

Improved apparatus and procedures for isopiestic studies at elevated temperatures

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A significantly improved apparatus for the isopiestic measurement of thermodynamic activities at elevated temperatures is described. Details of the new design and of an analysis of the propagation of the experimental errors are presented. The apparatus was tested by measurements of calcium chloride against sodium chloride at 353.15 K. Accuracies of better than 0.1% in the osmotic coefficient are routinely achieved. Data are also given for the osmotic coefficient of aqueous sodium hydroxide solutions at 353.15 K as a function of molality (up to 13 mol/kg), measured with respect to both sodium chloride and calcium chloride solutions as reference electrolytes. © 1997 American Institute of Physics. [S0034-6748(97)03106-7]

I. INTRODUCTION

The isopiestic equilibration method, in which solutions of nonvolatile solutes are brought to equilibrium by the transfer of solvent through the vapor phase, is currently regarded as the most convenient and reliable method for the determination of solvent activities of electrolyte solutions. Although the first experiments of this kind were described by Bousfield,¹ the technique was perfected and extensively applied to aqueous electrolyte solutions by Robinson and Stokes, as described in their well-known monograph,² and many other papers cited therein. The main attractions of isopiestic experiments are that the equilibrium molalities of the solutions can be determined accurately from the initial molalities and the mass changes alone and that the results are insensitive to minor impurities, such as dissolved gases (in contrast to direct vapor pressure measurements).

The experimental aspects of the isopiestic method, which are discussed in detail by Rard and Platford,^{3(a)} are considerably more involved than might be supposed, given the simplicity of the operating principle. Four particularly important prerequisites for successful application of the technique can be identified. These are

- (a) the availability of accurate direct measurements of solvent activity as a function of composition, for at least one of the equilibrated solutions (the reference electrolyte);
- (b) intimate thermal contact between the equilibrating solutions;
- (c) allowance of sufficient time to reach equilibrium: several days or weeks, depending on the concentrations; and
- (d) precise thermal control and stability (ideally to within 10 mK).³

Isopiestic experiments at elevated temperatures are considerably more difficult than those made under nearly ambient conditions (where most published isopiestic data have

been obtained). Apart from the obvious challenge of maintaining a high-temperature thermostat over extended periods with the appropriate stability, a specific difficulty arises from the difference between the equilibration temperature and the ambient laboratory temperature. This means that the cups containing the solutions must either be weighed *in situ* at the equilibration temperature, or sealed at the equilibration temperature and weighed at room temperature. Both these methods have been used in published designs of high-temperature isopiestic apparatus. Thus, at the Oak Ridge National Laboratory, an apparatus has been developed,^{3(b),3(c)} (which is also described by Rard and Platford^{3(a)}) incorporating a balance so that the weights of the cups containing the solutions are monitored *in situ*. In this way, the equilibrium composition of the system is determined without interrupting the experiment. This apparatus is capable of operating at temperatures between 110 and 250 °C. On the other hand, Grjotheim *et al.*⁴ have described a more traditional apparatus, designed to operate at around 100 °C, in which the solution cups are sealed at the equilibration temperature, allowed to cool, and then weighed accurately with appropriate corrections for air displacement. The relative simplicity and low cost of the Grjotheim *et al.* design are attractive, but their mechanism for sealing the cups is not entirely satisfactory, as outlined below.

The primary data utilized in isopiestic experiments are the initial and final weights and the initial molalities of the solutions. Transformation of these data into accurate values of the osmotic coefficient and water activity is a somewhat involved procedure, which involves three main steps. First, all weights must be corrected for air buoyancy. Second, the contribution of the vapor phase to the mass of each sealed cup must be estimated (this correction is negligible near room temperature but becomes critical in high-temperature measurements, where absolute solvent vapor pressures are appreciable). Finally, the errors in the resulting osmotic coefficient data should be calculated.

The present paper describes a significantly improved isopiestic apparatus based on the design of Grjotheim *et al.*⁴ but with a more reliable, robust, and convenient method of cup closure and built from higher-quality materials, intended

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for isopiestic measurements up to about 450 K. The implementation of the corrections identified above is considered in detail, and expressions derived for the uncertainty in the osmotic coefficient that can be expected from typical methods of solution preparation. The operation of the apparatus at 353.15 K and the calculations are tested by measurements of calcium chloride against sodium chloride; the osmotic coefficients of both these electrolytes are accurately known as a function of molality and temperature. Finally, some experimental data for NaOH solutions at 353.15 K are presented. These have been satisfactorily correlated using the Pitzer equation,⁵ as will be reported elsewhere.

II. THE NEW APPARATUS

A. Design concept

The apparatus of Grjotheim *et al.*⁴ is based on conventional isopiestic designs; the cups containing the electrolyte solutions are well seated in a metallic block to promote thermal equilibration, with the whole assembly enclosed in a metal chamber. Their apparatus features a novel method for closure of the isopiestic cups at the equilibration temperature: individual cup lids are pushed downwards by a pressure plate attached to a shaft through a vacuum-tight seal in the top of the chamber. Prior to equilibration, the lids are supported above their respective cups on sets of three pins, these being held up by friction in Teflon sleeves pressed into fine holes bored in the thermal block around each cup.

