation is given in Appendix 1.B.

Calculation of the anion diameter

The object of this procedure is to calculate the anion hard sphere diameter. The difference from the previous step for the cation is that it is determined using the size of the cation whereas the cation diameter is determined arbitrarily and independently. The procedure involves two steps as follows.

(1) Determination of the anion diameter and parameter (*P*) for the Stillinger-Lovett moment condition.

Here a suitable anion diameter, based on the given cation diameter at each different concentration, is estimated. The estimated cation and anion diameters are used to determine the *P* value, required for the satisfaction of the local electroneutrality condition of equation (6.36), in equation (6.35). Currently, a sophisticated algorithm for finding this *P* value has not been established, and so it is obtained by trial and error. This is possible since its value does not deviate significantly from 1. The *P* value is not empirical, but rather is the solution of the equation (6.36). Next, the cation and anion diameters and *P* value are used to calculate the osmotic coefficient at a given concentration and temperature. The calculated osmotic coefficient (ϕ_c) is converted to a ϕ_m value, by the conversion factor prepared in the previous step, for comparison with the experimental data. If necessary, the anion diameter, and thus the *P* value, are adjusted so as to give a reasonable fit at the given concentrations. The program for this procedure is introduced in the appendix 1.C.

(2) Analytical Construction of the anion diameter value with concentration.

The suitable anion diameters are determined at each given concentration data point in the former procedure. In this second step an analytical expression for the anion diameter is constructed via the perturbation method. The procedure is the same as for the cation case done previously. One difference from the cation case is that in most cases, the anion diameter is extremely large (about 10 Å) at dilute concentrations (0.001 M) and deceases rapidly until the concentration reaches 0.1 M. After this, the rate of change is less and shows behavior similar to the cation. As mentioned already, the diameter value is a hypothetical one, so that it may show abnormal behavior (in size) at the limiting concentration. This is the reason why a relatively large value of $r_{\min}$ is required for the anion as compared to the cation. The anion diameter tends to change with composition in the same manner as the osmotic coefficient. It does not decrease monotonically like the cation, so that the assumption used for the calculation of the cation diameter is invalid here. Also, the same anion can have different diameters at the same concentration and temperature if it is combined with a different cation, while the cation maintains the same diameter regardless of the counterpart ion. This seems physically unreasonable but there are two possible explanations for the these phenomena. The first one is that it is a hypothetical diameter. Secondly the cation tends to hydrate well, so that the cation sphere is protected by a water cosphere. As a consequence, the cation can maintain its property and this also may be the answer why the cation diameter decreases monotonically.

Generally, more coefficients are required for the regression of this value than for the cations due to the differences between the anion and cation diameter behavior. As stated earlier for the cation, the ultimate solution would be to develop a perturbation method suitable for ionic solutions in order to reduce the number of parameters. Alternatively, it may be possible to develop a better regression scheme. This parameter problem will be discussed again in the next chapter. Appendix 1.B contains the program used for this procedure.

Tables 7.3a and 7.3b show the required coefficients for the regression of the n value and $r_{\min}$ values for the calculation of the anion diameters. Figures 7.1, 7.2, 7.3 and 7.4 show the samples of

Table 7.3a. Regression Coefficients for the n value with concentration change and r_{min} values (anion).

Anion	concentration range(molarity)	Coefficient A/B/C/D/E/F/G
Br(Li) r_{min} $=16$ Å	$0 < M \leq 0.2$	1.1088E+00/4.6456E-03 /-9.1705E-05/1.3603E-06/ -6.8380E-09/ 1.2317E-11/-6.7375E-15
	$0.2 < M \leq 1.2$	6.5109E-06/ 4.2701E+00/-6.5905E+00/5.2101E+00/ -2.2240E+00/0.48630E+00/-4.2565E-02
	$1.2 < M \leq 16$	1.3054/-3.0876/20.598/-68.570/119.19/-103.40/ 35.29955
Br(Na) r_{min} $=15$ Å	$0 < M \leq 0.5$	1.1152E+00/ 6.7865E-03/-1.3850E-04/2.0293E-06/ -1.042439E-08/ 1.907260E-11/-1.052841E-14
	$0.5 < M \leq 1.6$	1.5857/-2.6880/6.0703/-7.1082/4.5597/-1.5159/ 0.20386
	$1.6 < M \leq 9.0$	2.0922/-18.184/147.66/-642.05/1547.3/-1946.0/ 995.1722
Br(H) r_{min} $=16$ Å	$0 < M \leq 1.0$	1.2686E+00/ 5.9771E-03/-4.5214E-05/1.2300E-07/ 4.8957E-10/-1.6540E-12/1.0875E-15
	$1.0 < M \leq 8.0$	2.5273/-9.8594/42.566/-98.254/125.07/-82.528/ 21.994

Table 7.3a. (Continuation)

Anion	concentration range(molarity)	Coefficient A/B/C/D/E/F/G
Cl(Li) $r_{\min}$ = 14 Å	$0 < M \leq 0.5$	1.1266E+00/4.6129E-04/7.1927E-05/-5.6717E-07/1.9577E-09/-2.8184E-12/1.3623E-15
	$0.5 < M \leq 3.0$	1.0502/0.3811/-1.3181/2.3454/-2.1434/0.96507/-0.16960
	$3.0 < M \leq 19.$	4.6532/-122.15/1738.9/-12861./51893.2/-108340./491590
Cl(K) $r_{\min}$ = 15 Å	$0 < M \leq 0.4$	1.0810E+00/4.7673E-03/-2.8214E-05/1.6669E-07/-2.2589E-11/-6.3912E-13/5.2462E-16
	$0.4 < M \leq 2.2$	1.1627/-0.51057/0.99494/-0.97019/0.51784/-0.14336/
	$2.2 < M \leq 5.0$	-2.9598/78.348/-613.22/2492.2/-5570.1/6503.1/-3100.8
Cl(Na) $r_{\min}$ = 15 Å	$0 < M \leq 0.2$	1.0948E+00/3.8342E-03/1.9762E-05/-4.4338E-07/2.6477E-09/-5.0835E-12/2.8590E-15
	$0.2 < M \leq 1.6$	1.0539/-1.0180E-02/4.9978E-02/-3.9610E-02/0.014931/-2.6863E-03/1.8386E-04
	$3.0 < M \leq 19.$	1.5577/-6.7575/39.778/-126.29/224.17/-209.09/79.75715

Table 7.3a. (Continuation)

Anion	concentration range(molarity)	Coefficient A/B/C/D/E/F/G
Cl(H)	$0 < M \le 1.4$	1.1889E+00/ 5.7164E-03/-1.3440E-04/1.9541E-06 /-9.7751E-09/1.7580E-11/-9.6121E-15
$r_{\min}$ =16 Å	$1.4 < M \le 10.$	1.9093/-9.3116/53.779/-166.71/285.38/-253.59/ 91.197
I(H)	$0 < M \le 1.7$	1.3794E+00/ 1.8806E-02/-4.9278E-04/5.8170E-06 /-2.6911E-08/4.6937E-11/-2.5335E-14
$r_{\min}$ =16 Å	$1.7 < M \le 8.$	2.6287/-12.381/50.120/-97.901/78.371/8.4390/ -32.862
I(Li)	$0 < M \le 0.2$	1.2876E+00/4.1755E-03/-5.3852E-05/6.2985E-07/ -2.5531E-09/ 4.0827E-12/-2.1004E-15
$r_{\min}$ =16 Å	$0.2 < M \le 1.7$	1.2047/-0.17411/0.29947/-0.18638/5.8875E-02/ -9.3542E-03/5.8925E-04
	$1.7 < M \le 3.0$	1.4064/-1.0569/1.6200/-0.83586/0/0/0

Table 7.3a. (Continuation)

Anion	concentration range(molarity)	Coefficient A/B/C/D/E/F/G
I(Na) $r_{\min}$ = 15 Å	$0 < M \leq 0.3$	1.1819E+00/3.6625E-03/-3.3389E-05/4.5125E-07/-1.8827E-09/2.9992E-12/-1.5278E-15
	$0.3 < M \leq 1.6$	1.568553/-1.992045/3.868205/-3.8259/2.0448/-0.56017/6.1525E-02
	$1.6 < M \leq 12.$	1.4566/-0.68149/-11.899/78.729/-198.79/230.19/-101.68
I(K) $r_{\min}$ = 15 Å	$0 < M \leq 0.4$	1.1753E+00/6.6929E-03/-1.2921E-04/1.7144E-06/-8.1964E-09/1.4480E-11/-7.8603E-15
	$0.4 < M \leq 1.8$	1.6175/-2.4290/4.8686/-4.8969/2.6446/-0.73030/0.080823
	$1.8 < M \leq 4.5$	2.5533/-22.228/147.56/-518.93/1009.2/-1023.5//422.19
NO_3(Na) $r_{\min}$ = 14 Å	$0 < M \leq 1.0$	1.0620E+00/5.5086E-03/-6.2879E-05/9.1491E-07/-4.6959E-09/8.6715E-12/-4.8180E-15
	$1.0 < M \leq 2.5$	2.3328/-9.7385/32.482/-58.422/58.855/-31.265/6.8222
	$2.5 < M \leq 10.83$	103.85/-1814.7/13402./-52858./117270./-138670/68261.

Table 7.3a. (Continuation)

Anion	concentration range(molarity)	Coefficient A/B/C/D/E/F/G
NO_3(Cs) r_{min} = 16 Å	$0 < M \leq 1.5$	1.0778E+00/1.1978E-02/-2.6197E-04/3.0819E-06/-1.4345E-08/2.5123E-11/-1.3588E-14
NO_3(Li) r_{min} = 14 Å	$0 < M \leq 0.5$	1.1053E+00/3.1661E-03/ 2.7347E-06/1.5500E-07/-1.1957E-09/2.5373E-12/-1.4928E-15
	$0.5 < M \leq 5.0$	1.0486/3.6933E-02/0.10552/-0.26746/0.31700/-0.19653/4.8497E-02
	$5.0 < M \leq 20.0$	2.2733/-38.178/517.17/-3766.6/15168./-30830./22858.
BrO_3(K) r_{min} = 14 Å	$0 < M \leq 0.2$	1.0080E+00/2.4144E-03/2.5999E-05/-1.4737E-07/4.7300E-10/-6.1205E-13/2.6823E-16
	$0.2 < M \leq 0.5$	4.3726/-2.7204/0.72653/-6.3208E-02/0/0/0
F(Na) r_{min} = 15 Å	$0 < M \leq 1.0$	1.0003E+00/5.5241E-03/-9.1653E-05/1.13306E-06/-5.0337E-09/ 8.5318E-12/-4.5342E-15

Table 7.3a. (Continuation)

Anion	concentration range(molarity)	Coefficient A/B/C/D/E/F/G
OH(Cs) r_{min} = 18 Å	$0 < M \leq 1.2$	1.3317E+00/2.8321E-02/-7.4132E-04/8.1094E-06/-3.6049E-08/ 6.1718E-11/-3.3025E-14
H_2PO_4(K) r_{min}	$0 < M \leq 0.7$	1.0112E+00/2.4030E-03/7.1231E-06/-6.3844E-08/4.3032E-10/-8.8788E-13/5.1896E-16
= 15 Å	$0.5 < M \leq 1.8$	-2.0010/18.159/-43.748/54.715/-37.707/13.621/-2.0188
ClO_4(Li) r_{min}	$0 < M \leq 0.3$	1.1841E+00/1.0066E-02/-2.1945E-04/2.3602E-06/-1.0138E-08/1.6980E-11/-8.9808E-15
= 17 Å	$0.3 < M \leq 1.5$	1.1494/9.1559E-02/-0.22912/0.29792/-0.19013/5.9268E-02/-7.2129E-03
	$1.5 < M \leq 4.5$	3.5565/-35.066/215.67/-704.44/1281.4/-1227.0/482.52
$S_2O_3(Na_2)$ r_{min}	$0 < M \leq 0.1$	1.0477E+00/3.5102E-03/-2.3245E-05/1.3090E-07/-3.1798E-10/3.7207E-13/-1.5434E-16
= 10 Å	$0.1 < M \leq 1.4$	1.021451/-4.640214E-02/ 5.411944E-02/-2.5689E-02/6.2852E-03/-7.3951E-04/3.1851E-05
	$1.4 < M \leq 4.052$	2.3979/-14.357/62.513/-144.81/186.36/-125.40/34.257

Table 7.3a. (Continuation)

Anion	concentration range(molarity)	Coefficient A/B/C/D/E/F/G
$CO_3(Na_2)$ r_{min} = 9.8 Å	$0 < M \leq 0.1$	1.0359E+00/3.5588E-03/-2.3459E-05/1.3617E-07/-3.4097E-10/4.0917E-13/-1.7107E-16
	$0.1 < M \leq 1.5$	0.98370/5.9951E-02/-8.2224E-02/0.06026/0.060257/-0.022217/3.9951E-03/-2.7666E-04
$HPO_4(Na_2)$ r_{min} = 10 Å	$0 < M \leq 0.01$	1.2165E+00/-1.1646E-03/2.6445E-05/-1.1262E-07/2.7626E-10/-3.1368E-11/1.3599E-16
	$0.01 < M \leq 0.1$	1.079676/-1.268527E-02/ 1.811354E-03/-9.1391E-05/2.2542E-06/-2.6253E-08/1.1178E-10
	$0.1 < M \leq 1.0$	0.80258/0.57895/-0.67826/0.40573/-0.12941/2.0875E-02/-1.3285E-03

Table 7.3a. (Continuation)

Anion	concentration range(molarity)	Coefficient A/B/C/D/E/F/G
$SO_4(Na_2)$ r_{min} = 9.5 Å	$0 < M \leq 0.01$	0.81950/7.3014E-03/-5.7905E-05/2.8812E-07/-6.8939E-10/7.9693E-13/-3.3185E-16
	$0.01 < M \leq 0.1$	1.0175/ 1.1592E-03/ 1.9473E-04/-1.0043E-05/2.1118E-07/-1.9523E-09/6.5669E-12
	$0.1 < M \leq 1.25$	0.9893/2.3971E-02/-1.7585E-02/7.3699E-03/-1.4828E-03/1.3941E-04/-4.9124E-06

where anion(*) : * is the counterpart cation.

The used equation is

$$n = A + B/M + C/M^2 + D/M^3 + E/M^4 + F/M^5 + G/M^6$$

where M is molarity.

Table 7.3b. Regression Coefficient for the n value with concentration change and r_{min} values (anion).

Anion	concentration range(molarity)	Coefficient A/B/C
SO_4(Mn)	$0 < M \leq 0.70$	1.0220/ 0.008591/0.0007171$^{(a)}$
r_{min}	$0.70 < M \leq 2.5$	1.1172/-0.1754/0.0981$^{(b)}$
= 6.18 Å	$2.50 < M \leq 4.20$	0.05749/-4.637/0.5208$^{(c)}$
SO_4(Zn)	$0 < M \leq 0.65$	1.0060/ -0.001475/0.0005$^{(a)}$
r_{min}	$0.65 < M \leq 1.55$	-0.08211/-0.7704/0.9956$^{(c)}$
= 6.18 Å	$1.55 < M \leq 3.60$	0.1471/-2.367/0.8477$^{(c)}$
SO_4(Mg)	$0 < M \leq 1.0$	0.9766/ 0.03802/0.01994$^{(d)}$
r_{min}	$1.0 < M \leq 3.0$	-0.0974/-1.0097/0.9561$^{(c)}$
= 6.18 Å		
SO_4(Cu)	$0 < M \leq 0.5$	1.0149/-0.0010/0.0003$^{(a)}$
r_{min}	$0.5 < M \leq 1.4$	-0.07312/-0.5517/0.9858$^{(c)}$
= 6.18 Å		

where all the notations are the same as the table 7.3b. The superscript attached to each coefficients represents the used equation.

(a) $n = A + B/M + C/M^2$ (b) $n = A + B\,M + C\,M^2$

(c) $n = 1/[A\,(M+B)^2 + C\,]$ (d) $n = A + B\,M + C/M$

the varying anion diameter and corresponding cation diameter at each different concentration (molarity). Figure 7.1 is the variation of the ion diameters for the CsOH solution. Generally, the Cs^+ ion is not hydrated, so that this cation may not have cospheres.(72) By this reason the cation diameter change is considered to be insensitive to the concentration change while the anion decreases monotonically.

Figure 7.2 is for the $MnSO_4$ solution. Here, the experimental data are supplied starting from 0.1 m. The rapid change of the anion diameter in the dilute solution is not shown, but the tendency is similar and the anion diameter does not change monotonically. Generally at higher concentrations, the osmotic coefficient increases and this increase is reflected in the anion diameter. Both ion sizes change rapidly compared with the other solutions. This is considered to be the effect of high valence.

Figure 7.3 is for the $NaNO_3$ solution. The behavior is the normal case for the 1-1 type electrolyte solution, i.e., the anion diameter changes steeply in the dilute region and comes to a minimum value around 1 m and then increases slowly.

Figure 7.4 depicts the LiCl solution. This shows that the ion size change at high concentrations is similar to that for the $NaNO_3$ solution. However the ion size is relatively insensitive to concentration changes.

All these values are hypothetical, but they are considered to be a reflection of the real situation.

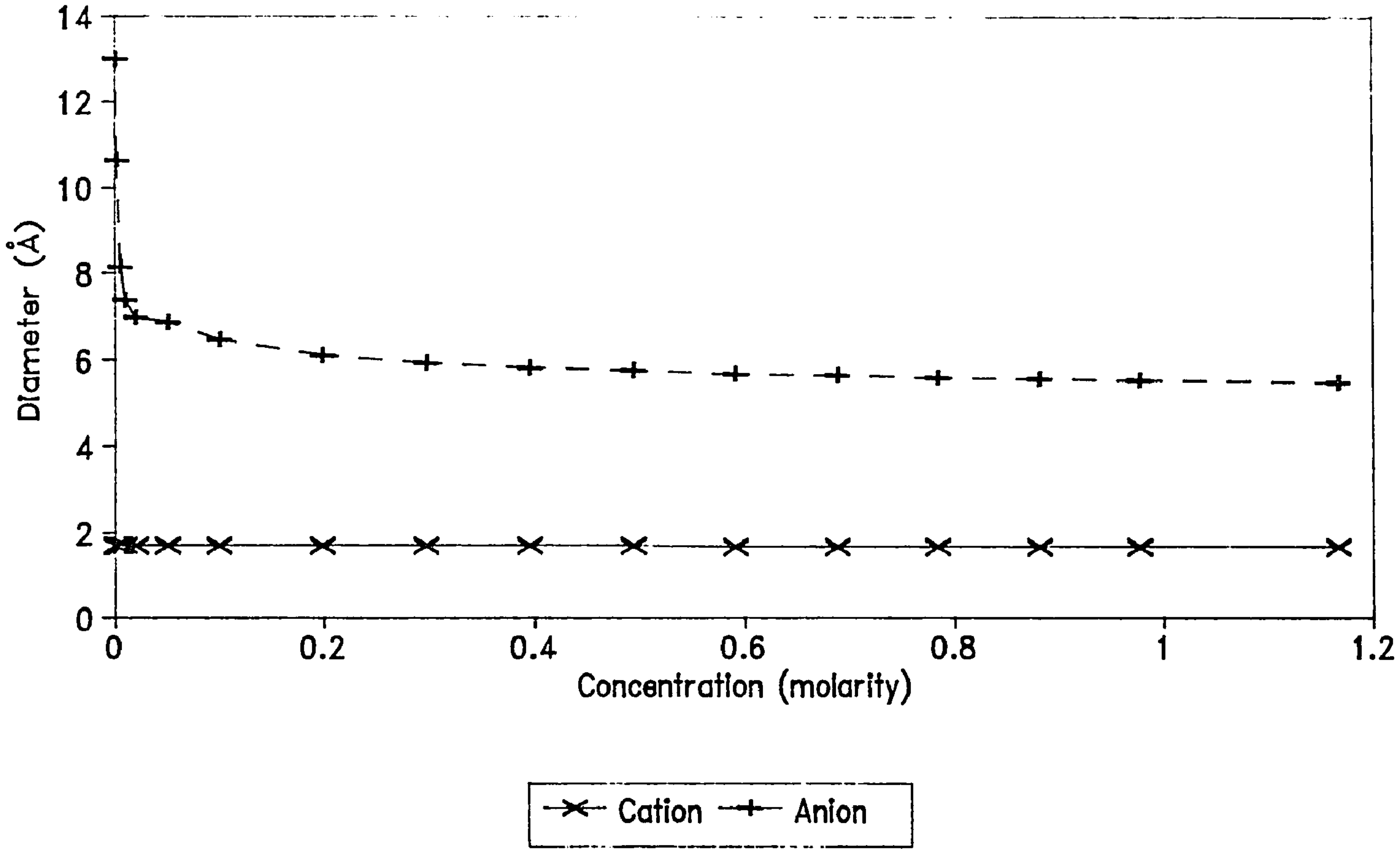


Fig. 7.1. Ion diameter change with concentration (CsOH : 0.000997 - 1.167612 M)

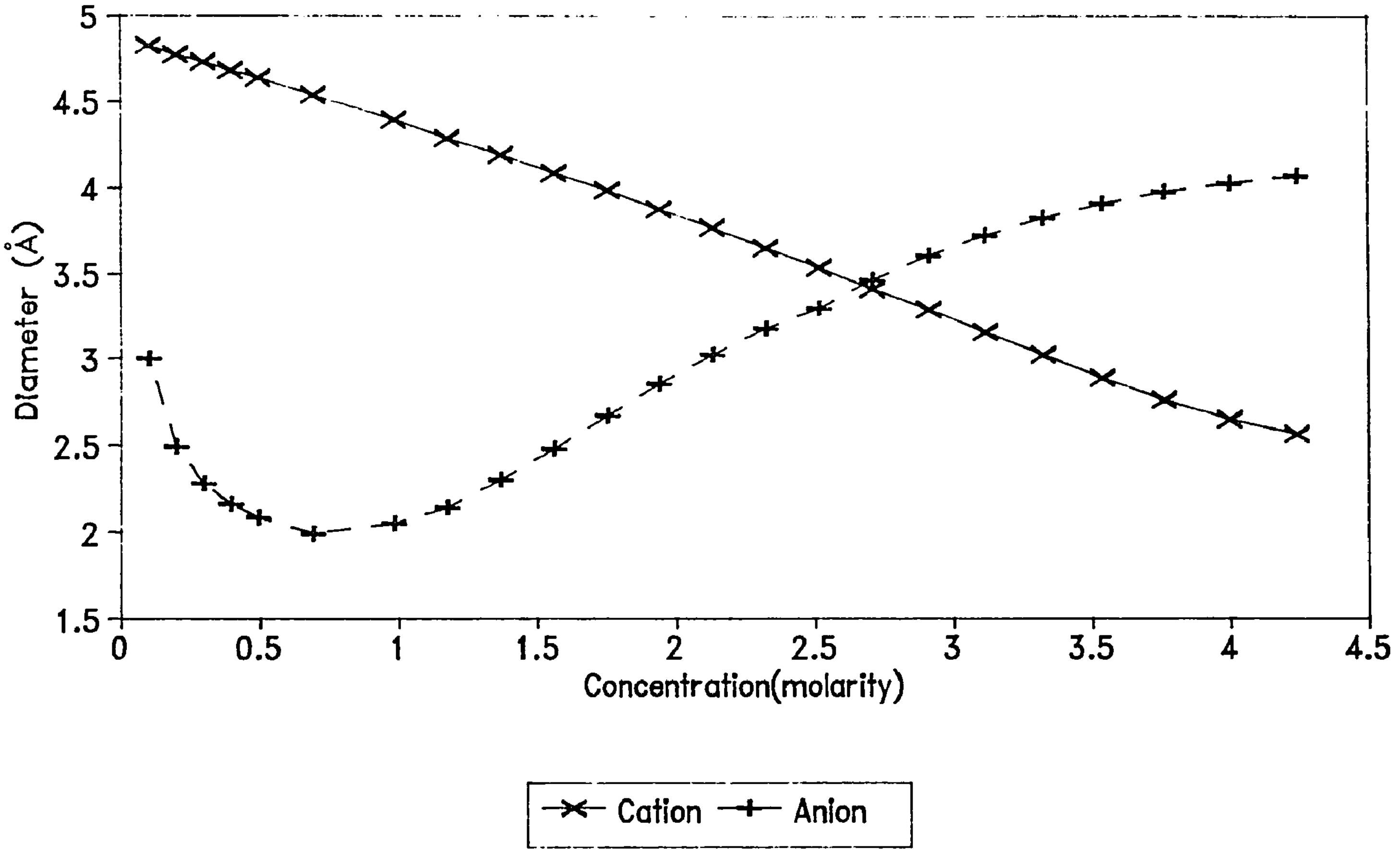


Fig. 7.2. Ion diameter change with concentration ($MnSO_4$: 0.009968 - 4.277151 M)

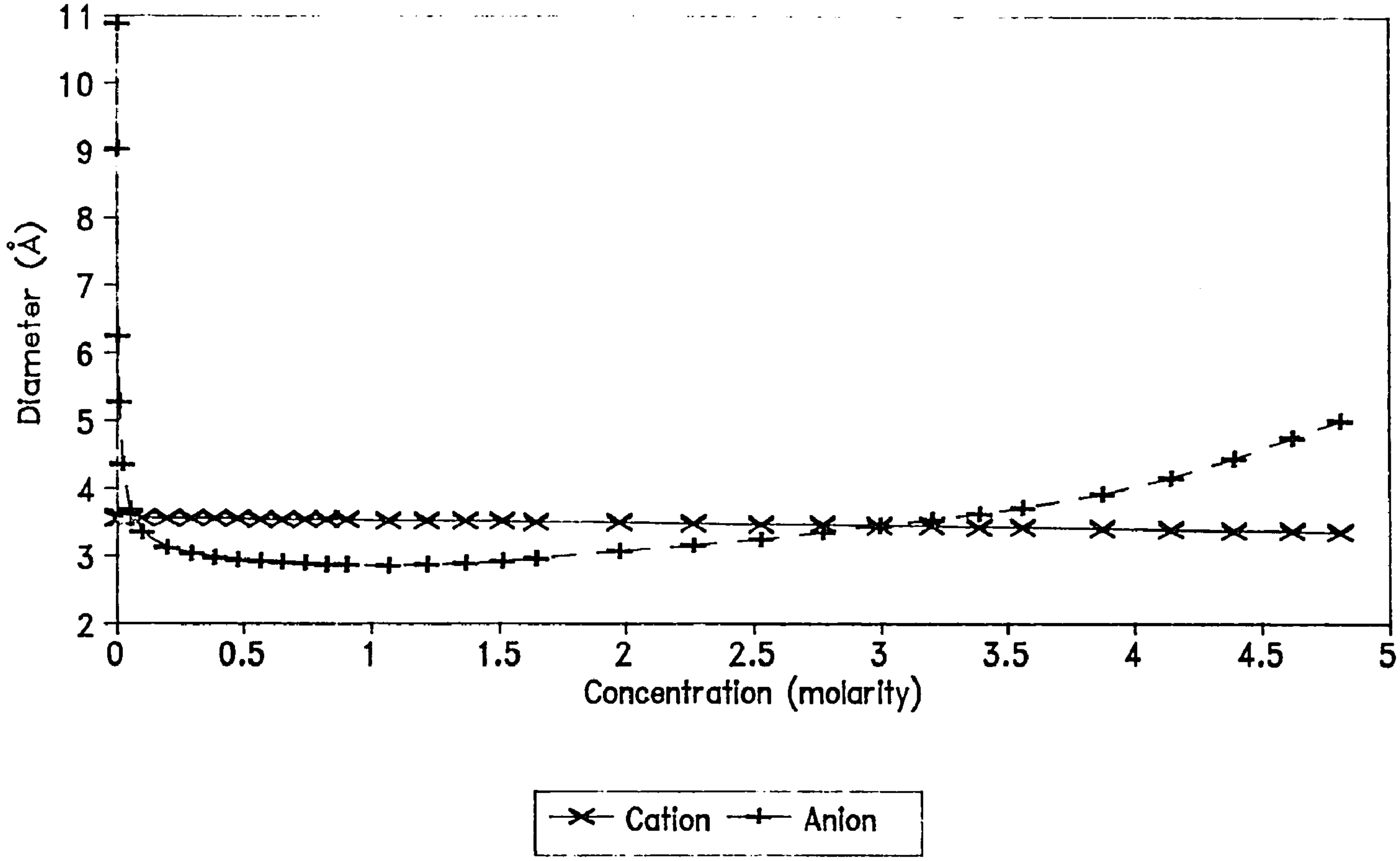


Fig. 7.3. Ion diameter change with concentration ($NaNO_3$: 0.000997 - 4.808119 M)

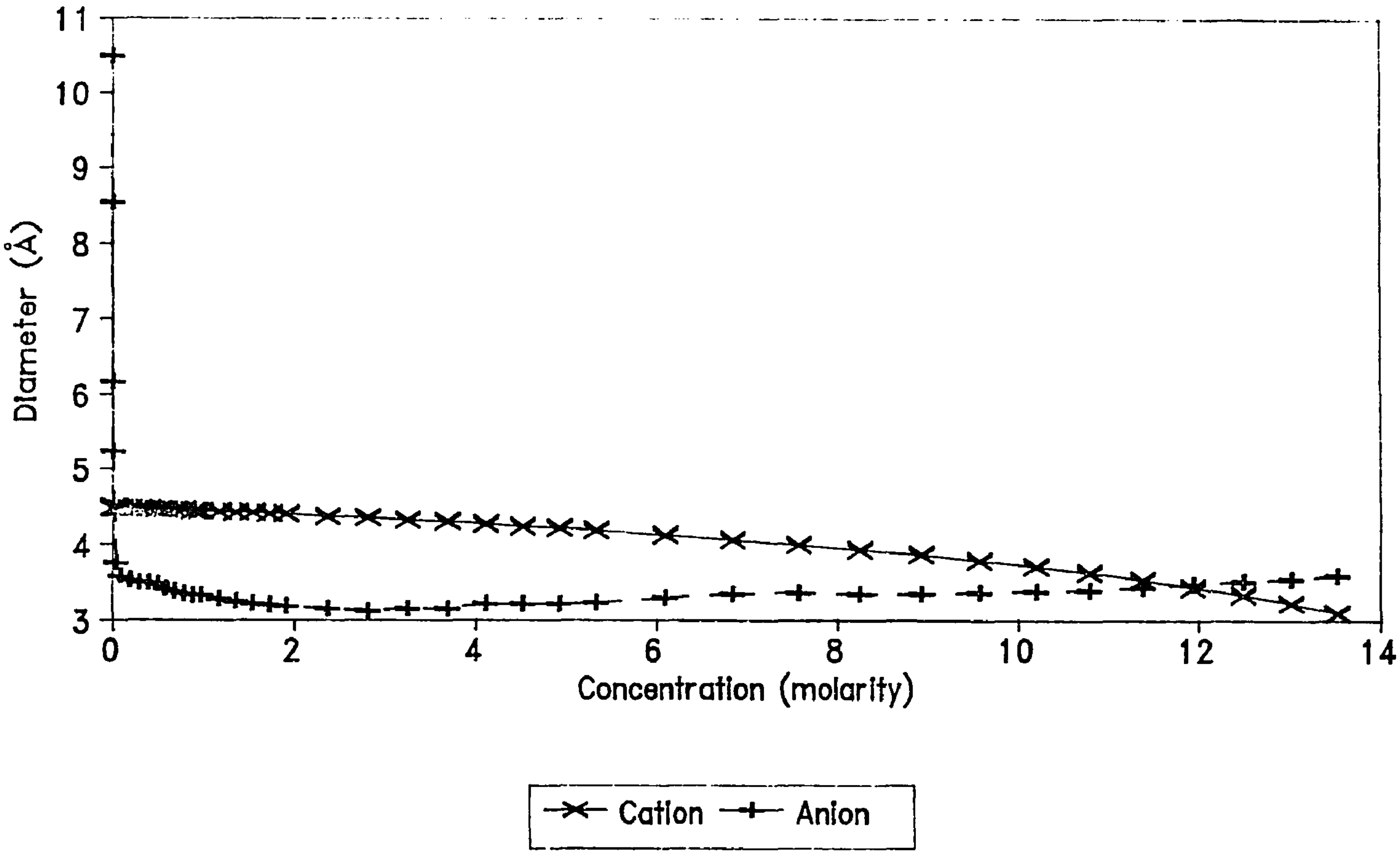


Fig. 7.4. Ion diameter change with concentration (LiCl : 0.000997 - 13.539350 M)

Final adjustment of the *P* value

Analytical expressions for the hypothetical diameters of the cation and anion are completed. The corresponding *P* value is now recalculated. The calculated values of cation, anion and *P* are used as the input for the osmotic coefficient calculation. Appendix 1.D gives the program for this procedure.

Calculation of the osmotic coefficient

The final step is to calculate the osmotic coefficient (ϕ_c) by the equation (3.12), and to convert it to ϕ_m for comparison with the experimental data. For reference purposes, we also calculate ϕ_m using Pitzer's model. It is important to keep in mind that the ionic interaction potential used here is for the charged hard sphere. Equation (3.12) can be changed to

$$\phi_c = 1 + \frac{2\pi}{3 \underset{i=1}{\Sigma} \rho_i} \frac{e^2}{\varepsilon_0 k T} \sum_{i=1}^{2} \sum_{j=1}^{2} \rho_i \rho_j z_i z_j \int_{d_{ij}}^{\infty} r g_{ij}(r)\, dr$$

$$+ \frac{2\pi}{3 \underset{i=1}{\Sigma} \rho_i} \sum_{i=1}^{2} \sum_{j=1}^{2} \rho_i \rho_j g_{ij}(d_{ij})\, d_{ij}^3 \qquad (7.1)$$

where $g_{ij}(r)$ is given in equation (6.35), and $g_{dij}(r)$ in equation

(6.35) is equivalent to equation (6.28). The contact value, $g_{ij}(d_{ij})$, is the case when $r = d_{ij}$ in equation (6.35), and the value of $g_{dij}(d_{ij})$ in this case is equivalent to equation (6.19), the so-called Carnanhan Starling rule.

There are two problems in the calculation of the equation (7.1). The first one is the determination of the integration range. In equation (7.1), the integration range is from zero to infinity, but this is of course impossible numerically. To solve this problem, the behavior of $g_{ij}(r)$ with respect to r should be considered. Generally the value of $g_{11}(r)$, $g_{22}(r)$, $g_{12}(r)$ and $g_{21}(r)$ are almost the same (i.e., unity) when the distance, r, is more than 6 or 7 times the diameter of the ion. If these values are almost the same, they cancel each other after this range in equation (7.1). This fact gives a practical definition of the upper limit of this integral, and so an upper limit equal to 10 times the ion diameter is used in the calculation of equation (7.1).

The second problem is the calculation of the pair correlation function for the hard sphere. This requires computation of the inverse Fourier transform, equation (6.17). Generally this requires N^2 operations where N is the number of integration steps, and as a result it requires a large amount of C.P.U. time. A Fast Fourier transform algorithm is adopted to solve this problem. This method executes the calculation of the discrete quantities with a kind of parallel processing algorithm. The Cooley and Tukey(101) calculation method is used and this calculation was done by the IMSL package. In general, this calculation requires $N \log N$ operations; since here N is 2048 steps, this calculation is about 600 times faster than the conventional Fourier transform calculation method. This is a very important savings in practice. Without this, the method developed here for the calculation of osmotic coefficients would be impractical. A test of the computing time on a VAX 6430 machine showed that for a particular calculation the Fast Fourier transform (F.F.T.) used 0.24 sec and the Fourier transform used 26.70 sec. The program used for this procedure is introduced in Appendix 1.E and the inputs and outputs are given in Appendix 2. Table 7.4 illustrates some sample input and output used and generated by the program for the example of a LiCl solution. All the calculated results are summarized and discussed in the next chapter.

B. Summary of Chapter 7.

The validity of the theoretical aspect of the new model is tested by the numerical calculations in this chapter. The numerical results for a total of 28 single salt solutions, at concentrations between 0.001 to 20 m have been obtained and compared with the experimental data and with the Pitzer model.

Table 7.4. Sample inputs and output for osmotic coefficient calculation.

INPUT A

molality	molarity	conversion rate	experimental data (ϕ_m)
1.0000000E-03	9.9705323E-04	0.9999831	0.988
2.0000001E-03	1.9940729E-03	0.9999661	0.984
4.9999999E-03	4.9849278E-03	0.9999149	0.976
9.9999998E-03	9.9690063E-03	0.9998290	0.969
2.0000000E-02	1.9934589E-02	0.9996555	0.960
5.0000001E-02	4.9810547E-02	0.9991270	0.947
0.1000000	9.9533461E-02	0.9982281	0.940
0.2000000	0.1987109	0.9963890	0.940
0.3000000	0.2975251	0.9945130	0.946
0.4000000	0.3959714	0.9926113	0.954
0.5000000	0.4940471	0.9906905	0.964
0.6000000	0.5917499	0.9887546	0.974
0.7000000	0.6890785	0.9868073	0.985
0.8000000	0.7860320	0.9848508	0.996
0.9000000	0.8826094	0.9828873	1.008
1.000000	0.9788108	0.9809180	1.020
1.200000	1.170086	0.9769689	1.044
1.400000	1.359858	0.9730118	1.068
1.600000	1.548132	0.9690538	1.093
1.800000	1.734916	0.9651000	1.119
2.000000	1.920217	0.9611548	1.145
2.500000	2.377046	0.9513484	1.213
3.000000	2.824838	0.9416520	1.284
3.500000	3.263784	0.9320898	1.361
4.000000	3.694090	0.9226772	1.441
4.500000	4.115968	0.9134243	1.525
5.000000	4.529634	0.9043368	1.613
5.500000	4.935302	0.8954184	1.703
6.000000	5.333189	0.8866705	1.794

INPUT A (continuation)

molality	molarity	conversion rate	experimental data (ϕ_m)
7.000000	6.106452	0.8696855	1.979
8.000000	6.851063	0.8533721	2.159
9.000000	7.568586	0.8377124	2.328
10.00000	8.260497	0.8226835	2.480
11.00000	8.928192	0.8082615	2.612
12.00000	9.572977	0.7944214	2.723
13.00000	10.19609	0.7811391	2.814
14.00000	10.79867	0.7683914	2.887
15.00000	11.38181	0.7561566	2.947
16.00000	11.94652	0.7444137	2.995
17.00000	12.49376	0.7331434	3.036
18.00000	13.02442	0.7223280	3.066
19.00000	13.53935	0.7119505	3.079

INPUT B

molality	cation diameter	anion diameter	*P* value
0.0009971	4.4701104	10.4927559	0.6544999
0.0019941	4.4700723	8.5468950	0.7642996
0.0049849	4.4699578	6.1682563	0.8405496
0.0099690	4.4697666	5.2322602	0.9130489
0.0199346	4.4693842	4.3810458	0.9558486
0.0498105	4.4682355	3.7479494	0.9944487
0.0995335	4.4663134	3.5789349	1.0068989
0.1987109	4.4624443	3.5174620	1.0108989
0.2975251	4.4585419	3.4997234	1.0128992
0.3959714	4.4546056	3.4901388	1.0142992
0.4940471	4.4506364	3.4833210	1.0157489
0.5917499	4.4466343	3.4064162	1.0168490
0.6890785	4.4425993	3.3804743	1.0194491
0.7860320	4.4385314	3.3509884	1.0202490
0.8826094	4.4344306	3.3369536	1.0219991
0.9788108	4.4302979	3.3232028	1.0252491
1.1700860	4.4219341	3.2874060	1.0276991
1.3598580	4.4134417	3.2504568	1.0335491
1.5481319	4.4048200	3.2199378	1.0360490
1.7349160	4.3960710	3.1966560	1.0426991
1.9202170	4.3871942	3.1789992	1.0448488
2.3770461	4.3644485	3.1483898	1.0557989
2.8248379	4.3409166	3.1249781	1.0670488
3.2637839	4.3166065	3.1576171	1.0786490
3.6940899	4.2915230	3.1503208	1.0902495
4.1159682	4.2656717	3.2217951	1.1019496
4.5296340	4.2390566	3.2142279	1.1215001
4.9353018	4.2116818	3.2133119	1.1345521

INPUT B (continuation)

molality	cation diameter	anion diameter	*P value*
5.3331890	4.1835475	3.2354853	1.1470531
6.1064520	4.1249990	3.3013134	1.1594527
6.8510628	4.0633831	3.3429906	1.2007025
7.5685859	3.9986243	3.3554935	1.2239531
8.2604971	3.9305894	3.3543208	1.2440000
8.9281921	3.8590701	3.3530166	1.2625004
9.5729771	3.7837646	3.3591506	1.2489487
10.1960897	3.7042530	3.3752270	1.2976509
10.7986698	3.6199667	3.4005048	1.2757521
11.3818102	3.5301359	3.4326570	1.2896007
11.9465199	3.4337244	3.4689543	1.3055497
12.4937601	3.3293123	3.5069368	1.3169987
13.0244198	3.2149184	3.5446846	1.3259488
13.5393496	3.0876713	3.5808637	1.3305489

OUTPUT

```
     molality                 OSMOTIC COEFFICIENT
                   New Model      experimental     Pitzer's
                                     value          model
 1.0000000E-03     0.9880040      0.9880000      0.9885255
 2.0000001E-03     0.9840007      0.9840000      0.9842656
 4.9999999E-03     0.9760000      0.9760000      0.9765961
 9.9999998E-03     0.9689896      0.9690000      0.9691004
 2.0000000E-02     0.9599574      0.9600000      0.9603496
 5.0000001E-02     0.9471748      0.9470000      0.9483732
 0.1000000         0.9398019      0.9400000      0.9416755
 0.2000000         0.9393156      0.9400000      0.9413663
 0.3000000         0.9455825      0.9460000      0.9467561
 0.4000000         0.9547470      0.9540000      0.9544517
 0.5000000         0.9655458      0.9640000      0.9633976
 0.6000000         0.9739342      0.9740000      0.9731456
 0.7000000         0.9850579      0.9850000      0.9834707
 0.8000000         0.9958987      0.9960000      0.9942461
 0.9000000          1.008098       1.008000       1.005394
  1.000000          1.020480       1.020000       1.016865
  1.200000          1.044570       1.044000       1.040640
  1.400000          1.069038       1.068000       1.065387
  1.600000          1.093458       1.093000       1.090991
  1.800000          1.118885       1.119000       1.117373
  2.000000          1.144370       1.145000       1.144476
  2.500000          1.211242       1.213000       1.215093
  3.000000          1.279059       1.284000       1.289386
  3.500000          1.360835       1.361000       1.366970
  4.000000          1.433727       1.441000       1.447561
  4.500000          1.536435       1.525000       1.530940
  5.000000          1.612716       1.613000       1.616937
  5.500000          1.690466       1.703000       1.705415
```

OUTPUT (continuation)

```
                      OSMOTIC COEFFICIENT
molality      New Model      experimental    Pitzer's
                                 value         model
6.000000      1.781104       1.794000       1.796267
7.000000      1.985174       1.979000       1.984755
8.000000      2.178133       2.159000       2.181870
9.000000      2.341894       2.328000       2.387248
10.00000      2.476626       2.480000       2.600631
11.00000      2.591044       2.612000       2.821835
12.00000      2.697319       2.723000       3.050725
13.00000      2.790150       2.814000       3.287197
14.00000      2.884246       2.887000       3.531178
15.00000      2.964470       2.947000       3.782605
16.00000      3.028820       2.995000       4.041435
17.00000      3.068908       3.036000       4.307630
18.00000      3.076946       3.066000       4.581162
19.00000      3.044519       3.079000       4.862008
Total # 42   ERROR %  RIM: 0.3073985 PITZER: 6.8005548
```

CHAPTER 8. RESULTS AND DISCUSSION

A. 1-1 type Electrolytes

The results can be classified into 3 categories, 1-1 type, 2-2 type and 1-2 type electrolytes. In this section, the results for the 1-1 type electrolytes are introduced. A total of 20 single salt solutions were treated and the results are shown in Table 8.1. The results are arranged in order of increasing maximum concentration where the new model is valid, and are compared with both Pitzer's model and the experimental data supplied by Hamer and Wu.(85) In most cases, the limiting maximum concentration range is determined by the extent of the experimental data. The exceptions are HCl, HBr and HI. For the case of HCl, experimental data are available up to 16 m, but the results are only shown up to 10 m. The reason is that the perturbation method does not work after 10 m due to the unrealistic behavior of the n value (i.e., it approaches 1) in the calculation of the hypothetical anion diameter. Similar things happen in the HBr and HI systems where the experimental data are available up to 11 m and 10 m, respectively. The common features of these systems is the H_3O^+ ion. As mentioned above, the hypothetical diameters of the cation and anion are correlated with each other, and the problems with these systems may be attributed to the selection of the hypothetical diameter of the cation, H_3O^+. Unlike the other cations, its diameter is determined somewhat arbitrarily because the Pauling radius of the

Table 8.1. Prediction of Osmotic Coefficients (1-1 type).