This method of sealing the cups is not ideal. Supporting the lids on pins is a delicate operation, sensitive to movement, and susceptible to misalignment. Given that the apparatus is being rocked during the experiment, premature cup closure or failure of the cups to seal can easily occur. Both, of course, are ruinous, either through the loss of time-consuming measurements, or worse, if the mishap is not detected.

Conceptually, the main problem is to find a better method of suspending the lids. These must be held above the cups during the equilibration period and then pressed down to seal them. However, they cannot just be attached to the pressure plate because they must remain securely positioned in the cups when the chamber is opened from the top and the pressure plate removed. Arrangements in which the pressure plate is separated from the chamber lid, in order that it be left behind over the cups, are precluded for several reasons. Since the lids must be in their open position when the chamber is sealed but closed when it is unfastened, the cup lids must be accessible from both above and below the pressure plate. There is also the need for highly reproducible alignments of the lids over the cups and the impracticality of repeatedly pushing the pressure plate shaft through its vacuum-tight seal.

Our solution to this problem is a simple one, as illustrated in Fig. 1. A holding plate is introduced between the cup lids and the pressure plate in the design of Grjotheim *et al.* and the cup lids modified by the addition of a welded, shaped pin (shank). The shanks are held firmly in position on the holding plate during the equilibration period by small circlips but are released when the lids are forced downwards

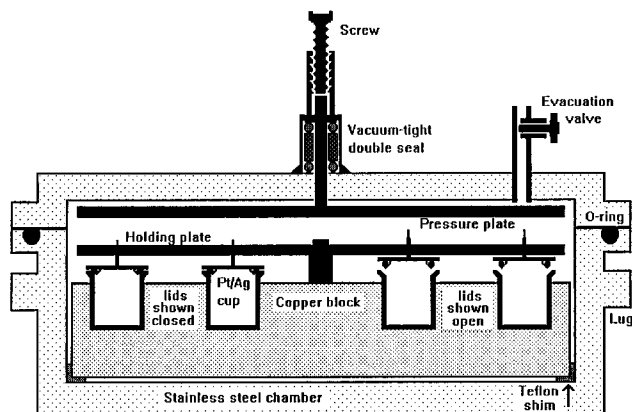


FIG. 1. Improved isopiestic apparatus for operation at elevated temperatures. Not to scale.

to seal the cups. In essence, then, the lids are supported precisely and robustly above the cups by the holding plate and are, thus, able to be depressed by the pressure plate without being attached to it. This design has now been in use for ca. 18 months and very few failures (perhaps 1% or 2%) have been experienced.

B. Construction

Details of the apparatus are shown schematically in Fig. 1. It differs from that of Grjotheim *et al.*⁴ in a number of respects relating to its construction. In particular, we have replaced their materials (mainly aluminum) used for block, chamber, and cups with more suitable metals and we have devised a more effective cup seal. To achieve strict temperature uniformity among the equilibrating cups, the block is made of massive, blowhole-free, high-purity (>99.99%) copper. This was cast oversize from electrical-grade metal under charcoal to minimize contamination by nonmetallic impurities such as oxygen, sulphur, and phosphorus, which are particularly deleterious to thermal conductivity.⁶ Copper is superior to aluminum both because it is chemically less reactive and because of its greater thermal conductivity and heat capacity; nevertheless, the block was gold plated to a thickness of about 5 μm to improve corrosion resistance even further.

As in the design of Grjotheim *et al.*, 12 cups are accommodated symmetrically in holes drilled into the block to a tolerance of 20 μm . Each cup has a diameter of about 27 mm and a depth of 25 mm, about 5 mm of which protrudes above the block. Two sets of cups were fabricated by Precious Metals Engineering Ltd., Welshpool, Western Australia. In addition to one set made entirely of platinum, a lower-cost alternative was initially investigated in which a thin inner wall of platinum (ca. 0.1 mm) was supported on a thicker (ca. 0.9 mm) outer layer of silver. This was achieved by “spinning” the platinum and then the silver over a mandrell, after which the cup exterior could be machined to size and gold plated. This method of cup fabrication has proved satisfactory but is not ideal; several cups have had to be scrapped because of a tendency for the lining to separate, particularly near the cup

lip, and the plating tends to wear away despite being of hard gold. The cup weights are approximately 35 g.

The cup lids are made of high grade (316) stainless steel and are intended to be as light as possible (<10 g). Each lid comprises a thin disk (1 mm) with its stepped shank spot welded on top and with a tapered ring machined below to hold up a gently tensioned Viton O ring (Ludovici). Sealing is accomplished by pressing the lid into the slightly flared cup lip.