Solution	Maximum Concentration(molality)	Error(%)	
		New Model	Pitzer
$KBrO_3$	0.5	0.020	0.050
NaF	1.0 (sat: 0.983)	0.231	0.047
CsOH	1.2	0.227	0.305
$CsNO_3$	1.5	0.111	0.289
KH_2PO_4	1.8	0.030	0.267
LiI	3.0	0.029	0.490
$LiClO_4$	4.5	0.030	0.150
KI	4.5	0.066	0.094
KCl	5.0 (sat: 4.803)	0.067	0.063
KBr	5.5	0.106	0.052
NaCl	6.144 (sat: 6.144)	0.030	0.065
HBr	8.0	0.092	0.674
HI	8.0	0.169	0.545
NaBr	9.0	0.326	0.515
HCl	10.0	0.075	0.618
$NaNO_3$	10.83 (sat: 10.83)	0.047	3.640
NaI	12.0	0.099	1.262
LiBr	16.0	0.315	2.233
LiCl	19.0 (sat:19.219)	0.307	6.800
$LiNO_3$	20.0	0.313	3.170

(sat: *) means saturation concentration is *.

hydrogen ion does not exist, and so it is established arbitrarily. This may explain why the current perturbation method becomes inefficient (slow convergence) in the high concentration range of these systems.

In the comparison with Pitzer's model, one of the things that should be considered is that generally the guaranteed maximum concentration range where Pitzer's model is valid is about 6 m (at best) for 1-1 type electrolyte solutions. Thus, this New Model is the first that is applicable for the higher concentration ranges.

In Table 8.1, a total of 20 different solutions are illustrated, and the New Model gives better results than Pitzer's for 17 of the 20. Furthermore, it is observed that the New Model works well not only at lower concentrations but also in the higher concentration ranges. Thus the New Model has a range well beyond that of Pitzer's model, and at the same time shows at least as good accuracy as Pitzer's in the low or dilute concentration ranges. In summary, the New Model shows better agreement with the experimental data than Pitzer's, especially for the higher concentration range. All the numerical data for each particular solution are given in Appendix 2.

The characteristics of these two models are well represented in Figures 8.1 through 8.4. All the numerical data for these figures are supplied in Appendix 2. Figure 8.1 shows the comparison of the New Model and Pitzer's model with experimental data for the $KBrO_3$ solution. This figure shows the behavior of the two models in the dilute concentration range and apparently there seems to be no significant difference between them. The New Model is slightly better, but both fit the experimental data well, and both are within the experimental error. Figure 8.2 shows the behavior of the osmotic coefficient in the NaCl solution. The concentration range is up to the saturation point (6.144 m), and the figure is divided into two ranges for the convenience of expression. This range is also within the range that Pitzer's model is guaranteed effective. As a consequence, both models show good agreement with the experimental data. Although the accuracy of the New Model is slightly higher, both are again within the experimental error. Figure 8.3 shows the behavior of the osmotic coefficient in the $NaNO_3$ solution up to a concentration high enough that Pitzer's model is no longer valid. The figure is also divided into two parts to better allow comparison with the experimental data. The importance of the new model is demonstrated by the behavior of the osmotic coefficient value as shown in Figure 8.3b. Figure 8.4 shows a case similar to Figure 8.3, but the concentration range is extended up to 19.219 m, which is the saturation point of the LiCl solution. The LiCl solution behavior can be predicted through the entire concentration range by the New Model, but not by Pitzer's model.

These four figures show the characteristics of only four solutions. The osmotic coefficients of the other solutions are given in Appendix 2 as tables. Generally, it can be stated that improvement of the accuracy has been achieved by introducing the Stillinger-Lovett moment condition (local electroneutrality condition) and a flexible ion size. This is possible with the help of the perturbation method for a 1-1 type electrolyte solution. By contrast, EXP theory (upon which the New Model is partially based) is valid up to 2 M (approximately 2m).

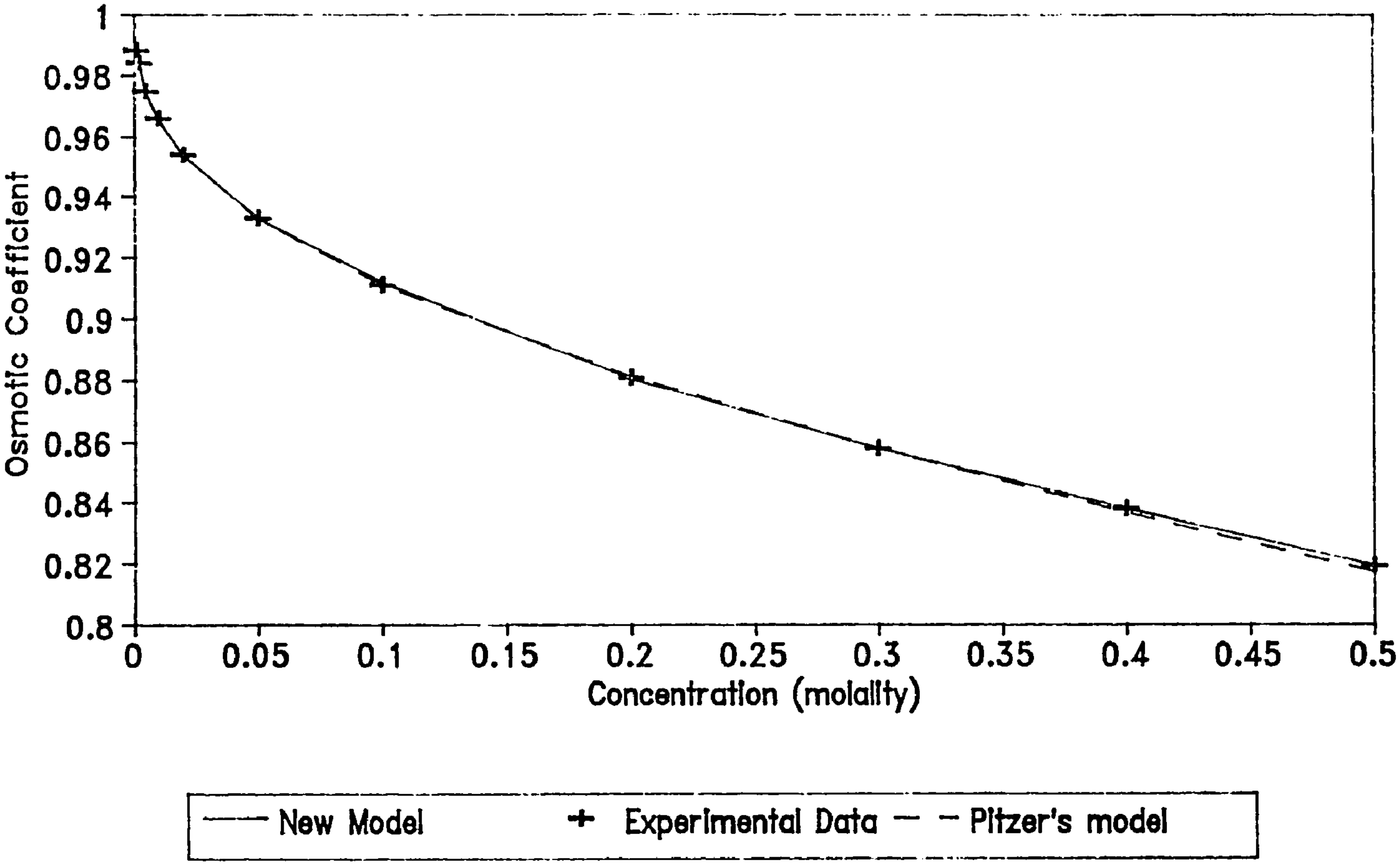


Fig. 8.1. Osmotic Coefficient with concentration change at room temperature and pressure ($KBrO_3$: 0.001 - 0.5 m)

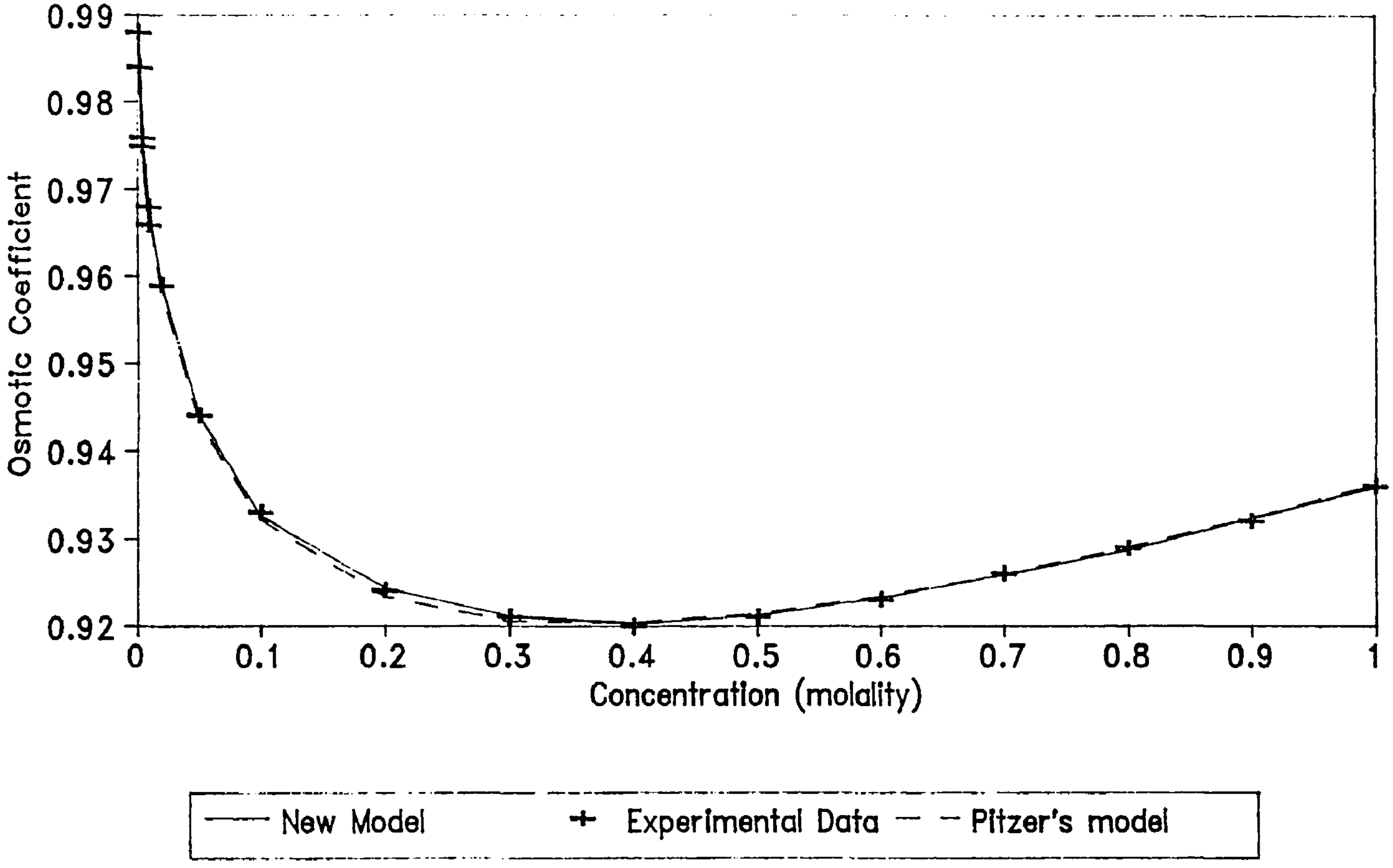


Fig. 8.2a. Osmotic Coefficient with concentration change at room temperature and pressure (NaCl : 0.001 - 1.0 m)

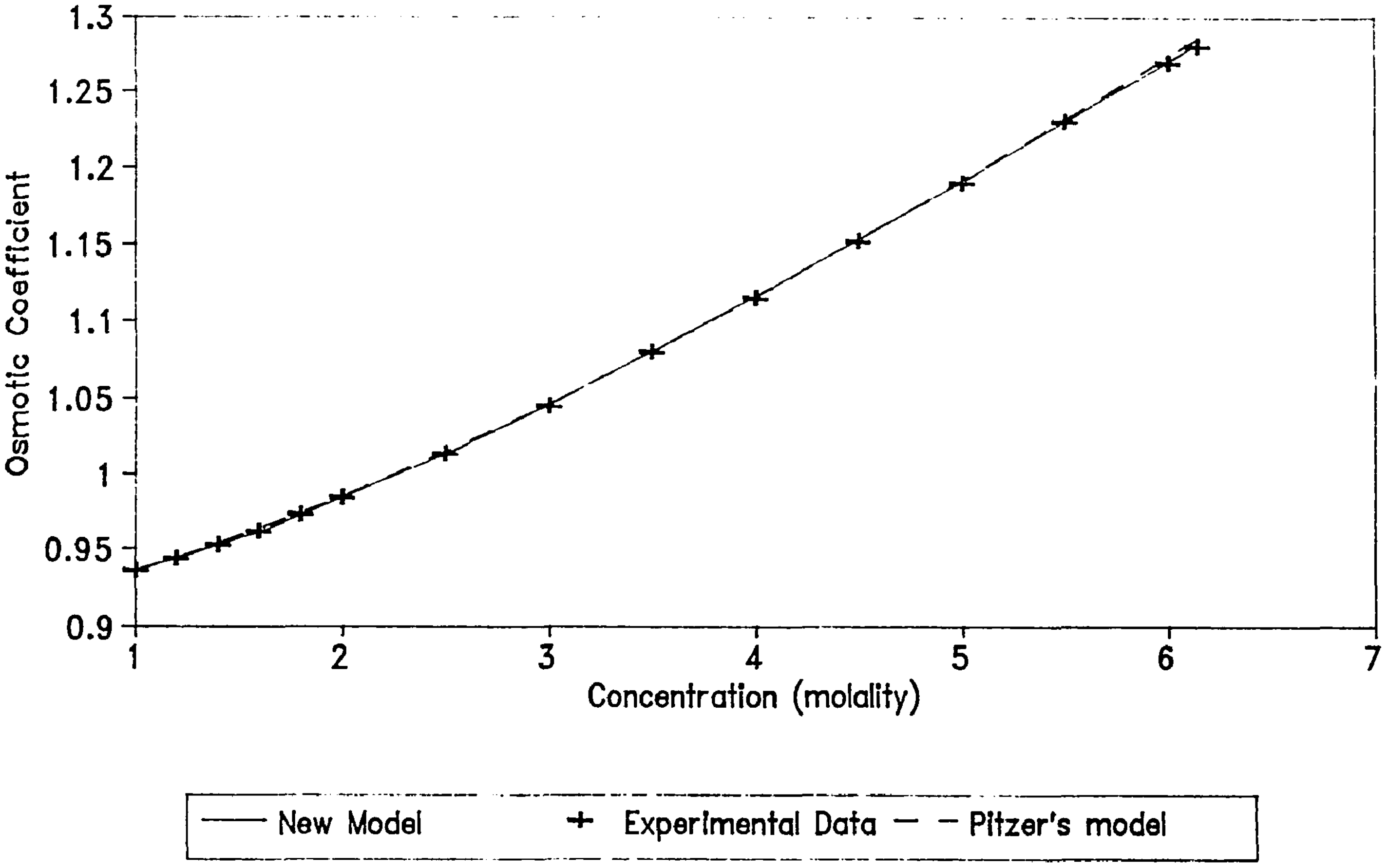


Fig. 8.2b. **Osmotic Coefficient with concentration change at room temperature and pressure (NaCl : 1.0 - 6.144 m)**

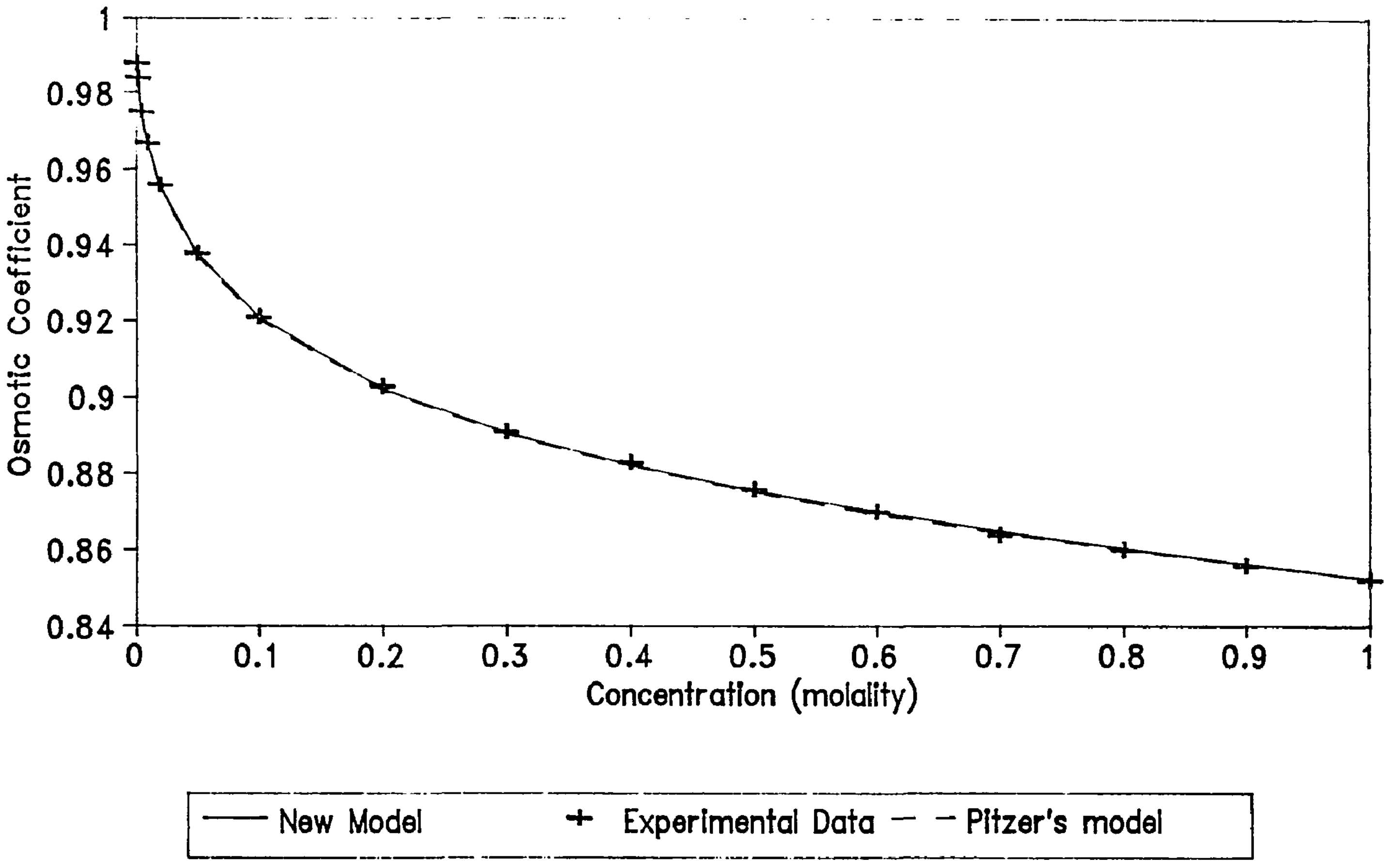


Fig. 8.3a. Osmotic Coefficient with concentration change at room temperature and pressure ($NaNO_3$: 0.001 - 1.0 m)

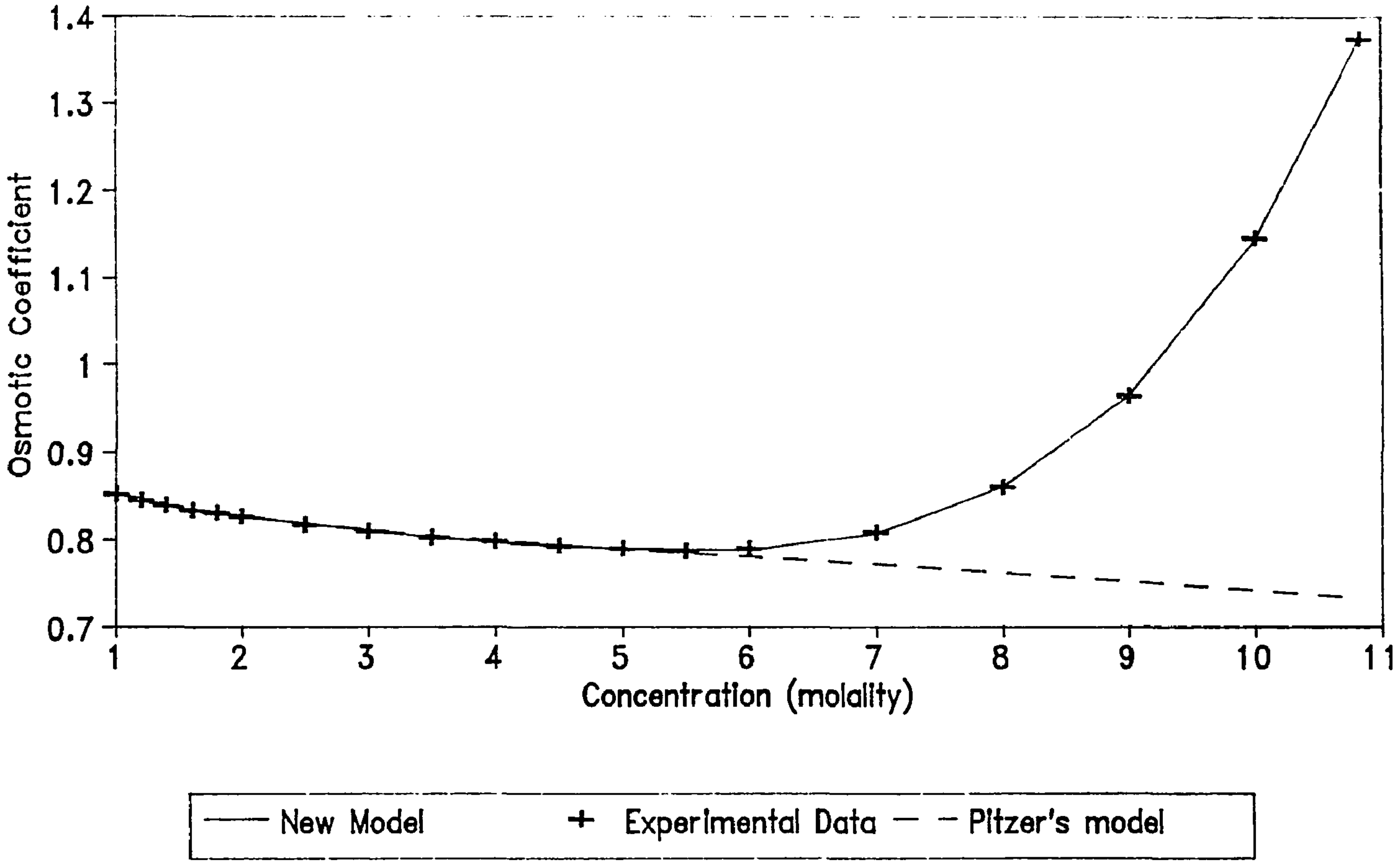


Fig. 8.3b. Osmotic Coefficient with concentration change at room temperature and pressure ($NaNO_3$: 1.0 - 10.83 m)

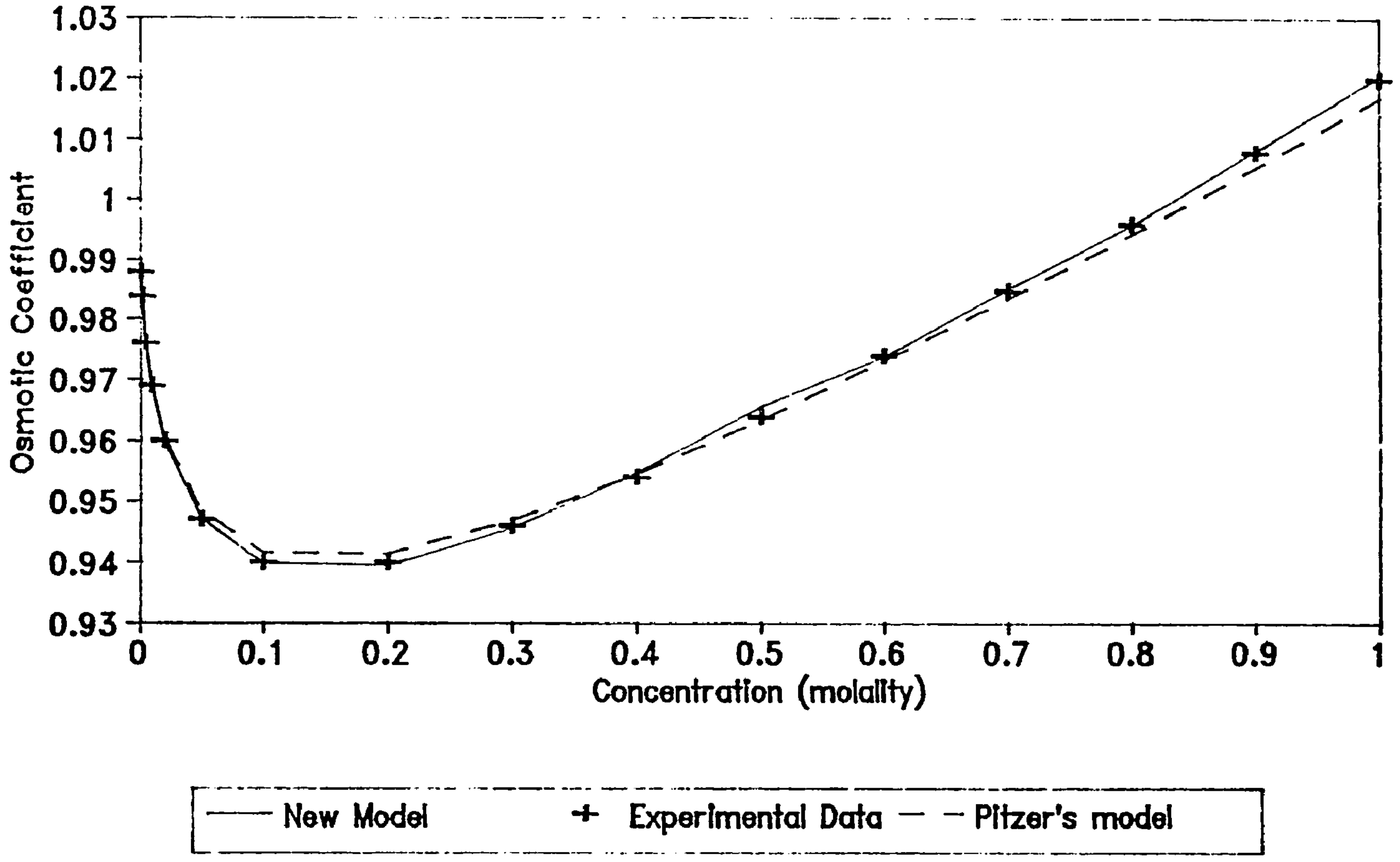


Fig. 8.4a. Osmotic Coefficient with concentration change at room temperature and pressure (LiCl : 0.001 - 1.0 m)

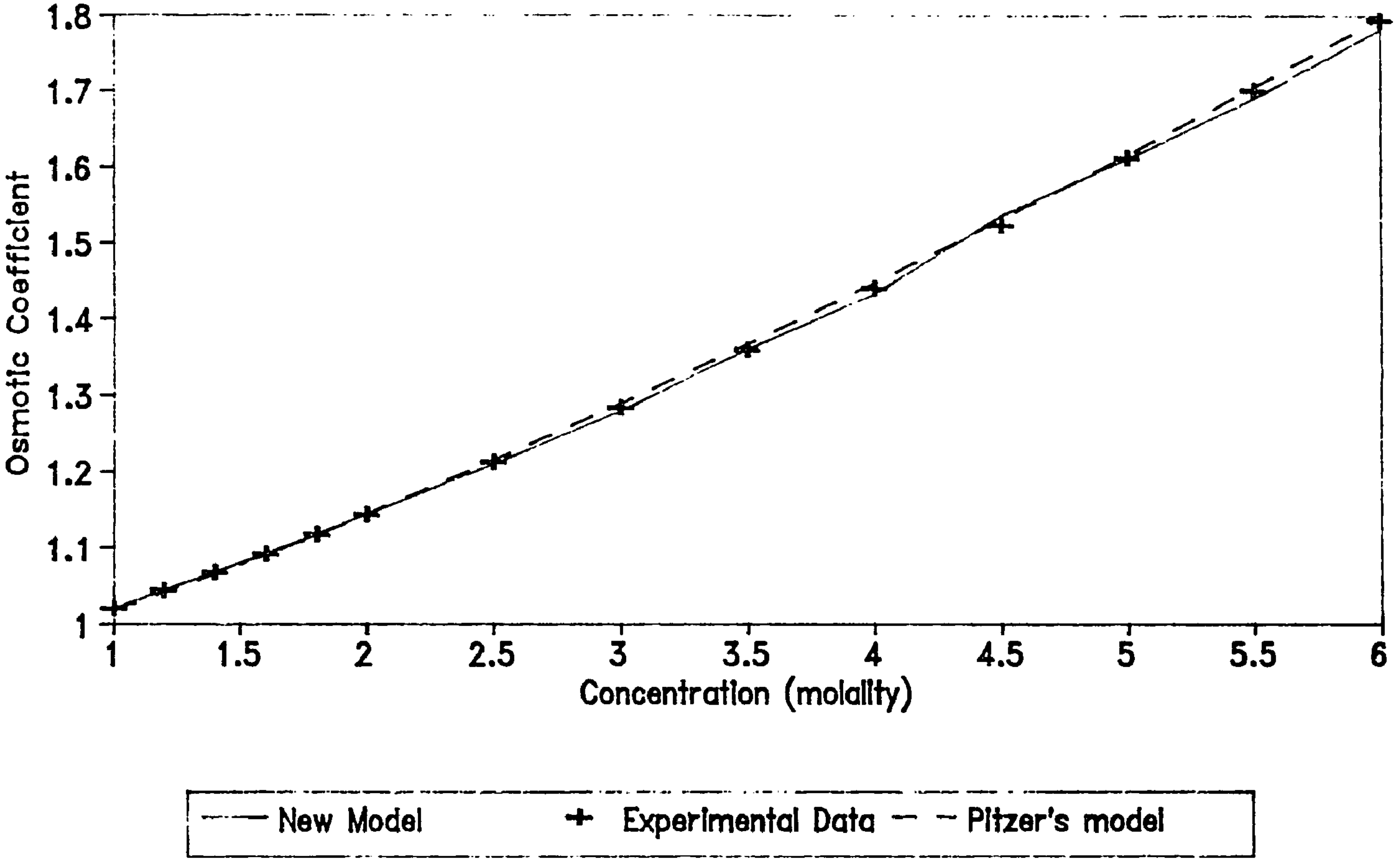


Fig. 8.4b. Osmotic Coefficient with concentration change at room temperature and pressure (LiCl : 1.0 - 6.0 m)

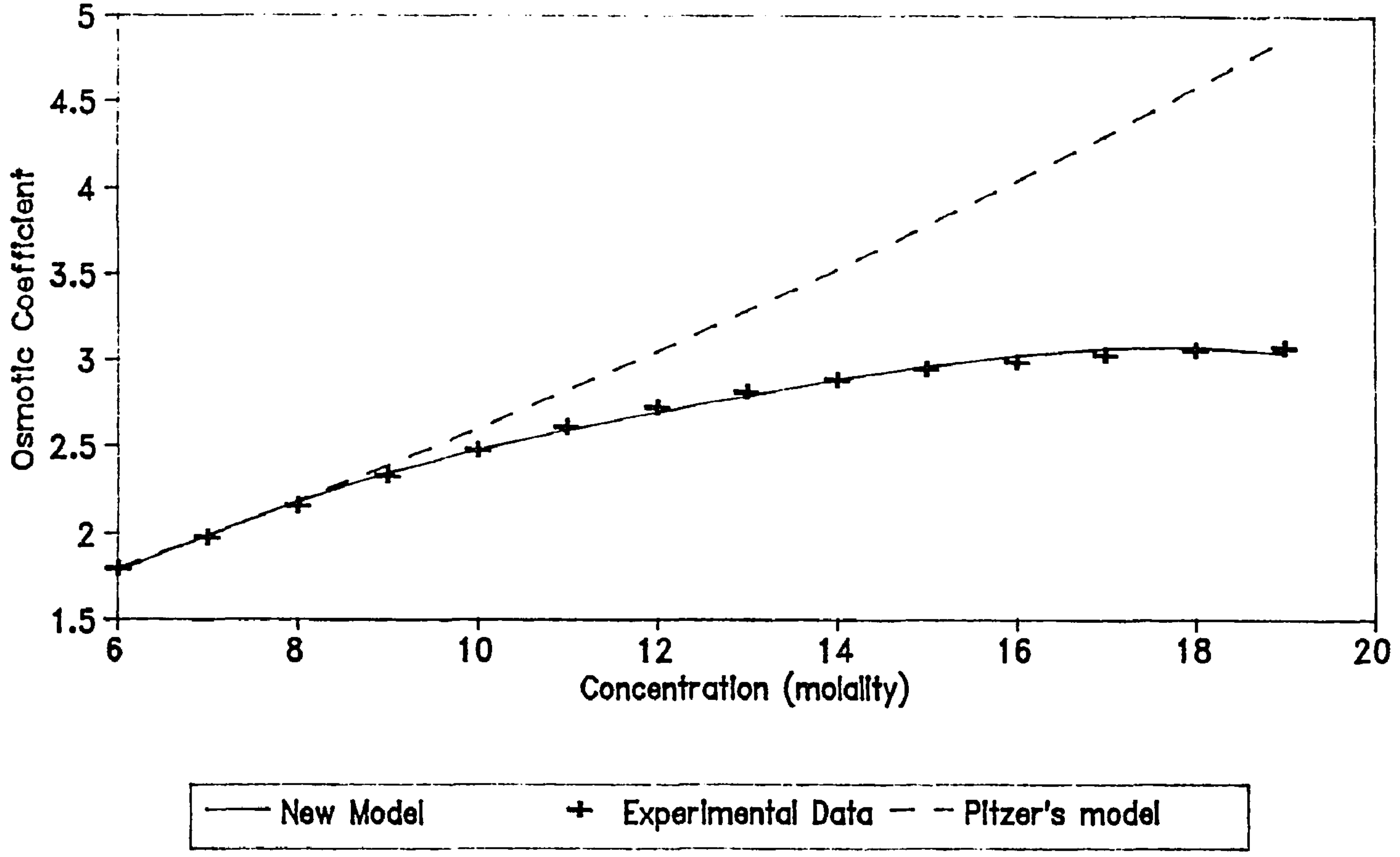


Fig. 8.4c. Osmotic Coefficient with concentration change at room temperature and pressure (LiCl : 6.0 - 19.0 m)

B. 1-2 type Electrolytes

Table 8.2 shows the results of the calculated osmotic coefficient for 1-2 type electrolytes. A total of 4 systems were studied and all the numerical data are given in Appendix 2. For this case, the calculation is not as easy to execute. The main problem lies in the perturbation procedure for the calculation of the hypothetical anion diameter. For solutions of Na_2HPO_4, Na_2CO_3 and Na_2SO_4, the hypothetical anion diameters are decreasing monotonically and come to a length of less than 1 Å. Thus, the n value of the charged soft sphere interaction potential decreases close to one, and it is impossible to get an equivalent hard sphere diameter at concentrations of more than 1 m. This is a reflection of the previously stated need for a suitable perturbation technique for ionic solutions. In spite of this problem, the performance of the new model exceeds that of Pitzer's for all four systems. One of the things that should also be considered is that Pitzer's model is also valid only in a limited concentration range. For the case of Na_2SO_4, $Na_2S_2O_3$, Na_2HPO_4 and Na_2CO_3, the valid concentration ranges are 1.3 m, 3.5 m, 1.0 m and 1.5 m respectively. But the experimental data(86) well exceed these ranges. For Na_2SO_4, $Na_2S_2O_3$, Na_2HPO_4 and Na_2CO_3, the data extend to 4.445 m, 4.052 m, 2.121 m and 3.0 m. These problems demonstrated that it is not easy to develop a suitable model for these solutions. As mentioned above, the suggestion to solve this problem is to develop a suitable perturbation technique.

Figures 8.5 through 8.8 illustrate the osmotic coefficient change

Table 8.2. Prediction of Osmotic Coefficients (1-2 type).

Solution	Maximum Concentration(molality)	Error(%)	
		New Model	Pitzer
Na_2HPO_4	1.0	0.078	0.327
Na_2SO_4	1.25	0.132	0.464
Na_2CO_3	1.5	0.102	2.704
$Na_2S_2O_3$	4.052 (sat: 4.052)	0.061	0.395

with concentration. Figure 8.5 shows the results for the Na_2HPO_4 solution. The figure is separated into two parts to better show the fitting of the experimental data. In the concentration range from 0.001 m to 0.01 m, both models and the data are in agreement. For the concentration range from 0.01 m to 0.3 m, the New Model is slightly better than Pitzer's model. In the final range, both models agree well with the experimental data. Generally both models fit the experimental data but the New Model slightly prevails over Pitzer's model.

Figure 8.6 shows analogous results for the Na_2SO_4 solution. The tendency is similar to the Na_2HPO_4 solution in the concentration range up to the 0.4 m. After this both models shows a slight deviation from the data, with the New Model showing slightly higher values than the data, while Pitzer's model shows lower values. Overall, the New Model shows better agreement with the experimental data.

Figure 8.7 shows the behavior of the Na_2CO_3 solution. The figure is again divided into a and b parts. In Figure 8.7b, the advantage of the New Model appears, as the Pitzer model begins to show a discrepancy after 0.1 m. However, after the concentration of 1.5 m, the New Model shows its limitation. Generally, if the osmotic coefficient is decreasing up to around 0.6, then it is very difficult to predict the behavior of a 1-2 type solution.

Figure 8.8 is divided into three parts due to the abundance of the experimental data for the $Na_2S_2O_3$ solution. The behavior of the two models are similar to those for the Na_2HPO_4 and Na_2SO_4 solutions up to 1 m. After this range, the disagreement of the Pitzer's model appears from 3.25 m, which is close to the stated effective concentration limit, 3.5 m, for Pitzer's model. Again the New Model

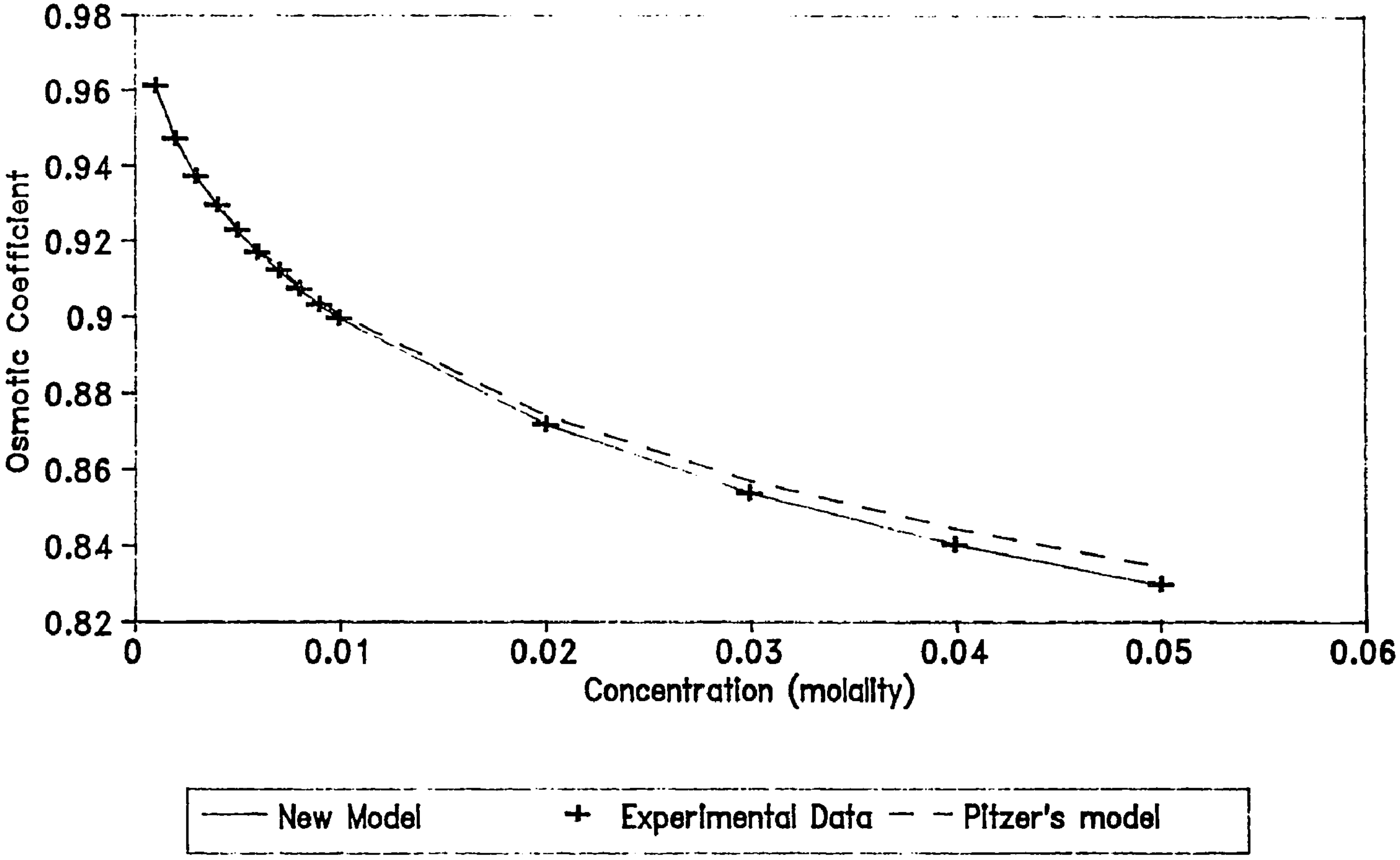


Fig. 8.5a. Osmotic Coefficient with concentration change at room temperature and pressure (Na_2HPO_4 : 0.001 - 0.05 m)

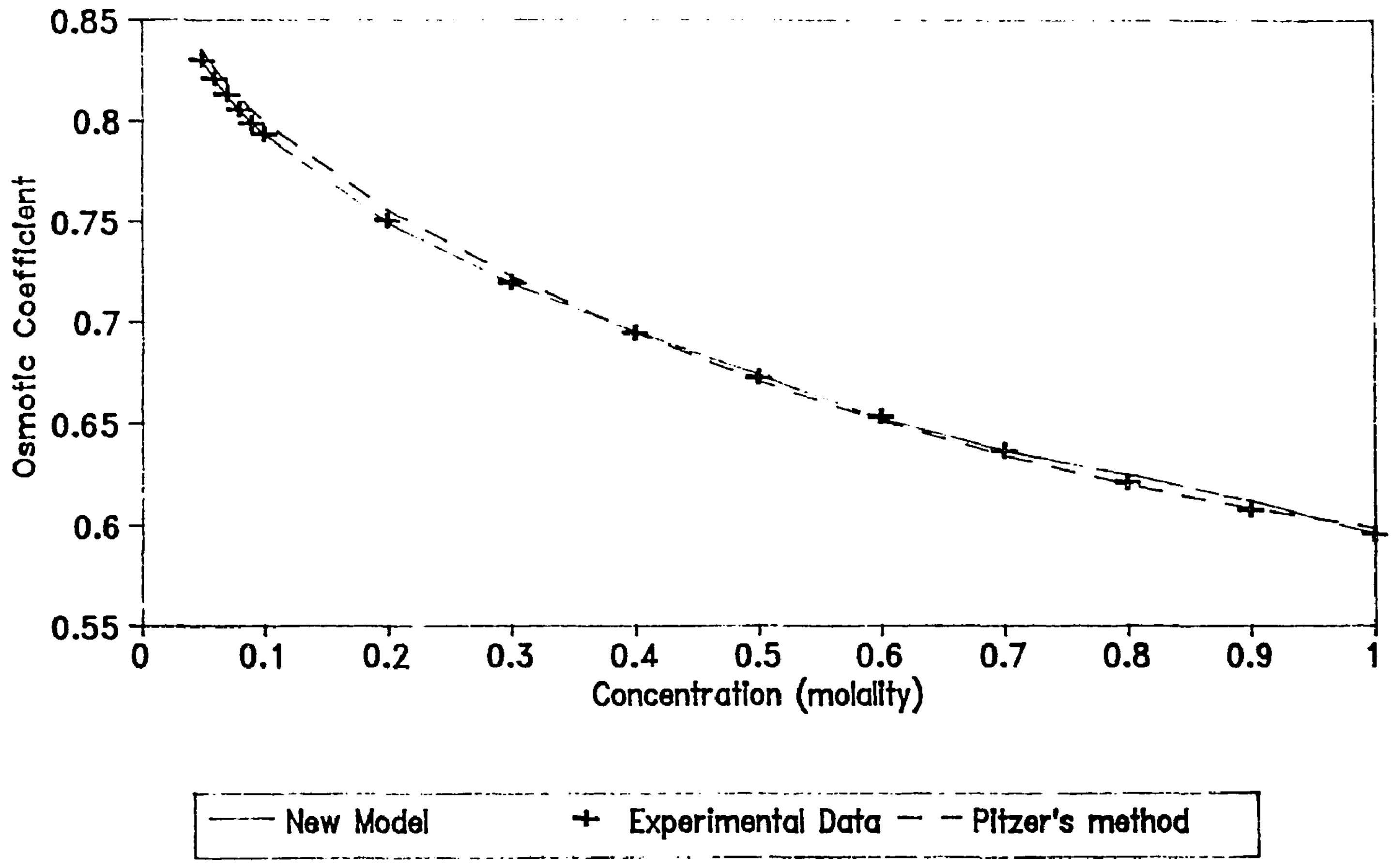


Fig. 8.5b. **Osmotic Coefficient with concentration change at room temperature and pressure** (Na_2HPO_4 : 0.05 - 1.0 m)

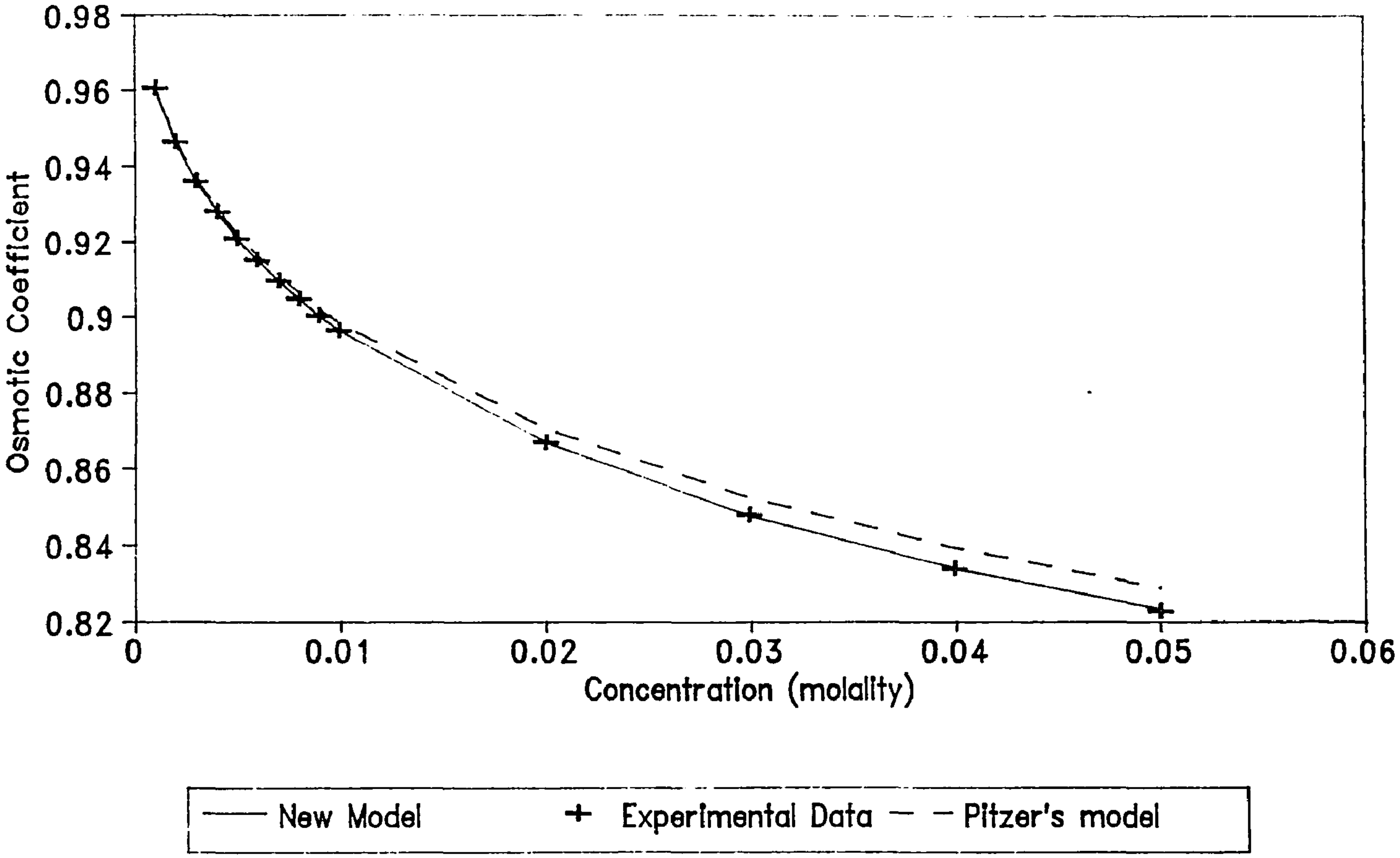


Fig. 8.6a. Osmotic Coefficient with concentration change at room temperature and pressure (Na_2SO_4 : 0.001 - 0.05 m)

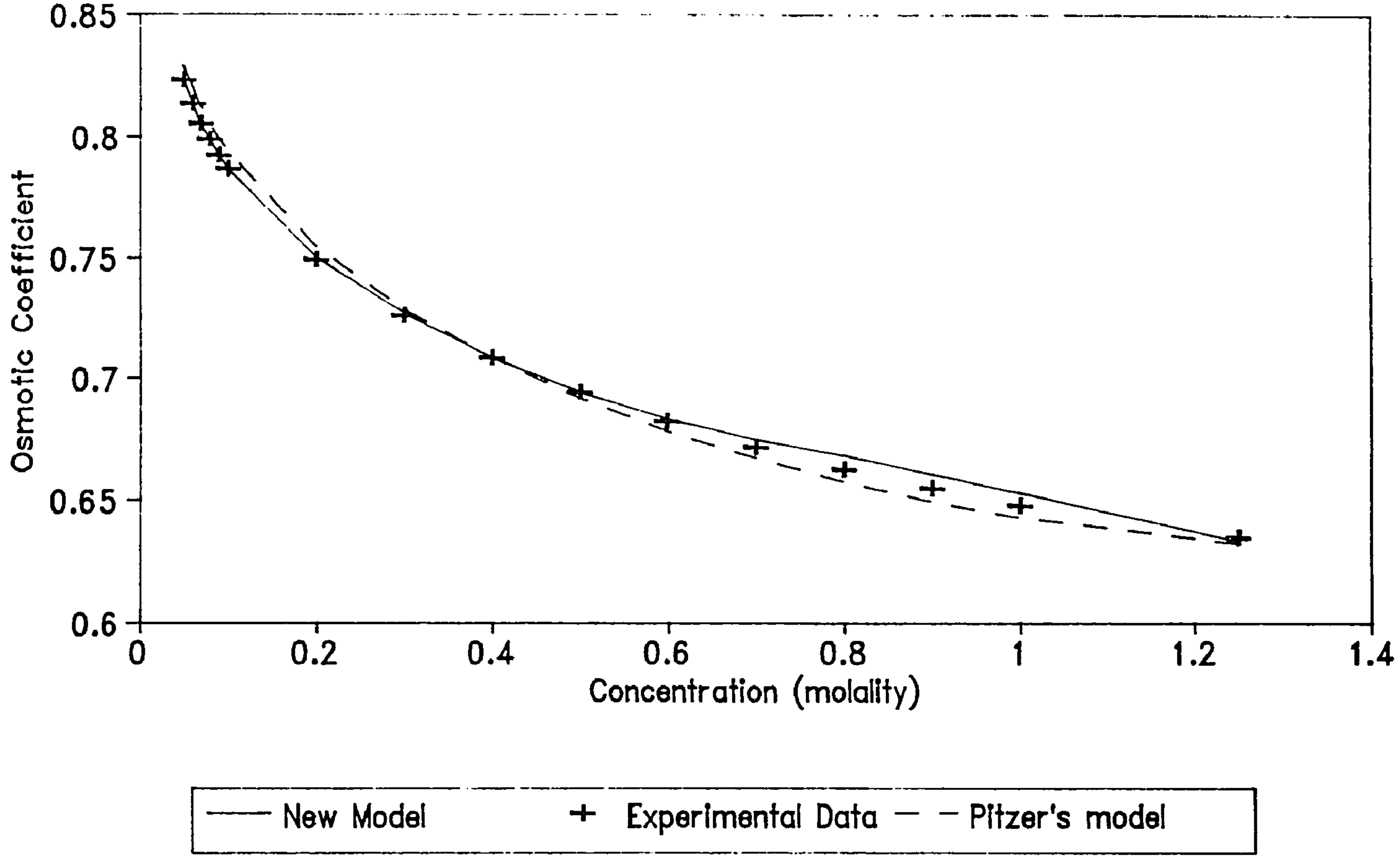


Fig. 8.6b. **Osmotic Coefficient with concentration change at room temperature and pressure** (Na_2SO_4 : 0.05 - 1.25 m)

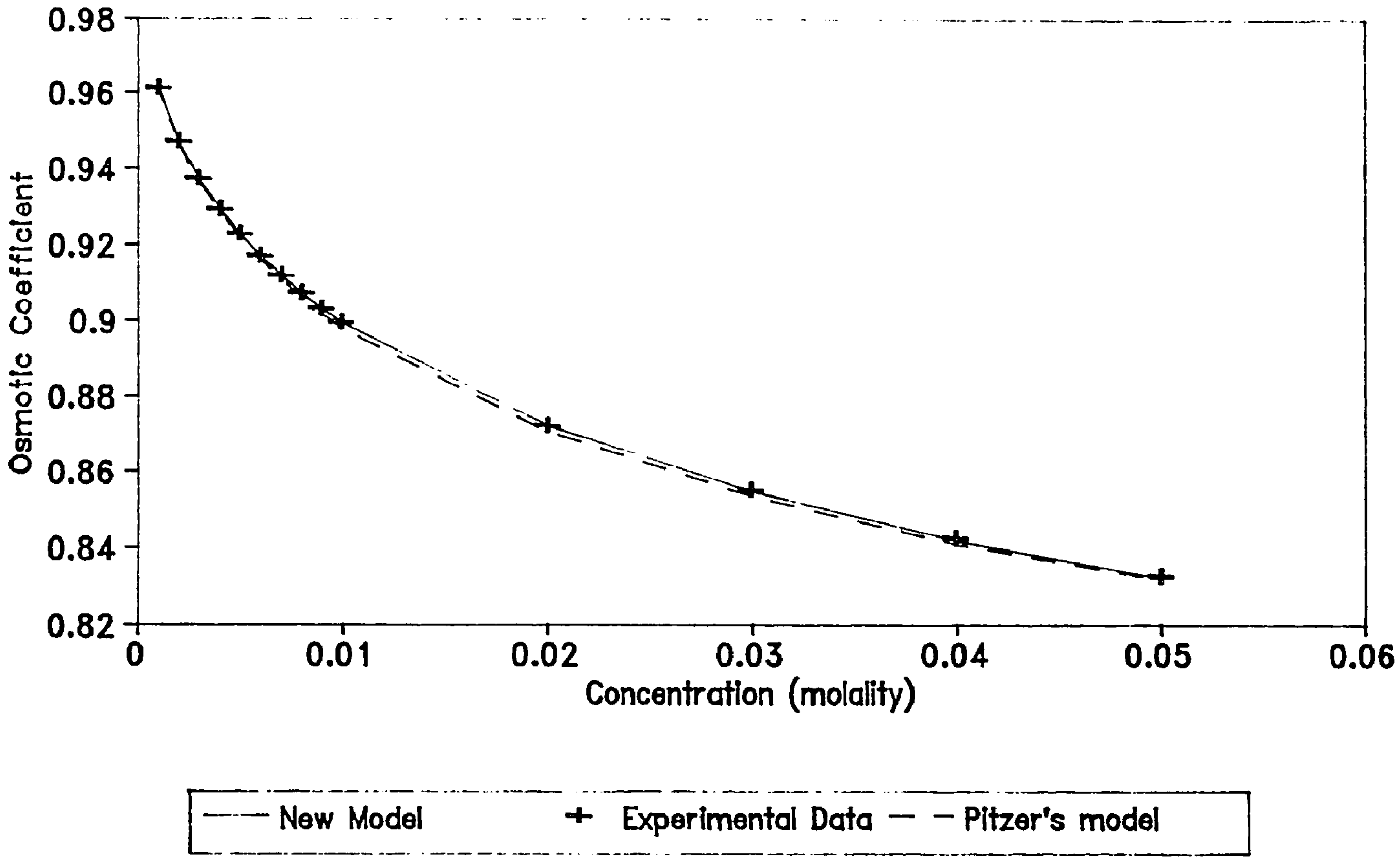


Fig. 8.7a. **Osmotic Coefficient with concentration change at room temperature and pressure (Na_2CO_3 : 0.001 - 0.05 m)**

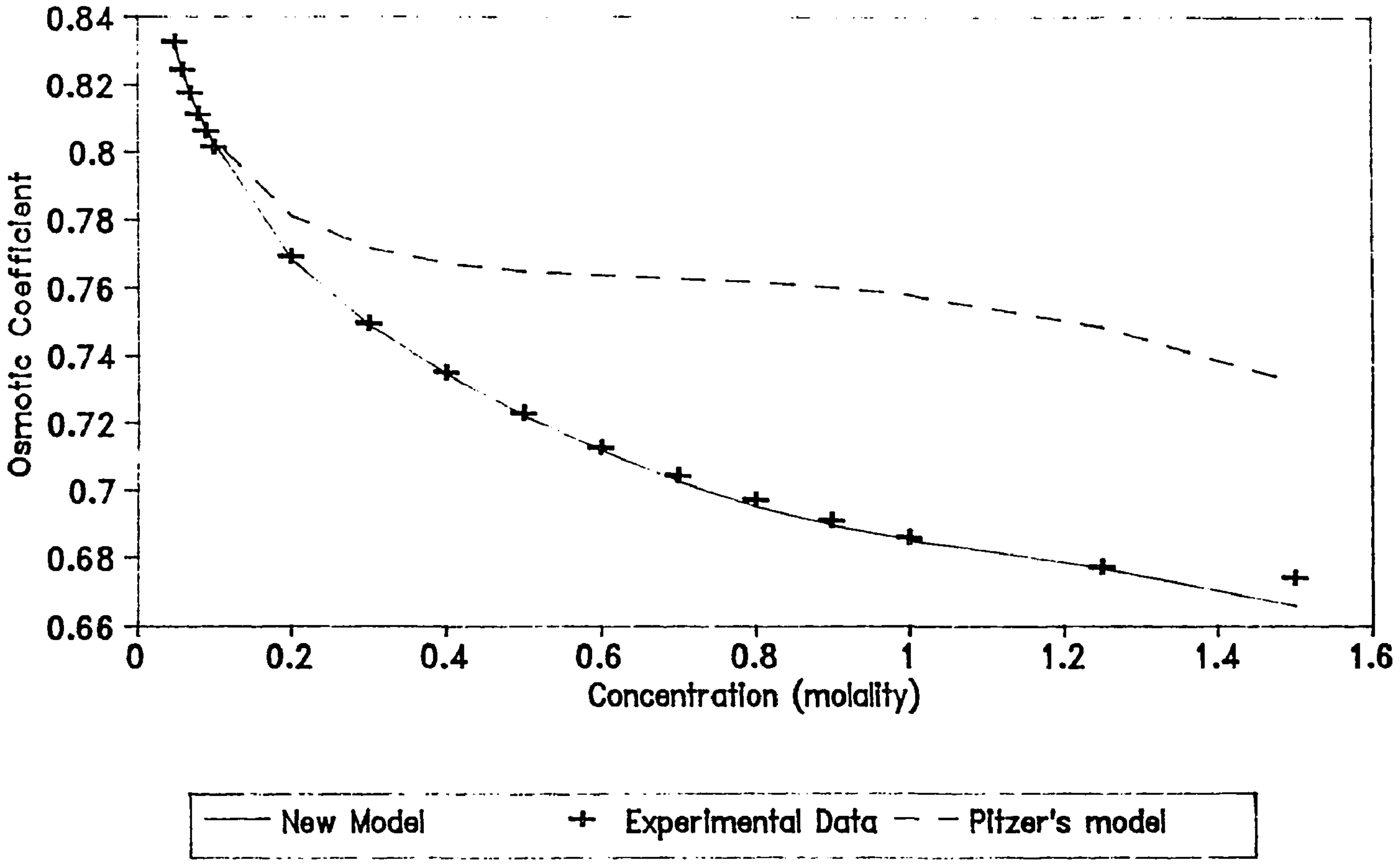


Fig. 8.7b. Osmotic Coefficient with concentration change at room temperature and pressure (Na_2CO_3 : 0.05 - 1.5 m)

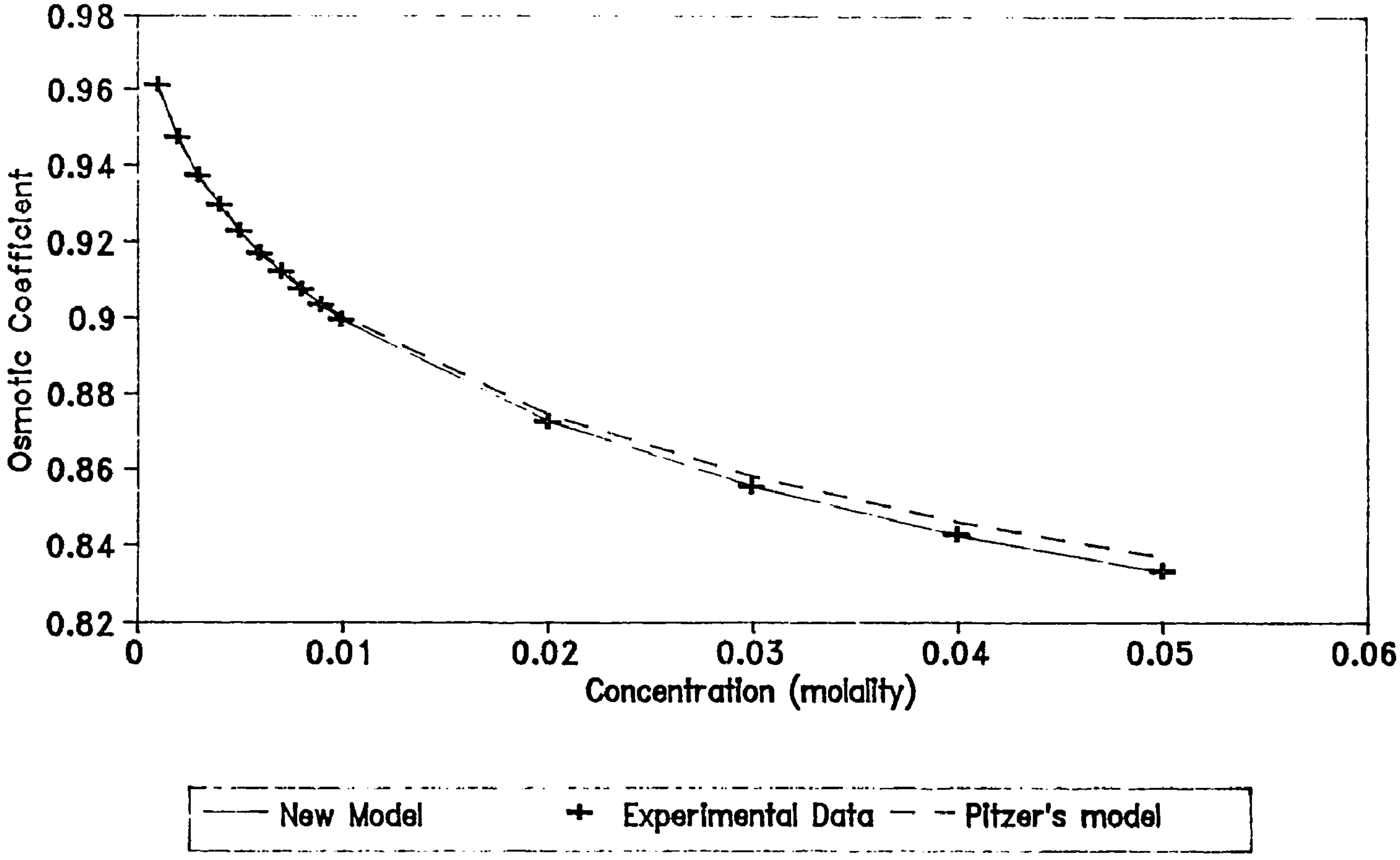


Fig. 8.8a. Osmotic Coefficient with concentration change at room temperature and pressure ($Na_2S_2O_3$: 0.001 - 0.05 m)

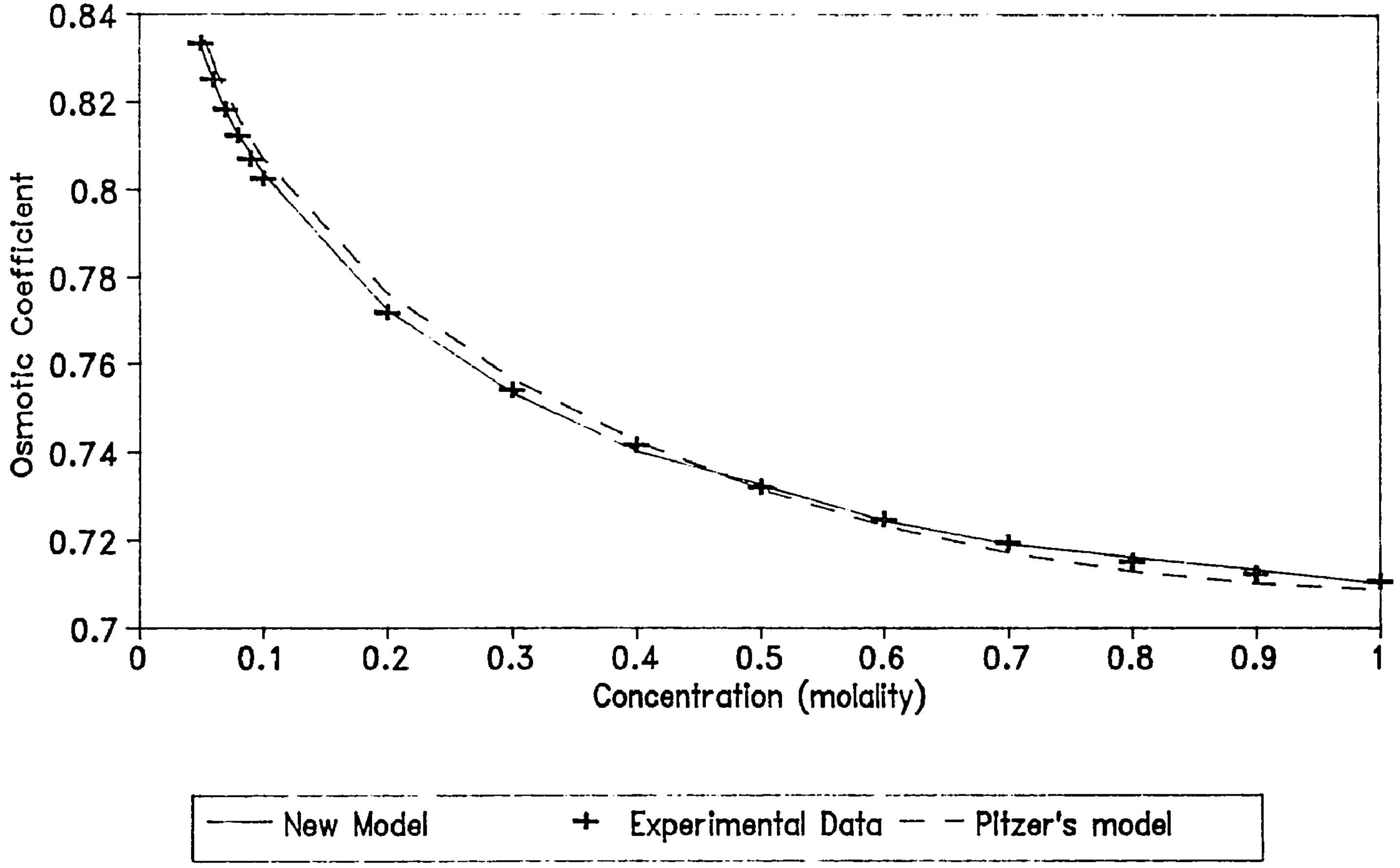


Fig. 8.8b. Osmotic Coefficient with concentration change at room temperature and pressure ($Na_2S_2O_3$: 0.05 - 1.0 m)

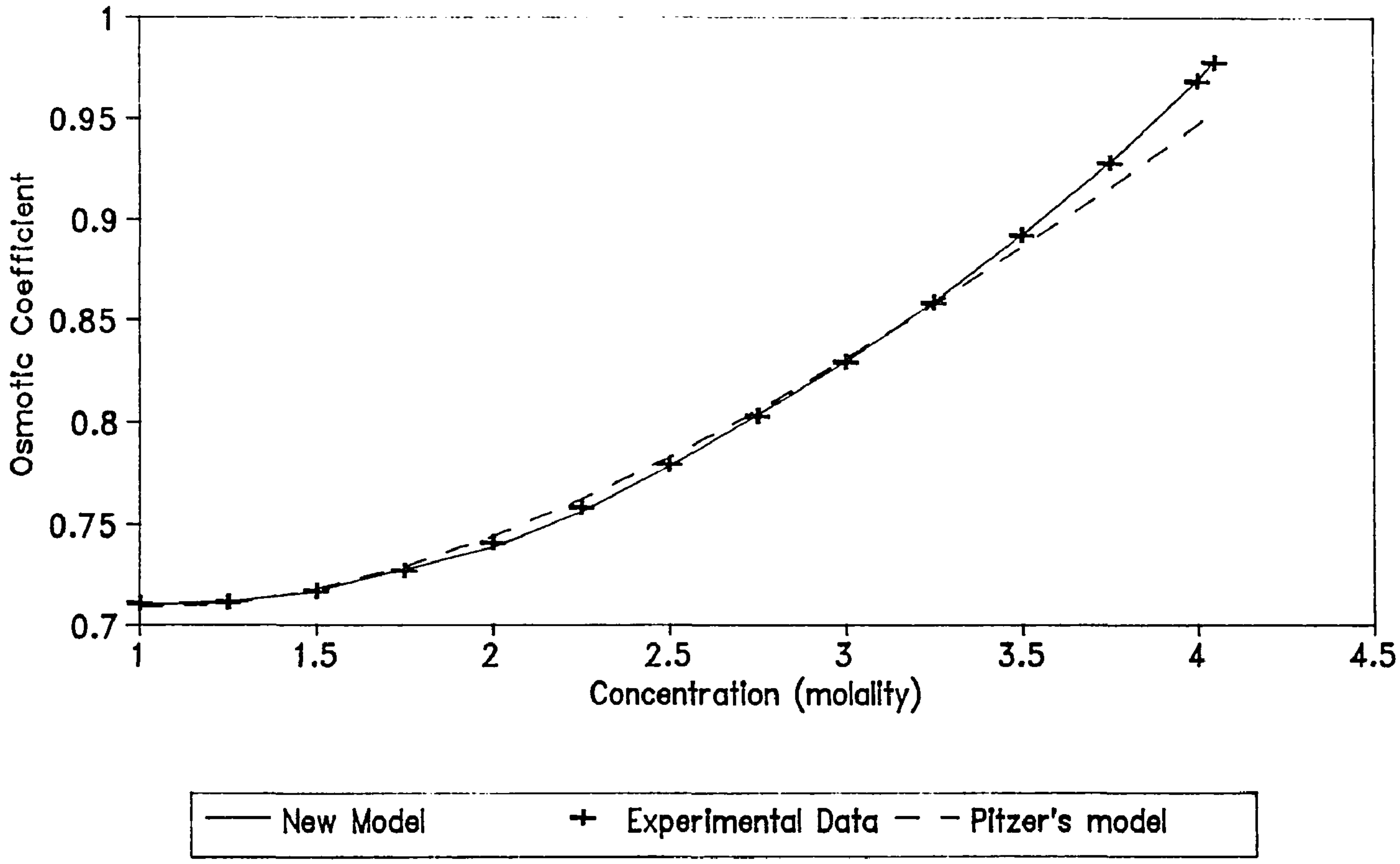


Fig. 8.8c. Osmotic Coefficient with concentration change at room temperature and pressure ($Na_2S_2O_3$: 1.0 - 4.052 m)

shows its advantage at concentrations beyond the concentration range where Pitzer's model is effective.

EXP theory only treats symmetrical systems, and so can not be used for this type of electrolyte.

It should be possible to obtain similar results for 2-1 type solutions by the New Model because there is no difference between the 1-2 type and the 2-1 type from the point of view of the New Model.

C. 2-2 type Electrolyte

In this case the original EXP theory also shows its validity up to 2 M, and the New Model shows an improvement. The results are shown in Table 8.3. A total of 4 species were tested using experimental data supplied by Robinson and Jones.(87) All the numerical data are included in Appendix 2. One of the differences from experimental data for the 1-1 type or 1-2 type electrolytes is that the number of data points is smaller than for the other types. This is the reason why the regression equation for the n value, presented in the former chapter, is of a different type.

Generally the results are good and the New Model shows better accuracy than Pitzer's. In spite of the low osmotic coefficient value, there was not such problem that happened in the 1-1 type or 1-2 type electrolyte cases, i.e., the perturbation was executed without any difficulty. Figures 8.9 through 8.12 represent the results for the osmotic coefficient of $CuSO_4$, $MgSO_4$, $ZnSO_4$, and $MnSO_4$ solutions. In

Table 8.3. Prediction of Osmotic Coefficients (2-2 type).

Solution	Maximum Concentration(molality)	Error(%) New Model	Error(%) Pitzer
$CuSO_4$	1.4	0.390	1.089
$MgSO_4$	3.0	0.536	0.660
$ZnSO_4$	3.6	0.624	0.723
$MnSO_4$	4.2	0.352	0.502

Figure 8.9, Pitzer's model shows some difference from the experimental data after a concentration of 0.5 m while the New Model shows good agreement with the experimental data. Generally, the Pitzer model is poor when the osmotic coefficient is extremely low. This is one case where the New Model is clearly better.

The other three figures show similar behavior and they all show good agreement with the experimental data.

D. Model Comparison

There was a comparison of the performance of the New Model and Pitzer's model in previous sections. From the viewpoint of performance, the New Model prevails over the Pitzer's model but each model has its own advantages and disadvantages. One of the problems is the total number of parameters. The general expression of Pitzer's model for the osmotic coefficient of a single salt is

$$\phi_m = 1 + |z_c z_a| \left[-\underline{A} \frac{I^{1/2}}{1 + 1.2\, I^{1/2}} \right] + m \left[\frac{2\, \upsilon_c\, \upsilon_a}{\upsilon} \right] [\beta_0 + \beta_1 \exp(-\alpha_1 I^{1/2}) + \beta_2 \exp(-\alpha_2\, I^{1/2})] + m^2 \left[\frac{2(\upsilon_c\, \upsilon_a)^{3/2}}{\upsilon} \right] \underline{C} \qquad (8.1)$$

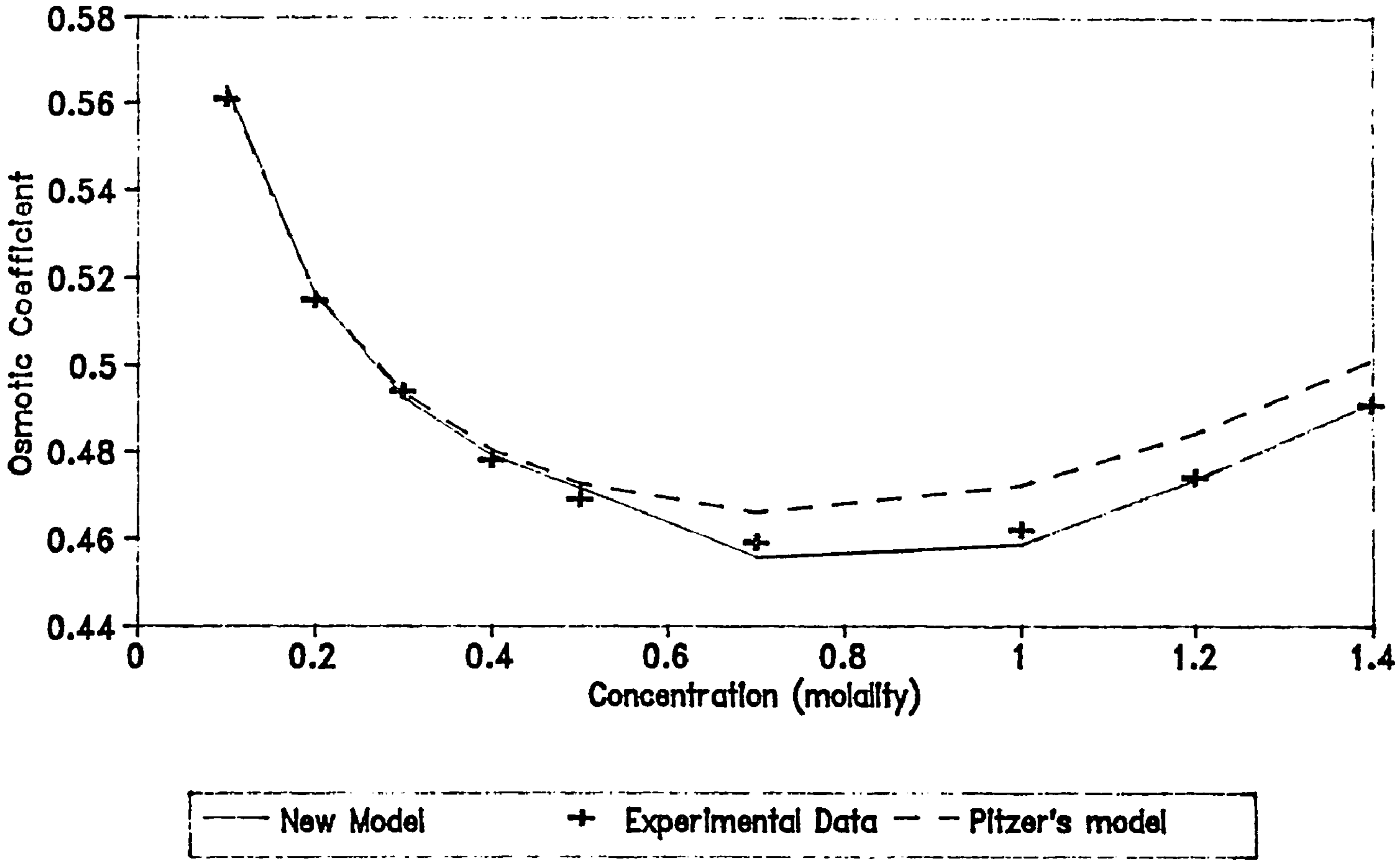


Fig. 8.9. Osmotic Coefficient with concentration change at room temperature and pressure ($CuSO_4$: 0.1 - 1.4 m)

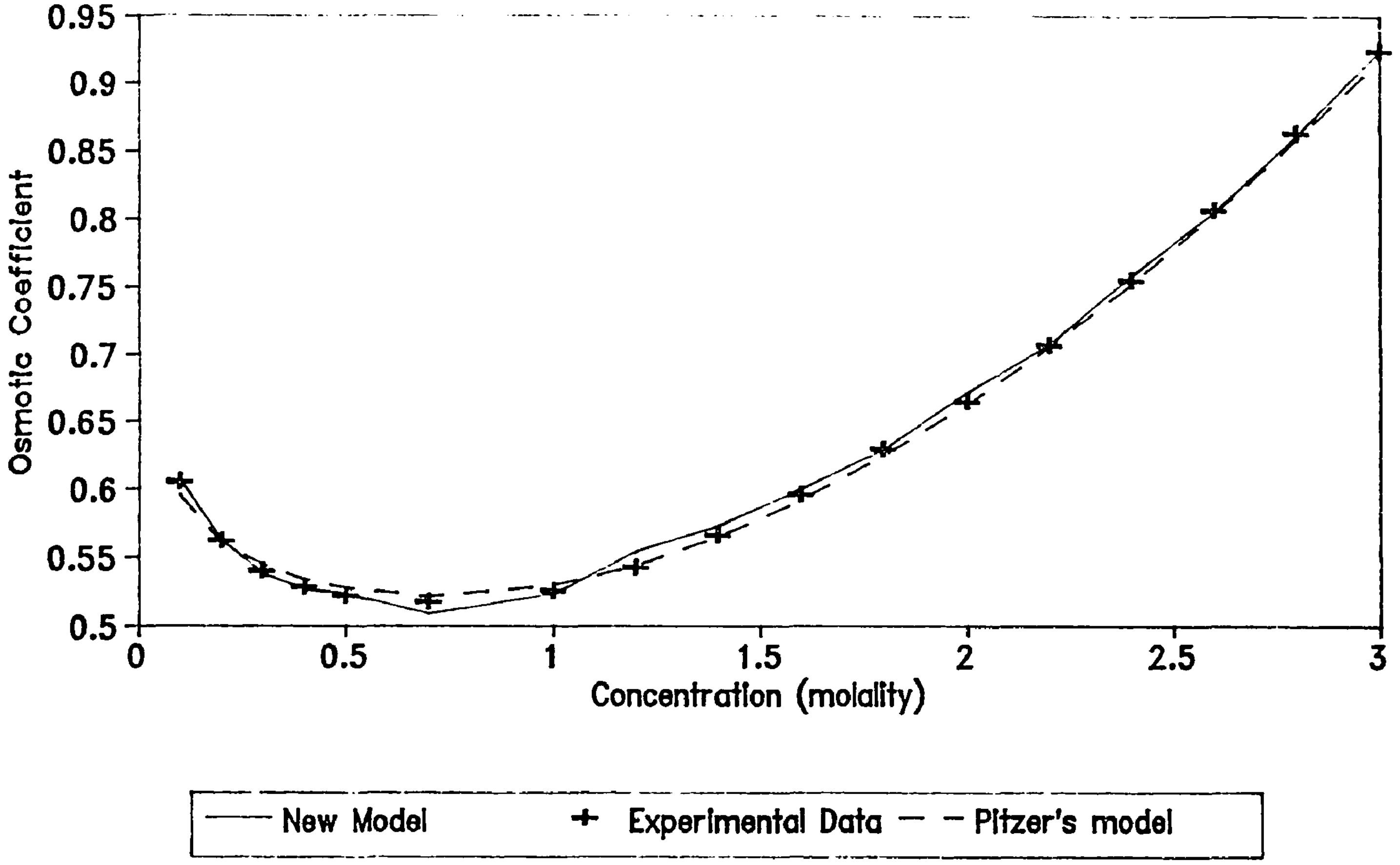


Fig. 8.10. Osmotic Coefficient with concentration change at room temperature and pressure ($MgSO_4$: 0.1 - 3.0 m)

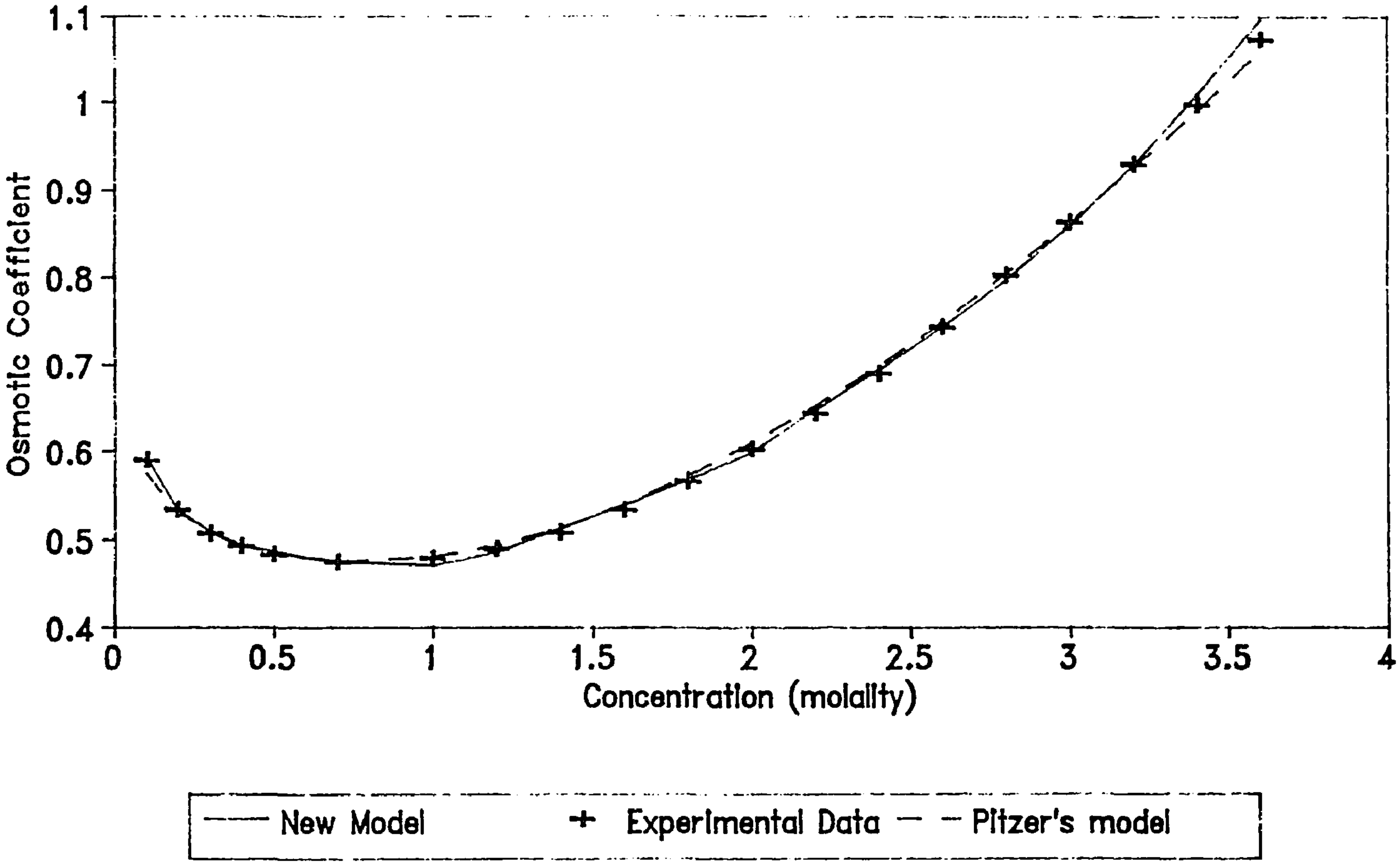


Fig. 8.11. Osmotic Coefficient with concentration change at room temperature and pressure ($ZnSO_4$: 0.1 - 3.6 m)

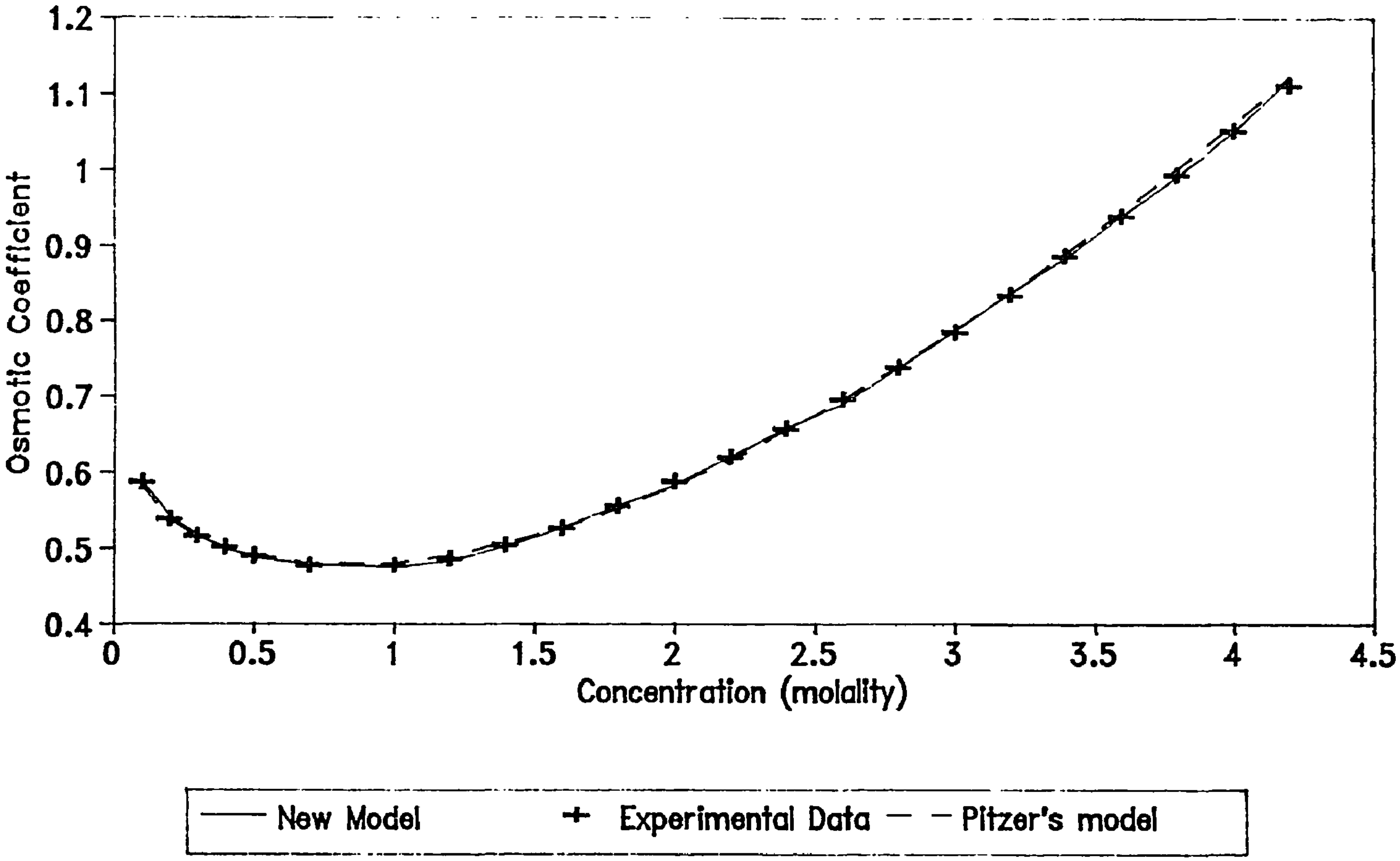


Fig. 8.12. Osmotic Coefficient with concentration change at room temperature and pressure ($MnSO_4$: 0.1 - 4.2 m)

where $\underline{A}$: the osmotic coefficient Debye-Hückel constant

I : the ionic strength

α_1= 1.4 for 2-2 electrolytes, =2.0 for others

α_2= 12.0 for 2-2 electrolytes, =0.0 for others

υ_c: number of cations in electrolyte

υ_a: number of anions in electrolyte

$\upsilon = \upsilon_c + \upsilon_a$

z_i: charge on ion i

$\underline{C}$: Pitzer parameter

β : Pitzer parameters

m : molality

For 1-1 and 1-2 type, the New model requires generally 10 parameters (see Table 7.2 and 7.3), while Pitzer's model requires the value of 5 parameters ($\underline{A}$, β_0, β_1, α_1, $\underline{C}$) at a given temperature and concentration. Also at a fixed temperature, the $\underline{A}$ and α_1 values are the same for all 1-1 type electrolyte solutions. For 2-2 type, the New Model requires 6 parameters and Pitzer's requires 7 parameters ($\underline{A}$, β_0, β_1, β_2,α_1,α_2,$\underline{C}$) but $\underline{A}$, α_1, α_2 values are constant at fixed temperature. From the viewpoint of parameter numbers, Pitzer's model appears better than the New Model. But as stated earlier, the parameters used in the New Model appear in a simple regression for the change of the n value with concentration. If an improved regression scheme is developed, the numbers will be reduced. An even better solution is to develop a suitable perturbation method.