The chamber is made of high-quality (316) stainless steel throughout, with both the lid and the lower body machined from single sections of metal. The walls of the chamber are 1 cm thick, both to contain solvent vapor pressures of up to 20 atm and to act as a thermal buffer. In combination with the high thermal conductivity and heat capacity of the copper block, which is held out of contact with the chamber walls and base by Teflon spacers, this creates a very effective thermally buffered system. The chamber seal is made by a large Viton O ring embedded in the lip of the lower section and compressed by 12 equally spaced bolts around the circumference of the lid; although degassing is not required by the technique, it shortens equilibration times,² so a moderate vacuum (<10 kPa) is routinely applied in all our experiments. For rocking purposes, the chamber is cradled in the thermostat bath and attached by a rod with two universal joints to a highly geared dc motor capable of smoothly varying the rate of oscillation from 0 to 20 rpm. Despite the buoyancy from immersion in the thermostatic liquid, the great weight of the chamber (about 15 kg) tends to create problems of wear and tear in various parts of this rocking mechanism, particularly the universal joint, the pivot lugs, and the cradle. It has been found that these can largely be controlled by the use of a hard composite material (polyetheretherketone: PEEK-BG, with Teflon, graphite, and carbon fiber; ERTA, Tielt, Belgium) machined to make a 3 mm thick sleeve for each of the lugs.

III. EXPERIMENT

A. Temperature control

Since maintenance of constant temperature is critical for successful isopiestic equilibration,^{3(a)} a thermostat bath of high precision and reliability is required. Long- and medium-term temperature stability is especially important since short-term fluctuations will be evened out by the thermal buffering of the chamber and block. Accordingly, a very well-insulated bath with large thermal mass has been custom built to thermostat the isopiestic chamber. The bath itself (50 L) and its housing (ca. 1 m³) are made from high-quality (316) stainless steel and are insulated from one another at the few points of contact either by Teflon sheeting (1.5 mm) or, where load bearing, by strips of compressed fibrocement (25 mm). Elsewhere, on the bottom and sides between the bath and the housing, there are two layers of space-filling insulation, the inner of compacted calcium silicate (25 mm) and the outer of rock wool (50 mm). On top, there are two stainless-steel covers separated by an air gap, each of which encases compacted calcium silicate. A fixed panel (30 mm thick \times 250 mm wide) insulated by a slab of Teflon (1 cm) is

located at one end of the bath adjacent to the lids to provide a convenient entry for the temperature-measuring devices.

The bath is heated by an electrical element (1 kW) connected to a (PID) controller of in-house construction. The temperature sensor is a four-wire, platinum-film resistor (1 k Ω , Degussa model GR2141) located in the end of a thin stainless-steel sheath placed centrally and near the bottom of the heating coil. A cooling coil around the outside of the heating element contains circulating thermostated (± 0.1 °C) liquid. This provides a constant heat sink that causes the PID controller to switch the heater on and off at approximately equal intervals. Both the heating and cooling coils are made of stainless steel. Two powerful fan-cooled electric motors suitable for continuous operation are mounted on top of a platform above the fixed access panel; these drive the stirring shafts, each with an impeller just below the surface of the bath liquid and a propeller (50 mm) near the bottom of the bath. The aim is to achieve vigorous and pervasive stirring by having a steady dominant flow downwards over the heater/cooler and lengthwise around the bath, but with a moderate component of turbulence imposed on it by the impellers and by the obstructive effect of the isopiestic chamber.

Lengthy testing indicates that the thermostat bath's performance is eminently satisfactory. All measurements were made in an air-conditioned laboratory (± 1 °C). Typical results at ca. 80 °C show that the maximum variation in temperature over six days was ± 7 mK, with a maximum daily variation of ± 5 mK. More importantly from the viewpoint of isopiestic equilibration, the daily average bath temperature varied by only ± 2 mK over the six days. Temperature changes were monitored by a thermistor calibrated against a quartz-crystal thermometer (Hewlett Packard Model 2804A), which was itself regularly calibrated in a triple-point apparatus.

B. Reference electrolytes

The primary reference electrolyte used in our experiments was sodium chloride of the highest obtainable purity. The osmotic coefficient of this reference electrolyte was determined as a function of temperature and molality by numerical interpolation from the table of critically assessed values presented by Rard and Platford.^{3(a)}