E. Summary of Chapter 8

A total of 28 strong electrolyte solutions, including all cases (1-1, 1-2, 2-2 type electrolytes), are analyzed from the viewpoint of the osmotic coefficient. The osmotic coefficient is well correlated by the New Model, with greater accuracy and greater range than Pitzer's model.

CHAPTER 9. CONCLUSIONS

The osmotic coefficients of 28 ionic solutions have been calculated by the New Model at room temperature and pressure. The New Model is a combination of the perturbation method and modified EXP theory which includes the electroneutrality condition and the charged soft sphere potential. In most cases, the New Model shows better performance, especially at high concentrations, than pre-existing models.

The following are recommended as future work.

(1) Development of a perturbation technique suitable for ionic solutions for the determination of the equivalent ion diameter of both ions (cation and anion).

(2) Obtain more osmotic coefficients for other ionic solutions.

(3) Extension to mixed salt solutions.

(4) Development of a more reasonable and simple ionic interaction model that reflects the effect of the solvent.

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APPENDIX 1.A

```
C
C     CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C     THIS PROGRAM IS DEVELOPED FOR THE PURPOSE OF
C     CONVERSION OF THE OSMOTIC COEFFICIENT WHICH
C     IS CALCULATED ON THE BASIS OF MOLARITY TO
C     THE OSMOTIC COEFFICIENT OF MOLALITY BASIS
C     (LiCl)
C     CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
C     INPUT DATA
C
      XI=0.001
      CALL CALC(XI)
C
      XI=0.002
      CALL CALC(XI)
C
      XI=0.005
      CALL CALC(XI)
C
      XI=0.01
      CALL CALC(XI)
C
      XI=0.02
      CALL CALC(XI)
C
      XI=0.05
      CALL CALC(XI)
C
      DO 10 I=1,10
        XI=0.1*I
        CALL CALC(XI)
   10 CONTINUE
C
      DO 20 I=1,5
        XI=1.+0.2*I
        CALL CALC(XI)
   20 CONTINUE
C
      DO 30 I=1,8
        XI=2.+0.5*I
        CALL CALC(XI)
   30 CONTINUE
C
      DO 40 I=1,13
        XI=6.+I
        CALL CALC(XI)
   40 CONTINUE
C
      XI=19.219
      CALL CALC(XI)
C
        STOP
        END
```

```
C
C     CCCCCCCCCCCCCCCCCCCC
      SUBROUTINE CALC(XM)
C     CCCCCCCCCCCCCCCCCCCC
C
      DATA  A,B,C,D/0.2554E-01,-0.2151E-02,
     1            -0.1896E-03, 0.3851E-04/
      DATA  E,W1,WLICL/-0.1422E-05,18.0154,42.394/
C
      D1=0.99707+A*XM+B*XM**1.5+C*XM**2.+D*XM**2.5
     1   +E*XM**3.
      DD=A+1.5*B*XM**0.5+2.*C*XM+2.5*D*XM**1.5
     1   +3.*E*XM**2.
      XC=XM*D1/(0.001*XM*WLICL+1.)
      V=XM*WLICL+1000.
      V=V/D1
      PARV=(W1/1000.)*(V-XM*(WLICL-V*DD)/D1)
      CONV=PARV/W1*XC/XM
C
      WRITE(1,*)XC
      WRITE(8,*)XM,XC,CONV
C
      RETURN
      END
```

APPENDIX 1.B

```
C
C     CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C     THIS PROGRAM IS FOR THE CALCULATION OF
C     EFFECTIVE DIAMETER OF LI AND CL ION. DE1
C     AND DE2 ARE CATION AND ANION DIAMETERS.
C     CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      DATA PAU1,PAU2/6.72,14.0/
      DATA  CA1,CA2,CA3,CA4,CA5,CA6,CA7/1.126598,
     1    4.612902E-04,7.192662E-05,-5.671713E-07,
     2    1.957671E-09,-2.818391E-12,1.362318E-15/
      DATA  CAA1,CAA2,CAA3,CAA4,CAA5,CAA6,CAA7/
     1    1.050151,0.3811103,-1.318081,2.345373,
     2    -2.143397,0.9650735,-0.1695988/
      DATA  CB1,CB2,CB3,CB4,CB5,CB6,CB7/4.653208,
     1    -122.1468,1738.935,-12861.13,51893.18,
     2    -108344.4,91594.38/
C
C     READ CONCENTRATION (AM)
C
   20 READ(1,*,ERR=100) AM
      AN1=3.8124+AM*(-0.0974)+(-0.0046)*AM**2.0
      IF (AM.LT.3.0) THEN
        IF (AM.LT.0.5) THEN
          AN2=CA1+CA2/AM+CA3/AM**2.+CA4/AM**3.
     1        +CA5/AM**4.+CA6/AM**5.+CA7/AM**6.
        ELSE
          AN2=CAA1+CAA2/AM+CAA3/AM**2.+CAA4/AM**3.
     1        +CAA5/AM**4.+ CAA6/AM**5.+CAA7/AM**6
        END IF
      ELSE
        AN2=CB1+CB2/AM+CB3/AM**2.+CB4/AM**3.
     1      +CB5/AM**4.+CB6/AM**5.+CB7/AM**6.
      END IF
      TEMP=298.15
      DEN=6.023E-4*AM
      EN1= 1.0*(4.8E-10)**2./(78.358*PAU1*1E-8)
     1    *(AN1-1.)/AN1
      EN2= 1.0*(4.8E-10)**2./(78.358*PAU2*1E-8)
     1    *(AN2-1.)/AN2
      AKT=1.3804E-16*TEMP
      B1=EN1/AKT
      B2=EN2/AKT
      B1=1./B1
      B2=1./B2
      S1=PAU1*AN1**(-1./(AN1-1.)
      S2=PAU2*AN2**(-1./(AN2-1.))
C
C     CALCULATION OF DB(BARKER HENDERSON DIAMETER)
C
      CALL  DDB(B1,DB1,PAU1,S1,AN1)
```

```
      CALL  DDB(B2,DB2,PAU2,S2,AN2)
C
C      CALCULATION OF SIG
C
      CALL  SSIG(B1,DB1,PAU1,S1,SIG1,AN1)
      CALL  SSIG(B2,DB2,PAU2,S2,SIG2,AN2)
C
C      CALCULATION OF EQUIVALENT DIAMETER DE
C
      CALL  DIA(DB1,SIG1,DEN,DE1)
      CALL  DIA(DB2,SIG2,DEN,DE2)
C
      WRITE(22,200)AM,DE1,DE2
      GO TO 20
C
  100 STOP
  200 FORMAT(2X,F10.7,2X,F10.7,2X,F10.7,2X,F10.7)
      END
C
C      CCCCCCCCCCCCCCCCCCCCCCCCC
      SUBROUTINE DDB(P,DB,PAU,S,AN)
C      CCCCCCCCCCCCCCCCCCCCCCCCC
C
C      ROMBERG ALGORITHM
C
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      DIMENSION R(2,15)
C
C      DEFINE FUNCTION F
C
      F(X) =X*DEXP(-1/P*(AN**(AN/(AN-1.))/(AN-1.))*
     1      ((S/X)**AN-(S/X))-1/P)*AN**(AN/(AN-1.))/
     2      (AN-1.)*(-1/P)*(-AN*(S/X)**(AN+1.)/
     3      S+(S/X)**2./S)
C
      A=0.1
      B=PAU
      N=15
      H = B-A
      R(1,1) = (F(A)+F(B))/2.0*H
C
C      APPROXIMATION FROM TRAPEZOIDAL METHOD
C
      DO 10 I=2,N
      SUM = 0.0
      M = 2**(I-2)
        DO 20 K=1,M
   20   SUM =SUM+F(A+(K-.5)*H)
      R(2,1) = (R(1,1)+H*SUM)/2
C
C      EXTRAPOLATION
C
```

```
        DO 30 J=2,I
        L = 2**(2*(J-1))
   30   R(2,J) = (L*R(2,J-1)-R(1,J-1))/(L-1)
      H = H/2
C
C      STEP 8
C      SINCE ONLY TWO ROWS ARE KEPT IN STORAGE,
C      THIS STEP IS TO PREPARE FOR THE NEXT ROW.
C      UPDATE ROW I OF R
C
        DO 40 J=1,I
   40   R(1,J) = R(2,J)
   10 CONTINUE
      DB=R(2,15)
C
      RETURN
      END
C
C      CCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
      SUBROUTINE SSIG(P,DB,PAU,S,SIG,AN)
C      CCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
C      ROMBERG ALGORITHM
C
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      DIMENSION R(2,15)
C
C      DEFINE FUNCTION F
C
      F(X)  =DEXP(-1/P*(AN**(AN/(AN-1.))/(AN-1.))*
     1    ((S/X)**AN-(S/X))-1/P)*AN**(AN/(AN-1.))
     2    /(AN-1.)*(-1/P)*(-AN*(S/X)**(AN+1.)/S+
     3    (S/X)**2./S)*(X/DB-1.)**2.
      A=0.1
      B=PAU
      N=15
      H = B-A
      R(1,1) = (F(A)+F(B))/2.0*H
C
C      APPROXIMATION FROM TRAPEZOIDAL METHOD
C
      DO 10 I=2,N
      SUM = 0.0
      M = 2**(I-2)
        DO 20 K=1,M
   20   SUM =SUM+F(A+(K-.5)*H)
      R(2,1) = (R(1,1)+H*SUM)/2
C
C      EXTRAPOLATION
C
        DO 30 J=2,I
        L = 2**(2*(J-1))
```

```
   30   R(2,J) = (L*R(2,J-1)-R(1,J-1))/(L-1)
      H = H/2
C
C      SINCE ONLY TWO ROWS ARE KEPT IN STORAGE,
C      THIS STEP IS TO PREPARE FOR THE NEXT ROW.
C      UPDATE ROW I OF R
C
        DO 40 J=1,I
   40   R(1,J) = R(2,J)
   10 CONTINUE
      SIG=R(2,15)
C
      RETURN
      END
C
C      CCCCCCCCCCCCCCCCCCCCCCCCCC
      SUBROUTINE DIA(DB,SIG,DEN,DE)
C      CCCCCCCCCCCCCCCCCCCCCCCCCC
C
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
C
C      INITIAL GUESS
C
      DE=DB
  100 DEA=DE
      ETA=1./6.*ATAN(1.)*4.*DEN*DE**3
      ETAW=ETA-1./16.*ETA**2
      ALP1=(1.-5.*ETAW-5*ETAW**2)/((1-ETAW)**3)
      ALP2=-3.*ETAW*(2.-4.*ETAW-7*ETAW**2)/
     1       (1-ETAW)**4
      SG=(1.-0.5*ETA)/(1.-ETA)**3
      AU=27./2.*ETAW**3/(1.-ETAW)**6*(1-0.7117
     1   *ETAW-0.114*ETAW**2)**2/(1+0.5*ETAW)
      A1=SG+ALP1-AU
      SS1=A1/(2.*SG)
      DE=DB*(1+SS1*SIG)
      DI=ABS(DE-DEA)
C
      IF (DI.LE.0.000001) THEN
        RETURN
      ELSE
        GO TO 100
      END IF
      END
```

APPENDIX 1.C

```
C
C     CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C                     LiCl SOLUTION
C     THIS PROGRAM TEST THE POSSIBILITY OF APPLYING THE
C     STILLINGER-LOVETTE MOMENT CONDITION. IN THIS
C     PROGRAM ONLY THE 1ST CONDITION(0 TH MOMENT
C     (CONDITION) WILL BE CONSIDERED FOR THE 1-1 TYPE
C     ELECTROLYTE SOLUTION.
C     CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
      COMMON/WORKSP/RWKSP
      COMMON/CCONC/CONC
      COMMON/CSIG/SIG(2),P1
      COMMON/ABC/AAA1,AAA2,BBB1,BBB2,CCC1,CCC2,MIT
      REAL RWKSP(5162)
C
C     PREPARATION FOR THE USE OF IMSL
C
      CALL IWKIN(5162)
C
C     READ BASIC DATA ( CONCENTRATION(MOLALITY,
C     MOLARITY),CONVERSION FACTOR, ANION, CATION
C     DIAMETER, P VALUE, EXPERIMENTAL DATA)
C
      MM=0
  100 READ(7,*,ERR=400) CONC,SIG(1),SIG(2),P1
      READ(8,*,ERR=400) CM,CONC,CONV,EXPR
      IF (MM.NE.0) THEN
        IF(MM.LE.2) SIG(2)=TSIG-3.0
        IF(MM.GT.2.AND.MM.LE.4) SIG(2)=TSIG-2.0
        IF(MM.GT.4.AND.MM.LE.6) SIG(2)=TSIG-1.0
        IF(MM.GT.6) SIG(2)=TSIG-0.5
      END IF
C
C     BASIC DATA
C
      DO 220 MMIT=1,2
        MIT=1
        NU=-1
        CALL  PARA(NU)
        SIG(2)=SIG(2)+1
  220 CONTINUE
C
      CALL EECP(NU,CM,CONV,EXPR)
C
      IF (NU.EQ.0) GO TO 270
      MIT=2
      SIG(2)=SIG(2)+1
      DO 250 MMIT=1,5
        NU=-1
        CALL PARA(NU)
        CALL EECP(NU,CM,CONV,EXPR)
```

```
         IF (NU.EQ.0) GO TO 270
         SIG(2)=SIG(2)+1
  250 CONTINUE
C
      STOP
C
  270 NU=0
      CALL PARA(NU)
      CALL EECP(NU,CM,CONV,EXPR)
C
      NU=1
      CALL PARA(NU)
      CALL EECP(NU,CM,CONV,EXPR)
C
      NU=2
      CALL PARA(NU)
      CALL EECP(NU,CM,CONV,EXPR)
C
      NU=3
      CALL PARA(NU)
      CALL EECP(NU,CM,CONV,EXPR)
C
      NU=4
      CALL PARA(NU)
      CALL EECP(NU,CM,CONV,EXPR)
C
      NU=5
      CALL PARA(NU)
      CALL EECP(NU,CM,CONV,EXPR)
C
      NU=6
      CALL PARA(NU)
      CALL EECP(NU,CM,CONV,EXPR)
C
      NU=7
      CALL PARA(NU)
      CALL EECP(NU,CM,CONV,EXPR)
C
      TSIG=SIG(2)
      TP1=P1
      MM=MM+1
      GO TO 100
C
  400 STOP
      END
C
C      CCCCCCCCCCCCCCCCCCC
      SUBROUTINE PARA(NNU)
C      CCCCCCCCCCCCCCCCCCC
C
      COMMON/WORKSP/RWKSP
      COMMON/CCONC/CONC
```

```
      COMMON/CSIG/SIG(2),P1
      COMMON/ABC/AAA1,AAA2,BBB1,BBB2,CCC1,CCC2,MIT
C
      CALL EXPLR1(R1,R2)
C
      IF ((ABS(R1)-ABS(R2)).GT.0) THEN
        AARP2=0.
        K=0
        DO 170 NJIT=1,4
          CALL  EXPLR1(R1,R2)
          AAR1=ABS(R1)
          AAR2=ABS(R2)
          DIFF1=AAR2-AAR1
          DIFF2=AARP2-AAR1
          IF (K.EQ.0) GO TO 160
          IF (DIFF1.GT.0.AND.DIFF2.LT.0) THEN
            P1=P1+0.1
            ARR2P=0.
            L1=0
            DO  150  I=1,20
              CALL  EXPLR1(R1,R2)
              AR1=ABS(R1)
              AR2=ABS(R2)
              DIFF1=AR2-AR1
              DIFF2=ARP2-AR1
             IF (L1.EQ.0) GO TO 120
             IF (DIFF1.GT.0.AND.DIFF2.LT.0) THEN
                P1=P1+0.01
                ARR2P=0.
                L=0
                DO 100 II=1,11
                  CALL  EXPLR1(RR1,RR2)
                  ARR1=ABS(RR1)
                  ARR2=ABS(RR2)
                  DIFF1=ARR2-ARR1
                  DIFF2=ARR2P-ARR1
                  IF (L.EQ.0) GO TO 80
                  IF (DIFF1.GT.0.AND.DIFF2.LT.0) THEN
                    P1=P1+0.001
                    ARR2P=0.
                    M=0
                    DO  50 III=1,11
                      CALL  EXPLR1(RRR1,RRR2)
                      ARRR1=ABS(RRR1)
                      ARRR2=ABS(RRR2)
                      DIFF1=ARRR2-ARRR1
                      DIFF2=ARRR2P-ARRR1
                      IF (M.EQ.0) GO TO 30
                      IF (DIFF1.GT.0.AND.DIFF2.LT.0)THEN
                        P1=P1+0.00005
                        CALL EXPLR1(RRRR1,RRRR2)
C
```

```
      IF (MIT.EQ.1.AND.NNU.EQ.-1)THEN
         WRITE(9,*)SIG(1),SIG(2),P1
         GO TO 330
      END IF
C
      IF (MIT.NE.1.AND.NNU.EQ.-1)THEN
         WRITE(9,*)AAA1,BBB1,CCC1
         WRITE(9,*)SIG(1),SIG(2),P1
         GO TO 330
      END IF
C
      IF (NNU.EQ.0) THEN
         WRITE(10,*)AAA1,BBB1,CCC1
         WRITE(10,*)SIG(1),SIG(2),P1
         WRITE(10,*)AAA2,BBB2,CCC2
         GO TO 330
      END IF
C
      IF (NNU.EQ.1) THEN
         WRITE(11,*)AAA1,BBB1,CCC1
         WRITE(11,*)SIG(1),SIG(2),P1
         WRITE(11,*)AAA2,BBB2,CCC2
         GO TO 330
      END IF
C
      IF (NNU.EQ.2) THEN
         WRITE(12,*)AAA1,BBB1,CCC1
         WRITE(12,*)SIG(1),SIG(2),P1
         WRITE(12,*)AAA2,BBB2,CCC2
         GO TO 330
      END IF
C
      IF (NNU.EQ.3) THEN
         WRITE(13,*)AAA1,BBB1,CCC1
         WRITE(13,*)SIG(1),SIG(2),P1
         WRITE(13,*)AAA2,BBB2,CCC2
         GO TO 330
      END IF
C
      IF (NNU.EQ.4) THEN
         WRITE(14,*)AAA1,BBB1,CCC
         WRITE(14,*)SIG(1),SIG(2),P1
         WRITE(14,*)AAA2,BBB2,CCC2
         GO TO 330
      END IF
C
      IF (NNU.EQ.5  THEN
         WRITE(15,*)AAA1,BBB1,CCC1
         WRITE(15,*)SIG(1),SIG(2),P1
         WRITE(15,*)AAA2,BBB2,CCC2
         GO TO 330
      END IF
```

```
C
                       IF (NNU.EQ.6) THEN
                         WRITE(16,*)AAA1,BBB1,CCC1
                         WRITE(16,*)SIG(1),SIG(2),P1
                         WRITE(16,*)AAA2,BBB2,CCC2
                         GO TO 330
                       END IF
C
                       IF (NNU.EQ.7) THEN
                         WRITE(17,*)SIG(1),SIG(2),P1
                         GO TO 330
                       END IF
                     END IF
   30              ARRR2P=ARRR2
                   P1=P1-0.0001
                   M=M+1
   50              CONTINUE
                 END IF
   80            ARR2P=ARR2
                 P1=P1-0.001
                 L=L+1
  100          CONTINUE
             END IF
  120        ARP2=AR2
             P1=P1-0.01
             L1=L1+1
  150       CONTINUE
          END IF
  160     AARP2=AAR2
          P1=P1-0.1
          K=K+1
  170   CONTINUE
C
      ELSE
C
        KK=0
        AARP2=0
        DO  320  NJIT=1,4
          CALL  EXPLR1(R1,R2)
          AAR1=ABS(R1)
          AAR2=ABS(R2)
          DIFF1=AAR2-AAR1
          DIFF2=AARP2-AAR1
          IF (KK.EQ.0) GO TO 310
          IF (DIFF1.LT.0.AND.DIFF2.GT.0) THEN
            P1=P1-0.1
            ARP2=0.
            LL1=0
            ARP2=0
            DO  300  J=1,11
              CALL  EXPLR1(R1,R2)
              AR1=ABS(R1)
```

```
          AR2=ABS(R2)
          DIFF1=AR2-AR1
          DIFF2=ARP2-AR1
          IF (LL1.EQ.0) GO TO 280
          IF (DIFF1.LT.0.AND.DIFF2.GT.0) THEN
            P1=P1-0.01
            ARR2P=0.
            LL=0
            DO 250 JJ=1,11
              CALL  EXPLR1(RR1,RR2)
              ARR1=ABS(RR1)
              ARR2=ABS(RR2)
              DIFF1=ARR2-ARR1
              DIFF2=ARR2P-ARR1
              IF (LL.EQ.0) GO TO 230
              IF (DIFF1.LT.0.AND.DIFF2.GT.0)THEN
                P1=P1-0.001
                ARRR2P=0.
                MM=0
                DO  200 JJJ=1,1
                  CALL  EXPLR1(RRR1,RRR2)
                  ARRR1=ABS(RRR1)
                  ARRR2=ABS(RRR2)
                  DIFF1=ARRR2-ARRR1
                  DIFF2=ARRR2P-ARRR1
                  IF (MM.EQ.0) GO TO 180
                  IF (DIFF1.LT.0.AND.DIFF2.GT.0)THEN
                    P1=P1-0.00005
                    CALL EXPLR1(RRRR1,RRRR2)
C
                    IF (MIT.EQ.1.AND.NNU.EQ.-1)THEN
                      WRITE(9,*)SIG(1),SIG(2),P1
                      GO TO 330
                    END IF
C
                    IF (MIT.NE.1.AND.NNU.EQ.-1)THEN
                      WRITE(9,*)AAA1,BBB1,CCC1
                      WRITE(9,*)SIG(1),SIG(2),P1
                      GO TO 330
                    END IF
C
                    IF (NNU.EQ.0)    THEN
                      WRITE(10,*)AAA1,BBB1,CCC1
                      WRITE(10,*)SIG(1),SIG(2),P1
                      WRITE(10,*)AAA2,BBB2,CCC2
                      GO TO 330
                    END IF
C
                    IF (NNU.EQ.1)    THEN
                      WRITE(11,*)AAA1,BBB1,CCC1
                      WRITE(11,*)SIG(1),SIG(2),P1
                      WRITE(11,*)AAA2,BBB2,CCC2
```

```
                    GO TO 330
                  END IF
C
                  IF (NNU.EQ.2)    THEN
                    WRITE(12,*)AAA1,BBB1,CCC1
                    WRITE(12,*)SIG(1),SIG(2),P1
                    WRITE(12,*)AAA2,BBB2,CCC2
                    GO TO 330
                  END IF
C
                  IF (NNU.EQ.3)    THEN
                    WRITE(13,*)AAA1,BBB1,CCC1
                    WRITE(13,*)SIG(1),SIG(2),P1
                    WRITE(13,*)AAA2,BBB2,CCC2
                    GO TO 330
                  END IF
C
                  IF (NNU.EQ.4)    THEN
                    WRITE(14,*)AAA1,BBB1,CCC1
                    WRITE(14,*)SIG(1),SIG(2),P1
                    WRITE(14,*)AAA2,BBB2,CCC2
                    GO TO 330
                  END IF
C
                  IF (NNU.EQ.5)    THEN
                    WRITE(15,*)AAA1,BBB1,CCC1
                    WRITE(15,*)SIG(1),SIG(2),P1
                    WRITE(15,*)AAA2,BBB2,CCC2
                    GO TO 330
                  END IF
C
                  IF (NNU.EQ.6)    THEN
                    WRITE(16,*)AAA1,BBB1,CCC1
                    WRITE(16,*)SIG(1),SIG(2),P1
                    WRITE(16,*)AAA2,BBB2,CCC2
                    GO TO 330
                  END IF
C
                  IF (NNU.EQ.7)    THEN
                    WRITE(17,*)SIG(1),SIG(2),P1
                    GO TO 330
                  END IF
C
                END IF
  180           ARRR2P=ARRR2
                P1=P1+0.0001
                MM=MM+1
  200         CONTINUE
            END IF
  230       ARR2P=ARR2
            P1=P1+0.001
            LL=LL+1
```

```
  250             CONTINUE
                END IF
  280           ARP2=AR2
                P1=P1+0.01
                LL1=LL1+1
  300         CONTINUE
            END IF
  310       AARP2=AAR2
            P1=P1+0.
            KK=KK+1
  320     CONTINUE
        END IF
C
          WRITE(9,*)'FAIL',SIG(2),'P1',P1,'SUB',R1,
     1            'SUMEXP',R2
  330 RETURN
      END
C
C      CCCCCCCCCCCCCCCCCCCCCCCCCC
      SUBROUTINE EXPLR1(SUB,SUMEXP)
C      CCCCCCCCCCCCCCCCCCCCCCCCCC
C
C      +, SMALL
C      -, BIG
C
      COMMON/CSIG/SIG(2),P1
      COMMON/CNC/NC
      COMMON/CZ/ Z(2)
      COMMON/CV/ V(2)
      COMMON/CCONC/ CONC
      COMMON/CRSTAR/ RSTAR
      COMMON/CALPHA/ ALPHA2
      COMMON/NITZS/ G11,G12,G22
      COMMON/CLRE/ EXPLRO
      COMMON/CLRGL/GLLSS(2048),GLLBB(2048),GLLSB(2048)
      COMMON/CDF/ DR,DK,NB
      DIMENSION YNTE(6,6),R(2048)
      DIMENSION GESS(2048),GEBB(2048),GESB(2048)
      DIMENSION CHSS(2048),CHBB(2048),CHSB(2048)
      DIMENSION RHO(2),GG(10,10)
      REAL K
C
C      BASIC DATA SUPPLY
C
      DR=0.01
      NB=2047
      NC=2
      V(1)=1.
      V(2)=1.
      Z(1)=1.
      Z(2)=-1.
      Z1=Z(1)
```

```
      Z2=Z(2)
      T=298.15
      AN=6.02252E+23
      K=1.38054E-23
      E=1.60210E-19
      P=78.54
      D=1.112647E-10*P
      PI=3.1415927
      BETA=((E*E)/(D*K*T))*1.E+10
      ALPHA2=4.*PI*BETA
      ALPHA=SQRT(ALPHA2)
      RSTAR=CONC*6.02252E-04
C
C      REDUCED DISTANCE,  R/SIG-
C
      DS=SIG(1)/SIG(2)
      DB=1.0
      DSB=(DS+DB)*0.5
C
C      LOWER INTEGRATION LIMITS, REDUCED SIGIJ
C
      NSS=DS/DR
      NBB=DB/DR
      NSB=DSB/DR
C
C      DETERMINE INTEGRATION GRID FROM R/SIGIJ TO
C      INFINITY=12SIG-
C
      R(1)=DR
      DO 15 J=2,NB
        R(J)=R(J-1)+DR
   15 CONTINUE
C
C      BEGIN- LRE OSMOTIC
C
      VT=0.
      RH=0.
      DO 25 J=1,NC
        VT=VT+V(J)
        RHO(J)=V(J)*RSTAR
        RH=RH+RHO(J)
   25 CONTINUE

C
C      REDUCED DENSITY(THE BASIC UNIT OF LENGTH IN THIS
C      PROGRAM IS THE SIG(2))
C
      RHRD=RH*SIG(2)*SIG(2)*SIG(2)
      DO 30 J=1,NB
        CHSS(J)=0.0
        CHBB(J)=0.0
        CHSB(J)=0.0
```

```
   30 CONTINUE
C
C      CALCULATION OF THE RENORMALIZED POTENTIAL
C
      CALL CHAIN(R,Z1,Z1,NSS,NB,CHSS)
      CALL CHAIN(R,Z2,Z2,NBB,NB,CHBB)
      CALL CHAIN(R,Z1,Z2,NSB,NB,CHSB)
      CALL GLLVW(RHRD,DB,DSB,DS)
C
      IF (NSS.LE.NBB) THEN
        IN=NSS
      ELSE
        IN=NBB
      END IF
  200 DO 1100 J=IN,NB
        GESS(J)=EXP(CHSS(J))*GLLSS(J)
        GEBB(J)=EXP(CHBB(J))*GLLBB(J)
        GESB(J)=EXP(CHSB(J))*GLLSB(J)
        IF (J.LT.NSS) GESS(J)=0.
        IF (J.LT.NBB) GEBB(J)=0.
        IF (J.LT.NSB) GESB(J)=0.
 1100 CONTINUE
C
C      CALCULATE  YNT=SIG-**2 (INTEGRAL(SIGIJ/SIG-TO INF)
C
      CALL YNTIJ1(R,DR,NSS,NB,GESS,YNTE(1,1))
      CALL YNTIJ1(R,DR,NBB,NB,GEBB,YNTE(2,2))
      CALL YNTIJ1(R,DR,NSB,NB,GESB,YNTE(1,2))
C
      YNTE(2,1)=YNTE(1,2)
      SUMEXP=0.
      DO 1220 J=1,NC
      DO 1210 KK=1,NC
        IF (J.NE.KK) YNTE(J,KK)=-YNTE(J,KK)
        SUMEXP=SUMEXP+YNTE(J,KK)
 1210 CONTINUE
 1220 CONTINUE
      SUB=-1./(2*PI*RHO(1))
C
      RETURN
      END

C
C     CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
      SUBROUTINE EECP(NNU,CM,CONV,EXPR)
C     CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
C     THIS PROGRAM CALCULATES THE OSMOTIC
C     COEFFICIENTS OF THE LiCl SOLUTION.
C     THERE IS A COMPARISON WITH THE
C     PITZER'S MODEL.
C
```

```
C     INPUT
C
      COMMON/WORKSP/RWKSP
      COMMON/CCONC/CONC
      COMMON/CSIG/SIG(2),P1
      COMMON/ABC/AAA1,AAA2,BBB1,BBB2,CCC1,CCC2
C
C     THESE ARE DATA OF THE PITZER MODEL PARAMETER AT
C     ROOM TEMPERATURE
C
      DATA A,BE0,BE1,CFI/0.3910,0.1494,0.3074,0.00359/
C
C     BEGIN DATA GENERATION
C     CALCULATION OF OSMOTIC COEFFICIENT BY PITZER
C     MODEL
C
      OSMO=1.-1.0*A*SQRT(CM)/(1.+1.2*SQRT(CM))+
     1  CM*(BE0+BE1*EXP(-2.0*SQRT(CM)))+CM**2.*CFI
      IF (NNU.EQ.-1)  CLOSE(9)
      IF (NNU.EQ.0)   CLOSE(10)
      IF (NNU.EQ.1)   CLOSE(11)
      IF (NNU.EQ.2)   CLOSE(12)
      IF (NNU.EQ.3)   CLOSE(13)
      IF (NNU.EQ.4)   CLOSE(14)
      IF (NNU.EQ.5)   CLOSE(15)
      IF (NNU.EQ.6)   CLOSE(16)
      IF (NNU.EQ.7)   CLOSE(17)
C
      DELOLD=0.0
  100 IF (NNU.EQ.-1)READ(9,*,Err=500)SIG(1),SIG(2),P1
      IF (NNU.EQ.0)READ(10,*,Err=500)SIG(1),SIG(2),P1
      IF (NNU.EQ.1)READ(11,*,Err=500)SIG(1),SIG(2),P1
      IF (NNU.EQ.2)READ(12,*,Err=500)SIG(1),SIG(2),P1
      IF (NNU.EQ.3)READ(13,*,Err=500)SIG(1),SIG(2),P1
      IF (NNU.EQ.4)READ(14,*,Err=500)SIG(1),SIG(2),P1
      IF (NNU.EQ.5)READ(15,*,Err=500)SIG(1),SIG(2),P1
      IF (NNU.EQ.6)READ(16,*,Err=500)SIG(1),SIG(2),P1
      IF (NNU.EQ.7)READ(17,*,Err=500)SIG(1),SIG(2),P1
C
      IF (NNU.EQ.7) THEN
        CALL FINAL(NNU,CM,CONV,EXPR,OSM,EXPT)
        RETURN
      END IF
C
      CALL EXPLR(CM,CONV,EXPR,EXPT)
      DELNEW=EXPT-EXPR
      CROSS=DELNEW*DELOLD
C
      IF (CROSS.LT.0.AND.NNU.EQ.-1) THEN
        NNU=0
        AAA2=SIG(1)
        BBB2=SIG(2)
```

```
          CCC2=P1
          SIG(2)=SIG(2)-0.5
          RETURN
        END IF
C
        IF (CROSS.LT.0.AND.NNU.EQ.0) THEN
          NNU=1
          AAA2=SIG(1)
          BBB2=SIG(2)
          CCC2=P1
          SIG(2)=SIG(2)-0.25
          RETURN
        END IF
C
        IF (CROSS.LT.0.AND.NNU.EQ.1) THEN
          NNU=2
          AAA2=SIG(1)
          BBB2=SIG(2)
          CCC2=P1
          SIG(2)=SIG(2)-0.125
          RETURN
        END IF
C
        IF (CROSS.LT.0.AND.NNU.EQ.2) THEN
          NNU=3
          AAA2=SIG(1)
          BBB2=SIG(2)
          CCC2=P1
          SIG(2)=SIG(2)-0.0625
          RETURN
        END IF
C
        IF (CROSS.LT.0.AND.NNU.EQ.3) THEN
          NNU=4
          AAA2=SIG(1)
          BBB2=SIG(2)
          CCC2=P1
          SIG(2)=SIG(2)-0.0325
          RETURN
        END IF
C
        IF (CROSS.LT.0.AND.NNU.EQ.4) THEN
          NNU=5
          AAA2=SIG(1)
          BBB2=SIG(2)
          CCC2=P1
          SIG(2)=SIG(2)-0.015625
          RETURN
        END IF
C
        IF (CROSS.LT.0.AND.NNU.EQ.5) THEN
          NNU=6
```

```
          AAA2=SIG(1)
          BBB2=SIG(2)
          CCC2=P1
          SIG(2)=SIG(2)-0.0078125
          RETURN
        END IF
C
        IF (CROSS.LT.0.AND.NNU.EQ.6) THEN
          NNU=7
          AAA2=SIG(1)
          BBB2=SIG(2)
          CCC2=P1
          SIG(2)=SIG(2)-0.00390625
          RETURN
        END IF
C
        DELOLD=DELNEW
        AAA1=SIG(1)
        BBB1=SIG(2)
        CCC1=P1
        GO TO 100
C
  500   RETURN
  700   FORMAT(1X,F9.7,2X,F10.7,2X,F9.7,2X,F9.7,2X,F9.7)
        END
C
C       CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
        SUBROUTINE FINAL(NNU,CM,CONV,EXPR,OSMO,EXPT)
C       CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
        COMMON/WORKSP/RWKSP
        COMMON/CCONC/CONC
        COMMON/CSIG/SIG(2),P1
C
        CALL EXPLR(CM,CONV,EXPR,EXPT)
C
        WRITE(18,700)CM,SIG(2),EXPT,EXPR,OSMO
        WRITE(19,*)CONC,SIG(2),P1
        WRITE(20,*)CONC
        CLOSE(20)
C
  700   FORMAT(1X,F10.7,2X,F10.7,2X,F9.7,2X,F9.7,2X,F9.7)
  800   RETURN
        END
C
C       CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
        SUBROUTINE EXPLR(CML,CONV,EXPR,EXPT)
C       CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
        COMMON/CSIG/SIG(2),P1
        COMMON/CNC/NC
        COMMON/CZ/ Z(2)
```

```
      COMMON/CV/ V(2)
      COMMON/CCONC/ CONC
      COMMON/CRSTAR/ RSTAR
      COMMON/CALPHA/ ALPHA2
      COMMON/NITZS/ G11,G12,G22
      COMMON/CLRE/ EXPLRO
      COMMON/CLRGL/GLLSS(2048),GLLBB(2048),GLLSB(2048)
      COMMON/CDF/ DR,DK,NB
C
      DIMENSION YNTE(6,6),R(2048)
      DIMENSION GESS(2048),GEBB(2048),GESB(2048)
      DIMENSION CHSS(2048),CHBB(2048),CHSB(2048)
      DIMENSION RHO(2),GG(10,10)
      REAL K
C
C      DETERMINATION OF THE NUMERICAL STEP
C
      DR=0.01
      NB=2047
C
C      NUMBER OF COMPONENTS
C
      NC=2
C
C      VOLUME (V(I)), VALENCE(Z(I))
C
      V(1)=1.
      V(2)=1.
      Z(1)=1.0
      Z(2)=-1.0
      Z1=Z(1)
      Z2=Z(2)
C
C     TEMP(T), AVOGADRO #(AN), BOLTZMAN CONSTANT(K),
C     ELECTRONIC CHARGE(E),DIELECTRIC CONSTANT AND
C     ITS UNIT CONVERSION(P & D), PI VALUE
C
      T=298.15
      AN=6.02252E+23
      K=1.38054E-23
      E=1.60210E-19
      P=78.54
      D=1.112647E-10*P
      PI=4.*ATAN(1.0)
C
C     BETA RELATED VALUE CALCULATION
C
      BETA=((E*E)/(D*K*T))*1.E+10
      ALPHA2=4.*PI*BETA
      ALPHA=SQRT(ALPHA2)
C
C     ION NUMBER CALCULATION
```

```
C
      RSTAR=CONC*6.02252E-04
C
C      REDUCED DISTANCE,  R/SIG(2)
C
      DS=SIG(1)/SIG(2)
      DB=1.0
      DSB=(DS+DB)*0.5
C
C      LOWER INTEGRATION LIMITS, REDUCED SIG(1),SIG(2)
C      AND  ITS AVERAGE VALUES
C
      NSS=DS/DR
      NBB=DB/DR
      NSB=DSB/DR
C
C      DETERMINE INTEGRATION GRID FROM R/SIG(IJ)
C      TO QUASI INFINITY
C      (=20.48*ANION DIAMETER)
C
      R(1)=DR
      DO 15 J=2,NB
       R(J)=R(J-1)+DR
   15 CONTINUE
C
C      BEGIN- LRE OSMOTIC
C
      VT=0.
      RH=0.
      DO 25 J=1,NC
        VT=VT+V(J)
        RHO(J)=V(J)*RSTAR
        RH=RH+RHO(J)
   25 CONTINUE
C
C      REDUCED DENSITY(THE BASIC UNIT OF LENGTH IN
C      THIS   PROGRAM IS SIG(2) VALUE)
C
      RHRD=RH*SIG(2)*SIG(2)*SIG(2)
C
C      CALCULATION OF THE RENORMALIZED POTENTIAL
C
      DO 30 J=1,NB
        CHSS(J)=0.0
        CHBB(J)=0.0
        CHSB(J)=0.0
   30 CONTINUE
C
      CALL CHAIN(R,Z1,Z1,NSS,NB,CHSS)
      CALL CHAIN(R,Z2,Z2,NBB,NB,CHBB)
      CALL CHAIN(R,Z1,Z2,NSB,NB,CHSB)
C
```

```
C     CALCULATION OF THE RADIAL DISTRIBUTION
C     FUNCTION FOR THE HARD SPHERE SYSTEM
C
      CALL GLLVW(RHRD,DB,DSB,DS)
C
C     CALCULATION OF THE TOTAL RADIAL
C     DISTRIBUTION FUNCTION (FOR LONG RANGE)
C
      IF (NSS.LE.NBB) THEN
        IN=NSS
      ELSE
        IN=NBB
      END IF
  200 DO 1100 J=IN,NB
        GESS(J)=EXP(CHSS(J))*GLLSS(J)
        GEBB(J)=EXP(CHBB(J))*GLLBB(J)
        GESB(J)=EXP(CHSB(J))*GLLSB(J)
        IF (J.LT.NSS) GESS(J)=0.
        IF (J.LT.NBB) GEBB(J)=0.
        IF (J.LT.NSB) GESB(J)=0.
 1100 CONTINUE
C
C     INTEGRATION OF THE PRODUCT
C     (DISTANCE*TOTAL RADIAL DISTRIBUTION FUNCTION)
C
      CALL YNTIJ(R,DR,NSS,NB,GESS,YNTE(1,1))
      CALL YNTIJ(R,DR,NBB,NB,GEBB,YNTE(2,2))
      CALL YNTIJ(R,DR,NSB,NB,GESB,YNTE(1,2))
      YNTE(2,1)=YNTE(1,2)
C
C     THE CALCULATION OF THE LONG RANGE CONTRIBUTION OF
C     THE  OSMOTIC COEFFICIENT VALUE.
C     COEF.=ALPHA2/(6*RH)*SUMI SUMJ(RHOJ ZI ZJ YNTIJ)
C
      SUMEXP=0.
      DO 1220 J=1,NC
      DO 1210 KK=1,NC
        SUMEXP=SUMEXP+RHO(J)*RHO(KK)*Z(J)*Z(KK)
     1       *YNTE(J,KK)
 1210 CONTINUE
 1220 CONTINUE
      EXPLRO=(ALPHA2*SUMEXP)/(6.*RH)
C
C     CALCULATION OF THE CONTRIBUTION BY THE  CONTACT
C     VALUE AMONG THE TOTAL OSMOTIC COEFFICIENT VALUE.
C
      SUMEXP=0.
      DO 1300 J=1,NC
      DO 1400 KK=1,NC
        IF (J.EQ.1.AND.KK.EQ.1) GG(J,KK)=G11*
     1     EXP(CHSS(NSS))*SIG(J)**3.
```

```
         IF (J.EQ.1.AND.KK.EQ.2) GG(J,KK)=G12
     1      *EXP(CHSB(NSB))*((SIG(J)+SIG(KK))/2.)**3.
         IF (J.EQ.2.AND.KK.EQ.1) GG(J,KK)=G12*
     1      EXP(CHSB(NSB))*((SIG(J)+SIG(KK))/2.)**3.
         IF (J.EQ.2.AND.KK.EQ.2) GG(J,KK)=G22*
     1      EXP(CHBB(NBB))*SIG(KK)**3.
         SUMEXP=SUMEXP+RHO(J)*RHO(KK)*GG(J,KK)
 1400 CONTINUE
 1300 CONTINUE
      EXPCO=(ALPHA2/BETA*SUMEXP)/(6.*RH)
      EXPT=EXPLRO+EXPCO+1.
C
C     CONVERSION TO MOLALITY BASIS OSMOTIC COEFFICIENT
C
      EXPT=EXPT*CONV
C
      RETURN
      END
C
C     CCCCCCCCCCCCCCCCCCCCCCCCCCCCC
      SUBROUTINE GLLVW(RH,DC1,DC12,DC2)
C     CCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
C     +, SMALL
C     -, BIG
C
C     HARD SPHERE RDF OF VERLET AND WEIS
C     GENERALIZED TO MIXTURES BY LEE AND LEVESQUE
C
C     CALLED BY LRE
C
      COMMON/CNC/NC
      COMMON/CV/V(2)
      COMMON/CLRGL/ G11(2048),G22(2048),G12(2048)
      COMMON/NITZS/COR11,COR12,COR22
      COMMON/JASPER/ NSMA, N11,N12,N22,M11,M12,M22,
     1              DSMA,NC1,NC2,NC12
      COMMON/HEIDG/ SMA
      COMMON/SPENGL/ A11,A12,A22
      COMMON/ZSE/RSR,ET,ET1,ET2
      COMMON/BOO/NS,DW,DV
      COMMON/YY/ YR12(2048),YR11(2048),YR22(2048)
      COMMON/YKY/ YK12(2048),YK11(2048),YK22(2048)
      COMMON/CDF/DX,DK,NM
      COMMON/CGC/ GC11,GC12,GC22
      COMMON/YHN/ RO1,RO2,X1,X2
C
      DOUBLE PRECISION GC11,GC12,GC22
      DOUBLE PRECISION RSR,ET,ET1,ET2,X1,X2
      DIMENSION R(2048)
      REAL MU1,MU2,MU3
C
```

```
      NSMA=1
      SMA=0.0001
      NS=NM
      DW=1.
C
      VT=0.
      DO 10 J=1,NC
        VT=VT+V(J)
   10 CONTINUE
      XI1=V(1)/VT
      XI2=1.-XI1
      X=XI1
      X1=XI2
C
      PI=3.14159265359
      RHO=RH*DC1*DC1*DC1
      D22=DC2/DC1
      D11=1.
      D12=.5*(D11+D22)
      ETA=PI*RHO*(XI1*D11**3+XI2*D22**3)/6.
      RHO1=RHO*X
      RHO2=RHO-RHO1
      RHO12=SQRT(RHO1*RHO2)
      RSR=D22
      HT=ETA
      HTW=HT-HT*HT/16.
      R(1)=DX
      DO 48 J=2,NM
   48 R(J)=R(J-1)+DX
      NC1=RSR/DX
      NC2=1./DX
      NC12=D12/DX
      M11=NC1-NSMA
      M12=NC12-NSMA
      M22=NC2-NSMA
      L1=NC1+NSMA
      L2=NC12+NSMA
      L3=NC2+NSMA
      X2=1.-X1
      RSR3=RSR**3
      ALPHA=(HT/HTW)**(1./3.)
      DV=1./ALPHA
      RO=RHO*(HTW/HT)
      RO1=RO*X1
      RO2=RO-RO1
      DX=DX*ALPHA
      DK=PI/(DX*(NM+1.))
      ET=PI*(RO1*RSR3+RO2)/6.
C
      CALL FINDA (RHO,ETA,RO,ET,D11,D22,ALPHA,X)
C
```

```
      ET1=PI*RO1*RSR3/6.
      ET2=ET-ET1
      ETA1=PI*RO1/6.
      ETA2=PI*RO2/6.
      QQ=1.+RSR+RSR*(ETA1*RSR*RSR+ETA2)
      PC=(1.+ET+ET*ET)*RO
      PC=PC-18.*ETA1*ETA2*(1.-RSR)*(1.-RSR)*QQ/PI
      PC=PC/((1.-ET)**3)
      QQ=ET*(ETA1*RSR*RSR+ETA2)**3
      PV=PC-18.*QQ/(PI*(1.-ET)**3)
      PC=PC/RO
      PV=PV/RO
C
      CALL YMIXT
C
      MU1=24.*A11/(D11*HTW*GC22)
      MU2=24.*A12/(D12*HTW*GC12)
      MU3=24.*A22/(D22*HTW*GC11)
      DO 21 J=1,NM
        G11(J)=0.
        G12(J)=0.
        G22(J)=0.
   21 CONTINUE
C
      MM=MM+1
      DO 22 N=NC1,NM
        DIS=R(N)-D22
        DISMU3=DIS*MU3
        IF (DISMU3.GT.170) DISMU3=170.
        G11(N)=YR11(N)+1.+A22*D22*EXP(-DISMU3)
     1          *COS(DISMU3)/R(N)
   22 CONTINUE
C
      DO 23 N=NC12,NM
        DIS=R(N)-D12
        DISMU2=DIS*MU2
        IF(DISMU2.GT. 170) DISMU2=170.
        G12(N)=YR12(N)+1.+A12*D12*EXP(-DISMU2)
     1          *COS(DISMU2)/R(N)
   23 CONTINUE
C
      DO 24 N=NC2,NM
        DIS=R(N)-D11
        DISMU1=DIS*MU1
        IF(DISMU1.GT. 170) DISMU1=170.
        G22(N)=YR22(N)+1.+A11*D11*EXP(-DISMU1)
     1          *COS(DISMU1)/R(N)
   24 CONTINUE
C
      RETURN
      END
```

```
C
C      CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
       SUBROUTINE FINDA(RHO,XY,RO,XI,D1,D2,ALPHA,X)
C      CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
C      CALLED BY GLLVW
C
       COMMON/CSIG/SIG(2),P1
       COMMON/NITZS/ G11,G12,G22
       COMMON/SPENGL/AD11,AD12,AD22
       COMMON/SOCRAT/DP1,Q
       COMMON/EURIPD/DD,AA1,ETAA1,ETAA2,AA2,UMB
       COMMON/PASCAL/D12,AL1,AL2,Y,PI
       COMMON/HODRLN/PY1,PY12,PY2
       DOUBLE PRECISION XI
C
       PI=3.1415926535
       D1=1.
       Y=1.-X
       D12=.5*(D1+D2)
       DD=D1+D2
       AL1=PI*D1**3*X/6.
       AL2=PI*D2**3*Y/6.
       XI1=AL1*RHO
       XI2=AL2*RHO
       XX=XI1/D1+XI2/D2
       Q=1./(1.-XY)
       G11=Q+3.*D1*XX*0.5*Q*Q+D1*D1*XX*XX*0.75*Q*Q*Q
       G22=Q+3.*D2*XX*0.5*Q*Q+D2*D2*XX*XX*0.75*Q*Q*Q
       TI=D1*D2/(D1+D2)
       G12=Q+3.*XX*Q*Q*TI+3.*XX*XX*Q*Q*Q*TI*TI
C
       CALL  PY (XY,RHO,D1,D2,X)
C
       G11=(2.*G11+PY1)/3.
       G12=(2.*G12+PY12)/3.
       G22=(2.*G22+PY2)/3.
       Z=RHO+2.*PI*(RHO*RHO*X*X*D1*D1*D1*G11
     1  +RHO*RHO*X*Y*2.*D12*D12*D12*G12
     2  +RHO*RHO*Y*Y*D2*D2*D2*G22)/3.
       Z=Z/RHO
       XE=XI
       Q=1./(1.-XI)
       WD1=D1*(ALPHA-1.)
       WD12=D12*(ALPHA-1.)
       WD2=D2*(ALPHA-1.)
C
       CALL PY (XE,RO,D1,D2,X)
C
       B1=ETAA1*D1**2*PY1**2+ETAA2*D12**2*PY12**2
       B1=-6.*B1
       B2=ETAA2*D2**2*PY2**2+ETAA1*D12**2*PY12**2
```

```
      B2=-6.*B2
      D=ETAA1*AA1+ETAA2*AA2
      D=0.5*D
      B=ETAA1*D1*PY1+ETAA2*D2*PY2
      B=-6.*B*D12*PY12
      DX11=B1+3.*D
      DX22=B2+3.*D*D2*D2
      DDX11=6.*D
      DDX22=6.*D*D2
      DDDX11=DDX11
      DDDX22=6.*D
      YAK=B*D2**2+4.*UMB*D*D2**3+D*D2**4
      DX12=-YAK/(D12*D12)
      YAL=2.*B*D2+12.*UMB*D*D2*D2+4.*D*D2*D2*D2
      DX12=DX12+YAL/D12
      DDX12=2.*YAK/D12**3
      DDX12=DDX12-2.*YAL/(D12*D12)
C
      YAM=2.*B+24.*UMB*D*D2+12.*D*D2*D2
      DDX12=DDX12+YAM/D12
      DDDX12=-6.*YAK/D12**4
      DDDX12=DDDX12+6.*YAL/D12**3
      DDDX12=DDDX12-3.*YAM/(D12*D12)
      DDDX12=DDDX12+(24.*UMB*D+24.*D*D2)/D12
      GG1=PY1+DX11*WD1+0.5*DDX11*WD1**2+DDDX11
     1    *WD1**3/6.
      AD11=G11-GG1
      GG2=PY2+DX22*WD2+0.5*DDX22*WD2**2+DDDX22
     1    *WD2**3/6.
      AD22=G22-GG2
      GG12=PY12+DX12*WD12+0.5*DDX12*WD12**2+DDDX12
     1      *WD12**3/6.
      AD12=G12-GG12
C
        RETURN
        END
C
C      CCCCCCCCCCCCCCCCCCCCCCCC
      SUBROUTINE PY (XI,RO,D1,D2,X)
C      CCCCCCCCCCCCCCCCCCCCCCCC
C
C      CALLED BY FINDA
C
      COMMON/SOCRAT/ DP1,Q
      COMMON/EURIPD/ DD,AA1,ETAA1,ETAA2,AA2,UMB
      COMMON/PASCAL/ D12,AL1,AL2,Y,PI
      COMMON/HODRLN/ PY1,PY12,PY2
C
      T=D1/D2
      S=D2/D1
      XI1=AL1*RO
      XI2=AL2*RO
```

```
      ETAA1=PI*RO*X/6.
      ETAA2=PI*RO*Y/6.
      UMB=0.5*(D1-D2)
C
      CALL A1 (T,XI1,XI2,XI)
C
      AA1=DP1
C
      CALL A1 (S,XI2,XI1,XI)
C
      AA2=DP1
      PY1=1.+0.5*XI
      PY1=PY1+3.*ETAA2*D2**2*UMB
      PY1=PY1*Q**2
      PY2=1.+0.5*XI
      PY2=PY2-3.*ETAA1*D1**2*UMB
      PY2=PY2*Q**2
      PY12=D2*PY1+D1*PY2
      PY12=PY12/(D1+D2)
C
      RETURN
      END
C
C     CCCCCCCCCCCCCCCCCCCCCCC
      SUBROUTINE A1 (T,XI1,XI2,XI)
C     CCCCCCCCCCCCCCCCCCCCCCC
C
C     CALLED BY PY
C
      COMMON/SOCRAT/DP1,Q
C
      DP=(1.+XI+XI**2)*Q**3
      DP=DP+(2.+XI)**2*(XI1+T**3*XI2)*Q**4
      DP=DP-3.*XI2*(1.-T)**2*(1.+T+2.*XI1+T*XI2)
     1   *Q**3
      DP1=DP-9.*XI1*XI2*(1.-T)**2*(1.+T+T*XI2+XI1)
     1    *Q**4
      RETURN
      END
C
C     CCCCCCCCCCCCCCCC
      SUBROUTINE YMIXT
C     CCCCCCCCCCCCCCCC
C
C     CALLED BY MAIN
C
      COMMON/HEIDG/SMA
      COMMON/JASPER/NSMA,N11,N12,N22,M11,M12,M22,DSMA,NC1,NC2
     1              ,NC12
      COMMON/BOO/ NS,DW,DV
      COMMON/CC/CK11,CK22,CK12
      COMMON/YY/YR12(2048),YR11(2048),YR22(2048)
```

```
      COMMON/YKY/YK12(2048),YK11(2048),YK22(2048)
      COMMON/YHN/RO1,RO2,X1,X2
      COMMON/BG/ XK
      COMMON/CDF/ DX,DK,NM
      COMMON/CGC/GC11,GC12,GC22
      COMMON/WQ/A1,A2,B1R1,B2R2,BR2,DR1,DR2
      COMMON/ZSE/RSR,ET,ET1,ET2
C
      DOUBLE PRECISION CK11,CK12,CK22
      DOUBLE PRECISION RSR,ET,ET1,ET2,X1,X2
      DOUBLE PRECISION A1,A2,B1R1,B2R2,BR2,DR1,DR2
      DOUBLE PRECISION E,E2,E3,E4,AST,PR,RSR3
      DOUBLE PRECISION GC11,GC12,GC22
C
      D1=1.
      DH=0.5
      D3H=1.5
      DSMA=DX*SMA
      N11=NC1+NSMA
      N12=NC12+NSMA
      N22=NC2+NSMA
      PI=3.14159265359
      CONS=0.5/PI/PI
      CON1=1./(RO1*(2.*PI)**3)
      CON2=1./(RO2*(2.*PI)**3)
      XC=X1/X2
      RSR3=RSR**3
      E=D1/(D1-ET)
      E2=E*E
      E3=E*E2
      E4=E*E3
C
      GC11=E2*(1.+0.5*ET-1.5*ET2*(1.-RSR))
      GC22=E2*(1.+0.5*ET+1.5*ET1*(1./RSR-1.))
      GC12=(GC11+RSR*GC22)/(1.+RSR)
C
      PR1=1+ET+ET**2.
      PR2=ET1+RSR**3.*ET2
      PR3=1+2*ET
      PR4=1+ET1+RSR*(1+ET2)
      PR5=1/(1-ET)**3.
      PR6=1/(1-ET)**4.
C
      AA11=PR1+PR2*PR3-3.*ET2*(1-RSR)**2.*PR4-3*ET1
     1      *ET2*(1-RSR)**2.
      AA12=3.*(PR2*PR1-3.*ET1*ET2*(1-RSR)**2*PR4)
      A1=AA11*PR5 + AA12*PR6
      AA21=PR1*RSR**3.+PR2*PR3-3.*ET1*(1-RSR)**2.
     1      *PR4-3*ET1*ET2*(1-RSR)**2.*RSR
      AA22=AA12
      A2=AA21*PR5/RSR**3. + AA22*PR6/RSR**3.
```

```
C
      B1R1=-6.*(ET1*GC11**2+0.25*ET2*RSR*(1.+RSR)**2
     1     *GC12**2)
      B2R2=-6.*(ET2*GC22**2+0.25*ET1*(1.+1./RSR)**2
     1     *GC12**2/RSR)
      BR2=-3.*(ET1*GC11/RSR**2+  ET2*GC22)*(1.+RSR)
     1     *GC12
      DR2=0.5*(ET1*A1/RSR3+ET2*A2)
      DR1=RSR3*DR2
C
      DO 20 N=1,NS
        XK=N*DK*DW
        CALL LEBO
        DEN=(1.-CK11)*(1.-CK22)-XC*CK12**2.
        YK11(N)=(CK11**2.*(1-CK22)+XC*CK12**2*(1+CK11))
     1          /DEN
        YK11(N)=YK11(N)/RO1
        YK12(N)=CK12*(1./DEN-1.)
        YK12(N)=YK12(N)/RO2
        YK22(N)=(CK22**2.*(1.-CK11)+XC*CK12**2.
     1          *(1.+CK22))/DEN
        YK22(N)=YK22(N)/RO2
   20 CONTINUE
C
      XR=DX
      XK=DK
      CALL FOURI (YK11,CONS,XR,XK,YR11)
      CALL FOURI (YK12,CONS,XR,XK,YR12)
      CALL FOURI (YK22,CONS,XR,XK,YR22)
C
      RETURN
      END
C
C      CCCCCCCCCCCCCCC
      SUBROUTINE LEBO
C      CCCCCCCCCCCCCCC
C
C      CALLED BY YMIXT
C
      COMMON/CC/ CK11,CK22,CK12
      COMMON/BG/ XK
      COMMON/CDF/ DX,DK,NM
      COMMON/WQ/A1,A2,B1R1,B2R2,BR2,DR1,DR2
      COMMON/ZSE/RSR,ET,ET1,ET2
      COMMON/YHN/RO1,RO2,X1,X2
C
      DOUBLE PRECISION  CK11,CK22,CK12
      DOUBLE PRECISION  RSR,ET,ET1,ET2
      DOUBLE PRECISION  A1,A2,B1R1,B2R2,BR2,DR1,DR2
      DOUBLE PRECISION  UP,UM,FSP,FCP,FSM,FCM
      DOUBLE PRECISION  Q2,Q3,Q4,Q6,Q12,Q24,FS,FC,UK
      DOUBLE PRECISION  D1C1,D1C2,D1C3,D2C1,D2C2,D2C3
```

```
      DOUBLE PRECISION  EC1,EC2,EC3,EC4
      DOUBLE PRECISION  UKZ,FSZ,FCZ
      DOUBLE PRECISION  U1,U2,U3
C
      PI=3.14159265359
      UK=XK
      FS=DSIN(UK)
      FC=DCOS(UK)
      UKZ=UK*RSR
      FSZ=DSIN(UKZ)
      FCZ=DCOS(UKZ)
      Q2=2.
      Q3=3.
      Q4=4.
      Q5=5.
      Q6=6.
      Q12=12.
      Q24=24.
      D1C2=(Q2*UKZ*FSZ-(UKZ**Q2-Q2)*FCZ-Q2)/UKZ**Q4
      D1C1=(FSZ-UKZ*FCZ)/UKZ**Q3
      D1C3=((Q4*UKZ**Q3-Q24*UKZ)*FSZ-
     1     (UKZ**Q4-Q12*UKZ**Q2+Q24)*FCZ+Q24)/UKZ**Q6
      D2C1=(FS-UK*FC)/UK**Q3
      D2C2=(Q2*UK*FS-(UK**Q2-Q2)*FC-Q2)/UK**Q4
      D2C3=((Q4*UK**Q3-Q24*UK)*FS-
     1     (UK**Q4-Q12*UK**Q2+Q24)*FC+Q24)/UK**Q6
      UP=0.5*(1.+RSR)
      UM=0.5*(1.-RSR)
      FSP=DSIN(UK*UP)
      FCP=DCOS(UK*UP)
      FSM=DSIN(UK*UM)
      FCM=DCOS(UK*UM)
C
      U1=(1+RSR)*0.5*UK
      U2=(1-RSR)*0.5*UK
      U3=RSR*UK
C
      EC1=DSIN(U1)-U1*DCOS(U1)
      EC2=2.*U3*DSIN(U3)+(2.-U3**2.)*DCOS(U3)-2.
      EC3=2.*U3*DCOS(U3)+(U3**2.-2.)*DSIN(U3)
      EC4=(3.*U3**2.-6.)*DSIN(U3)+(6.*U3-U3**3.)
     1    *DCOS(U3)
      EC5=(3.*U3**2.-6)*DCOS(U3)+(U3**3.-6.*U3)
     1    *DSIN(U3)+6.
      EC6=DSIN(U3)*(4.*U3**3.-24.*U3)-DCOS(U3)
     1    *(U3**4.-12.*U3**2.+24.)+24.
      CK11=-ET1*(A1*D1C1+B1R1*D1C2+DR1*D1C3)*24.
      CK12=-ET2*(A1*EC1/UK**3.+BR2/UK**4.*(DCOS(U2)
     1    *EC2+DSIN(U2)*EC3)+2.*(1-RSR)/UK**5.*DR2
     2    *(DCOS(U2)*EC4+DSIN(U2)*EC5)+(DCOS(U2)
     3    *EC6+U3**4.*DSIN(U2)*DSIN(U3)-4.*DSIN(U2)
     4    *EC(4)*DR2/UK**6)*24
```

```
      CK22=-ET2*(A2*D2C1+B2R2*D2C2+DR2*D2C3)*24.
C
      RETURN
      END
C
C      CCCCCCCCCCCCCCCCCCCCCCCCCCCCC
      SUBROUTINE FOURI (H,CONS,DK,DS,FH)
C      CCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
C      CALLED BY YMIXT
C
C      USE OF FAST FOURIER TRANSFORM BY IMSL
C
      COMMON/CDF/ DD,DDD,NM
      COMMON/BOO/ NS,DW,DV
      DIMENSION H(2048),FH(2048),SEQ(2048),Q(2048)
C
      PI=3.14159265359
      DO 2 I=1,NM
        Q(I)=DS*I
        H(I)=H(I)*Q(I)
    2 CONTINUE
C
      CALL UMACH(2,NOUT)
      CALL FSINT(NM,H,SEQ)
C
      X=0.
      DO 4 K=1,NM
        X=X+DK
        FH(K)=0.5*DS*SEQ(K)* CONS/X
    4 CONTINUE
C
      RETURN
      END
C
C      CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
      SUBROUTINE CHAIN(R,Z1,Z2,NN,MM,CHIJ)
C      CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
      COMMON/CNC/  NC
      COMMON/CZ/ Z(2)
      COMMON/CV/ V(2)
      COMMON/CSIG/ SIG(2),P1
      COMMON/CRSTAR/ RSTAR
      COMMON/CALPHA/ ALPHA2
      COMMON/CDF/DR,DK,NB
C
      DIMENSION R(2048),CHIJ(2048),RHO(2)
      REAL KP,KPSUM
C
C      SUPPLY THE BASIC DATA AND PARAMETER VALUE
C
```

```
      PI=3.1415927
      AL2=ALPHA2/SIG(2)
      BETA=AL2/(4.*PI)
      KPSUM=0.
      RAD=NN*DR
C
C      KAPPA
C
      DO 10 K=1,NC
        RHO(K)=V(K)*RSTAR*SIG(2)*SIG(2)*SIG(2)
        KPSUM=KPSUM+RHO(K)*Z(K)*Z(K)
   10 CONTINUE
      KP=SQRT(AL2*KPSUM)
C
C      CHAIN SUM. THIS IS THE MODIFICATION OF THE
C      ORIGINAL EXP TYPE MODEL
C
      DO 20 J=NN,MM
        CHIJ(J)=(-BETA*Z1*Z2*EXP(-KP*P1*(R(J)-RAD)))/
     1           ((1.+KP*P1*RAD)*R(J))
   20 CONTINUE
C
      RETURN
      END
C
C      CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
      SUBROUTINE YNTIJ1(R,DR,NIJ,INF,GIJ,YNT)
C      CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
C      THIS PART IS USED FOR THE CALCULATION OF
C      INTEGRANDS OF GIJ*R**2
C
      COMMON/CSIG/SIG(2), P1
      DIMENSION R(2048),GIJ(2048)
C
      Y=0.
      N=NIJ+1
      M=INF-1
      VDEMI=0.5*R(NIJ)**2.*GIJ(NIJ)
      YDEMI=0.5*R(INF)**2.*GIJ(INF)
      DO 5 J=N,M
    5 Y=Y+R(J)**2.*GIJ(J)
      Y=VDEMI+Y+YDEMI
      Y=Y*DR
C
C      CONVERSION FROM THE DIMENSIONLESS(REDUCED)
C      FROM WHICHIS BASED ON THE SIG(2) REFERENCED
C      SCALE TO THE REAL SCALE
C
      YNT=SIG(2)*SIG(2)*SIG(2)*Y
C
      RETURN
      END
```

```
C
C      CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
       SUBROUTINE YNTIJ(R,DR,NIJ,INF,GIJ,YNT)
C      CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
C      THIS PART IS USED FOR THE CALCULATION OF
C      INTEGRANDS OF GIJ*R**2
C
       COMMON/CSIG/SIG(2), P1
       DIMENSION R(2048),GIJ(2048)
C
       Y=0.
       N=NIJ+1
       M=INF-1
C
       VDEMI=0.5*R(NIJ)*GIJ(NIJ)
       YDEMI=0.5*R(INF)*GIJ(INF)
C
       DO 5 J=N,M
         Y=Y+R(J)*GIJ(J)
     5 COMTINUE
C
C      CONVERSION FROM THE DIMENSIONLESS(REDUCED)
C      FROM WHICH IS BASED ON THE SIG(2) REFERENCED
C      SCALE TO THE REAL SCALE
C
       Y=VDEMI+Y+YDEMI
       Y=Y*DR
       YNT=SIG(2)*SIG(2)*Y
C
       RETURN
       END
```

APPENDIX 1.D

```
C
C      CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C      THIS PROGRAM TEST THE POSSIBILITY OF APPLYING THE
C      STILLINGER-LOVETT MOMENT CONDITION. IN THIS PROGRAM
C      ONLY THE 1ST CONDITION(0 TH MOMENT * CONDITION) WILL
C      BE CONSIDERED C FOR THE 1-1 TYPE ELECTROLYTE SOLUTION.
C      (LICL)
C      CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
       COMMON/WORKSP/RWKSP
       COMMON/CCONC/CONC
       COMMON/CSIG/SIG(2),P1
       REAL RWKSP(5162)
C
C      PREPARATION FOR THE USE OF IMSL
C
       CALL IWKIN(5162)
C
   10  READ(22,*,err=400) CONC,SIG(1),SIG(2),P1
C
C      BASIC DATA
C
       CALL EXPLR(R1,R2)
C
       IF ((ABS(R1)-ABS(R2)).GT.0) THEN
         ARP2=0.
         K=0
         DO  150  I=1,11
           CALL  EXPLR(R1,R2)
           AR1=ABS(R1)
           AR2=ABS(R2)
           DIFF1=AR2-AR1
           DIFF2=ARP2-AR1
           IF (K.EQ.0) GO TO 120
           IF (DIFF1.GT.0.AND.DIFF2.LT.0) THEN
             P1=P1+0.01
             ARR2P=0.
             L=0
             DO 100 II=1,11
               CALL  EXPLR(RR1,RR2)
               ARR1=ABS(RR1)
               ARR2=ABS(RR2)
               DIFF1=ARR2-ARR1
               DIFF2=ARR2P-ARR1
               IF (L.EQ.0) GO TO 80
               IF (DIFF1.GT.0.AND.DIFF2.LT.0) THEN
                 P1=P1+0.001
                 ARR2P=0.
                 M=0
                 DO  50 III=1,11
                   CALL  EXPLR(RRR1,RRR2)
                   ARRR1=ABS(RRR1)
```

```
                  ARRR2=ABS(RRR2)
                  DIFF1=ARRR2-ARRR1
                  DIFF2=ARRR2P-ARRR1
                  IF (M.EQ.0) GO TO 30
                  IF (DIFF1.GT.0.AND.DIFF2.LT.0)THEN
                    P1=P1+0.00005
                    CALL EXPLR(RRRR1,RRRR2)
                    WRITE(23,450)CONC,SIG(1),SIG(2),P1
                    WRITE(24,*)CONC
                    GO TO 330
                  END IF
   30             ARRR2P=ARRR2
                  P1=P1-0.0001
                  M=M+1
   50           CONTINUE
              END IF
   80         ARR2P=ARR2
              P1=P1-0.001
              L=L+1
  100       CONTINUE
          END IF
  120     ARP2=AR2
          P1=P1-0.01
          K=K+1
  150   CONTINUE
C
      ELSE
C
        KK=0
        DO 300  J=1,11
          CALL  EXPLR(R1,R2)
          AR1=ABS(R1)
          AR2=ABS(R2)
          DIFF1=AR2-AR1
          DIFF2=ARP2-AR1
          IF (KK.EQ.0) GO TO 280
          IF (DIFF1.LT.0.AND.DIFF2.GT.0) THEN
            P1=P1-0.01
            ARR2P=0.
            LL=0
            DO 250 JJ=1,11
              CALL  EXPLR(RR1,RR2)
              ARR1=ABS(RR1)
              ARR2=ABS(RR2)
              DIFF1=ARR2-ARR1
              DIFF2=ARR2P-ARR1
              IF (LL.EQ.0) GO TO 230
              IF (DIFF1.LT.0.AND.DIFF2.GT.0) THEN
                P1=P1-0.001
                ARRR2P=0.
                MM=0
                DO  200 JJJ=1,11
```

```
                CALL  EXPLR(RRR1,RRR2)
                ARRR1=ABS(RRR1)
                ARRR2=ABS(RRR2)
                DIFF1=ARRR2-ARRR1
                DIFF2=ARRR2P-ARRR1
                IF (MM.EQ.0) GO TO 180
                IF (DIFF1.LT.0.AND.DIFF2.GT.0)THEN
                  P1=P1-0.00005
                  CALL EXPLR(RRRR1,RRRR2)
                  WRITE(23,450)CONC,SIG(1),SIG(2),P1
                  WRITE(24,*)CONC
                  GO TO 330
                END IF
  180           ARRR2P=ARRR2
                P1=P1+0.0001
                MM=MM+1
  200         CONTINUE
            END IF
  230       ARR2P=ARR2
            P1=P1+0.001
            LL=LL+1
  250     CONTINUE
        END IF
  280   ARP2=AR2
        P1=P1+0.01
        KK=KK+1
  300 CONTINUE
      END IF
C
C      ERROR MESSAGE
C
      WRITE(23,*)'FAIL',SIG(2),'P1',P1,'SUB',R1,
     1            'SUMEXP',R2
330   GO TO 10
400   STOP
450   FORMAT(1X,F10.7,2X,F10.7,2X,F10.7,2X,F10.7)
      END
C
C      CCCCCCCCCCCCCCCCCCCCCCCCC
      SUBROUTINE EXPLR(SUB,SUMEXP)
C      CCCCCCCCCCCCCCCCCCCCCCCCC
C
C      +, SMALL
C      -, BIG
C
      COMMON/CSIG/SIG(2),P1
      COMMON/CNC/NC
      COMMON/CZ/ Z(2)
      COMMON/CV/ V(2)
      COMMON/CCONC/ CONC
      COMMON/CRSTAR/ RSTAR
      COMMON/CALPHA/ ALPHA2
```

```
      COMMON/NITZS/ G11,G12,G22
      COMMON/CLRE/ EXPLRO
      COMMON/CLRGL/GLLSS(2048),GLLBB(2048),GLLSB(2048)
      COMMON/CDF/ DR,DK,NB
      DIMENSION YNTE(6,6),R(2048)
      DIMENSION GESS(2048),GEBB(2048),GESB(2048)
      DIMENSION CHSS(2048),CHBB(2048),CHSB(2048)
      DIMENSION RHO(2),GG(10,10)
      REAL K
C
C     SUPPLY OF THE BASIC DATA
C
      DR=0.01
      NB=2047
      NC=2
      V(1)=1.
      V(2)=1.
      Z(1)=1
      Z(2)=-1.
      Z1=Z(1)
      Z2=Z(2)
      T=298.15
      AN=6.02252E+23
      K=1.38054E-23
      E=1.60210E-19
      P=78.54
      D=1.112647E-10*P
      PI=3.1415927
      BETA=((E*E)/(D*K*T))*1.E+10
      ALPHA2=4.*PI*BETA
      ALPHA=SQRT(ALPHA2)
      RSTAR=CONC*6.02252E-04
C
C     REDUCED DISTANCE,  R/SIG-
C
      DS=SIG(1)/SIG(2)
      DB=1.0
      DSB=(DS+DB)*0.5
C
C     LOWER INTEGRATION LIMITS, REDUCED SIGIJ
C
      NSS=DS/DR
      NBB=DB/DR
      NSB=DSB/DR
C
C     DETERMINE INTEGRATION GRID FROM R/SIGIJ TO
C     INFINITY
C
      R(1)=DR
      DO 15 J=2,NB
   15 R(J)=R(J-1)+DR
```

```
C
C     BEGIN- LRE OSMOTIC
C
      VT=0.
      RH=0.
      DO 25 J=1,NC
        VT=VT+V(J)
        RHO(J)=V(J)*RSTAR
        RH=RH+RHO(J)
   25 CONTINUE
C
C     REDUCED DENSITY(THE BASIC UNIT OF LENGTH
C     IN THIS PROGRAM IS THE SIG(2))
C
      RHRD=RH*SIG(2)*SIG(2)*SIG(2)
      DO 30 J=1,NB
        CHSS(J)=0.0
        CHBB(J)=0.0
        CHSB(J)=0.0
   30 CONTINUE
C
C     CALCULATION OF THE RENORMALIZED POTENTIAL
C
      CALL CHAIN(R,Z1,Z1,NSS,NB,CHSS)
      CALL CHAIN(R,Z2,Z2,NBB,NB,CHBB)
      CALL CHAIN(R,Z1,Z2,NSB,NB,CHSB)
      CALL GLLVW(RHRD,DB,DSB,DS)
C
      IF (NSS.LE.NBB) THEN
        IN=NSS
      ELSE
        IN=NBB
      END IF
C
  200 DO 1100 J=IN,NB
        GESS(J)=EXP(CHSS(J))*GLLSS(J)
        GEBB(J)=EXP(CHBB(J))*GLLBB(J)
        GESB(J)=EXP(CHSB(J))*GLLSB(J)
        IF (J.LT.NSS) GESS(J)=0.
        IF (J.LT.NBB) GEBB(J)=0.
        IF (J.LT.NSB) GESB(J)=0.
 1100 CONTINUE
C
C     CALCULATE  YNT=SIG-**2 (INTEGRAL(SIGIJ/SIG-TO INF)
C     R*R*GIJ(RR))
C
      CALL YNTIJ(R,DR,NSS,NB,GESS,YNTE(1,1))
      CALL YNTIJ(R,DR,NBB,NB,GEBB,YNTE(2,2))
      CALL YNTIJ(R,DR,NSB,NB,GESB,YNTE(1,2))
      YNTE(2,1)=YNTE(1,2)
      SUMEXP=0.
```

```
C
      DO 1220 J=1,NC
        DO 1210 KK=1,NC
          IF (J.NE.KK) YNTE(J,KK)= -YNTE(J,KK)
          SUMEXP=SUMEXP+YNTE(J,KK)
 1210   CONTINUE
 1220 CONTINUE
      SUB=-1./(2*PI*RHO(1))
C
      RETURN
      END
C
C      CCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
      SUBROUTINE GLLVW(RH,DC1,DC12,DC2)
C      CCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
C      HARD SPHERE RDF OF VERLET AND WEIS
C      GENERALIZED TO MIXTURES BY LEE AND LEVESQUE
C
C      CALLED BY LRE
C
      COMMON/CNC/NC
      COMMON/CV/V(2)
      COMMON/CLRGL/ G11(2048),G22(2048),G12(2048)
C
C      NOTE:   SMALL,+  BIG,-
C
      COMMON/NITZS/COR11,COR12,COR22
      COMMON/JASPER/ NSMA, N11,N12,N22,M11,M12,M22,
     1               DSMA,NC1,NC2,NC12
      COMMON/HEIDG/ SMA
      COMMON/SPENGL/ A11,A12,A22
      COMMON/ZSE/RSR,ET,ET1,ET2
      COMMON/BOO/NS,DW,DV
      COMMON/YY/ YR12(2048),YR11(2048),YR22(2048)
      COMMON/YKY/ YK12(2048),YK11(2048),YK22(2048)
      COMMON/CDF/DX,DK,NM
      COMMON/CGC/ GC11,GC12,GC22
      COMMON/YHN/ RO1,RO2,X1,X2
      DOUBLE PRECISION GC11,GC12,GC22
      DOUBLE PRECISION RSR,ET,ET1,ET2,X1,X2
      DIMENSION R(2048)
      REAL MU1,MU2,MU3
C
      NSMA=1
      SMA=0.0001
      NS=NM
      DW=1.
C
      VT=0.
      DO 10 J=1,NC
        VT=VT+V(J)
   10 CONTINUE
```

```
      XI1=V(1)/VT
      XI2=1.-XI1
      X=XI1
      X1=XI2
C
      PI=3.14159265359
      RHO=RH*DC1*DC1*DC1
      D22=DC2/DC1
      D11=1.
      D12=.5*(D11+D22)
      ETA=PI*RHO*(XI1*D11**3+XI2*D22**3)/6.
      RHO1=RHO*X
      RHO2=RHO-RHO1
      RHO12=SQRT(RHO1*RHO2)
      RSR=D22
      HT=ETA
      HTW=HT-HT*HT/16.
      R(1)=DX
      DO 48 J=2,NM
        R(J)=R(J-1)+DX
   48 CONTINUE
      NC1=RSR/DX
      NC2=1./DX
      NC12=D12/DX
      M11=NC1-NSMA
      M12=NC12-NSMA
      M22=NC2-NSMA
      L1=NC1+NSMA
      L2=NC12+NSMA
      L3=NC2+NSMA
      X2=1.-X1
      RSR3=RSR**3
      ALPHA=(HT/HTW)**(1./3.)
      DV=1./ALPHA
      RO=RHO*(HTW/HT)
      RO1=RO*X1
      RO2=RO-RO1
      DX=DX*ALPHA
      DK=PI/(DX*(NM+1.))
      ET=PI*(RO1*RSR3+RO2)/6.
C
      CALL FINDA (RHO,ETA,RO,ET,D11,D22,ALPHA,X)
C
      ET1=PI*RO1*RSR3/6.
      ET2=ET-ET1
      ETA1=PI*RO1/6.
      ETA2=PI*RO2/6.
      QQ=1.+RSR+RSR*(ETA1*RSR*RSR+ETA2)
      PC=(1.+ET+ET*ET)*RO
      PC=PC-18.*ETA1*ETA2*(1.-RSR)*(1.-RSR)*QQ/PI
      PC=PC/((1.-ET)**3)
      QQ=ET*(ETA1*RSR*RSR+ETA2)**3
```

```
      PV=PC-18.*QQ/(PI*(1.-ET)**3)
      PC=PC/RO
      PV=PV/RO
C
      CALL YMIXT
C
      MU1=24.*A11/(D11*HTW*GC22)
      MU2=24.*A12/(D12*HTW*GC12)
      MU3=24.*A22/(D22*HTW*GC11)
      DO 21 J=1,NM
        G11(J)=0.
        G12(J)=0.
        G22(J)=0.
   21 CONTINUE
      MM=MM+1
      DO 22 N=NC1,NM
        DIS=R(N)-D22
        DISMU3=DIS*MU3
        IF (DISMU3.GT.170) DISMU3=170.
        G11(N)=YR11(N)+1.+A22*D22*EXP(-DISMU3)
     1         *COS(DISMU3)/R(N)
   22 CONTINUE
      DO 23 N=NC12,NM
        DIS=R(N)-D12
        DISMU2=DIS*MU2
        IF(DISMU2.GT. 170) DISMU2=170.
        G12(N)=YR12(N)+1.+A12*D12*EXP(-DISMU2)*COS(DISMU2)/R(N)
   23 CONTINUE
      DO 24 N=NC2,NM
        DIS=R(N)-D11
        DISMU1=DIS*MU1
        IF(DISMU1.GT. 170) DISMU1=170.
        G22(N)=YR22(N)+1.+A11*D11*EXP(-DISMU1)*COS(DISMU1)/R(N)
   24 CONTINUE
C
      RETURN
      END
C
C     CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
      SUBROUTINE FINDA(RHO,XY,RO,XI,D1,D2,ALPHA,X)
C     CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
C     CALLED BY GLLVW
C
      COMMON/CSIG/SIG(2),P1
      COMMON/NITZS/ G11,G12,G22
      COMMON/SPENGL/AD11,AD12,AD22
      COMMON/SOCRAT/DP1,Q
      COMMON/EURIPD/DD,AA1,ETAA1,ETAA2,AA2,UMB
      COMMON/PASCAL/D12,AL1,AL2,Y,PI
      COMMON/HODRLN/PY1,PY12,PY2
      DOUBLE PRECISION XI
```

```
C
      PI=3.1415926535
      D1=1.
      Y=1.-X
      D12=.5*(D1+D2)
      DD=D1+D2
      AL1=PI*D1**3*X/6.
      AL2=PI*D2**3*Y/6.
      XI1=AL1*RHO
      XI2=AL2*RHO
      XX=XI1/D1+XI2/D2
      Q=1./(1.-XY)
      G11=Q+3.*D1*XX*0.5*Q*Q+D1*D1*XX*XX*0.75*Q*Q*Q
      G22=Q+3.*D2*XX*0.5*Q*Q+D2*D2*XX*XX*0.75*Q*Q*Q
      TI=D1*D2/(D1+D2)
      G12=Q+3.*XX*Q*Q*TI+3.*XX*XX*Q*Q*Q*TI*TI
C
      CALL  PY (XY,RHO,D1,D2,X)
C
      G11=(2.*G11+PY1)/3.
      G12=(2.*G12+PY12)/3.
      G22=(2.*G22+PY2)/3.
      Z=RHO+2.*PI*(RHO*RHO*X*X*D1*D1*D1*G11
     1     +RHO*RHO*X*Y*2.*D12*D12*D12*G12
     2     +RHO*RHO*Y*Y*D2*D2*D2*G22)/3.
      Z=Z/RHO
      XE=XI
      Q=1./(1.-XI)
      WD1=D1*(ALPHA-1.)
      WD12=D12*(ALPHA-1.)
      WD2=D2*(ALPHA-1.)
C
      CALL PY (XE,RO,D1,D2,X)
C
      B1=ETAA1*D1**2*PY1**2+ETAA2*D12**2*PY12**2
      B1=-6.*B1
      B2=ETAA2*D2**2*PY2**2+ETAA1*D12**2*PY12**2
      B2=-6.*B2
      D=ETAA1*AA1+ETAA2*AA2
      D=0.5*D
      B=ETAA1*D1*PY1+ETAA2*D2*PY2
      B=-6.*B*D12*PY12
      DX11=B1+3.*D
      DX22=B2+3.*D*D2*D2
      DDX11=6.*D
      DDX22=6.*D*D2
      DDDX11=DDX11
      DDDX22=6.*D
      YAK=B*D2**2+4.*UMB*D*D2**3+D*D2**4
      DX12=-YAK/(D12*D12)
      YAL=2.*B*D2+12.*UMB*D*D2*D2+4.*D*D2*D2*D2
      DX12=DX12+YAL/D12
```

```
      DDX12=2.*YAK/D12**3
      DDX12=DDX12-2.*YAL/(D12*D12)
C
      YAM=2.*B+24.*UMB*D*D2+12.*D*D2*D2
      DDX12=DDX12+YAM/D12
      DDDX12=-6.*YAK/D12**4
      DDDX12=DDDX12+6.*YAL/D12**3
      DDDX12=DDDX12-3.*YAM/(D12*D12)
      DDDX12=DDDX12+(24.*UMB*D+24.*D*D2)/D12
      GG1=PY1+DX11*WD1+0.5*DDX11*WD1**2+DDDX11*WD1
     1         **3/6.
      AD11=G11-GG1
      GG2=PY2+DX22*WD2+0.5*DDX22*WD2**2+DDDX22*WD2
     1         **3/6.
      AD22=G22-GG2
      GG12=PY12+DX12*WD12+0.5*DDX12*WD12**2+DDDX12
     1         *WD12**3/6.
      AD12=G12-GG12
C
      RETURN
      END
C
C      CCCCCCCCCCCCCCCCCCCCCCCC
      SUBROUTINE PY (XI,RO,D1,D2,X)
C      CCCCCCCCCCCCCCCCCCCCCCCC
C
C      CALLED BY FINDA
C
      COMMON/SOCRAT/ DP1,Q
      COMMON/EURIPD/ DD,AA1,ETAA1,ETAA2,AA2,UMB
      COMMON/PASCAL/ D12,AL1,AL2,Y,PI
      COMMON/HODRLN/ PY1,PY12,PY2
C
      T=D1/D2
      S=D2/D1
      XI1=AL1*RO
      XI2=AL2*RO
      ETAA1=PI*RO*X/6.
      ETAA2=PI*RO*Y/6.
      UMB=0.5*(D1-D2)
C
      CALL A1 (T,XI1,XI2,XI)
C
      AA1=DP1
      CALL A1 (S,XI2,XI1,XI)
C
      AA2=DP1
      PY1=1.+0.5*XI
      PY1=PY1+3.*ETAA2*D2**2*UMB
      PY1=PY1*Q**2
      PY2=1.+0.5*XI
      PY2=PY2-3.*ETAA1*D1**2*UMB
```

```
      PY2=PY2*Q**2
      PY12=D2*PY1+D1*PY2
      PY12=PY12/(D1+D2)
      RETURN
      END
C
C      CCCCCCCCCCCCCCCCCCCCCC
      SUBROUTINE A1 (T,XI1,XI2,XI)
C      CCCCCCCCCCCCCCCCCCCCCC
C
C      CALLED BY PY
C
      COMMON/SOCRAT/DP1,Q
C
      DP=(1.+XI+XI**2)*Q**3
      DP=DP+(2.+XI)**2*(XI1+T**3*XI2)*Q**4
      DP=DP-3.*XI2*(1.-T)**2*(1.+T+2.*XI1+T*XI2)
     1       *Q**3
      DP1=DP-9.*XI1*XI2*(1.-T)**2*(1.+T+T*XI2+XI1)
     1       *Q**4
C
      RETURN
      END
C
C      CCCCCCCCCCCCCCC
      SUBROUTINE YMIXT
C      CCCCCCCCCCCCCCC
C
C      CALLED BY MAIN
C
      COMMON/HEIDG/SMA
      COMMON/JASPER/NSMA,N11,N12,N22,M11,M12,M22,
     1             DSMA,NC1,NC2,NC12
      COMMON/BOO/ NS,DW,DV
      COMMON/CC/CK11,CK22,CK12
      COMMON/YY/YR12(2048),YR11(2048),YR22(2048)
      COMMON/YKY/YK12(2048),YK11(2048),YK22(2048)
      COMMON/YHN/RO1,RO2,X1,X2
      COMMON/BG/ XK
      COMMON/CDF/ DX,DK,NM
      COMMON/CGC/GC11,GC12,GC22
      COMMON/WQ/A1,A2,B1R1,B2R2,BR2,DR1,DR2
      COMMON/ZSE/RSR,ET,ET1,ET2
C
      DOUBLE PRECISION CK11,CK12,CK22
      DOUBLE PRECISION RSR,ET,ET1,ET2,X1,X2
      DOUBLE PRECISION A1,A2,B1R1,B2R2,BR2,DR1,DR2
      DOUBLE PRECISION E,E2,E3,E4,AST,PR,RSR3
      DOUBLE PRECISION GC11,GC12,GC22
C
      D1=1.
      DH=0.5
```

```
      D3H=1.5
      DSMA=DX*SMA
      N11=NC1+NSMA
      N12=NC12+NSMA
      N22=NC2+NSMA
      PI=3.14159265359
      CONS=0.5/PI/PI
      CON1=1./(RO1*(2.*PI)**3)
      CON2=1./(RO2*(2.*PI)**3)
      XC=X1/X2
      RSR3=RSR**3
      E=D1/(D1-ET)
      E2=E*E
      E3=E*E2
      E4=E*E3
      GC11=E2*(1.+0.5*ET-1.5*ET2*(1.-RSR))
      GC22=E2*(1.+0.5*ET+1.5*ET1*(1./RSR-1.))
      GC12=(GC11+RSR*GC22)/(1.+RSR)
      PR1=1+ET+ET**2.
      PR2=ET1+RSR**3.*ET2
      PR3=1+2*ET
      PR4=1+ET1+RSR*(1+ET2)
      PR5=1/(1-ET)**3.
      PR6=1/(1-ET)**4.
      AA11=PR1+PR2*PR3-3.*ET2*(1-RSR)**2.*PR4-3*ET1
     1         *ET2*(1-RSR)**2.
      AA12=3.*(PR2*PR1-3.*ET1*ET2*(1-RSR)**2*PR4)
      A1=AA11*PR5  +  AA12*PR6
      AA21=PR1*RSR**3.+PR2*PR3-3.*ET1*(1-RSR)**2.
     1         *PR4-3*ET1*ET2*(1-RSR)**2.*RSR
      AA22=AA12
      A2=AA21*PR5/RSR**3. + AA22*PR6/RSR**3.
      B1R1=-6.*(ET1*GC11**2+0.25*ET2*RSR*(1.+RSR)
     1         **2*GC12**2)
      B2R2=-6.*(ET2*GC22**2+0.25*ET1*(1.+1./RSR)
     1         **2*GC12**2/RSR)
      BR2=-3.*(ET1*GC11/RSR**2+  ET2*GC22)*(1.+RSR)
     1         *GC12
      DR2=0.5*(ET1*A1/RSR3+ET2*A2)
      DR1=RSR3*DR2
C
      DO 20 N=1,NS
        XK=N*DK*DW
C
        CALL LEBO
C
        DEN=(1.-CK11)*(1.-CK22)-XC*CK12**2.
        YK11(N)=(CK11**2.*(1-CK22)+XC*CK12**2*(1+CK11))/DEN
        YK11(N)=YK11(N)/RO1
        YK12(N)=CK12*(1./DEN-1.)
        YK12(N)=YK12(N)/RO2
        YK22(N)=(CK22**2.*(1.-CK11)+XC*CK12**2.*(1.+CK22))/DEN
```

```
         YK22(N)=YK22(N)/RO2
   20 CONTINUE
      XR=DX
      XK=DK
      CALL FOURI (YK11,CONS,XR,XK,YR11)
      CALL FOURI (YK12,CONS,XR,XK,YR12)
      CALL FOURI (YK22,CONS,XR,XK,YR22)
C
      RETURN
      END
C
C      CCCCCCCCCCCCCCC
      SUBROUTINE LEBO
C      CCCCCCCCCCCCCCC
C
C      CALLED BY YMIXT
C
      COMMON/CC/ CK11,CK22,CK12
      COMMON/BG/ XK
      COMMON/CDF/ DX,DK,NM
      COMMON/WQ/A1,A2,B1R1,B2R2,BR2,DR1,DR2
      COMMON/ZSE/RSR,ET,ET1,ET2
      COMMON/YHN/RO1,RO2,X1,X2
      DOUBLE PRECISION  CK11,CK22,CK12
      DOUBLE PRECISION  RSR,ET,ET1,ET2
      DOUBLE PRECISION  A1,A2,B1R1,B2R2,BR2,DR1,DR2
      DOUBLE PRECISION  UP,UM,FSP,FCP,FSM,FCM
      DOUBLE PRECISION  Q2,Q3,Q4,Q6,Q12,Q24,FS,FC,UK
      DOUBLE PRECISION  D1C1,D1C2,D1C3,D2C1,D2C2,D2C3
      DOUBLE PRECISION  EC1,EC2,EC3,EC4
      DOUBLE PRECISION  UKZ,FSZ,FCZ
      DOUBLE PRECISION  U1,U2,U3
C
      PI=3.14159265359
      UK=XK
      FS=DSIN(UK)
      FC=DCOS(UK)
      UKZ=UK*RSR
      FSZ=DSIN(UKZ)
      FCZ=DCOS(UKZ)
      Q2=2.
      Q3=3.
      Q4=4.
      Q5=5.
      Q6=6.
      Q12=12.
      Q24=24.
      D1C2=(Q2*UKZ*FSZ-(UKZ**Q2-Q2)*FCZ-Q2)/UKZ**Q4
      D1C1=(FSZ-UKZ*FCZ)/UKZ**Q3
      D1C3=((Q4*UKZ**Q3-Q24*UKZ)*FSZ-(UKZ**Q4-Q12*
     1        (UKZ**Q2+Q24)*FCZ+Q24)/UKZ**Q6
      D2C1=(FS-UK*FC)/UK**Q3
```

```
      D2C2=(Q2*UK*FS-(UK**Q2-Q2)*FC-Q2)/UK**Q4
      D2C3=((Q4*UK**Q3-Q24*UK)*FS-(UK**Q4-Q12*UK**
     1        Q2+Q24)*FC+Q24)/UK**Q6
      UP=0.5*(1.+RSR)
      UM=0.5*(1.-RSR)
      FSP=DSIN(UK*UP)
      FCP=DCOS(UK*UP)
      FSM=DSIN(UK*UM)
      FCM=DCOS(UK*UM)
      U1=(1+RSR)*0.5*UK
      U2=(1-RSR)*0.5*UK
      U3=RSR*UK
      EC1=DSIN(U1)-U1*DCOS(U1)
      EC2=2.*U3*DSIN(U3)+(2.-U3**2.)*DCOS(U3)-2.
      EC3=2.*U3*DCOS(U3)+(U3**2.-2.)*DSIN(U3)
      EC4=(3.*U3**2.-6.)*DSIN(U3)+(6.*U3-U3**3.)
     1        *DCOS(U3)
      EC5=(3.*U3**2.-6)*DCOS(U3)+(U3**3.-6.*U3)
     1        *DSIN(U3)+6.
      EC6=DSIN(U3)*(4.*U3**3.-24.*U3)-DCOS(U3)*
     1        (U3**4.-12.*U3**2.+24.)+24.
      CK11=-ET1*(A1*D1C1+B1R1*D1C2+DR1*D1C3)*24.
      CK12=-ET2*(A1*EC1/UK**3.+BR2/UK**4.
     1*(DCOS(U2)*EC2+DSIN(U2)*EC3)  +2.*(1-RSR)/UK**5.
     2*DR2*(DCOS(U2)*EC4+DSIN(U2)*EC5)+(DCOS(U2)
     3*EC6+U3**4.*DSIN(U2)*DSIN(U3)-4.*DSIN(U2)
     4*EC4)*DR2/UK**6)*24
      CK22=-ET2*(A2*D2C1+B2R2*D2C2+DR2*D2C3)*24.
C
      RETURN
      END
C
C      CCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
      SUBROUTINE FOURI (H,CONS,DK,DS,FH)
C      CCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C      CALLED BY YMIXT
C
      COMMON/CDF/ DD,DDD,NM
      COMMON/BOO/ NS,DW,DV
      DIMENSION H(2048),FH(2048),SEQ(2048),Q(2048)
C
      PI=3.14159265359
      DO 2 I=1,NM
        Q(I)=DS*I
        H(I)=H(I)*Q(I)
    2 CONTINUE
C
      CALL UMACH(2,NOUT)
C
      CALL FSINT(NM,H,SEQ)
C
      X=0.
```

```
      DO 4 K=1,NM
        X=X+DK
        FH(K)=0.5*DS*SEQ(K)* CONS/X
    4 CONTINUE
C
      RETURN
      END
C
C      CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
      SUBROUTINE CHAIN(R,Z1,Z2,NN,MM,CHIJ)
C      CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
      COMMON/CNC/  NC
      COMMON/CZ/ Z(2)
      COMMON/CV/ V(2)
      COMMON/CSIG/ SIG(2),P1
      COMMON/CRSTAR/ RSTAR
      COMMON/CALPHA/ ALPHA2
      COMMON/CDF/DR,DK,NB
      DIMENSION R(2048),CHIJ(2048),RHO(2)
      REAL KP,KPSUM
C
C      SUPPLY THE BASIC DATA AND PARAMETER VALUE
C
      PI=3.1415927
      AL2=ALPHA2/SIG(2)
      BETA=AL2/(4.*PI)
      KPSUM=0.
      RAD=NN*DR
C
      DO 10 K=1,NC
        RHO(K)=V(K)*RSTAR*SIG(2)*SIG(2)*SIG(2)
        KPSUM=KPSUM+RHO(K)*Z(K)*Z(K)
   10 CONTINUE
      KP=SQRT(AL2*KPSUM)
C
C      CHAIN SUM. THIS IS THE MODIFICATION OF THE ORIGINAL
C      EXP TYPE MODEL
C
      DO 20 J=NN,MM
        CHIJ(J)=(-BETA*Z1*Z2*EXP(-KP*P1*(R(J)-RAD)))/
     1           ((1.+KP*P1*RAD)*R(J))
   20 CONTINUE
C
      RETURN
      END
C
C      CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
      SUBROUTINE YNTIJ(R,DR,NIJ,INF,GIJ,YNT)
C      CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
```

```
C     THIS PART IS USED FOR THE CALCULATION OF
C     INTEGRANDS OF GIJ*R**2
C
      COMMON/CSIG/SIG(2),P1
      DIMENSION R(2048),GIJ(2048)
C
      Y=0.
      N=NIJ+1
      M=INF-1
C
      VDEMI=0.5*R(NIJ)**2.*GIJ(NIJ)
      YDEMI=0.5*R(INF)**2.*GIJ(INF)
C
      DO 5 J=N,M
    5 Y=Y+R(J)**2.*GIJ(J)
C
C     CONVERSION FROM THE DIMENSIONLESS(REDUCED)
C     FORM WHICH IS BASED ON THE SIG(2) REFERENCED
C     SCALE TO THE REAL SCALE
C
      Y=VDEMI+Y+YDEMI
      Y=Y*DR
      YNT=SIG(2)*SIG(2)*SIG(2)*Y
C
      RETURN
      END
```