The solubility of NaCl (about 6 mol/kg at 298 K) limits the usefulness of this substance as a reference electrolyte to solutions of water activity 0.78 or above. For solutions with lower water activities, CaCl₂ was used as a reference electrolyte. CaCl₂ is a somewhat surprising choice as an isopiestic reference since, unlike NaCl, it is not readily obtained in high purity and it is very hygroscopic. Clearly, it is selected because of its particularly large osmotic coefficients and correspondingly wide range of accessible water activities. The purity of the salt (CaCl₂·2H₂O), especially with regard to water content, is problematic. The older literature⁷ suggests that there may be some decomposition on heating, but our thermogravimetric analysis indicated that the dehydration process is quite normal and well defined, with at least two temperatures suitable for analytical purposes. An assay of 99.95% for the solute was, thus, achieved by gravimetric

analysis of the stock solution through careful evaporation below 100 °C, followed by dehydration at 200 °C. This is consistent with our isopiestic data, which correspond to an assay of 100.0±0.1%. As a cross check, it was also supported by a titration of Ca content against standard EDTA solution, to the limits of accuracy of the titration (about 0.5%). The osmotic coefficient of this electrolyte was determined as a function of molality and temperature from the extended Pitzer-type correlation constructed by Ananthaswamy and Atkinson⁸ from a wide range of critically assessed data.

IV. THEORETICAL ANALYSIS

Although Rard and Platford^{3(a)} state that the application of buoyancy corrections is desirable, and provide an estimate of the vapor-phase mass contribution that can be expected in a typical experiment, they do not consider explicitly the problem of calculating these corrections and estimating the uncertainties in osmotic-coefficient data. Here, we describe the implementation of the various corrections required, and we analyze the propagation of errors in the initial conditions into the isopiestic molalities and osmotic coefficient data.

A. Error analysis

The reliability of the osmotic coefficient data derived from isopiestic equilibration experiments depends on the accuracy with which the initial and final masses and the initial molalities of the equilibrated solutions are known. Accurate specification of the initial conditions requires application of buoyancy corrections to weights of solution components. With high-temperature measurements, an additional correction needs to be applied for the water vapor above the solutions in the sealed cups. Initially, both the mass and molality of the solution are known but, finally, only the mass of the solution plus vapor is known.

1. Buoyancy corrections

The manner in which buoyancy corrections should be applied has been discussed by Battino and Williamson.⁹ For single-pan mechanical balances, the corrected and apparent weights w_{cor} and w_{app} are related by

$$w_{\text{cor}} = w_{\text{app}} \frac{1 - \rho_a / \rho_w}{1 - \rho_a / \rho_0}, \quad (1)$$

where ρ_a , ρ_0 , and ρ_w are the densities of air, the object, and the balance weights, respectively. For a single-pan electronic balance (which does not contain weights), the formula is

$$w_{\text{cor}} = w_{\text{app}} (1 - \rho_a / \rho_0). \quad (2)$$

Application of these formulae requires the density of the air, which can, in turn, be related to the atmospheric pressure p_a (Torr), temperature T (K), and vapor pressure p_w (Torr) of water as described in the Handbook of Chemistry and Physics.¹⁰

$$\rho_a = 1.2929 \times 10^{-3} \left(\frac{273.13}{T} \right) (p_a - 0.3783 p_w) / 760. \quad (3)$$

This density is in g/mL. The vapor pressure of water is obtained by interpolation from the NBS/NRC Steam Tables

(Haar *et al.*¹¹). It should, however, be noted that the effect of fluctuating atmospheric humidity on weighing errors is considerably less than that of the other variables.

2. Initial molalities and uncertainties

The starting solutions of electrolytes in isopiestic equilibration experiments can be prepared either by mixing and/or dilution of appropriate stock solutions, or from pure solvent and solutes. Consideration of the method of preparation is of importance in the calculation of the uncertainties in the initial molalities. Since our ultimate interest was in determining the water activity in aluminate solutions, which may be formally regarded as mixtures of NaOH and NaAl(OH)₄, we present in this section general formulae for the uncertainties in molalities of a solution of two electrolytes of molar masses M_1 and M_2 , (g/mol), prepared by mixing w_0 g of water and masses w_1 and w_2 of stock solutions with molalities m_{01} and m_{02} . The molality of each solute is

$$m_1 = \frac{1000n_1}{W_0} \quad \text{and} \quad m_2 = \frac{1000n_2}{W_0}, \quad (4a)$$

where W_0 is the *total* mass of solvent in the mixture,

$$W_0 = w_0 + w_1 \frac{1000}{1000 + m_{01}M_1} + w_2 \frac{1000}{1000 + m_{02}M_2},$$

and n_1 and n_2 are the respective numbers of moles of the solutes:

$$n_1 = \frac{m_{01}w_1}{1000 + m_{01}M_1} \quad \text{and} \quad n_2 = \frac{m_{02}w_2}{1000 + m_{02}M_2}.$$

The uncertainty in the molality $m_{1,2}$ of each solute of the resulting solution contains contributions from the uncertainties in w_0 , w_1 , w_2 , m_{01} , and m_{02} , and is given by

$$\begin{aligned} \delta m_{1,2} \approx & \left| \frac{\partial m_{1,2}}{\partial w_0} \right| \delta w_0 + \left| \frac{\partial m_{1,2}}{\partial w_1} \right| \delta w_1 + \left| \frac{\partial m_{1,2}}{\partial w_2} \right| \delta w_2 \\ & + \left| \frac{\partial m_{1,2}}{\partial m_{01}} \right| \delta m_{01} + \left| \frac{\partial m_{1,2}}{\partial m_{02}} \right| \delta m_{02}. \end{aligned} \quad (5a)$$