APPENDIX 1.E

```
C
C     CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C     THIS PROGRAM CALCULATES THE OSMOTIC
C     COEFFICIENTS OF LICL SOLUTION. THERE
C     IS A COMPARISON WITH THE PITZER'S MODEL.
C     CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
C     INPUT
C
      COMMON/WORKSP/RWKSP
      COMMON/CCONC/CONC
      COMMON/CSIG/SIG(2),P1
C
C     THESE ARE DATA OF THE PITZER MODEL PARAMETER AT ROOM
C     TEMPERATURE
C
      DATA A,BE0,BE1,CFI/0.3910,0.1494,0.3074,0.00359/
      REAL RWKSP(5162)
C
C     BEGIN DATA GENERATION
C
      CALL IWKIN(5162)
C
      MM=0
      SUM=0.0
      SUM1=0.0
  100 READ(23,*,Err=500)CONC,SIG(1),SIG(2),P1
      READ(8,*,Err=500)CM,CONC,CONV,EXPR
C
C     CHECK THE LOGICAL ERROR
C
      CALL EXPLR(CM,CONV,EXPR,EXPT)
C
C     CALCULATION OF OSMOTIC COEFFICIENT BY PITZER
C     MODEL
C
      SMO=1.-1.0*A*SQRT(CM)/(1.+1.2*SQRT(CM))+
     1  CM*(BE0+BE1*EXP(-2.0*SQRT(CM)))+CM**2.*CFI
      DEL=ABS(EXPT-EXPR)/EXPR*100
      DEL1=ABS(OSMO-EXPR)/EXPR*100
C
      SUM=SUM+DEL
      SUM1=SUM1+DEL1
      MM=MM+1
      WRITE(24,*)CM,EXPT,EXPR,OSMO
      GO TO 100
C
  500 AVG=SUM/MM
      AVG1=SUM1/MM
      WRITE(24,600)MM,AVG,AVG1
  600 FORMAT(1X,'DATA #',2X,I3,'  ERROR %  RIM:',F10.7,
     1          ' PITZER:',F 10.7)
```

```
      STOP
      END
C
C      CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
      SUBROUTINE EXPLR(CML,CONV,EXPR,EXPT)
C      CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
      COMMON/CSIG/SIG(2),P1
      COMMON/CNC/NC
      COMMON/CZ/ Z(2)
      COMMON/CV/ V(2)
      COMMON/CCONC/ CONC
      COMMON/CRSTAR/ RSTAR
      COMMON/CALPHA/ ALPHA2
      COMMON/NITZS/ G11,G12,G22
      COMMON/CLRE/ EXPLRO
      COMMON/CLRGL/GLLSS(2048),GLLBB(2048),GLLSB(2048)
      COMMON/CDF/ DR,DK,NB
C
      DIMENSION  YNTE(6,6),R(2048)
      DIMENSION  GESS(2048),GEBB(2048),GESB(2048)
      DIMENSION  CHSS(2048),CHBB(2048),CHSB(2048)
      DIMENSION  RHO(2),GG(10,10)
      REAL  K
C
C      DETERMINATION  OF  THE  NUMERICAL  STEP
C
      DR=0.01
      NB=2047
C
C      NUMBER  OF  COMPONENTS
C
      NC=2
C
C      VOLUME  (V(I)),  VALENCE(Z(I))
C
      V(1)=1.
      V(2)=1.
      Z(1)=1.0
      Z(2)=-1.0
      Z1=Z(1)
      Z2=Z(2)
C
C     TEMP(T),  AVOGADRO  #(AN),  BOLTZMAN  CONSTANT(K),
C     ELECTRONIC  CHARGE(E),DIELECTRIC  CONSTANT  AND
C     ITS  UNIT  CONVERSION(P  &  D),  PI  VALUE
C
      T=298.15
      AN=6.02252E+23
      K=1.38054E-23
      E=1.60210E-19
      P=78.54
```

```
      D=1.112647E-10*P
      PI=4.*ATAN(1.0)
C
C      BETA RELATED VALUE CALCULATION
C
      BETA=((E*E)/(D*K*T))*1.E+10
      ALPHA2=4.*PI*BETA
      ALPHA=SQRT(ALPHA2)
C
C      ION NUMBER CALCULATION
C
      RSTAR=CONC*6.02252E-04
C
C      REDUCED DISTANCE,  R/SIG(2)
C
      DS=SIG(1)/SIG(2)
      DB=1.0
      DSB=(DS+DB)*0.5
C
C      LOWER INTEGRATION LIMITS, REDUCED SIG(1),SIG(2) AND
C      ITS AVERAGE VALUES
C
      NSS=DS/DR
      NBB=DB/DR
      NSB=DSB/DR
C
C      DETERMINE INTEGRATION GRID FROM R/SIG(IJ) TO QUASI
C      INFINITY
C      (=20.48*ANION DIAMETER)
C
      R(1)=DR
      DO 15 J=2,NB
   15 R(J)=R(J-1)+DR
C
C      BEGIN- LRE OSMOTIC
C
      VT=0.
      RH=0.
      DO 25 J=1,NC
        VT=VT+V(J)
        RHO(J)=V(J)*RSTAR
        RH=RH+RHO(J)
   25 CONTINUE
C
C      REDUCED DENSITY(THE BASIC UNIT OF LENGTH IN THIS
C      PROGRAM IS SIG(2) VALUE)
C
      RHRD=RH*SIG(2)*SIG(2)*SIG(2)
C
C      CALCULATION OF THE RENORMALIZED POTENTIAL
C
```

```
      DO 30 J=1,NB
        CHSS(J)=0.0
        CHBB(J)=0.0
        CHSB(J)=0.0
   30 CONTINUE
C
      CALL CHAIN(R,Z1,Z1,NSS,NB,CHSS)
      CALL CHAIN(R,Z2,Z2,NBB,NB,CHBB)
      CALL CHAIN(R,Z1,Z2,NSB,NB,CHSB)
C
C     CALCULATION OF THE RADIAL DISTRIBUTION FUNCTION
C     FOR THE HARD SPHERE SYSTEM
C
      CALL GLLVW(RHRD,DB,DSB,DS)
C
C     CALCULATION OF THE TOTAL RADIAL DISTRIBUTION
C     FUNCTION(FOR LONG RANGE)
C
      IF (NSS.LE.NBB) THEN
        IN=NSS
      ELSE
        IN=NBB
      END IF
C
  200 DO 1100 J=IN,NB
        GESS(J)=EXP(CHSS(J))*GLLSS(J)
        GEBB(J)=EXP(CHBB(J))*GLLBB(J)
        GESB(J)=EXP(CHSB(J))*GLLSB(J)
        IF (J.LT.NSS) GESS(J)=0.
        IF (J.LT.NBB) GEBB(J)=0.
        IF (J.LT.NSB) GESB(J)=0.
 1100 CONTINUE
C
C     INTEGRATION OF THE PRODUCT(DISTANCE*TOTAL RADIAL
C     DISTRIBUTION FUNCTION)
C
      CALL YNTIJ(R,DR,NSS,NB,GESS,YNTE(1,1))
      CALL YNTIJ(R,DR,NBB,NB,GEBB,YNTE(2,2))
      CALL YNTIJ(R,DR,NSB,NB,GESB,YNTE(1,2))
      YNTE(2,1)=YNTE(1,2)
C
C     THE CALCULATION OF THE LONG RANGE CONTRIBUTION OF
C     THE  OSMOTIC COEFFICIENT VALUE.
C
      SUMEXP=0.
      DO 1220 J=1,NC
        DO 1210 KK=1,NC
          SUMEXP=SUMEXP+RHO(J)*RHO(KK)*Z(J)*Z(KK)
     1               *YNTE(J,KK)
 1210   CONTINUE
 1220 CONTINUE
      EXPLRO=(ALPHA2*SUMEXP)/(6.*RH)
```

```
C
C     CALCULATION OF THE CONTRIBUTION BY THE  CONTACT
C     VALUE AMONG  THE TOTAL OSMOTIC COEFFICIENT VALUE.
C
      SUMEXP=0.
      DO 1300 J=1,NC
        DO 1400 KK=1,NC
          IF (J.EQ.1.AND.KK.EQ.1) GG(J,KK)=
     1       G11*EXP(CHSS(NSS))*SIG(J)**3.
         IF (J.EQ.1.AND.KK.EQ.2) GG(J,KK)=G12
     1       *EXP(CHSB(NSB))*((SIG(J)+SIG(KK))/2.)**3.
          IF (J.EQ.2.AND.KK.EQ.1) GG(J,KK)=G12*
     1       EXP(CHSB(NSB))*((SIG(J)+SIG(KK))/2.)**3.
          IF (J.EQ.2.AND.KK.EQ.2) GG(J,KK)=G22*
     1       EXP(CHBB(NBB))*SIG(KK)**3.
            SUMEXP=SUMEXP+RHO(J)*RHO(KK)*GG(J,KK)
 1400   CONTINUE
 1300 CONTINUE
C
C     CONVERSION TO MOLALITY BASIS OSMOTIC COEFFICIENT
C
      EXPCO=(ALPHA2/BETA*SUMEXP)/(6.*RH)
      EXPT=EXPLRO+EXPCO+1.
      EXPT=EXPT*CONV
C
      RETURN
      END
C
C     CCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C     SUBROUTINE GLLVW(RH,DC1,DC12,DC2)
C     CCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
C     HARD SPHERE RDF OF VERLET AND WEIS
C     GENERALIZED TO MIXTURES BY LEE AND LEVESQUE
C
C     CALLED BY LRE
C
C     NOTE : SMALL,+  BIG,-
C
      COMMON/CNC/NC
      COMMON/CV/V(2)
      COMMON/CLRGL/ G11(2048),G22(2048),G12(2048)
      COMMON/NITZS/COR11,COR12,COR22
      COMMON/JASPER/ NSMA, N11,N12,N22,M11,M12,M22,
     1               DSMA,NC1,NC2,NC12
      COMMON/HEIDG/ SMA
      COMMON/SPENGL/ A11,A12,A22
      COMMON/ZSE/RSR,ET,ET1,ET2
      COMMON/BOO/NS,DW,DV
      COMMON/YY/ YR12(2048),YR11(2048),YR22(2048)
      COMMON/YKY/ YK12(2048),YK11(2048),YK22(2048)
      COMMON/CDF/DX,DK,NM
```

```
      COMMON/CGC/ GC11,GC12,GC22
      COMMON/YHN/ RO1,RO2,X1,X2
C
      DOUBLE PRECISION GC11,GC12,GC22
      DOUBLE PRECISION RSR,ET,ET1,ET2,X1,X2
      DIMENSION R(2048)
      REAL MU1,MU2,MU3
C
      NSMA=1
      SMA=0.0001
      NS=NM
      DW=1.
C
      VT=0.
      DO 10 J=1,NC
   10 VT=VT+V(J)
      XI1=V(1)/VT
      XI2=1.-XI1
      X=XI1
      X1=XI2
C
      PI=4.0*ATAN(1.0)
      RHO=RH*DC1*DC1*DC1
      D22=DC2/DC1
      D11=1.
      D12=.5*(D11+D22)
      ETA=PI*RHO*(XI1*D11**3+XI2*D22**3)/6.
      RHO1=RHO*X
      RHO2=RHO-RHO1
      RHO12=SQRT(RHO1*RHO2)
      RSR=D22
      HT=ETA
      HTW=HT-HT*HT/16.
C
      R(1)=DX
      DO 48 J=2,NM
   48 R(J)=R(J-1)+DX
      NC1=RSR/DX
      NC2=1./DX
      NC12=D12/DX
      M11=NC1-NSMA
      M12=NC12-NSMA
      M22=NC2-NSMA
      L1=NC1+NSMA
      L2=NC12+NSMA
      L3=NC2+NSMA
      X2=1.-X1
      RSR3=RSR**3
      ALPHA=(HT/HTW)**(1./3.)
      DV=1./ALPHA
      RO=RHO*(HTW/HT)
      RO1=RO*X1
```

```
      RO2=RO-RO1
      DX=DX*ALPHA
      DK=PI/(DX*(NM+1.))
      ET=PI*(RO1*RSR3+RO2)/6.
C
      CALL FINDA (RHO,ETA,RO,ET,D11,D22,ALPHA,X)
C
      ET1=PI*RO1*RSR3/6.
      ET2=ET-ET1
      ETA1=PI*RO1/6.
      ETA2=PI*RO2/6.
      QQ=1.+RSR+RSR*(ETA1*RSR*RSR+ETA2)
      PC=(1.+ET+ET*ET)*RO
      PC=PC-18.*ETA1*ETA2*(1.-RSR)*(1.-RSR)*QQ/PI
      PC=PC/((1.-ET)**3)
      QQ=ET*(ETA1*RSR*RSR+ETA2)**3
      PV=PC-18.*QQ/(PI*(1.-ET)**3)
      PC=PC/RO
      PV=PV/RO
C
      CALL YMIXT
C
      MU1=24.*A11/(D11*HTW*GC22)
      MU2=24.*A12/(D12*HTW*GC12)
      MU3=24.*A22/(D22*HTW*GC11)
      DO 21 J=1,NM
        G11(J)=0.
        G12(J)=0.
        G22(J)=0.
   21 CONTINUE
C
      MM=MM+1
      DO 22 N=NC1,NM
        DIS=R(N)-D22
        DISMU3=DIS*MU3
        IF (DISMU3.GT.170) DISMU3=170.
        G11(N)=YR11(N)+1.+A22*D22*EXP(-DISMU3)*COS(DISMU3)/R(N)
   22 CONTINUE
C
      DO 23 N=NC12,NM
        DIS=R(N)-D12
        DISMU2=DIS*MU2
        IF(DISMU2.GT. 170) DISMU2=170.
        G12(N)=YR12(N)+1.+A12*D12*EXP(-DISMU2)*COS(DISMU2)/R(N)
   23 CONTINUE
C
      DO 24 N=NC2,NM
        DIS=R(N)-D11
        DISMU1=DIS*MU1
        IF(DISMU1.GT. 170) DISMU1=170.
        G22(N)=YR22(N)+1.+A11*D11*EXP(-DISMU1)*COS(DISMU1)/R(N)
   24 CONTINUE
```

```
C
      RETURN
      END
C
C      CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
      SUBROUTINE FINDA(RHO,XY,RO,XI,D1,D2,ALPHA,X)
C      CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
C      CALLED BY GLLVW
C
      COMMON/CSIG/SIG(2),P1
      COMMON/NITZS/ G11,G12,G22
      COMMON/SPENGL/AD11,AD12,AD22
      COMMON/SOCRAT/DP1,Q
      COMMON/EURIPD/DD,AA1,ETAA1,ETAA2,AA2,UMB
      COMMON/PASCAL/D12,AL1,AL2,Y,PI
      COMMON/HODRLN/PY1,PY12,PY2
      DOUBLE PRECISION XI
C
      PI=4.0*ATAN(1.0)
      D1=1.
      Y=1.-X
      D12=.5*(D1+D2)
      DD=D1+D2
      AL1=PI*D1**3*X/6.
      AL2=PI*D2**3*Y/6.
      XI1=AL1*RHO
      XI2=AL2*RHO
      XX=XI1/D1+XI2/D2
      Q=1./(1.-XY)
      G11=Q+3.*D1*XX*0.5*Q*Q+D1*D1*XX*XX*0.75*Q*Q*Q
      G22=Q+3.*D2*XX*0.5*Q*Q+D2*D2*XX*XX*0.75*Q*Q*Q
      TI=D1*D2/(D1+D2)
      G12=Q+3.*XX*Q*Q*TI+3.*XX*XX*Q*Q*Q*TI*TI
C
      CALL  PY (XY,RHO,D1,D2,X)
C
      G11=(2.*G11+PY1)/3.
      G12=(2.*G12+PY12)/3.
      G22=(2.*G22+PY2)/3.
      Z=RHO+2.*PI*(RHO*RHO*X*X*D1*D1*D1*G11
     1          +RHO*RHO*X*Y*2.*D12*D12*D12*G12
     1          +RHO*RHO*Y*Y*D2*D2*D2*G22)/3.
      Z=Z/RHO
      XE=XI
      Q=1./(1.-XI)
      WD1=D1*(ALPHA-1.)
      WD12=D12*(ALPHA-1.)
      WD2=D2*(ALPHA-1.)
C
      CALL PY (XE,RO,D1,D2,X)
C
```

```
      B1=ETAA1*D1**2*PY1**2+ETAA2*D12**2*PY12**2
      B1=-6.*B1
      B2=ETAA2*D2**2*PY2**2+ETAA1*D12**2*PY12**2
      B2=-6.*B2
      D=ETAA1*AA1+ETAA2*AA2
      D=0.5*D
      B=ETAA1*D1*PY1+ETAA2*D2*PY2
      B=-6.*B*D12*PY12
      DX11=B1+3.*D
      DX22=B2+3.*D*D2*D2
      DDX11=6.*D
      DDX22=6.*D*D2
      DDDX11=DDX11
      DDDX22=6.*D
      YAK=B*D2**2+4.*UMB*D*D2**3+D*D2**4
      DX12=-YAK/(D12*D12)
      YAL=2.*B*D2+12.*UMB*D*D2*D2+4.*D*D2*D2*D2
      DX12=DX12+YAL/D12
      DDX12=2.*YAK/D12**3
      DDX12=DDX12-2.*YAL/(D12*D12)
C
      YAM=2.*B+24.*UMB*D*D2+12.*D*D2*D2
      DDX12=DDX12+YAM/D12
      DDDX12=-6.*YAK/D12**4
      DDDX12=DDDX12+6.*YAL/D12**3
      DDDX12=DDDX12-3.*YAM/(D12*D12)
      DDDX12=DDDX12+(24.*UMB*D+24.*D*D2)/D12
      GG1=PY1+DX11*WD1+0.5*DDX11*WD1**2+DDDX11*WD1
     1        **3/6.
      AD11=G11-GG1
      GG2=PY2+DX22*WD2+0.5*DDX22*WD2**2+DDDX22*WD2
     1         **3/6.
      AD22=G22-GG2
      GG12=PY12+DX12*WD12+0.5*DDX12*WD12**2+DDDX12
     1          *WD12**3/6.
      AD12=G12-GG12
C
      RETURN
      END
C
C     CCCCCCCCCCCCCCCCCCCCCCCCC
      SUBROUTINE PY (XI,RO,D1,D2,X)
C     CCCCCCCCCCCCCCCCCCCCCCCCC
C
C     CALLED BY FINDA
C
      COMMON/SOCRAT/ DP1,Q
      COMMON/EURIPD/ DD,AA1,ETAA1,ETAA2,AA2,UMB
      COMMON/PASCAL/ D12,AL1,AL2,Y,PI
      COMMON/HODRLN/ PY1,PY12,PY2
C
```

```
      T=D1/D2
      S=D2/D1
      XI1=AL1*RO
      XI2=AL2*RO
      ETAA1=PI*RO*X/6.
      ETAA2=PI*RO*Y/6.
      UMB=0.5*(D1-D2)
C
      CALL A1 (T,XI1,XI2,XI)
C
      AA1=DP1
      CALL A1 (S,XI2,XI1,XI)
C
      AA2=DP1
      PY1=1.+0.5*XI
      PY1=PY1+3.*ETAA2*D2**2*UMB
      PY1=PY1*Q**2
      PY2=1.+0.5*XI
      PY2=PY2-3.*ETAA1*D1**2*UMB
      PY2=PY2*Q**2
      PY12=D2*PY1+D1*PY2
      PY12=PY12/(D1+D2)
C
      RETURN
      END
C
C      CCCCCCCCCCCCCCCCCCCCCCC
      SUBROUTINE A1 (T,XI1,XI2,XI)
C      CCCCCCCCCCCCCCCCCCCCCCC
C
C      CALLED BY PY
C
      COMMON/SOCRAT/DP1,Q
      DP=(1.+XI+XI**2)*Q**3
      DP=DP+(2.+XI)**2*(XI1+T**3*XI2)*Q**4
      DP=DP-3.*XI2*(1.-T)**2*(1.+T+2.*XI1+T*XI2)
     1         *Q**3
      DP1=DP-9.*XI1*XI2*(1.-T)**2*(1.+T+T*XI2+XI1)
     1         *Q**4
C
      RETURN
      END
C
C      CCCCCCCCCCCCCCCC
      SUBROUTINE YMIXT
C      CCCCCCCCCCCCCCCC
C
C      CALLED BY MAIN
C
      COMMON/HEIDG/SMA
      COMMON/JASPER/NSMA,N11,N12,N22,M11,M12,M22,
     1              DSMA,NC1,NC2,NC12
```

```
      COMMON/BOO/ NS,DW,DV
      COMMON/CC/CK11,CK22,CK12
      COMMON/YY/YR12(2048),YR11(2048),YR22(2048)
      COMMON/YKY/YK12(2048),YK11(2048),YK22(2048)
      COMMON/YHN/RO1,RO2,X1,X2
      COMMON/BG/ XK
      COMMON/CDF/ DX,DK,NM
      COMMON/CGC/GC11,GC12,GC22
      COMMON/WQ/A1,A2,B1R1,B2R2,BR2,DR1,DR2
      COMMON/ZSE/RSR,ET,ET1,ET2
C
      DOUBLE PRECISION CK11,CK12,CK22
      DOUBLE PRECISION RSR,ET,ET1,ET2,X1,X2
      DOUBLE PRECISION A1,A2,B1R1,B2R2,BR2,DR1,DR2
      DOUBLE PRECISION E,E2,E3,E4,AST,PR,RSR3
      DOUBLE PRECISION GC11,GC12,GC22
C
      D1=1.
      DH=0.5
      D3H=1.5
      DSMA=DX*SMA
      N11=NC1+NSMA
      N12=NC12+NSMA
      N22=NC2+NSMA
C
      PI=4.0*ATAN(1.0)
      CONS=0.5/PI/PI
      CON1=1./(RO1*(2.*PI)**3)
      CON2=1./(RO2*(2.*PI)**3)
      XC=X1/X2
      RSR3=RSR**3
      E=D1/(D1-ET)
      E2=E*E
      E3=E*E2
      E4=E*E3
C
      GC11=E2*(1.+0.5*ET-1.5*ET2*(1.-RSR))
      GC22=E2*(1.+0.5*ET+1.5*ET1*(1./RSR-1.))
      GC12=(GC11+RSR*GC22)/(1.+RSR)
C
      PR1=1+ET+ET**2.
      PR2=ET1+RSR**3.*ET2
      PR3=1+2*ET
      PR4=1+ET1+RSR*(1+ET2)
      PR5=1/(1-ET)**3.
      PR6=1/(1-ET)**4.
C
      AA11=PR1+PR2*PR3-3.*ET2*(1-RSR)**2.*PR4-3*ET1
     1         *ET2*(1-RSR)**2.
      AA12=3.*(PR2*PR1-3.*ET1*ET2*(1-RSR)**2*PR4)
      A1=AA11*PR5 + AA12*PR6
```

```
      AA21=PR1*RSR**3.+PR2*PR3-3.*ET1*(1-RSR)**2.
     1        *PR4-3*ET1*ET2*(1-RSR)**2.*RSR
      AA22=AA12
      A2=AA21*PR5/RSR**3. + AA22*PR6/RSR**3.
      B1R1=-6.*(ET1*GC11**2+0.25*ET2*RSR*(1.+RSR)**2
     1        *GC12**2)
      B2R2=-6.*(ET2*GC22**2+0.25*ET1*(1.+1./RSR)**2
     1        *GC12**2/RSR)
      BR2=-3.*(ET1*GC11/RSR**2+ ET2*GC22)*(1.+RSR)
     1        *GC12
      DR2=0.5*(ET1*A1/RSR3+ET2*A2)
      DR1=RSR3*DR2
C
      DO 20 N=1,NS
        XK=N*DK*DW
C
        CALL LEBO
C
        DEN=(1.-CK11)*(1.-CK22)-XC*CK12**2.
        YK11(N)=(CK11**2.*(1-CK22)+XC*CK12**2*(1+CK11))
     1          /DEN
        YK11(N)=YK11(N)/RO1
        YK12(N)=CK12*(1./DEN-1.)
        YK12(N)=YK12(N)/RO2
        YK22(N)=(CK22**2.*(1.-CK11)+XC*CK12**2.*(1.+
     1          CK22))/DEN
        YK22(N)=YK22(N)/RO2
   20 CONTINUE
C
      XR=DX
      XK=DK
C
      CALL FOURI (YK11,CONS,XR,XK,YR11)
      CALL FOURI (YK12,CONS,XR,XK,YR12)
      CALL FOURI (YK22,CONS,XR,XK,YR22)
C
      RETURN
      END
C
C     CCCCCCCCCCCCCCC
      SUBROUTINE LEBO
C     CCCCCCCCCCCCCCC
C
C     CALLED BY YMIXT
C
      COMMON/CC/ CK11,CK22,CK12
      COMMON/BG/ XK
      COMMON/CDF/ DX,DK,NM
      COMMON/WQ/A1,A2,B1R1,B2R2,BR2,DR1,DR2
      COMMON/ZSE/RSR,ET,ET1,ET2
      COMMON/YHN/RO1,RO2,X1,X2
C
```

```
      DOUBLE PRECISION  CK11,CK22,CK12
      DOUBLE PRECISION  RSR,ET,ET1,ET2
      DOUBLE PRECISION  A1,A2,B1R1,B2R2,BR2,DR1,DR2
      DOUBLE PRECISION  UP,UM,FSP,FCP,FSM,FCM
      DOUBLE PRECISION  Q2,Q3,Q4,Q6,Q12,Q24,FS,FC,UK
      DOUBLE PRECISION  D1C1,D1C2,D1C3,D2C1,D2C2,D2C3
      DOUBLE PRECISION  EC1,EC2,EC3,EC4
      DOUBLE PRECISION  UKZ,FSZ,FCZ
      DOUBLE PRECISION  U1,U2,U3
C
      PI=4.0*ATAN(1.0)
      UK=XK
      FS=DSIN(UK)
      FC=DCOS(UK)
      UKZ=UK*RSR
      FSZ=DSIN(UKZ)
      FCZ=DCOS(UKZ)
      Q2=2.
      Q3=3.
      Q4=4.
      Q5=5.
      Q6=6.
      Q12=12.
      Q24=24.
      D1C2=(Q2*UKZ*FSZ-(UKZ**Q2-Q2)*FCZ-Q2)/UKZ**Q4
      D1C1=(FSZ-UKZ*FCZ)/UKZ**Q3
      D1C3=((Q4*UKZ**Q3-Q24*UKZ)*FSZ-(UKZ**Q4-Q12
     1      *UKZ**Q2+Q24)*FCZ+Q24)/UKZ**Q6
      D2C1=(FS-UK*FC)/UK**Q3
      D2C2=(Q2*UK*FS-(UK**Q2-Q2)*FC-Q2)/UK**Q4
      D2C3=((Q4*UK**Q3-Q24*UK)*FS-(UK**Q4-Q12
     1      *UK**Q2+Q24)*FC+Q24)/UK**Q6
      UP=0.5*(1.+RSR)
      UM=0.5*(1.-RSR)
      FSP=DSIN(UK*UP)
      FCP=DCOS(UK*UP)
      FSM=DSIN(UK*UM)
      FCM=DCOS(UK*UM)
C
      U1=(1+RSR)*0.5*UK
      U2=(1-RSR)*0.5*UK
      U3=RSR*UK
C
      EC1=DSIN(U1)-U1*DCOS(U1)
      EC2=2.*U3*DSIN(U3)+(2.-U3**2.)*DCOS(U3)-2.
      EC3=2.*U3*DCOS(U3)+(U3**2.-2.)*DSIN(U3)
      EC4=(3.*U3**2.-6.)*DSIN(U3)+(6.*U3-U3**3.)
     1    *DCOS(U3)
      EC5=(3.*U3**2.-6)*DCOS(U3)+(U3**3.-6.*U3)
     1    *DSIN(U3)+6.
      EC6=DSIN(U3)*(4.*U3**3.-24.*U3)-DCOS(U3)
     1    *(U3**4.-12.*U3**2.+24.)+24.
```

```
C
      CK11=-ET1*(A1*D1C1+B1R1*D1C2+DR1*D1C3)*24.

      CK12=-ET2*(A1*EC1/UK**3.+BR2/UK**4.*(DCOS(U2)*EC2
     1     +DSIN(U2)*EC3)+2.*(1-RSR)/UK**5.*DR2*(DCOS(U2)
     2     *EC4+DSIN(U2)*EC5)+(DCOS(U2)*EC6+U3**4.
     3     *DSIN(U2)*DSIN(U3)-4.*DSIN(U2)*EC4)
     4     *DR2/UK**6)*24
C
      RETURN
      END
C
C      CCCCCCCCCCCCCCCCCCCCCCCCCCCCC
      SUBROUTINE FOURI (H,CONS,DK,DS,FH)
C      CCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
C      CALLED BY YMIXT
C      FAST FOURIER TRANSFORM
C
      COMMON/CDF/DD,DDD,NM
      COMMON/BOO/ NS,DW,DV
      DIMENSION H(2048),FH(2048),SEQ(2048),Q(2048)
C
      PI=4.0*ATAN(1.0)
      DO 2 I=1,NM
        Q(I)=DS*I
        H(I)=H(I)*Q(I)
    2 CONTINUE
C
      CALL UMACH(2,NOUT)
      CALL FSINT(NM,H,SEQ)
C
      X=0.
      DO 4 K=1,NM
        X=X+DK
        FH(K)=0.5*DS*SEQ(K)* CONS/X
    4 CONTINUE
C
      RETURN
      END
C
C     CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
      SUBROUTINE CHAIN(R,Z1,Z2,NN,MM,CHIJ)
C     CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
      COMMON/CNC/ NC
      COMMON/CZ/ Z(2)
      COMMON/CV/ V(2)
      COMMON/CSIG/ SIG(2),P1
      COMMON/CRSTAR/ RSTAR
      COMMON/CALPHA/ ALPHA2
      COMMON/CDF/DR,DK,NB
```

```
      DIMENSION R(2048),CHIJ(2048),RHO(2)
      REAL KP,KPSUM
C
      PI=4.0*ATAN(1.0)
      AL2=ALPHA2/SIG(2)
      BETA=AL2/(4.*PI)
C
C      CHOOSE THE OPTION OF THE ORIGINAL FORM OR THE
C      MODIFIED FORM
C
      IF (P1.EQ.1.0) THEN
        RAD=0.0
      ELSE
        RAD=NN*DR
      END IF
C
C      CALCULATION OF THE KAPPA VALUE(KP)
C
      KPSUM=0.
      DO 10 K=1,NC
        RHO(K)=V(K)*RSTAR*SIG(2)*SIG(2)*SIG(2)
        KPSUM=KPSUM+RHO(K)*Z(K)*Z(K)
   10 CONTINUE
        KP=SQRT(AL2*KPSUM)
C
C      CORRECTION OF KP VALUE BY INTROUCING THE MOMENT
C      CONDITION
C
      KP=KP*P1
C
C      CALCULATION OF THE RENORMALIZED POTENTIAL
C

      DO 20 J=NN,MM
        CHIJ(J)=(-BETA*Z1*Z2*EXP(-KP*(R(J)-RAD)))/
     1          (R(J)*(1.+KP*RAD))
   20 CONTINUE
C
      RETURN
      END
C
C     CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
      SUBROUTINE YNTIJ(R,DR,NIJ,INF,GIJ,YNT)
C     CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
      COMMON/CSIG/SIG(2),P1
      DIMENSION R(2048),GIJ(2048)
C
      Y=0.
      N=NIJ+1
      M=INF-1
```

```
C
C      NUMERICAL TREATMENT OF THE BOUNDARY VALUE
C
      VDEMI=0.5*R(NIJ)*GIJ(NIJ)
      YDEMI=0.5*R(INF)*GIJ(INF)
C
C      INTEGRATION OF THE PRODUCT VALUE
C      (DISTANCE*RADIAL DISTRIBUTION FUNCTION)
C
      DO 5 J=N,M
    5 Y=Y+R(J)*GIJ(J)
      Y=VDEMI+Y+YDEMI
      Y=Y*DR
      YNT=SIG(2)*SIG(2)*Y
C
      RETURN
      END
```

APPENDIX 2

* MAIN INPUT AND OUTPUT FOR THE PROGRAM OF
* OSMOTIC COEFFICIENT CALCULATION.