The errors δw_0 , δw_1 , and δw_2 can be set equal to δw , the nominal balance error in grams. The partial derivatives occurring in this expression are

$$\frac{\partial m_{1,2}}{\partial w_0} = - \frac{1000n_{1,2}}{W_0^2},$$

$$\frac{\partial m_{1,2}}{\partial w_1} = - \frac{1000n_{1,2}}{W_0^2} \frac{\partial W_0}{\partial w_1} + \frac{1000}{W_0} \times \frac{\partial n_{1,2}}{\partial w_1},$$

$$\frac{\partial m_{1,2}}{\partial w_2} = - \frac{1000n_{1,2}}{W_0^2} \frac{\partial W_0}{\partial w_2},$$

$$\frac{\partial m_{1,2}}{\partial m_{01}} = - \frac{1000n_{1,2}}{W_0^2} \frac{\partial W_0}{\partial m_{01}} + \frac{1000}{W_0} \times \frac{\partial n_{1,2}}{\partial m_{01}},$$

$$\frac{\partial m_{1,2}}{\partial m_{02}} = - \frac{1000n_{1,2}}{W_0^2} \frac{\partial W_0}{\partial m_{02}} + \frac{1000}{W_0} \times \frac{\partial n_{1,2}}{\partial m_{02}},$$

and the derivatives of W_0 and the solute mole numbers can be obtained by tedious but straightforward calculus:

$$\frac{\partial n_1}{\partial w_1} = \frac{n_1}{w_1}, \quad \frac{\partial n_1}{\partial w_0} = 0, \quad \frac{\partial n_1}{\partial m_{01}} = n_1 \left(\frac{1}{m_{01}} - \frac{M_1}{m_{01}w_1} \right),$$

$$\frac{\partial n_1}{\partial m_{02}} = 0,$$

$$\frac{\partial n_2}{\partial w_2} = \frac{n_2}{w_2}, \quad \frac{\partial n_2}{\partial w_1} = 0, \quad \frac{\partial n_2}{\partial m_{02}} = n_2 \left(\frac{1}{m_{02}} - \frac{M_2}{m_{02}w_2} \right),$$

$$\frac{\partial n_2}{\partial m_{01}} = 0,$$

$$\frac{\partial W_0}{\partial w_0} = 1, \quad \frac{\partial W_0}{\partial m_{01,02}} = - \frac{1000M_{1,2}w_{1,2}}{(1000 + m_{01,02}M_{1,2})^2},$$

and

$$\frac{\partial W_0}{\partial w_{1,2}} = \frac{1000}{1000 + m_{01,02}M_{1,2}}.$$

The corresponding results for the case of a solution prepared directly from the pure solutes and solvent are much simpler. Representing the mass of solute 1 or 2 as $w_{1,2}$, the corresponding molality is

$$m_{1,2} = \frac{1000w_{1,2}}{M_{1,2}w_0} \quad (4b)$$

from which it follows that the uncertainty in m is

$$\delta m_{1,2} = m_{1,2} \left[\frac{1}{w_1} + \frac{1}{w_0} \right] \delta w. \quad (5b)$$

If one or both of these solid solutes is hydrated, the calculation of the solution molality must consider the mass of water contained in the starting material and the contribution of this water of crystallization to the solute molar mass. Accordingly, it is assumed here that the mass of water contained in the solid solute is included in w_0 , and that the solute molar mass that appears in Eq. (4b) is that of the corresponding anhydrous salt.

Calculation of the equilibrium molality in each sealed cup requires knowledge of the mass change of the contents of that cup. The experimental measurements from which this mass can be obtained are the weight of the sealed cup, the mass of the cup and lid, and the mass of the solution initially present. The determination of this equilibrium mass can be represented by the following scheme:

weight of sealed cup+lid+contents
 \downarrow buoyancy correction

mass of sealed cup + lid + contents, M .

Then

$$M - (\text{mass of cup+lid}) - (\text{mass of initial contents}) \\ - (\text{mass of water in vapor}) = \text{mass change of the solution.}$$

The application of the buoyancy correction to the sealed cup and its contents can be carried out with an average density,

obtained approximately by dividing the weight of the cup by its external volume (as determined, for example, by water displacement).