* INPUT (1st column: molarity, 2nd column: cation diameter
3rd column: anion diameter, 4th column: *P* value)

* OUTPUT (1st column: molality, 2nd column: ϕ_m (New Model)
3rd column: ϕ_m (experimental), 4th column: ϕ_m (Pitzer)

Table A.2.1.$KBrO_3$

INPUT

```
0.0009970   3.0568125  10.9548235   0.6918507
0.0019941   3.0567739   9.1000252   0.8035014
0.0049848   3.0566585   6.2748303   0.8496010
0.0099687   3.0564659   4.9342871   0.8949505
0.0199341   3.0560799   3.8715208   0.9299509
0.0498101   3.0549164   2.8638852   0.9692507
0.0994996   3.0529613   2.3590214   0.9949502
0.1979655   3.0490127   2.0196698   1.0139998
0.2938896   3.0450695   2.4122598   1.0201001
0.3853953   3.0412178   3.2497787   1.0171990
0.4704381   3.0375588   4.3266864   1.0165499
```

OUTPUT

```
  1.0000000E-03      0.9880034        0.9880000        0.9881993
  2.0000001E-03      0.9840037        0.9840000        0.9836157
   4.9999999E-03      0.9749928        0.9750000        0.9749830
  9.9999998E-03      0.9659953        0.9660000        0.9658993
  2.0000000E-02      0.9540058        0.9540000        0.9540129
   5.0000001E-02      0.9327757        0.9330000        0.9328169
   0.1000000          0.9117312        0.9110000        0.9110954
   0.2000000          0.8805351        0.8810000        0.8813807
   0.3000000          0.8577525        0.8580000        0.8578069
   0.4000000          0.8381202        0.8380000        0.8367704
   0.5000000          0.8191282        0.8190000        0.8171128
DATA #     11   ERROR %   RIM: 0.0198618 PITZER: 0.0496127
```

Table A.2.2. NaF

INPUT

```
0.0009971   3.5752268  10.7393503   0.6751509
0.0019941   3.5752008   8.8598251   0.7875007
0.0049854   3.5751219   6.5340862   0.8673012
0.0099707   3.5749903   4.9648743   0.8966007
0.0199416   3.5747266   3.9379489   0.9337002
0.0498560   3.5739312   3.2201736   0.9835005
0.0997203   3.5725915   2.7233570   1.0022509
0.1994711   3.5698586   2.2631426   1.0140029
0.2992359   3.5670552   2.0202160   1.0192039
0.3989964   3.5641823   1.8592938   1.0232041
0.4987418   3.5612409   1.7413408   1.0258502
0.5984721   3.5582311   1.6504916   1.0288501
0.6982005   3.5551531   1.5785201   1.0310999
0.7979532   3.5520070   1.5204101   1.0332488
0.8977718   3.5487912   1.4727985   1.0348479
0.9807106   3.5460684   1.4395276   1.0364478
0.9977120   3.5455048   1.4333051   1.0371478
```

OUTPUT

```
    1.0000000E-03  0.9879870      0.9880000      0.9883068
    2.0000001E-03  0.9839993      0.9840000      0.9838329
    4.9999999E-03  0.9760086      0.9760000      0.9755366
    9.9999998E-03  0.9670043      0.9670000      0.9670293
    2.0000000E-02  0.9559771      0.9560000      0.9563326
    5.0000001E-02  0.9392908      0.9390000      0.9388776
    0.1000000      0.9237889      0.9240000      0.9237121
    0.2000000      0.9066660      0.9080000      0.9077358
    0.3000000      0.8965522      0.8990000      0.8983623
    0.4000000      0.8899615      0.8920000      0.8917993
    0.5000000      0.8851581      0.8870000      0.8867954
    0.6000000      0.8821065      0.8830000      0.8827886
    0.7000000      0.8800343      0.8800000      0.8794813
    0.8000000      0.8791569      0.8770000      0.8766977
    0.9000000      0.8791235      0.8740000      0.8743252
    0.9830000      0.8798386      0.8710000      0.8726131
     1.000000     0.8802630      0.8710000      0.8722879
DATA #    17  ERROR %  RIM: 0.2311646 PITZER: 0.0476924
```

Table A.2.3. CsOH

INPUT

0.0009970	1.6747289	13.0021505	0.8094500
0.0019941	1.6747169	10.6550465	0.8797000
0.0049848	1.6746811	8.1337347	0.9389002
0.0099685	1.6746211	7.3917117	0.9815500
0.0199328	1.6744999	6.9984040	1.0020499
0.0498006	1.6741284	6.8690429	1.0120500
0.0994983	1.6734819	6.4856186	1.0182000
0.1985932	1.6720871	6.1142097	1.0257999
0.2972935	1.6705565	5.9386230	1.0312501
0.3956019	1.6688907	5.8323469	1.0376505
0.4935176	1.6670895	5.7582140	1.0433502
0.5910385	1.6651531	5.7016048	1.0500500
0.6881606	1.6630815	5.6556187	1.0557504
0.7848794	1.6608745	5.6165771	1.0616502
0.8811899	1.6585321	5.5823412	1.0676504
0.9770860	1.6560540	5.5515838	1.0734506
1.1676120	1.6506891	5.4973097	1.0802501

OUTPUT

1.0000000E-03	0.9891335	0.9890000	0.9885191
2.0000001E-03	0.9850097	0.9850000	0.9842532
4.9999999E-03	0.9769977	0.9770000	0.9765668
9.9999998E-03	0.9699972	0.9700000	0.9690455
2.0000000E-02	0.9619189	0.9620000	0.9602486
5.0000001E-02	0.9525062	0.9520000	0.9481576
0.1000000	0.9459311	0.9460000	0.9413065
0.2000000	0.9440215	0.9460000	0.9407377
0.3000000	0.9481686	0.9520000	0.9458707
0.4000000	0.9555423	0.9590000	0.9532818
0.5000000	0.9644288	0.9660000	0.9619006
0.6000000	0.9743553	0.9750000	0.9712700
0.7000000	0.9848329	0.9840000	0.9811596
0.8000000	0.9957194	0.9930000	0.9914390
0.9000000	1.006871	1.002000	1.002028
1.000000	1.018110	1.011000	1.012873
1.200000	1.039618	1.029000	1.035198

DATA # 17 ERROR % RIM: 0.2273266 PITZER: 0.3052092

Table A.2.4. $CsNO_3$

INPUT

```
0.0009969   1.6747289  11.6045589   0.7365498
0.0019934   1.6747169   8.9840221   0.7964499
0.0049804   1.6746812   6.8003111   0.8842997
0.0099510   1.6746213   5.9431057   0.9477994
0.0198626   1.6745008   5.1014700   0.9812995
0.0493639   1.6741339   4.6295023   1.0074000
0.0977661   1.6735049   4.2335510   1.0156001
0.1917905   1.6721874   3.8892705   1.0210501
0.2822767   1.6707987   3.7330065   1.0239501
0.3694177   1.6693484   3.6427159   1.0267001
0.4533966   1.6678448   3.5833220   1.0273999
0.5343870   1.6662954   3.5409293   1.0290499
0.6125535   1.6647066   3.5089154   1.0303999
0.6880530   1.6630838   3.4837186   1.0314499
0.7610349   1.6614321   3.4632494   1.0324001
0.8316414   1.6597553   3.4461994   1.0317501
0.9662675   1.6563410   3.4191818   1.0330508
1.0929530   1.6528622   3.3984649   1.0342518
1.1536160   1.6511035   3.3897371   1.0348018
```

OUTPUT

```
1.0000000E-03   0.9879829     0.9880000     0.9879490
2.0000001E-03   0.9829992     0.9830000     0.9831306
4.9999999E-03   0.9739996     0.9740000     0.9738452
9.9999998E-03   0.9649948     0.9650000     0.9637835
2.0000000E-02   0.9520051     0.9520000     0.9502024
5.0000001E-02   0.9290887     0.9290000     0.9251377
0.1000000       0.9038677     0.9040000     0.8992336
0.2000000       0.8693819     0.8700000     0.8655769
0.3000000       0.8438749     0.8440000     0.8413243
0.4000000       0.8230844     0.8220000     0.8215367
0.5000000       0.8045294     0.8040000     0.8044008
0.6000000       0.7882710     0.7870000     0.7890280
0.7000000       0.7734979     0.7720000     0.7749124
0.8000000       0.7598702     0.7590000     0.7617366
0.9000000       0.7472223     0.7460000     0.7492884
 1.000000       0.7347748     0.7350000     0.7374188
 1.200000       0.7134386     0.7150000     0.7150071
 1.400000       0.6949238     0.6980000     0.6939097
 1.500000       0.6866664     0.6900000     0.6837354
DATA #    19   ERROR %   RIM: 0.1114529  PITZER: 0.2886417
```

Table A.2.5. KH_2PO_4

INPUT

```
0.0009969   3.0568125  11.1242085   0.7041503
0.0019935   3.0567739   8.4397058   0.7562004
0.0049814   3.0566585   6.1136732   0.8369498
0.0099548   3.0564663   4.7263246   0.8783997
0.0198778   3.0560820   3.8145669   0.9255499
0.0494563   3.0549302   2.9551127   0.9735498
0.0981210   3.0530159   2.5100145   0.9989499
0.1931076   3.0492098   2.2076793   1.0151498
0.2850346   3.0454376   2.0837016   1.0212001
0.3739840   3.0417030   2.0147927   1.0242499
0.4600407   3.0380101   1.9706088   1.0259998
0.5432904   3.0343621   1.9397635   1.0272999
0.6238192   3.0307617   1.9169648   1.0280501
0.7017128   3.0272110   1.9926752   1.0282001
0.7770569   3.0237122   1.9646235   1.0288501
0.8499362   3.0202670   2.0011456   1.0282998
0.9886374   3.0135424   2.0904143   1.0273999
1.1184820   3.0070438   2.2149234   1.0271001
1.2401230   3.0007737   2.3611302   1.0258501
1.3542030   2.9947293   2.4858677   1.0242000
```

OUTPUT

```
   1.0000000E-03  0.9879960        0.9880000        0.9879219
   2.0000001E-03  0.9830046        0.9830000        0.9830784
   4.9999999E-03  0.9740036        0.9740000        0.9737233
   9.9999998E-03  0.9639973        0.9640000        0.9635581
   2.0000000E-02  0.9510301        0.9510000        0.9498002
   5.0000001E-02  0.9270253        0.9270000        0.9243452
   0.1000000      0.9019660        0.9020000        0.8980519
   0.2000000      0.8688365        0.8690000        0.8641269
   0.3000000      0.8445010        0.8450000        0.8399825
   0.4000000      0.8242735        0.8240000        0.8205253
   0.5000000      0.8062360        0.8060000        0.8038667
   0.6000000      0.7898622        0.7900000        0.7890741
   0.7000000      0.7744614        0.7750000        0.7756135
   0.8000000      0.7631566        0.7620000        0.7631488
   0.9000000      0.7489639        0.7490000        0.7514542
    1.000000     0.7372213        0.7370000        0.7403708
    1.200000     0.7159023        0.7160000        0.7196021
    1.400000     0.6982433        0.6980000        0.7002107
    1.600000     0.6827414        0.6820000        0.6818107
    1.800000     0.6681207        0.6680000        0.6641510
DATA #    20   ERROR %   RIM: 0.0300193 PITZER: 0.2668613
```

Table A.2.6. LiI

INPUT

```
0.0009970   4.4590158  11.8140221   0.7486498
0.0019940   4.4589949   9.4768839   0.8252492
0.0049844   4.4589319   7.2912760   0.9072990
0.0099671   4.4588265   6.0599828   0.9498487
0.0199269   4.4586158   5.5267596   0.9859986
0.0497630   4.4579782   5.2278090   1.0041490
0.0993466   4.4568992   5.0873055   1.0073991
0.1979807   4.4546781   4.9933333   1.0094990
0.2959111   4.4523740   4.8279114   1.0103489
0.3931442   4.4499893   4.7314582   1.0120490
0.4896855   4.4475245   4.6395774   1.0150990
0.5855402   4.4449811   4.5554471   1.0169991
0.6807132   4.4423604   4.4790082   1.0189999
0.7752094   4.4396639   4.4116321   1.0193511
0.8690332   4.4368920   4.3536711   1.0233020
0.9621894   4.4340467   4.3045502   1.0254022
1.1465180   4.4281387   4.2286134   1.0276030
1.3282350   4.4219489   4.1751351   1.0350533
1.5073820   4.4154854   4.1369677   1.0369041
1.6840010   4.4087558   4.1090660   1.0453550
1.8581400   4.4017668   4.1100912   1.0509559
2.2829621   4.3832030   4.1287060   1.0609571
2.6934290   4.3631477   4.1632681   1.0767579
```

OUTPUT

```
1.0000000E-03  0.9890066      0.9890000      0.9886481
2.0000001E-03  0.9849972      0.9850000      0.9845076
4.9999999E-03  0.9779933      0.9780000      0.9771857
9.9999998E-03  0.9710023      0.9710000      0.9702471
2.0000000E-02  0.9639867      0.9640000      0.9625569
5.0000001E-02  0.9562372      0.9560000      0.9535115
0.1000000      0.9552351      0.9560000      0.9512249
0.2000000      0.9658318      0.9650000      0.9587868
0.3000000      0.9780940      0.9780000      0.9713138
0.4000000      0.9929367      0.9930000      0.9856840
0.5000000       1.008175       1.008000       1.000974
0.6000000       1.022880       1.023000       1.016814
0.7000000       1.037356       1.037000       1.033027
0.8000000       1.051738       1.052000       1.049521
0.9000000       1.066632       1.067000       1.066240
 1.000000      1.081186       1.082000       1.083153
 1.200000      1.111616       1.112000       1.117473
 1.400000      1.143634       1.143000       1.152367
 1.600000      1.176237       1.176000       1.187763
 1.800000      1.210163       1.211000       1.223611
 2.000000      1.249098       1.249000       1.259870
 2.500000      1.353920       1.353000       1.352097
 3.000000      1.470941       1.471000       1.446236
DATA #    23  ERROR %  RIM: 0.0290175  PITZER: 0.4909641
```

Table A.2.7. $LiClO_4$

INPUT

0.0009970	4.4590158	11.8462400	0.7505496
0.0019940	4.4589949	9.4917784	0.8261492
0.0049843	4.4589319	7.3142552	0.9082492
0.0099665	4.4588265	6.0817213	0.9505986
0.0199244	4.4586158	5.5649476	0.9863984
0.0497469	4.4579787	5.2746606	1.0040989
0.0992792	4.4569006	5.0024266	1.0072491
0.1976985	4.4546843	4.7777858	1.0093992
0.2952608	4.4523897	4.6785245	1.0110991
0.3919725	4.4500184	4.5707664	1.0128499
0.4878419	4.4475727	4.5095444	1.0136001
0.5828781	4.4450531	4.4507689	1.0167511
0.6770900	4.4424620	4.4085135	1.0172009
0.7704870	4.4398007	4.3734531	1.0208020
0.8630785	4.4370708	4.3437734	1.0210521
0.9548731	4.4342737	4.3188539	1.0233030
1.1361099	4.4284825	4.2803550	1.0300040
1.3142660	4.4224377	4.2520971	1.0321550
1.4894100	4.4161501	4.2297606	1.0370059
1.6616040	4.4096289	4.2122412	1.0422570
1.8309079	4.4028831	4.2022276	1.0475070
2.2418890	4.3850937	4.1764278	1.0609579
2.6359529	4.3660855	4.1583939	1.0746089
3.0137911	4.3459787	4.1528640	1.0886101
3.3760040	4.3248887	4.1502118	1.1020101
3.7231190	4.3029242	4.1537433	1.1290611

OUTPUT

```
      1.0000000E-03  0.9890255       0.9890000       0.9886599
      2.0000001E-03  0.9850034       0.9850000       0.9845300
      4.9999999E-03  0.9780028       0.9780000       0.9772356
      9.9999998E-03  0.9709983       0.9710000       0.9703340
      2.0000000E-02  0.9639921       0.9640000       0.9626961
      5.0000001E-02  0.9562294       0.9560000       0.9537089
      0.1000000      0.9534138       0.9540000       0.9513361
      0.2000000      0.9593420       0.9600000       0.9583738
      0.3000000      0.9709231       0.9710000       0.9701243
      0.4000000      0.9830309       0.9830000       0.9835752
      0.5000000      0.9968960       0.9970000       0.9978577
      0.6000000       1.011193        1.011000        1.012632
      0.7000000       1.025814        1.026000        1.027743
      0.8000000       1.041166        1.041000        1.043110
      0.9000000       1.056342        1.057000        1.058688
       1.000000      1.072267        1.072000        1.074453
       1.200000      1.104729        1.105000        1.106474
       1.400000      1.137581        1.138000        1.139088
       1.600000      1.171408        1.171000        1.172242
       1.800000      1.205772        1.206000        1.205895
       2.000000      1.241230        1.240000        1.240015
       2.500000      1.329054        1.329000        1.327162
       3.000000      1.416929        1.418000        1.416633
       3.500000      1.506657        1.508000        1.508095
       4.000000      1.595114        1.596000        1.601276
       4.500000      1.683469        1.683000        1.695954
DATA #    26   ERROR %   RIM: 0.0302413 PITZER: 0.1498412
```

Table A.2.8. KI

INPUT

0.0009970	3.0569351	11.0061884	0.6956999
0.0019940	3.0568948	9.1398449	0.8059997
0.0049842	3.0567732	6.8937044	0.8886499
0.0099663	3.0565710	5.7880435	0.9408997
0.0199236	3.0561666	4.9923496	0.9770495
0.0497416	3.0549538	4.6010623	1.0042001
0.0992576	3.0529337	4.3882480	1.0103011
0.1976101	3.0488999	4.2326941	1.0127989
0.2950584	3.0448749	4.1669750	1.0146489
0.3916084	3.0408590	4.1289768	1.0159992
0.4872676	3.0368519	4.0169725	1.0170491
0.5820449	3.0328541	3.9743874	1.0169989
0.6759495	3.0288656	3.9264569	1.0186989
0.7689906	3.0248866	3.8996301	1.0197999
0.8611783	3.0209169	3.8795297	1.0209000
0.9525217	3.0169568	3.8579509	1.0203000
1.1327159	3.0090652	3.8092053	1.0223498
1.3096480	3.0012119	3.7662582	1.0255001
1.4833950	2.9933977	3.7402215	1.0252498
1.6540270	2.9856224	3.7334692	1.0297999
1.8216180	2.9778862	3.7351100	1.0320500
2.2277291	2.9587190	3.7045906	1.0378501
2.6162760	2.9398000	3.6749980	1.0433494
2.9882259	2.9211307	3.6754215	1.0489991
3.3444970	2.9027104	3.6827385	1.0523989
3.6859691	2.8845370	3.6899374	1.0568990

OUTPUT

```
       1.0000000E-03  0.9880213      0.9880000      0.9883984
       2.0000001E-03  0.9840014      0.9840000      0.9840141
       4.9999999E-03  0.9759998      0.9760000      0.9759800
       9.9999998E-03  0.9680382      0.9680000      0.9678956
       2.0000000E-02  0.9579706      0.9580000      0.9580109
       5.0000001E-02  0.9432256      0.9430000      0.9428331
       0.1000000      0.9314223      0.9320000      0.9311590
       0.2000000      0.9217896      0.9220000      0.9215427
       0.3000000      0.9192494      0.9190000      0.9180328
       0.4000000      0.9196832      0.9180000      0.9170061
       0.5000000      0.9184079      0.9180000      0.9172943
       0.6000000      0.9194883      0.9190000      0.9183837
       0.7000000      0.9209512      0.9210000      0.9200075
       0.8000000      0.9234450      0.9230000      0.9220107
       0.9000000      0.9263527      0.9250000      0.9242954
        1.000000     0.9285815      0.9280000      0.9267966
        1.200000     0.9337130      0.9330000      0.9322754
        1.400000     0.9386942      0.9390000      0.9382005
        1.600000     0.9437586      0.9450000      0.9444214
        1.800000     0.9517331      0.9510000      0.9508364
        2.000000     0.9596488      0.9570000      0.9573712
        2.500000     0.9747706      0.9720000      0.9738858
        3.000000     0.9875426      0.9870000      0.9901851
        3.500000      1.002809       1.003000       1.005854
        4.000000      1.018490       1.018000       1.020600
        4.500000      1.032710       1.033000       1.034206
DATA #    26   ERROR %   RIM: 0.0660753 PITZER: 0.0940386
```

Table A.2.9. KCl

INPUT

0.0009971	3.0569351	10.9526777	0.6917503
0.0019941	3.0568948	9.0913105	0.8029998
0.0049849	3.0567732	6.8221231	0.8848495
0.0099687	3.0565710	5.3037605	0.9182992
0.0199332	3.0561662	4.6011996	0.9657488
0.0498003	3.0549512	3.9805129	0.9996490
0.0994859	3.0529244	3.6581044	1.0100999
0.1984865	3.0488639	3.4494500	1.0142499
0.2969667	3.0447960	3.3681431	1.0155499
0.3949064	3.0407212	3.3237619	1.0170000
0.4922932	3.0366406	3.2167478	1.0173001
0.5891188	3.0325546	3.1713223	1.0185001
0.6853785	3.0284636	3.1191642	1.0190002
0.7810694	3.0243678	3.0765848	1.0188498
0.8761908	3.0202677	3.0414927	1.0201502
0.9707430	3.0161636	3.0114043	1.0197499
1.1581470	3.0079429	2.9633646	1.0218002
1.3433011	2.9997065	2.9311690	1.0215999
1.5262320	2.9914553	2.9138412	1.0226001
1.7069710	2.9831891	2.9088359	1.0234998
1.8855470	2.9749088	2.9130678	1.0243500
2.3227301	2.9541466	2.8975668	1.0289011
2.7469990	2.9333024	2.9143739	1.0300021
3.1586130	2.9123886	2.9491403	1.0333520
3.5576530	2.8914270	2.9828148	1.0371529
3.9440000	2.8704524	3.0350571	1.0414041
4.1718240	2.8577549	3.0694633	1.0472039
4.3173380	2.8495121	3.0900013	1.0459541

OUTPUT

```
     1.0000000E-03  0.9880050    0.9880000    0.9883351
     2.0000001E-03  0.9839983    0.9840000    0.9838893
     4.9999999E-03  0.9759947    0.9760000    0.9756774
     9.9999998E-03  0.9670141    0.9670000    0.9673101
     2.0000000E-02  0.9569558    0.9570000    0.9568919
     5.0000001E-02  0.9404035    0.9400000    0.9402660
     0.1000000      0.9260505    0.9270000    0.9264684
     0.2000000      0.9123409    0.9130000    0.9131948
     0.3000000      0.9061574    0.9060000    0.9064922
     0.4000000      0.9034832    0.9020000    0.9025743
     0.5000000      0.8997826    0.9000000    0.9001927
     0.6000000      0.8988519    0.8990000    0.8987874
     0.7000000      0.8976517    0.8980000    0.8980617
     0.8000000      0.8969281    0.8980000    0.8978407
     0.9000000      0.8970478    0.8980000    0.8980123
      1.000000      0.8969063    0.8980000    0.8985009
      1.200000      0.8983560    0.9000000    0.9002272
      1.400000      0.8999786    0.9020000    0.9027305
      1.600000      0.9031464    0.9050000    0.9058340
      1.800000      0.9071393    0.9080000    0.9094195
      2.000000      0.9118903    0.9120000    0.9134020
      2.500000      0.9227110    0.9230000    0.9247058
      3.000000      0.9352181    0.9360000    0.9374259
      3.500000      0.9503068    0.9500000    0.9511257
      4.000000      0.9647231    0.9650000    0.9655064
      4.500000      0.9809306    0.9810000    0.9803516
      4.803000      0.9908478    0.9900000    0.9895035
      5.000000      0.9963713    0.9970000    0.9954991
DATA #    28   ERROR %   RIM: 0.0672588 PITZER: 0.0627408
```

Table A.2.10. KBr

INPUT

0.0009970	3.0569351	10.9684801	0.6928996
0.0019940	3.0568948	9.1063557	0.8038995
0.0049847	3.0567732	6.8444247	0.8860492
0.0099680	3.0565710	5.7081242	0.9376991
0.0199304	3.0561664	4.9146919	0.9750991
0.0497827	3.0549519	4.2786441	1.0024490
0.0994161	3.0529273	3.9381452	1.0103501
0.1982116	3.0488753	3.7059889	1.0134999
0.2963572	3.0448213	3.6125057	1.0149001
0.3938372	3.0407660	3.5607166	1.0163000
0.4906430	3.0367100	3.4982777	1.0164499
0.5867702	3.0326540	3.4441831	1.0170001
0.6822168	3.0285983	3.3998084	1.0183001
0.7769831	3.0245433	3.3652632	1.0191499
0.8710713	3.0204892	3.3358343	1.0187501
0.9644838	3.0164361	3.3092024	1.0201501
1.1492990	3.0083334	3.2623067	1.0201999
1.3314660	3.0002365	3.2241137	1.0224011
1.5110281	2.9921453	3.1946220	1.0238521
1.6880310	2.9840608	3.1728430	1.0234519
1.8625250	2.9759829	3.1573627	1.0246029
2.2880859	2.9558179	3.1361208	1.0277028
2.6989570	2.9356983	3.2045822	1.0344520
3.0957589	2.9156277	3.2284770	1.0361519
3.4790101	2.8956134	3.2416184	1.0437509
3.8491220	2.8756673	3.2712321	1.0496010
4.2064009	2.8558056	3.2992408	1.0507499
4.5510612	2.8360498	3.3345628	1.0603489

OUTPUT

```
  1.0000000E-03  0.9880098       0.9880000       0.9883521
  2.0000001E-03  0.9839993       0.9840000       0.9839229
  4.9999999E-03  0.9759980       0.9760000       0.9757592
  9.9999998E-03  0.9680017       0.9680000       0.9674691
  2.0000000E-02  0.9579931       0.9580000       0.9571981
  5.0000001E-02  0.9419655       0.9420000       0.9409789
  0.1000000      0.9282095       0.9280000       0.9277920
  0.2000000      0.9152848       0.9160000       0.9156023
  0.3000000      0.9097429       0.9100000       0.9098737
  0.4000000      0.9075686       0.9070000       0.9068568
  0.5000000      0.9059274       0.9060000       0.9053218
  0.6000000      0.9050034       0.9050000       0.9047188
  0.7000000      0.9050425       0.9050000       0.9047583
  0.8000000      0.9056852       0.9050000       0.9052698
  0.9000000      0.9060722       0.9060000       0.9061444
   1.000000      0.9071342       0.9070000       0.9073089
   1.200000      0.9090325       0.9100000       0.9103125
   1.400000      0.9118183       0.9130000       0.9140010
   1.600000      0.9150648       0.9170000       0.9182038
   1.800000      0.9178894       0.9220000       0.9228062
   2.000000      0.9217133       0.9270000       0.9277258
   2.500000      0.9321630       0.9400000       0.9410332
   3.000000      0.9539246       0.9540000       0.9552810
   3.500000      0.9695909       0.9690000       0.9700377
   4.000000      0.9839689       0.9850000       0.9850057
   4.500000       1.000430        1.000000       0.9999686
   5.000000       1.014896        1.015000        1.014763
   5.500000       1.030496        1.029000        1.029264
DATA #   28   ERROR %   RIM: 0.1063552  PITZER: 0.0524273
```

Table A.2.11. NaCl

INPUT

0.0009971	3.5769482	10.7877712	0.6789498
0.0019941	3.5769162	8.8803740	0.7888497
0.0049851	3.5768206	6.5570254	0.8686997
0.0099696	3.5766613	5.3563328	0.9205993
0.0199368	3.5763426	4.7304645	0.9694988
0.0498235	3.5753844	4.0503173	0.9993000
0.0995806	3.5737824	3.7324309	1.0088011
0.1988734	3.5705602	3.5485358	1.0122509
0.2978479	3.5673144	3.3873472	1.0141009
0.3964849	3.5640450	3.2706337	1.0148509
0.4947705	3.5607524	3.1934621	1.0161510
0.5926944	3.5574369	3.1392071	1.0171001
0.6902481	3.5540986	3.0952806	1.0172001
0.7874261	3.5507376	3.0575864	1.0177499
0.8842233	3.5473540	3.0247295	1.0194499
0.9806364	3.5439475	2.9960067	1.0194501
1.1723000	3.5370662	2.9488866	1.0221502
1.3624049	3.5300934	2.9125924	1.0239002
1.5509460	3.5230284	2.8842564	1.0244501
1.7379240	3.5158696	2.8783226	1.0261998
1.9233470	3.5086162	2.8773143	1.0295500
2.3801501	3.4900591	2.8733096	1.0345510
2.8274331	3.4708776	2.8963356	1.0399020
3.2653480	3.4510462	2.9264436	1.0456520
3.6940069	3.4305396	2.9583793	1.0515022
4.1134648	3.4093335	2.9938159	1.0581031
4.5237021	3.3874059	3.0334988	1.0647041
4.9246202	3.3647394	3.0765128	1.0717040
5.3160410	3.3413212	3.1211791	1.0787529
5.4269748	3.3344364	3.1341019	1.0753530

OUTPUT

```
  1.0000000E-03  0.9880143      0.9880000      0.9884141
  2.0000001E-03  0.9840006      0.9840000      0.9840448
  4.9999999E-03  0.9759951      0.9760000      0.9760535
  9.9999998E-03  0.9679990      0.9680000      0.9680355
  2.0000000E-02  0.9589968      0.9590000      0.9582727
  5.0000001E-02  0.9441307      0.9440000      0.9434116
  0.1000000      0.9326388      0.9330000      0.9321840
  0.2000000      0.9242820      0.9240000      0.9233410
  0.3000000      0.9210539      0.9210000      0.9205644
  0.4000000      0.9201649      0.9200000      0.9202914
  0.5000000      0.9211314      0.9210000      0.9213837
  0.6000000      0.9231906      0.9230000      0.9233449
  0.7000000      0.9258108      0.9260000      0.9259191
  0.8000000      0.9287382      0.9290000      0.9289588
  0.9000000      0.9324175      0.9320000      0.9323716
   1.000000     0.9358636      0.9360000      0.9360960
   1.200000     0.9442161      0.9440000      0.9443182
   1.400000     0.9525000      0.9530000      0.9533948
   1.600000     0.9611768      0.9620000      0.9631849
   1.800000     0.9719972      0.9730000      0.9735931
   2.000000     0.9840190      0.9840000      0.9845490
   2.500000      1.012615       1.013000       1.014004
   3.000000      1.045530       1.045000       1.045956
   3.500000      1.080322       1.080000       1.079997
   4.000000      1.116135       1.116000       1.115837
   4.500000      1.153243       1.153000       1.153259
   5.000000      1.191584       1.191000       1.192095
   5.500000      1.231017       1.231000       1.232214
   6.000000      1.270828       1.270000       1.273513
   6.144000      1.282562       1.281000       1.285614
DATA #    30   ERROR %   RIM: 0.0302467  PITZER: 0.0648041
```

Table A.2.12. HBr

INPUT

0.0009970	3.8185010	12.0233498	0.7608495
0.0019940	3.8184044	9.7341843	0.8390495
0.0049848	3.8181140	7.0323105	0.8954994
0.0099684	3.8176301	6.0293245	0.9492491
0.0199320	3.8166623	5.6997900	0.9888988
0.0497944	3.8137591	5.3014698	1.0052491
0.0994684	3.8089216	5.0849061	1.0082489
0.1984503	3.7992513	4.9454126	1.0104991
0.2969402	3.7895885	4.8879657	1.0127989
0.3949363	3.7799337	4.8534141	1.0149491
0.4924392	3.7702880	4.8284769	1.0154988
0.5894507	3.7606514	4.8085022	1.0175991
0.6859727	3.7510245	4.7914376	1.0197991
0.7820087	3.7414076	4.7762380	1.0218991
0.8775616	3.7318013	4.7623143	1.0241491
0.9726350	3.7222056	4.7493105	1.0264989
1.1613600	3.7030475	4.7113013	1.0313489
1.3482130	3.6839354	4.7106743	1.0360990
1.5332290	3.6648705	4.6915355	1.0414991
1.7164390	3.6458552	4.6851401	1.0524510
1.8978750	3.6268904	4.6879096	1.0580009
2.3439021	3.5797114	4.6985884	1.0695001
2.7794690	3.5328853	4.7019963	1.0939980
3.2049530	3.4864399	4.7060785	1.1038980
3.6206629	3.4404068	4.7150612	1.1276971
4.0268388	3.3948214	4.7280278	1.1623470
4.4236588	3.3497233	4.7424879	1.1673479
4.8112369	3.3051565	4.7562008	1.2091992
5.1896329	3.2611687	4.7676840	1.2096988
5.9188561	3.1751423	4.7814078	1.2553967
6.6108279	3.0921042	4.7827010	1.3046968

OUTPUT

```
  1.0000000E-03  0.9889956     0.9890000     0.9886181
  2.0000001E-03  0.9849995     0.9850000     0.9844484
  4.9999999E-03  0.9770039     0.9770000     0.9770418
  9.9999998E-03  0.9700030     0.9700000     0.9699681
  2.0000000E-02  0.9629802     0.9630000     0.9620220
  5.0000001E-02  0.9532590     0.9530000     0.9522814
  0.1000000      0.9488817     0.9490000     0.9489856
  0.2000000      0.9533503     0.9540000     0.9548802
  0.3000000      0.9640406     0.9650000     0.9660729
  0.4000000      0.9773652     0.9780000     0.9793729
  0.5000000      0.9916248     0.9920000     0.9938239
  0.6000000       1.007175      1.007000      1.009036
  0.7000000       1.023307      1.022000      1.024819
  0.8000000       1.039822      1.039000      1.041074
  0.9000000       1.056641      1.055000      1.057739
   1.000000       1.073687      1.072000      1.074776
   1.200000       1.106605      1.107000      1.109874
   1.400000       1.144086      1.143000      1.146235
   1.600000       1.179608      1.181000      1.183778
   1.800000       1.218062      1.219000      1.222444
   2.000000       1.257994      1.258000      1.262188
   2.500000       1.362905      1.361000      1.366028
   3.000000       1.470271      1.470000      1.475907
   3.500000       1.581281      1.583000      1.591467
   4.000000       1.698131      1.701000      1.712431
   4.500000       1.819706      1.822000      1.838578
   5.000000       1.947173      1.947000      1.969735
   5.500000       2.075805      2.073000      2.105760
   6.000000       2.207383      2.200000      2.246538
   7.000000       2.459310      2.452000      2.542002
   8.000000       2.682996      2.692000      2.855560
DATA #    31  ERROR %  RIM: 0.0919538 PITZER: 0.6740525
```

Table A.2.13. HI

INPUT

0.0009970	3.8185010	12.1126633	0.7656996
0.0019940	3.8184044	9.7576275	0.8402492
0.0049844	3.8181140	7.6461110	0.9218991
0.0099671	3.8176303	6.8974485	0.9716989
0.0199269	3.8166628	6.2923026	0.9950489
0.0497624	3.8137622	6.1141405	1.0061489
0.0993417	3.8089340	5.8647537	1.0087990
0.1979508	3.7993002	5.6366720	1.0122991
0.2958308	3.7896976	5.5310178	1.0143988
0.3929885	3.7801261	5.4669838	1.0183492
0.4894315	3.7705860	5.4218688	1.0215489
0.5851685	3.7610774	5.3869448	1.0249989
0.6802079	3.7516005	5.3581529	1.0257990
0.7745588	3.7421551	5.3333507	1.0291991
0.8682297	3.7327411	5.3113027	1.0324491
0.9612291	3.7233586	5.2912450	1.0356991
1.1452490	3.7046885	5.2552743	1.0428488
1.3266850	3.6861446	5.2230496	1.0497488
1.5056030	3.6677260	5.1933460	1.0566987
1.6820641	3.6494334	5.1654696	1.0642998
1.8561280	3.6312659	5.0987382	1.0740001
2.2811680	3.5863948	5.0607347	1.0879499
2.6923950	3.5423050	5.0433340	1.1055502
3.0905471	3.4989958	5.0318770	1.1388501
3.4762909	3.4564660	5.0266013	1.1496499
3.8502340	3.4147146	5.0270119	1.1924011
4.2129331	3.3737402	5.0310211	1.2095009
4.5649061	3.3335402	5.0363684	1.2138501
4.9066362	3.2941103	5.0413227	1.2679491
5.5611610	3.2175398	5.0462527	1.3351489
6.1798782	3.1439714	5.0425606	1.3361491

OUTPUT

```
    1.0000000E-03  0.9890477    0.9890000    0.9886917
    2.0000001E-03  0.9849988    0.9850000    0.9845939
    4.9999999E-03  0.9779989    0.9780000    0.9773971
    9.9999998E-03  0.9720082    0.9720000    0.9706608
    2.0000000E-02  0.9649191    0.9650000    0.9633597
    5.0000001E-02  0.9586037    0.9580000    0.9554116
    0.1000000      0.9578920    0.9580000    0.9548253
    0.2000000      0.9673616    0.9700000    0.9655443
    0.3000000      0.9820611    0.9850000    0.9810589
    0.4000000      0.9993517     1.002000    0.9983252
    0.5000000       1.017922     1.020000     1.016459
    0.6000000       1.037317     1.039000     1.035112
    0.7000000       1.056696     1.057000     1.054121
    0.8000000       1.076966     1.076000     1.073405
    0.9000000       1.097449     1.095000     1.092916
     1.000000       1.118116     1.115000     1.112624
     1.200000       1.159830     1.154000     1.152567
     1.400000       1.201643     1.193000     1.193138
     1.600000       1.243384     1.234000     1.234281
     1.800000       1.285002     1.274000     1.275952
     2.000000       1.315772     1.315000     1.318116
     2.500000       1.421238     1.421000     1.425483
     3.000000       1.532443     1.531000     1.535320
     3.500000       1.646496     1.646000     1.647289
     4.000000       1.765149     1.765000     1.761119
     4.500000       1.887715     1.888000     1.876588
     5.000000       2.015389     2.016000     1.993518
     5.500000       2.148600     2.146000     2.111765
     6.000000       2.280731     2.279000     2.231210
     7.000000       2.547641     2.548000     2.473326
     8.000000       2.809254     2.809000     2.719275
DATA #    31   ERROR %   RIM: 0.1689737 PITZER: 0.5448135
```

Table A.2.14. NaBr

INPUT

0.0009971	3.5769482	10.7169924	0.6732998
0.0019941	3.5769162	8.8918953	0.7896494
0.0049849	3.5768206	6.5796065	0.8700994
0.0099689	3.5766613	5.7644753	0.9395488
0.0199340	3.5763426	4.7639222	0.9703982
0.0498060	3.5753849	4.2694321	1.0014992
0.0995112	3.5737846	4.0113358	1.0090491
0.1986009	3.5705693	3.8184326	1.0120990
0.2972438	3.5673342	3.7366488	1.0132991
0.3954244	3.5640802	3.6901622	1.0135489
0.4931322	3.5608075	3.6593826	1.0149491
0.5903597	3.5575163	3.5553186	1.0149988
0.6871014	3.5542068	3.5349824	1.0159490
0.7833537	3.5508792	3.4965498	1.0175990
0.8791142	3.5475335	3.4703259	1.0173489
0.9743813	3.5441697	3.4537208	1.0182490
1.1634330	3.5373878	3.4291120	1.0212489
1.3505120	3.5305343	3.4096136	1.0234491
1.5356250	3.5236082	3.4012699	1.0256490
1.7187870	3.5166094	4.1304755	1.0367996
1.9000160	3.5095377	3.4015312	1.0301489
2.3447630	3.4915330	3.4116628	1.0340489
2.7778921	3.4730539	3.4449599	1.0414010
3.1997521	3.4540865	3.4631140	1.0523499
3.6106820	3.4346149	3.4891272	1.0560001
4.0109921	3.4146235	3.5138438	1.0687499
4.4009571	3.3940959	3.5338664	1.0714991
4.7808180	3.3730168	3.5502653	1.0865979
5.1507769	3.3513713	3.5650198	1.0876974
5.8616219	3.3063269	3.5948486	1.1169978
6.5344248	3.2588704	3.6277001	1.1366992
7.1696229	3.2089465	3.6621759	1.1568491

OUTPUT

```
1.0000000E-03  0.9879518     0.9880000     0.9884468
2.0000001E-03  0.9839995     0.9840000     0.9841096
4.9999999E-03  0.9760010     0.9760000     0.9762126
9.9999998E-03  0.9690008     0.9690000     0.9683474
2.0000000E-02  0.9589801     0.9590000     0.9588801
5.0000001E-02  0.9452451     0.9450000     0.9448574
0.1000000      0.9348285     0.9350000     0.9349377
0.2000000      0.9277568     0.9290000     0.9285351
0.3000000      0.9273996     0.9280000     0.9280685
0.4000000      0.9298530     0.9290000     0.9300277
0.5000000      0.9341782     0.9320000     0.9333000
0.6000000      0.9357308     0.9360000     0.9374039
0.7000000      0.9411448     0.9410000     0.9420931
0.8000000      0.9459540     0.9460000     0.9472266
0.9000000      0.9509079     0.9510000     0.9527165
 1.000000     0.9569103     0.9570000     0.9585049
 1.200000     0.9695416     0.9690000     0.9708239
 1.400000     0.9827307     0.9830000     0.9839672
 1.600000     0.9968448     0.9970000     0.9978023
 1.800000      1.103788      1.012000      1.012239
 2.000000      1.027042      1.027000      1.027210
 2.500000      1.067050      1.068000      1.066660
 3.000000      1.112707      1.112000      1.108558
 3.500000      1.156926      1.157000      1.152503
 4.000000      1.203325      1.203000      1.198208
 4.500000      1.250556      1.249000      1.245453
 5.000000      1.296909      1.296000      1.294070
 5.500000      1.341879      1.341000      1.343928
 6.000000      1.385771      1.386000      1.394921
 7.000000      1.470220      1.470000      1.499988
 8.000000      1.549030      1.547000      1.608759
 9.000000      1.619320      1.619000      1.720886
DATA #    32   ERROR %   RIM: 0.3264112  PITZER: 0.5148209
```

Table A.2.15. HCl

INPUT

0.0009971	3.8185010	11.9759130	0.7581494
0.0019941	3.8184044	8.7934561	0.7827494
0.0049850	3.8181140	7.0093827	0.8942992
0.0099692	3.8176301	5.9980412	0.9481992
0.0199352	3.8166621	5.1095700	0.9788989
0.0498140	3.8137572	4.7849145	1.0036991
0.0995467	3.8089139	4.6150546	1.0082991
0.1987607	3.7992210	4.4837122	1.0102991
0.2976317	3.7895205	4.4256878	1.0121990
0.3961532	3.7798138	4.3907990	1.0126488
0.4943208	3.7701013	4.3661375	1.0139490
0.5921311	3.7603846	4.3469019	1.0152990
0.6895816	3.7506638	4.3308988	1.0168991
0.7866707	3.7409399	4.3169851	1.0183989
0.8833970	3.7312133	4.3045068	1.0200491
0.9797593	3.7214849	4.2930617	1.0216988
1.1713910	3.7020249	4.2723160	1.0252991
1.3615650	3.6825640	4.2535014	1.0288491
1.5502830	3.6631062	4.2373691	1.0326489
1.7375500	3.6436553	4.2395492	1.0405493
1.9233741	3.6242146	4.2289729	1.0450491
2.3816741	3.5756800	4.2219605	1.0527991
2.8311651	3.5272789	4.2323947	1.0706511
3.2720301	3.4790554	4.2382851	1.0770512
3.7044661	3.4310501	4.2395320	1.0925509
4.1286702	3.3833008	4.2400541	1.1158509
4.5448370	3.3358436	4.2419777	1.1197501
4.9531522	3.2887135	4.2456775	1.1462510
5.3537951	3.2419436	4.2506499	1.1463509
6.1327000	3.1496193	4.2614346	1.2009521
6.8827038	3.0591393	4.2695012	1.2338508
7.6047249	2.9707830	4.2725892	1.2681512
8.2994423	2.8848505	4.2703657	1.3022507

OUTPUT

```
 1.0000000E-03  0.9889680      0.9890000      0.9885415
 2.0000001E-03  0.9839990      0.9840000      0.9842982
 4.9999999E-03  0.9770008      0.9770000      0.9766804
 9.9999998E-03  0.9700024      0.9700000      0.9692755
 2.0000000E-02  0.9609758      0.9610000      0.9607160
 5.0000001E-02  0.9501115      0.9500000      0.9493588
 0.1000000      0.9440861      0.9440000      0.9437723
 0.2000000      0.9451118      0.9460000      0.9458200
 0.3000000      0.9524775      0.9530000      0.9536409
 0.4000000      0.9621549      0.9630000      0.9637888
 0.5000000      0.9735640      0.9740000      0.9751819
 0.6000000      0.9858634      0.9860000      0.9873571
 0.7000000      0.9987808      0.9980000       1.000079
 0.8000000       1.012090       1.011000       1.013216
 0.9000000       1.025693       1.025000       1.026683
  1.000000      1.039504       1.038000       1.040429
  1.200000      1.067560       1.067000       1.068612
  1.400000      1.095880       1.095000       1.097564
  1.600000      1.124512       1.125000       1.127164
  1.800000      1.156507       1.155000       1.157327
  2.000000      1.186081       1.186000       1.187991
  2.500000      1.263917       1.265000       1.266540
  3.000000      1.347545       1.346000       1.347364
  3.500000      1.431302       1.429000       1.430072
  4.000000      1.514737       1.513000       1.514376
  4.500000      1.597004       1.597000       1.600058
  5.000000      1.680144       1.682000       1.686950
  5.500000      1.762848       1.766000       1.774916
  6.000000      1.847062       1.849000       1.863850
  7.000000      2.011691       2.011000       2.044291
  8.000000      2.169229       2.165000       2.227750
  9.000000      2.312757       2.309000       2.413870
  10.00000      2.436656       2.441000       2.602400
DATA #    33   ERROR %   RIM: 0.0749945  PITZER: 0.6180441
```

Table A.2.16. $NaNO_3$

INPUT

0.0009970	3.5769482	10.8819323	0.6860997
0.0019938	3.5769162	9.0314360	0.7989491
0.0049829	3.5768206	6.2509594	0.8473987
0.0099611	3.5766616	5.2880225	0.9167984
0.0199028	3.5763435	4.3724298	0.9563480
0.0496124	3.5753911	3.7030706	0.9946977
0.0987435	3.5738094	3.3639338	1.0077481
0.1955747	3.5706680	3.1301754	1.0131481
0.2905236	3.5675557	3.0353394	1.0153481
0.3836237	3.5644732	2.9831200	1.0163481
0.4749096	3.5614204	2.9496746	1.0166481
0.5644164	3.5583980	2.9261823	1.0179479
0.6521793	3.5554056	2.9086120	1.0178478
0.7382331	3.5524435	2.8948581	1.0183978
0.8226126	3.5495119	2.8837123	1.0196979
0.9053522	3.5466106	2.8744309	1.0203979
1.0660460	3.5408993	2.8616788	1.0217481
1.2205790	3.5353096	2.8744762	1.0218481
1.3692060	3.5298412	2.9003839	1.0240980
1.5121750	3.5244937	2.9384048	1.0252479
1.6497231	3.5192659	2.9796140	1.0249981
1.9713629	3.5067122	3.0787866	1.0300479
2.2638850	3.4948781	3.1768286	1.0315480
2.5303359	3.4837341	3.2685759	1.0355481
2.7734909	3.4732468	3.3690174	1.0429482
2.9958811	3.4633772	3.4629207	1.0446470
3.1998241	3.4540832	3.5528541	1.0539449
3.3874481	3.4453194	3.6395602	1.0563461
3.5607109	3.4370379	3.7269697	1.0618949
3.8712630	3.4217215	3.9272754	1.0843009
4.1444530	3.4077194	4.1769428	1.1110018
4.3915491	3.3946042	4.4633503	1.1316018
4.6224489	3.3819408	4.7652621	1.1850518
4.8081188	3.3714583	5.0167699	1.2541507