B. Determination of the isopiestic molalities

The relation connecting the initial and final molalities m' and m'' of an isopiastically equilibrated solution to its initial mass w and mass change Δw can be readily derived by noting that the equilibrium mass of solvent is

$$W = \Delta w + \frac{1000w}{1000 + m'M}, \quad (6)$$

where M is the molar mass of solute, and that the (constant) number of moles of solute is

$$n = \frac{m'w}{1000 + m'M}. \quad (7)$$

Applying the definition of molality [cf., Eq. (4a)] and rearranging, we obtain

$$m'' = \frac{1000n}{W} = 1000 \frac{m'w/(1000 + m'M)}{\Delta w + 1000w/(1000 + m'M)} \\ = \frac{m'}{1 + (1 + m'M/1000)\Delta w/w}. \quad (8)$$

Knowledge of the initial molality and the *relative* mass change of the solution is, therefore, sufficient to calculate the equilibrium molality. In applying these equations, it is necessary to recognize that the above scheme yields a value for the mass of the total contents of the cup, including the water vapor in the head space above the solution at the time of sealing, i.e., at the equilibration temperature. To calculate the equilibrium molality, it is, therefore, necessary to know the liquid-phase mass fraction in each cup. The determination of these mass fractions is an intricate process, which consists of the following steps:

- (i) the equilibrium compositions of the reference cups are determined separately,
- (ii) the equilibrium reference molalities are averaged,
- (iii) the water activity corresponding to this average reference molality is calculated,
- (iv) the vapor density is adjusted iteratively to correspond to the water activity,
- (v) the liquid-phase mass fraction in each cup is determined iteratively,
- (vi) the equilibrium molality of each solution is calculated, and
- (vii) the osmotic coefficient in each solution is calculated.

Steps (i), (iv), and (v) involve iteration loops, which are now discussed in detail.

1. Step (i)

The equilibrium composition of the reference cup at the equilibration temperature T , as expressed by the molality of the liquid and the density of the vapor in equilibrium with it, can be determined from the condition that the fugacities of water in the liquid and vapor phases are equal,

$$f_{w,l} = f_{w,v} \quad (9)$$

If the liquid and vapor phase fugacities are expressed, respectively, in terms of the water activity a_w and the pressure p above the solution, this equation can be written

$$a_w f_{w,l}^0 \exp\left[\frac{\int_{p_s}^p v_w dp}{RT}\right] = \phi p, \quad (10)$$

where ϕ is the fugacity coefficient of the vapor, and v_w is the partial molal volume of water in the solution. The reference fugacity $f_{w,l}^0$ is given by (Prausnitz *et al.*¹²)

$$f_{w,l}^0 = \phi_s p_s \exp\left[\frac{\int_0^p v_s dp}{RT}\right], \quad (11)$$

where v_s is the molar volume of pure water in equilibrium with pure steam, and p_s and ϕ_s are the saturation pressure and fugacity coefficient, respectively. At 353 K, the vapor pressure of water is about 47 kPa, the molar volume v_s of the saturated liquid is $1.8 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$, and $RT \approx 2.9 \text{ kJ mol}^{-1}$. Assuming that v_s is independent of pressure, the argument of the exponential in Eq. (10) is found to be approximately 2.9×10^{-4} . For isopiestic experiments at this temperature, the Poynting (exponential) correction factors in Eqs. (10) and (11) are, therefore, negligibly different from unity, so that the equilibrium condition reduces to

$$a_w = \frac{\phi p}{\phi_s p_s}, \quad (12)$$

which is easily recognized as a generalization of Raoult's law for a solution with only one volatile component. Since for the reference electrolyte, the osmotic coefficient (and, hence, the water activity) is known as a function of solute molality, application of Eq. (12) requires a suitable equation of state for the vapor and saturated vapor. Rard and Platford^{3(a)} suggest that vapor-phase nonideality in systems of this kind can be adequately treated by use of the truncated virial equation

$$z \equiv \frac{pv}{RT} = 1 + \frac{b(T)}{v}, \quad (13)$$

where v is the molar volume of vapor, z is the compressibility factor, and $b(T)$ is the second virial coefficient. The suitability of Eq. (13) for the saturated fluid can be examined by comparing the pressure estimated from it with the tabulated values under the same conditions. For $T=353.15 \text{ K}$ Rard and Platford give a value of $b = -0.567 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}$, while from the Steam Tables,¹¹ $p_s = 47\,373 \text{ Pa}$ and the specific volume is $3.4088 \text{ m}^3 \text{ kg}^{-1}$, which gives $v = 61.410 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}$. Thus,

$$\frac{p_s v}{RT} = \frac{(47\,373 \text{ Pa}) \times (61.410 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1})}{(8.314\,31 \text{ J K}^{-1} \text{ mol}^{-1}) \times (353.15 \text{ K})} = 0.9908,$$

while from the virial equation,

$$1 + \frac{b(T)}{v} = 1 + \frac{(5.67 \times 10^{-4} \text{ m}^3 \text{ mol}^{-1})}{(61.410 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1})} = 0.9908.$$

From this calculation, it can be concluded not only that the equation of state is valid for both the saturated and unsatur-

ated vapor at 353.15 K, but also that the nonideality effects are small. Discrepancies become more pronounced at higher temperatures and higher vapor pressures. For example, at 523.15 K, $b = -1.52 \times 10^{-4} \text{ m}^3 \text{ mol}^{-1}$, the molar volume of the saturated vapor is $9.02 \times 10^{-4} \text{ m}^3 \text{ mol}^{-1}$, and the vapor pressure is 3.98 MPa. The compressibility factor under these conditions is $z = 0.825$, while the right-hand side of Eq. (13) gives 0.831. (Interestingly, the error resulting from the use of Eq. (13) is seen to be much less than that resulting from the assumption of ideal-gas behavior, i.e., $z = 1$.) The fugacity coefficient for a gas obeying the truncated virial Eq. (13) is given by Prausnitz *et al.*^{12,13} as

$$\phi = \frac{1}{z} \exp\left[-\frac{2b(T)}{v}\right]. \quad (14)$$

The amount of solute in the cup is fixed by the initial conditions, and the total mass of material in the cup (distributed between liquid and vapor phases) is also known, in addition to the volume of the cup and the temperature. By Duhem's theorem (as discussed by Smith and Van Ness¹⁴), the equilibrium state of the system is properly determined, and in view of the material balance conditions that apply to each component, it is sufficient to find the fraction x of the mass that is concentrated in the liquid phase. This problem is superficially similar to a "flash" vapor-liquid equilibrium calculation, but differs from it in that only one component is distributed between the two phases. More importantly, since the total *volume* of the system rather than the pressure is specified, it is necessary to know the density of the liquid as a function of molality, since this is required for estimation of the volumes occupied by the liquid and vapor. The steps involved in the iterative determination of x are as follows:

(1) For a given value of x , the liquid molality is given by an appropriate modification of Eq. (8), in which the mass change of the solution is

$$\Delta w = x w_{1r} - w_{0r}. \quad (15)$$

Thus,

$$m_{1r}(x) = \frac{m_{0r}}{1 + (1 + m_{0r} M_r / 1000)(x w_{1r} - w_{0r}) / w_{0r}}, \quad (16)$$

where the subscripts "0r" and "1r" refer to the reference solution, before and after equilibration, respectively.

(2) At this molality, the solution density, ρ_l , and osmotic coefficient ϕ are determined from tabulated data. It is now possible to estimate the vapor density

$$\rho_g = \frac{\text{mass of gas}}{\text{volume of gas}} = \frac{(1-x)w_{1r}}{v_c - w_{1r}x/\rho_l}, \quad (17)$$

where v_c is the internal volume of the sealed cup. The molar volume, the pressure, and compressibility factor of the vapor then follow from Eq. (13), and the fugacity coefficient from Eq. (14). (The fugacity coefficient of the saturated fluid depends only on the temperature.)

(3) The left- and right-hand sides of Eq. (9) are compared.

(4) The value of x is adjusted and steps 1–3 are repeated until Eq. (9) is satisfied to the required degree of approximation.

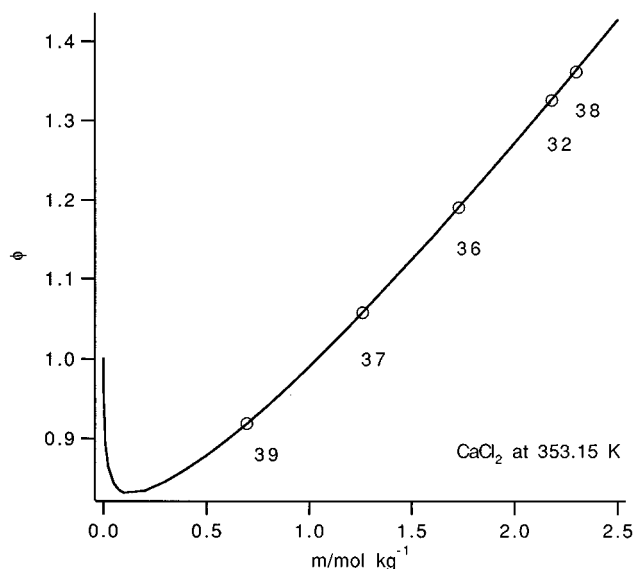


FIG. 2. Osmotic coefficient of $\text{CaCl}_2(\text{aq})$ as a function of concentration at 353.15 K, measured against $\text{NaCl}(\text{aq})$ as the reference electrolyte. Numbers refer to experimental "runs." Solid line calculated from the model of Ananthaswamy and Atkinson (Ref. 8).

The density and osmotic coefficient corresponding to each assumed value of x and the saturated pressure and molar volume are determined by interpolation from published tables. The second virial coefficient is given by an empirical function quoted by Rard and Platford,^{3(a)}

$$b(T) = \frac{27.02}{1 + T/10000} - \frac{13193}{T} - 16.9704 \times (1 - e^{-1500/T})^{5/2} e^{1500/T} \left(\frac{T}{1500}\right)^{1/2}. \quad (18)$$

2. Step (iv)

The replacement of the reference molalities by their average value requires that the vapor density has to be adjusted iteratively so as to satisfy the equilibrium condition expressed by Eq. (9).