OUTPUT

```
 1.0000000E-03  0.9880010      0.9880000      0.9882617
 2.0000001E-03  0.9840003      0.9840000      0.9837443
 4.9999999E-03  0.9750011      0.9750000      0.9753225
 9.9999998E-03  0.9669989      0.9670000      0.9666170
 2.0000000E-02  0.9559873      0.9560000      0.9555500
 5.0000001E-02  0.9379920      0.9380000      0.9371051
 0.1000000      0.9212375      0.9210000      0.9205135
 0.2000000      0.9023345      0.9030000      0.9021177
 0.3000000      0.8908880      0.8910000      0.8906373
 0.4000000      0.8824850      0.8830000      0.8821460
 0.5000000      0.8757155      0.8760000      0.8753269
 0.6000000      0.8702377      0.8700000      0.8695800
 0.7000000      0.8650159      0.8640000      0.8645833
 0.8000000      0.8605632      0.8600000      0.8601443
 0.9000000      0.8563928      0.8560000      0.8561391
  1.000000     0.8524390      0.8520000      0.8524830
  1.200000     0.8449411      0.8450000      0.8459913
  1.400000     0.8386940      0.8390000      0.8403432
  1.600000     0.8337722      0.8340000      0.8353397
  1.800000     0.8297732      0.8300000      0.8308483
  2.000000     0.8256682      0.8260000      0.8267745
  2.500000     0.8177503      0.8170000      0.8179934
  3.000000     0.8096051      0.8100000      0.8106726
  3.500000     0.8024498      0.8030000      0.8043569
  4.000000     0.7972747      0.7980000      0.7987427
  4.500000     0.7924935      0.7930000      0.7936144
  5.000000     0.7892656      0.7890000      0.7888129
  5.500000     0.7876023      0.7870000      0.7842171
  6.000000     0.7884779      0.7890000      0.7797328
  7.000000     0.8068057      0.8080000      0.7708157
  8.000000     0.8603672      0.8600000      0.7616221
  9.000000     0.9652063      0.9650000      0.7518578
  10.00000      1.144181       1.146000      0.7413179
  10.83000      1.374476       1.374000      0.7318750
DATA #    34  ERROR %  RIM: 0.0469702 PITZER: 3.6395054
```

Table A.2.17. NaI

INPUT

0.0009970	3.5769482	12.1371202	0.7670496
0.0019940	3.5769162	8.9203711	0.7915494
0.0049845	3.5768206	7.1828680	0.9028991
0.0099673	3.5766613	5.8209124	0.9418988
0.0199276	3.5763428	5.1099629	0.9792984
0.0497667	3.5753863	4.6828675	1.0034990
0.0993585	3.5737896	4.5013285	1.0089492
0.1980150	3.5705884	4.3888011	1.0112991
0.2959689	3.5673761	4.3431044	1.0121489
0.3932226	3.5641537	4.2467136	1.0139489
0.4897794	3.5609205	4.2293911	1.0142491
0.5856439	3.5576768	4.1887388	1.0154991
0.6808206	3.5544229	4.1476593	1.0176991
0.7753145	3.5511584	4.1258850	1.0173990
0.8691306	3.5478840	4.1108079	1.0186989
0.9622741	3.5445991	4.0957313	1.0201491
1.1465640	3.5379989	4.0644164	1.0241989
1.3282270	3.5313582	4.0407991	1.0274489
1.5073040	3.5246773	4.0316124	1.0306489
1.6838380	3.5179563	4.0232673	1.0341991
1.8578700	3.5111954	4.0058866	1.0378491
2.2822649	3.4941206	4.0202765	1.0441988
2.6918960	3.4768007	4.0301185	1.0530990
3.0873661	3.4592376	4.0360689	1.0692492
3.4692640	3.4414318	4.0488958	1.0745469
3.8381679	3.4233835	4.0686712	1.0838461
4.1946492	3.4050906	4.0918970	1.1045959
4.5392699	3.3865492	4.1153440	1.1084949
4.8725920	3.3677537	4.1369429	1.1335940
5.5075660	3.3293631	4.1710858	1.1643021
6.1040182	3.2898133	4.1924715	1.1715519
6.6663909	3.2489376	4.2030921	1.2159522
7.1991439	3.2064898	4.2055421	1.2142512
7.7067528	3.1621220	4.2020359	1.2648512
8.1937227	3.1153548	4.1942344	1.2528008

OUTPUT

```
   1.0000000E-03  0.9890006     0.9890000     0.9885299
   2.0000001E-03  0.9839981     0.9840000     0.9842725
   4.9999999E-03  0.9770008     0.9770000     0.9766049
   9.9999998E-03  0.9689988     0.9690000     0.9691001
   2.0000000E-02  0.9599760     0.9600000     0.9603010
   5.0000001E-02  0.9471286     0.9470000     0.9480406
   0.1000000      0.9386627     0.9390000     0.9406068
   0.2000000      0.9355728     0.9360000     0.9382993
   0.3000000      0.9388851     0.9380000     0.9412866
   0.4000000      0.9429824     0.9430000     0.9463264
   0.5000000      0.9499752     0.9500000     0.9524370
   0.6000000      0.9570289     0.9570000     0.9592132
   0.7000000      0.9642000     0.9640000     0.9664574
   0.8000000      0.9718780     0.9720000     0.9740613
   0.9000000      0.9805741     0.9810000     0.9819608
    1.000000     0.9893752     0.9890000     0.9901145
    1.200000      1.006752      1.007000      1.007080
    1.400000      1.024713      1.025000      1.024812
    1.600000      1.043949      1.044000      1.043221
    1.800000      1.063330      1.063000      1.062243
    2.000000      1.081378      1.083000      1.081830
    2.500000      1.134862      1.134000      1.133018
    3.000000      1.188304      1.187000      1.187003
    3.500000      1.241689      1.242000      1.243422
    4.000000      1.296686      1.298000      1.301995
    4.500000      1.354152      1.356000      1.362503
    5.000000      1.414262      1.415000      1.424771
    5.500000      1.476324      1.474000      1.488661
    6.000000      1.538109      1.535000      1.554059
    7.000000      1.660201      1.656000      1.689031
    8.000000      1.777124      1.775000      1.829130
    9.000000      1.884006      1.890000      1.973972
    10.00000      1.986622      1.996000      2.123285
    11.00000      2.079929      2.088000      2.276873
    12.00000      2.174867      2.164000      2.434594
DATA #    35   ERROR %   RIM:  0.0989389  PITZER:  1.2617799
```

Table A.2.18. LiBr

INPUT

0.0009970	4.4701104	11.8141832	0.7486496
0.0019940	4.4700723	8.5596085	0.7652490
0.0049847	4.4699578	6.7047648	0.8773485
0.0099683	4.4697666	5.6219311	0.9330482
0.0199316	4.4693847	4.6735749	0.9668479
0.0497924	4.4682360	4.2298088	0.9999480
0.0994618	4.4663162	4.0136957	1.0076481
0.1984311	4.4624553	3.8577452	1.0105481
0.2969083	4.4585662	3.7823067	1.0120981
0.3948953	4.4546490	3.7267549	1.0135980
0.4923953	4.4507036	3.6737368	1.0151981
0.5894120	4.4467306	3.6686299	1.0167480
0.6859495	4.4427295	3.6345658	1.0174980
0.7820122	4.4387012	3.6184380	1.0190480
0.8776044	4.4346447	3.6200271	1.0207980
0.9727313	4.4305606	3.6234970	1.0225980
1.1616091	4.4223089	3.5902865	1.0283482
1.3486850	4.4139471	3.5821786	1.0326482
1.5340019	4.4054742	3.6153481	1.0373492
1.7176030	4.3968902	3.5974970	1.0392001
1.8995310	4.3881950	3.5806572	1.0437509
2.3473229	4.3659663	3.5902154	1.0597519
2.7856209	4.3430281	3.6140838	1.0682510
3.2151110	4.3193645	3.6198082	1.0878514
3.6364660	4.2949557	3.6104772	1.0946505
4.0503559	4.2697763	3.5938978	1.1067499
4.4574318	4.2437949	3.5754452	1.1197001
4.8583369	4.2169752	3.5579591	1.1316510
5.2537031	4.1892724	3.5426486	1.1436007
6.0302801	4.1310039	3.5193408	1.1844523
6.7919922	4.0684714	3.5040245	1.1897018
7.5435171	4.0009823	3.4937425	1.2126508
8.2893896	3.9276192	3.4860291	1.2332019
9.0340347	3.8471522	3.4791832	1.2522521
9.7817698	3.7579112	3.4721239	1.2675021
10.5368299	3.6575673	3.4641924	1.3212013
11.3033504	3.5427542	3.4550042	1.2931008
12.0854301	3.4083450	3.4443431	1.3007009
12.8870802	3.2459645	3.4320948	1.2973508

OUTPUT

```
   1.0000000E-03  0.9890221      0.9890000      0.9885014
   2.0000001E-03  0.9840003      0.9840000      0.9842200
   4.9999999E-03  0.9770036      0.9770000      0.9764943
   9.9999998E-03  0.9699959      0.9700000      0.9689231
   2.0000000E-02  0.9610106      0.9610000      0.9600639
   5.0000001E-02  0.9500404      0.9500000      0.9479626
   0.1000000      0.9438000      0.9440000      0.9414327
   0.2000000      0.9443284      0.9440000      0.9422055
   0.3000000      0.9509508      0.9510000      0.9492434
   0.4000000      0.9598998      0.9600000      0.9589352
   0.5000000      0.9697599      0.9700000      0.9701190
   0.6000000      0.9822932      0.9820000      0.9822845
   0.7000000      0.9937828      0.9940000      0.9951671
   0.8000000       1.006729       1.007000       1.008613
   0.9000000       1.021068       1.021000       1.022527
    1.000000       1.035955       1.035000       1.036843
    1.200000       1.063525       1.064000       1.066512
    1.400000       1.093741       1.095000       1.097377
    1.600000       1.130159       1.127000       1.129290
    1.800000       1.160517       1.160000       1.162151
    2.000000       1.191835       1.195000       1.195886
    2.500000       1.281366       1.284000       1.283703
    3.000000       1.379748       1.377000       1.376027
    3.500000       1.479693       1.473000       1.472443
    4.000000       1.578956       1.572000       1.572660
    4.500000       1.677079       1.674000       1.676460
    5.000000       1.776016       1.777000       1.783677
    5.500000       1.876478       1.883000       1.894181
    6.000000       1.979384       1.990000       2.007870
    7.000000       2.193702       2.210000       2.244488
    8.000000       2.423541       2.437000       2.493037
    9.000000       2.664535       2.670000       2.753182
    10.00000       2.913339       2.905000       3.024687
    11.00000       3.163718       3.138000       3.307382
    12.00000       3.406100       3.364000       3.601145
    13.00000       3.621417       3.574000       3.905882
    14.00000       3.808497       3.761000       4.221523
    15.00000       3.925512       3.920000       4.548013
    16.00000       3.948540       4.040000       4.885312
DATA #    39   ERROR %   RIM: 0.3153575 PITZER: 2.2326441
```

Table A.2.19. LiCl

INPUT

0.0009971	4.4701104	10.4927559	0.6544999
0.0019941	4.4700723	8.5468950	0.7642996
0.0049849	4.4699578	6.1682563	0.8405496
0.0099690	4.4697666	5.2322602	0.9130489
0.0199346	4.4693842	4.3810458	0.9558486
0.0498105	4.4682355	3.7479494	0.9944487
0.0995335	4.4663134	3.5789349	1.0068989
0.1987109	4.4624443	3.5174620	1.0108989
0.2975251	4.4585419	3.4997234	1.0128992
0.3959714	4.4546056	3.4901388	1.0142992
0.4940471	4.4506364	3.4833210	1.0157489
0.5917499	4.4466343	3.4064162	1.0168490
0.6890785	4.4425993	3.3804743	1.0194491
0.7860320	4.4385314	3.3509884	1.0202490
0.8826094	4.4344306	3.3369536	1.0219991
0.9788108	4.4302979	3.3232028	1.0252491
1.1700860	4.4219341	3.2874060	1.0276991
1.3598580	4.4134417	3.2504568	1.0335491
1.5481319	4.4048200	3.2199378	1.0360490
1.7349160	4.3960710	3.1966560	1.0426991
1.9202170	4.3871942	3.1789992	1.0448488
2.3770461	4.3644485	3.1483898	1.0557989
2.8248379	4.3409166	3.1249781	1.0670488
3.2637839	4.3166065	3.1576171	1.0786490
3.6940899	4.2915230	3.1503208	1.0902495
4.1159682	4.2656717	3.2217951	1.1019496
4.5296340	4.2390566	3.2142279	1.1215001
4.9353018	4.2116818	3.2133119	1.1345521
5.3331890	4.1835475	3.2354853	1.1470531
6.1064520	4.1249990	3.3013134	1.1594527
6.8510628	4.0633831	3.3429906	1.2007025
7.5685859	3.9986243	3.3554935	1.2239531
8.2604971	3.9305894	3.3543208	1.2440000
8.9281921	3.8590701	3.3530166	1.2625004
9.5729771	3.7837646	3.3591506	1.2489487
10.1960897	3.7042530	3.3752270	1.2976509
10.7986698	3.6199667	3.4005048	1.2757521
11.3818102	3.5301359	3.4326570	1.2896007
11.9465199	3.4337244	3.4689543	1.3055497
12.4937601	3.3293123	3.5069368	1.3169987
13.0244198	3.2149184	3.5446846	1.3259488
13.5393496	3.0876713	3.5808637	1.3305489

OUTPUT

```
 1.0000000E-03  0.9880040      0.9880000      0.9885255
 2.0000001E-03  0.9840007      0.9840000      0.9842656
 4.9999999E-03  0.9760000      0.9760000      0.9765961
 9.9999998E-03  0.9689896      0.9690000      0.9691004
 2.0000000E-02  0.9599574      0.9600000      0.9603496
 5.0000001E-02  0.9471748      0.9470000      0.9483732
 0.1000000      0.9398019      0.9400000      0.9416755
 0.2000000      0.9393156      0.9400000      0.9413663
 0.3000000      0.9455825      0.9460000      0.9467561
 0.4000000      0.9547470      0.9540000      0.9544517
 0.5000000      0.9655458      0.9640000      0.9633976
 0.6000000      0.9739342      0.9740000      0.9731456
 0.7000000      0.9850579      0.9850000      0.9834707
 0.8000000      0.9958987      0.9960000      0.9942461
 0.9000000       1.008098       1.008000       1.005394
  1.000000       1.020480       1.020000       1.016865
  1.200000       1.044570       1.044000       1.040640
  1.400000       1.069038       1.068000       1.065387
  1.600000       1.093458       1.093000       1.090991
  1.800000       1.118885       1.119000       1.117373
  2.000000       1.144370       1.145000       1.144476
  2.500000       1.211242       1.213000       1.215093
  3.000000       1.279059       1.284000       1.289386
  3.500000       1.360835       1.361000       1.366970
  4.000000       1.433727       1.441000       1.447561
  4.500000       1.536435       1.525000       1.530940
  5.000000       1.612716       1.613000       1.616937
  5.500000       1.690466       1.703000       1.705415
  6.000000       1.781104       1.794000       1.796267
  7.000000       1.985174       1.979000       1.984755
  8.000000       2.178133       2.159000       2.181870
  9.000000       2.341894       2.328000       2.387248
  10.00000       2.476626       2.480000       2.600631
  11.00000       2.591044       2.612000       2.821835
  12.00000       2.697319       2.723000       3.050725
  13.00000       2.790150       2.814000       3.287197
  14.00000       2.884246       2.887000       3.531178
  15.00000       2.964470       2.947000       3.782605
  16.00000       3.028820       2.995000       4.041435
  17.00000       3.068908       3.036000       4.307630
  18.00000       3.076946       3.066000       4.581162
  19.00000       3.044519       3.079000       4.862008
DATA #    42   ERROR %   RIM: 0.3073985  PITZER: 6.8005548
```

Table A.2.20. $LiNO_3$

INPUT

0.0009970	4.4701104	10.5077600	0.6556997
0.0019940	4.4700723	8.5677166	0.7658995
0.0049846	4.4699578	6.1958184	0.8426990
0.0099678	4.4697666	5.2777267	0.9156484
0.0199298	4.4693847	4.4429975	0.9584481
0.0497809	4.4682364	3.8195851	0.9954479
0.0994159	4.4663181	3.5758522	1.0068480
0.1982470	4.4624624	3.4400728	1.0114480
0.2964932	4.4585829	3.3904741	1.0132482
0.3941565	4.4546785	3.3636563	1.0141479
0.4912395	4.4507508	3.3461919	1.0162481
0.5877459	4.4467993	3.5006092	1.0171977
0.6836789	4.4428244	3.2456753	1.0189980
0.7790427	4.4388261	3.1976283	1.0207980
0.8738409	4.4348049	3.1773467	1.0237980
0.9680780	4.4307613	3.1562099	1.0244979
1.1548851	4.4226060	3.1080685	1.0284978
1.3394960	4.4143620	3.0606880	1.0325978
1.5219460	4.4060311	3.0181291	1.0384480
1.7022671	4.3976145	2.9807279	1.0429481
1.8804940	4.3891139	2.9478879	1.0450978
2.3171079	4.3675041	2.8813469	1.0587981
2.7413230	4.3454008	2.8307421	1.0700979
3.1536081	4.3228273	2.7908964	1.0771480
3.5544050	4.2998047	2.7586091	1.0916483
3.9441290	4.2763553	2.7318134	1.0976477
4.3231730	4.2525005	2.7091236	1.1064976
4.6919088	4.2282610	2.6895797	1.1228491
5.0506859	4.2036567	2.6740911	1.1319995
5.7396870	4.1534276	2.7529123	1.1395479
6.3926501	4.1019530	2.7612848	1.1546983
7.0118361	4.0493526	2.7708168	1.1681988
7.5993261	3.9957230	2.7875767	1.1914009
8.1570501	3.9411361	2.8100398	1.1891992
8.6868219	3.8856368	2.8364182	1.1957989
9.1903429	3.8292425	2.8652806	1.2210490
9.6692410	3.7719395	2.8954766	1.2113489
10.1250601	3.7136853	2.9260807	1.2159991
10.5592899	3.6544027	2.9563746	1.2437979
10.9733696	3.5939782	2.9858327	1.2260972
11.3686895	3.5322583	3.0140941	1.2535969
11.7466002	3.4690425	3.0409365	1.2323451
12.1084299	3.4040730	3.0662432	1.2598950

OUTPUT

```
1.0000000E-03  0.9880034      0.9880000      0.9884905
2.0000001E-03  0.9840016      0.9840000      0.9841970
4.9999999E-03  0.9759974      0.9760000      0.9764312
9.9999998E-03  0.9690020      0.9690000      0.9687848
2.0000000E-02  0.9599924      0.9600000      0.9597548
5.0000001E-02  0.9470980      0.9470000      0.9470405
0.1000000      0.9386777      0.9390000      0.9392826
0.2000000      0.9358224      0.9360000      0.9371184
0.3000000      0.9395845      0.9400000      0.9407678
0.4000000      0.9461260      0.9460000      0.9467163
0.5000000      0.9544806      0.9530000      0.9538488
0.6000000      0.9712617      0.9610000      0.9616825
0.7000000      0.9699488      0.9700000      0.9699703
0.8000000      0.9777619      0.9780000      0.9785708
0.9000000      0.9872820      0.9870000      0.9873954
 1.000000     0.9963868      0.9970000      0.9963859
 1.200000      1.014622       1.015000       1.014711
 1.400000      1.032479       1.034000       1.033329
 1.600000      1.050663       1.052000       1.052107
 1.800000      1.068154       1.071000       1.070953
 2.000000      1.085597       1.089000       1.089800
 2.500000      1.129104       1.135000       1.136606
 3.000000      1.171419       1.179000       1.182525
 3.500000      1.212412       1.222000       1.227155
 4.000000      1.251972       1.264000       1.270207
 4.500000      1.289294       1.304000       1.311464
 5.000000      1.325027       1.344000       1.350757
 5.500000      1.357987       1.382000       1.387955
 6.000000      1.389376       1.418000       1.422952
 7.000000      1.488849       1.490000       1.486019
 8.000000      1.553611       1.550000       1.539448
 9.000000      1.608980       1.610000       1.582892
 10.00000      1.658192       1.660000       1.616104
 11.00000      1.703188       1.700000       1.638910
 12.00000      1.741819       1.740000       1.651179
 13.00000      1.772220       1.770000       1.652815
 14.00000      1.798701       1.800000       1.643746
 15.00000      1.817585       1.820000       1.623915
 16.00000      1.827199       1.830000       1.593277
 17.00000      1.833424       1.830000       1.551799
 18.00000      1.828972       1.830000       1.499453
 19.00000      1.822168       1.820000       1.436216
 20.00000      1.804738       1.810000       1.362071
DATA #     43   ERROR %   RIM: 0.3130423  PITZER: 3.1690826
```

Table A.2.21. Na_2HPO_4

INPUT

0.0009970	3.5769482	8.7241039	0.8716499
0.0019938	3.5769162	6.9557114	0.9138000
0.0029903	3.5768845	6.1915841	0.9374999
0.0039867	3.5768526	5.7616916	0.9532494
0.0049830	3.5768206	5.4805179	0.9648992
0.0059790	3.5767889	5.2759414	0.9733491
0.0069748	3.5767572	5.1195760	0.9798490
0.0079704	3.5767252	4.9972601	0.9848486
0.0089659	3.5766933	4.9003463	0.9888484
0.0099611	3.5766616	4.8228931	0.9920984
0.0199030	3.5763435	4.3522158	1.0073990
0.0298259	3.5760257	4.0914631	1.0134490
0.0397296	3.5757084	3.9134760	1.0165989
0.0496144	3.5753911	3.7794881	1.0181991
0.0594802	3.5750742	3.6559749	1.0204492
0.0693271	3.5747573	3.5450909	1.0210991
0.0791552	3.5744410	3.4498870	1.0228989
0.0889645	3.5741248	3.3708980	1.0226490
0.0987551	3.5738091	3.3070288	1.0232489
0.1956457	3.5706656	2.6563580	1.0304489
0.2907319	3.5675488	2.2526641	1.0355991
0.3840723	3.5644581	1.9405830	1.0422492
0.4757234	3.5613933	1.7095051	1.0458488
0.5657389	3.5583532	1.4550674	1.0537992
0.6541703	3.5553372	1.2823184	1.0604492
0.7410670	3.5523455	1.1792819	1.0635487
0.8264759	3.5493770	1.0675433	1.0672487
0.9104414	3.5464313	0.9078435	1.0759498

OUTPUT

```
    1.0000000E-03  0.9613039      0.9613000      0.9614833
    2.0000001E-03  0.9474967      0.9475000      0.9477701
    3.0000003E-03  0.9375947      0.9376000      0.9380116
    4.0000002E-03  0.9296898      0.9297000      0.9302570
    5.0000004E-03  0.9231178      0.9231000      0.9237576
    6.0000005E-03  0.9173895      0.9174000      0.9181331
    7.0000002E-03  0.9123027      0.9123000      0.9131600
    8.0000004E-03  0.9077073      0.9077000      0.9086932
    9.0000005E-03  0.9035285      0.9035000      0.9046335
    9.9999998E-03  0.8996947      0.8997000      0.9009089
    2.0000000E-02  0.8720039      0.8720000      0.8743756
    2.9999999E-02  0.8540241      0.8540000      0.8573902
    3.9999999E-02  0.8405319      0.8405000      0.8447233
    5.0000001E-02  0.8296189      0.8297000      0.8345129
    5.9999999E-02  0.8207322      0.8205000      0.8258746
    7.0000000E-02  0.8123776      0.8126000      0.8183203
    7.9999998E-02  0.8056406      0.8055000      0.8115537
    8.9999996E-02  0.7988656      0.7991000      0.8053822
    0.1000000      0.7934535      0.7933000      0.7996749
    0.2000000      0.7491940      0.7504000      0.7557586
    0.3000000      0.7190725      0.7199000      0.7226598
    0.4000000      0.6954712      0.6948000      0.6950678
    0.5000000      0.6743413      0.6731000      0.6715505
    0.6000000      0.6527658      0.6538000      0.6514611
    0.7000000      0.6366504      0.6367000      0.6344044
    0.8000000      0.6248639      0.6213000      0.6200966
    0.9000000      0.6119453      0.6077000      0.6083159
     1.000000     0.5957890      0.5955000      0.5988816
DATA #    28   ERROR %   RIM: 0.0782984 PITZER: 0.3273459
```

Table A.2.22. Na_2SO_4

INPUT

0.0009971	3.5769482	8.3841019	0.8549998
0.0019941	3.5769162	6.5845995	0.8967997
0.0029912	3.5768845	5.8054771	0.9219494
0.0039883	3.5768526	5.3480244	0.9388493
0.0049854	3.5768206	5.0319915	0.9511990
0.0059825	3.5767889	4.8086019	0.9607985
0.0069795	3.5767570	4.6408768	0.9688483
0.0079766	3.5767250	4.5050368	0.9752982
0.0089737	3.5766933	4.3873315	0.9803978
0.0099707	3.5766613	4.2800527	0.9845977
0.0199409	3.5763423	3.7741456	1.0071479
0.0299098	3.5760231	3.5056512	1.0156980
0.0398772	3.5757034	3.3556178	1.0206479
0.0498426	3.5753837	3.2295239	1.0237979
0.0598057	3.5750637	3.1201034	1.0260481
0.0697664	3.5747433	3.0260360	1.0276479
0.0797243	3.5744226	2.9455435	1.0298979
0.0896794	3.5741019	2.8766243	1.0302979
0.0996313	3.5737808	2.8174031	1.0315471
0.1989515	3.5705578	2.3950927	1.0369968
0.2978471	3.5673144	2.0909634	1.0402470
0.3962656	3.5640521	1.8199621	1.0461972
0.4941798	3.5607722	1.6358134	1.0493472
0.5915739	3.5574751	1.5044507	1.0505478
0.6884369	3.5541608	1.3975313	1.0525478
0.7847573	3.5508304	1.2993597	1.0557487
0.8805215	3.5474839	1.2022630	1.0586487
0.9757115	3.5441225	1.1037400	1.0622988
1.2109990	3.5356591	0.8837720	1.0716481

OUTPUT

```
 1.0000000E-03  0.9607971      0.9608000      0.9611658
 2.0000001E-03  0.9465970      0.9466000      0.9471724
 3.0000003E-03  0.9364014      0.9364000      0.9371564
 4.0000002E-03  0.9281850      0.9282000      0.9291614
 5.0000004E-03  0.9212220      0.9212000      0.9224361
 6.0000005E-03  0.9151677      0.9152000      0.9165980
 7.0000002E-03  0.9098626      0.9099000      0.9114221
 8.0000004E-03  0.9050600      0.9050000      0.9067626
 9.0000005E-03  0.9006157      0.9006000      0.9025189
 9.9999998E-03  0.8964583      0.8965000      0.8986185
 2.0000000E-02  0.8672255      0.8672000      0.8706745
 2.9999999E-02  0.8478926      0.8482000      0.8527257
 3.9999999E-02  0.8341445      0.8341000      0.8394009
 5.0000001E-02  0.8229815      0.8229000      0.8287604
 5.9999999E-02  0.8135218      0.8136000      0.8198710
 7.0000000E-02  0.8052995      0.8056000      0.8122104
 7.9999998E-02  0.7986811      0.7986000      0.8054573
 8.9999996E-02  0.7921110      0.7924000      0.7993999
 0.1000000      0.7868839      0.7869000      0.7938921
 0.2000000      0.7506371      0.7494000      0.7547652
 0.3000000      0.7271591      0.7262000      0.7286366
 0.4000000      0.7086356      0.7088000      0.7084221
 0.5000000      0.6944922      0.6945000      0.6919987
 0.6000000      0.6832270      0.6824000      0.6783957
 0.7000000      0.6749342      0.6720000      0.6670520
 0.8000000      0.6683909      0.6629000      0.6575947
 0.9000000      0.6608467      0.6550000      0.6497532
  1.000000     0.6530832      0.6481000      0.6433200
  1.250000     0.6333838      0.6351000      0.6323936
DATA #    29   ERROR %   RIM: 0.1315456 PITZER: 0.4633841
```

Table A.2.23. Na_2CO_3

INPUT

0.0009971	3.5769481	8.6614932	0.8687498
0.0019942	3.5769162	6.8500932	0.9092495
0.0029913	3.5768844	6.0848700	0.9335496
0.0039885	3.5768525	5.6464672	0.9496493
0.0049857	3.5768206	5.3502919	0.9615495
0.0059830	3.5767888	5.1417202	0.9706493
0.0069802	3.5767569	4.9880601	0.9773989
0.0079775	3.5767250	4.8692812	0.9826488
0.0089748	3.5766931	4.7733456	0.9871485
0.0099721	3.5766612	4.6929753	0.9906483
0.0199468	3.5763421	4.2258267	1.0077490
0.0299237	3.5760226	3.9727357	1.0143490
0.0399025	3.5757027	3.8019814	1.0173990
0.0498830	3.5753824	3.6768547	1.0186490
0.0598651	3.5750617	3.5804861	1.0210990
0.0698485	3.5747407	3.5036498	1.0223490
0.0798331	3.5744192	3.4407795	1.0219990
0.0898187	3.5740974	3.3882847	1.0228990
0.0998052	3.5737752	3.3437319	1.0233990
0.1996921	3.5705336	2.7852552	1.0272990
0.2995494	3.5672582	2.4628840	1.0295490
0.3992998	3.5639511	2.1997380	1.0338990
0.4988846	3.5606138	1.9933858	1.0346480
0.5982584	3.5572474	1.8064260	1.0390480
0.6973857	3.5538530	1.6529544	1.0414980
0.7962392	3.5504310	1.5313676	1.0424490
0.8947985	3.5469820	1.4336463	1.0455490
0.9930487	3.5435063	1.3514659	1.0478500
1.2372690	3.5347001	1.1740857	1.0539000
1.4794640	3.5257249	1.0023580	1.0581500

OUTPUT

```
      1.0000000E-03  0.9613029      0.9613000      0.9610735
      2.0000001E-03  0.9473978      0.9474000      0.9470160
      3.0000003E-03  0.9375011      0.9375000      0.9369527
      4.0000002E-03  0.9296049      0.9296000      0.9289235
      5.0000004E-03  0.9229802      0.9230000      0.9221747
      6.0000005E-03  0.9172769      0.9173000      0.9163225
      7.0000002E-03  0.9122078      0.9122000      0.9111405
      8.0000004E-03  0.9076456      0.9076000      0.9064821
      9.0000005E-03  0.9035295      0.9035000      0.9022462
      9.9999998E-03  0.8997189      0.8997000      0.8983597
      2.0000000E-02  0.8725736      0.8725000      0.8708096
      2.9999999E-02  0.8550686      0.8552000      0.8535802
      3.9999999E-02  0.8421071      0.8426000      0.8411924
      5.0000001E-02  0.8319409      0.8326000      0.8316482
      5.9999999E-02  0.8241926      0.8243000      0.8239772
      7.0000000E-02  0.8172997      0.8174000      0.8176312
      7.9999998E-02  0.8116093      0.8113000      0.8122698
      8.9999996E-02  0.8068341      0.8059000      0.8076668
      0.1000000      0.8026511      0.8012000      0.8036646
      0.2000000      0.7682288      0.7692000      0.7809681
      0.3000000      0.7492372      0.7496000      0.7715717
      0.4000000      0.7347512      0.7349000      0.7670482
      0.5000000      0.7222734      0.7230000      0.7647507
      0.6000000      0.7122456      0.7129000      0.7634634
      0.7000000      0.7025710      0.7044000      0.7624998
      0.8000000      0.6949098      0.6971000      0.7614192
      0.9000000      0.6897154      0.6910000      0.7599140
       1.000000     0.6850986      0.6859000      0.7577569
       1.250000     0.6768345      0.6772000      0.7484518
       1.500000     0.6656139      0.6738000      0.7321609
 DATA #    30  ERROR %  RIM:  0.1023893 PITZER:  2.7035532
```

Table A.2.24.$Na_2S_2O_3$

INPUT

0.0009970	3.5769482	8.6887922	0.8699498
0.0019940	3.5769162	6.9208121	0.9123999
0.0029908	3.5768845	6.1603198	0.9361498
0.0039876	3.5768526	5.7183604	0.9520496
0.0049843	3.5768206	5.4246554	0.9635991
0.0059809	3.5767889	5.2212343	0.9719987
0.0069775	3.5767570	5.0731683	0.9786987
0.0079739	3.5767250	4.9595833	0.9840483
0.0089703	3.5766933	4.8682408	0.9885982
0.0099666	3.5766613	4.7918892	0.9918982
0.0199251	3.5763428	4.3491492	1.0073979
0.0298755	3.5760243	4.1110997	1.0131481
0.0398181	3.5757053	3.9522355	1.0157979
0.0497528	3.5753865	3.8370283	1.0180482
0.0596798	3.5750678	3.7491181	1.0192981
0.0695990	3.5747488	3.6795945	1.0199980
0.0795104	3.5744295	3.6231129	1.0201979
0.0894142	3.5741105	3.5762484	1.0214481
0.0993104	3.5737913	3.5366952	1.0209979
0.1978550	3.5705936	3.0282035	1.0247480
0.2956477	3.5673869	2.7438068	1.0240480
0.3926892	3.5641713	2.5070977	1.0252481
0.4889741	3.5609474	2.3461146	1.0272472
0.5844944	3.5577159	2.2151599	1.0265962
0.6792402	3.5544772	2.1065361	1.0272461
0.7732010	3.5512319	2.0188856	1.0289462
0.8663659	3.5479808	1.9507380	1.0292959
0.9587247	3.5447249	1.8998935	1.0282462
1.1860310	3.5365677	1.8312626	1.0290959
1.4081050	3.5283949	1.8108983	1.0277961
1.6248490	3.5202174	1.8437257	1.0267999
1.8362060	3.5120447	1.8712832	1.0279502
2.0421600	3.5038855	1.9682034	1.0253999
2.2427371	3.4957473	2.0806763	1.0251999
2.4380000	3.4876363	2.1929824	1.0280999
2.6280489	3.4795570	2.3075576	1.0279001
2.8130181	3.4715123	2.4273541	1.0334003
2.9930739	3.4635036	2.5520499	1.0379509
3.1684110	3.4555304	2.6791377	1.0404009
3.3392539	3.4475906	2.8055866	1.0474011
3.3742471	3.4459429	2.8315551	1.0535010

OUTPUT

```
   1.0000000E-03  0.9612923      0.9613000      0.9614224
   2.0000001E-03  0.9475064      0.9475000      0.9476683
   3.0000003E-03  0.9376035      0.9376000      0.9378811
   4.0000002E-03  0.9297180      0.9297000      0.9301069
   5.0000004E-03  0.9231161      0.9231000      0.9235957
   6.0000005E-03  0.9173532      0.9174000      0.9179661
   7.0000002E-03  0.9123150      0.9124000      0.9129935
   8.0000004E-03  0.9078037      0.9078000      0.9085326
   9.0000005E-03  0.9037758      0.9037000      0.9044834
   9.9999998E-03  0.8999829      0.8999000      0.9007738
   2.0000000E-02  0.8729076      0.8729000      0.8745741
   2.9999999E-02  0.8555913      0.8557000      0.8581582
   3.9999999E-02  0.8427420      0.8432000      0.8462203
   5.0000001E-02  0.8330008      0.8333000      0.8368568
   5.9999999E-02  0.8250685      0.8252000      0.8291568
   7.0000000E-02  0.8184162      0.8183000      0.8226140
   7.9999998E-02  0.8127187      0.8124000      0.8169184
   8.9999996E-02  0.8084894      0.8072000      0.8118672
   0.1000000      0.8040079      0.8025000      0.8073214
   0.2000000      0.7723230      0.7719000      0.7762561
   0.3000000      0.7535800      0.7540000      0.7566962
   0.4000000      0.7401606      0.7415000      0.7423759
   0.5000000      0.7325873      0.7320000      0.7314914
   0.6000000      0.7245002      0.7247000      0.7232214
   0.7000000      0.7190116      0.7192000      0.7170815
   0.8000000      0.7159297      0.7151000      0.7127399
   0.9000000      0.7130267      0.7123000      0.7099485
    1.000000     0.7101203      0.7107000      0.7085124
    1.250000     0.7114484      0.7110000      0.7098783
    1.500000     0.7164078      0.7166000      0.7169566
    1.750000     0.7273011      0.7269000      0.7285206
    2.000000     0.7384742      0.7410000      0.7437159
    2.250000     0.7559170      0.7586000      0.7619288
    2.500000     0.7784694      0.7793000      0.7827088
    2.750000     0.8035208      0.8030000      0.8057179
    3.000000     0.8296955      0.8295000      0.8306991
    3.250000     0.8587338      0.8590000      0.8574543
    3.500000     0.8922434      0.8918000      0.8858281
    3.750000     0.9284914      0.9282000      0.9156985
    4.000000     0.9690025      0.9688000      0.9469670
    4.052000     0.9782297      0.9778000      0.9536390
DATA #    41   ERROR %   RIM:  0.0608560 PITZER:  0.3953283
```

Table A.2.25. $CuSO_4$

INPUT

```
 9.9718823E-02   5.297991     1.98224    1.243
 0.19937410      5.206170     1.62816    1.2428
 0.29886260      5.113540     1.55623    1.2285
 0.39809820      5.020307     1.53666    1.219
 0.49700670      4.926694     1.53091    1.2148
 0.69358720      4.739329     1.58538    1.201
 0.98459300      4.462658     1.87349    1.175
 1.1755490       4.286040     2.11245    1.160
 1.3637850       4.121109     2.34731    1.149
```

OUTPUT

```
         0.1000000      0.5638291      0.5610000      0.5628874
         0.2000000      0.5164084      0.5150000      0.5165371
         0.3000000      0.4926288      0.4940000      0.4939046
         0.4000000      0.4791579      0.4780000      0.4806161
         0.5000000      0.4715515      0.4690000      0.4724767
         0.7000000      0.4557311      0.4590000      0.4658572
          1.000000      0.4584308      0.4620000      0.4720671
          1.200000      0.4733270      0.4740000      0.4840955
          1.400000      0.4912333      0.4910000      0.5011246
# OF DATA   9   AVG(RIM)=   0.3906521      AVG(PITZER)=    1.089744
```

Table A.2.26. $MgSO_4$

INPUT

```
9.9532545E-02  5.26    3.0    1.171
0.1988325      5.215   2.5    1.171
0.2979709      5.169   2.2    1.174
0.3969678      5.123   2.08   1.171
0.4958207      5.076   2.0    1.171
0.6930248      4.98    1.92   1.160
0.9871823      4.836   1.97   1.158
1.181847       4.738   2.17   1.152
1.375100       4.640   2.29   1.145
1.566758       4.541   2.46   1.13812
1.756676       4.441   2.654  1.129
1.944761       4.342   2.85   1.129
2.130967       4.242   3.05   1.1215
2.315301       4.143   3.25   1.125
2.497819       4.045   3.44   1.125
2.678628       3.948   3.63   1.1247
2.857885       3.85    3.82   1.131
```

OUTPUT

```
        0.1000000       0.6077805       0.6060000       0.5960175
        0.2000000       0.5628056       0.5620000       0.5614644
        0.3000000       0.5388190       0.5400000       0.5446813
        0.4000000       0.5269344       0.5290000       0.5342613
        0.5000000       0.5231882       0.5220000       0.5274649
        0.7000000       0.5088531       0.5180000       0.5217282
         1.000000       0.5229944       0.5260000       0.5292881
         1.200000       0.5542232       0.5430000       0.5437405
         1.400000       0.5727508       0.5670000       0.5648916
         1.600000       0.5998541       0.5970000       0.5921258
         1.800000       0.6294151       0.6300000       0.6249036
         2.000000       0.6719040       0.6660000       0.6627576
         2.200000       0.7068783       0.7070000       0.7052849
         2.400000       0.7577631       0.7550000       0.7521412
         2.600000       0.8053608       0.8070000       0.8030305
         2.800000       0.8606779       0.8630000       0.8577000
         3.000000       0.9230776       0.9240000       0.9159325
# OF DATA 17   AVG(RIM)=   0.5355862       AVG(PITZER)=   0.6598032
```

Table A.2.27. $ZnSO_4$

INPUT

```
9.8448284E-02   5.9725605   2.0906949   1.1865
0.1943333       5.9435631   1.4482375   1.2022
0.2876334       5.9153866   1.2402832   1.2026
0.3783559       5.8880564   1.1623485   1.1991
0.4665261       5.8615899   1.1317066   1.1975
0.6353801       5.8112708   1.1162298   1.1940
0.8708766       5.7422381   1.1397383   1.1964
1.016950        5.7003190   1.3621059   1.1861
1.155188        5.6614408   1.6103643   1.179
1.286476        5.6253464   1.8406332   1.1740
1.411787        5.5917504   2.0468246   1.172
1.532165        5.5603539   2.2316828   1.17
1.648720        5.5308550   2.4795423   1.1686
1.762619        5.5029597   2.6560908   1.1695
1.875079        5.4763917   2.7788658   1.1728
 1.987362       5.4509013   2.8661467   1.1728
2.100771        5.4262756   2.9266201   1.182
2.216643        5.4023500   2.9643099   1.183
2.336348        5.3790196   2.9803157   1.189
2.461287        5.3562547   2.9733172   1.196
```

OUTPUT

```
  0.1000000      0.5929157      0.5900000      0.5746945
  0.2000000      0.5333449      0.5330000      0.5301232
  0.3000000      0.5075737      0.5060000      0.5074401
  0.4000000      0.4927066      0.4920000      0.4931479
  0.5000000      0.4856314      0.4830000      0.4836559
  0.7000000      0.4740539      0.4740000      0.4744826
   1.000000     0.4693473      0.4790000      0.4792155
   1.200000     0.4860435      0.4900000      0.4924853
   1.400000     0.5115426      0.5080000      0.5127457
   1.600000     0.5386709      0.5330000      0.5392893
   1.800000     0.5674494      0.5660000      0.5715390
   2.000000     0.5987399      0.6020000      0.6090159
   2.200000     0.6469779      0.6430000      0.6513203
   2.400000     0.6946408      0.6900000      0.6981163
   2.600000     0.7437591      0.7440000      0.7491202
   2.800000     0.7978587      0.8030000      0.8040918
   3.000000     0.8598409      0.8630000      0.8628265
   3.200000     0.9291662      0.9300000      0.9251497
   3.400000      1.008577      0.9980000      0.9909114
   3.600000      1.095030       1.073000       1.059983
DATA #    20  ERROR %  RIM: 0.6241877 PITZER: 0.7229677
```

Table A.2.28. $MnSO_4$

INPUT

9.9679433E-02	4.818083	2.998818	1.196000
0.1992833	4.772834	2.489896	1.201900
0.2987571	4.727048	2.276998	1.196750
0.3980420	4.680749	2.159009	1.189699
0.4970835	4.6339612	2.0837841	1.1848488
0.6942599	4.5389900	1.9931340	1.1815499
0.9873350	4.3932199	2.0475791	1.1664988
1.180819	4.293859	2.141237	1.157650
1.372895	4.192669	2.297562	1.147050
1.5638120	4.0894918	2.4805851	1.1374500
1.7539480	3.9840910	2.6678560	1.1314498
1.9438010	3.8761580	2.8486900	1.1221497
2.133972	3.765326	3.019019	1.118900
2.325165	3.651192	3.177947	1.116950
2.518172	3.533354	3.293210	1.120350
2.713870	3.411479	3.463608	1.118050
2.9132090	3.2854340	3.6045780	1.1261498
3.117213	3.155502	3.723460	1.128500
3.326966	3.022774	3.824268	1.139650
3.543613	2.889802	3.909062	1.151850
3.768352	2.761635	3.978576	1.160850
4.0024328	2.6471770	4.0325251	1.1727998
4.2471509	2.5601950	4.0697541	1.1765997

OUTPUT

0.1000000	0.5877089	0.5870000	0.5808574
0.2000000	0.5413668	0.5380000	0.5366003
0.3000000	0.5170035	0.5160000	0.5145957
0.4000000	0.4998455	0.5010000	0.5004664
0.5000000	0.4883711	0.4900000	0.4907036
0.7000000	0.4784047	0.4760000	0.4799840
1.000000	0.4748308	0.4760000	0.4804141
1.200000	0.4828419	0.4860000	0.4896716
1.400000	0.5006191	0.5040000	0.5050617
1.600000	0.5264957	0.5270000	0.5258963
1.800000	0.5561081	0.5560000	0.5516062
2.000000	0.5836740	0.5880000	0.5817149
2.200000	0.6204672	0.6200000	0.6158221
2.400000	0.6575953	0.6570000	0.6535900
2.600000	0.6890033	0.6960000	0.6947325
2.800000	0.7369364	0.7380000	0.7390067
3.000000	0.7862164	0.7840000	0.7862052
3.200000	0.8364082	0.8340000	0.8361509
3.400000	0.8838408	0.8870000	0.8886915
3.600000	0.9398224	0.9400000	0.9436959
3.800000	0.9904578	0.9950000	1.001051
4.000000	1.050202	1.053000	1.060658
4.200000	1.119535	1.112000	1.122432

DATA # 23 ERROR % RIM: 0.3516464 PITZER: 0.5015548