3. Step (v)

With the vapor-phase density known, the liquid-phase mass fraction can now be found in each of the equilibrated cups, by an iterative procedure very similar to that used in step (ii).

4. Step (vi)

The equilibrium molalities of solutes 1 and 2 for the i th cup are given by equations similar to Eq. (16):

$$m_{11i}(x_{\text{eq},i}) = \frac{m_{01i}}{1 + [1 + (m_{01i}M_{1i} + m_{02i}M_{2i})/1000]\Delta w_i/w_{0i}}, \quad (19a)$$

$$m_{12i}(x_{\text{eq},i}) = \frac{m_{02i}}{1 + [1 + (m_{01i}M_{1i} + m_{02i}M_{2i})/1000]\Delta w_i/w_{0i}}, \quad (19b)$$

where the mass increment Δw_i for each cup is related to the corresponding equilibrium liquid mass fraction $x_{\text{eq},i}$ by

$$\Delta w_i \equiv x_{\text{eq},i}w_{1i} - w_{0i}. \quad (19c)$$

The uncertainty in these equilibrium molalities contains contributions from the uncertainties in the initial molalities of solutes 1 and 2, the mass change, and the initial mass. These contributions can be estimated from the partial derivatives of the equilibrium molality with respect to each of these quantities, viz.,

$$\frac{\partial m_{1ji}}{\partial m_{01i}} = \frac{m_{1ji}}{m_{01i}} \left[1 - \frac{M_{1i}\Delta w_i}{1000w_{0i}} m_{1ji} \right], \quad (20)$$

$$\frac{\partial m_{1ji}}{\partial m_{02i}} = \frac{m_{1ji}}{m_{02i}} \left[1 - \frac{M_{2i}\Delta w_i}{1000w_{0i}} m_{1ji} \right], \quad (21)$$

$$\frac{\partial m_{1ji}}{\partial \Delta w_i} = - \left(1 + \frac{m_{01i}M_{1i} + m_{02i}M_{2i}}{1000} \right) \frac{1}{w_{0i}} \frac{m_{1ji}^2}{m_{0ji}}, \quad (22)$$

$$\frac{\partial m_{1ji}}{\partial w_{0i}} = \left(1 + \frac{m_{01i}M_{1i} + m_{02i}M_{2i}}{1000} \right) \frac{m_{1ji}^2}{m_{0ji}} \frac{\Delta w_i}{w_{0i}^2}, \quad (23)$$

TABLE I. Initial masses (w_i), molalities (m_i), and mass changes (Δw). Uncertainties in molalities as estimated by Eqs. (4) and (5).

Cup No.	Solute	Initial mass (g)	Molality (mol/kg)	Uncertainty (\pm mol/kg)	Cup+lid mass (g)	Final mass (g)	Mass change (g)
1	NaCl	2.745 04	2.003 66	0.0025	43.796 94	46.538 64	-0.003 34
2	NaOH	2.713 23	1.992 70	0.0028	43.882 04	46.534 74	-0.060 53
3	CaCl_2	2.751 06	1.239 23	0.0019	41.743 38	44.444 14	-0.050 30
4	NaCl	2.747 81	1.999 53	0.0025	42.082 24	44.821 44	-0.008 61
5	NaOH	2.713 25	1.992 70	0.0028	41.456 56	44.111 64	-0.058 17
6	NaCl	2.742 89	2.009 33	0.0025	41.198 73	43.945 94	0.004 32
7	CaCl_2	2.742 79	1.243 39	0.0019	41.585 48	44.303 64	-0.024 63
8	NaOH	2.717 96	1.992 70	0.0028	42.470 47	45.127 84	-0.060 59
9	CaCl_2	2.757 41	1.242 34	0.0019	41.432 27	44.087 04	-0.060 28
10	NaOH	2.715 05	1.992 70	0.0028	43.691 71	46.401 24	-0.021 65
11	CaCl_2	2.731 18	1.245 47	0.0019	43.691 71	46.401 24	-0.021 65

TABLE II. Mass fractions (x), cup contents masses, and molalities (m_{1r}) of reference electrolyte cups.

Cup No.	Mass fraction (x)	Liquid mass (g)	Vapor mass (g)	Total mass (g)	Molality (mol/kg)
1	0.999 01	2.738 99	0.002 71	2.741 70	2.008 60
4	0.999 01	2.736 49	0.002 71	2.739 20	2.008 77
6	0.999 01	2.744 50	0.002 71	2.747 21	2.008 00

where $j = 1$ or 2 . The uncertainty in the equilibrium molality can then be estimated from

$$|\delta m_{1ji}| = \left| \frac{\partial m_{1ji}}{\partial m_{01i}} \right| |\delta m_{01i}| + \left| \frac{\partial m_{1ji}}{\partial m_{02i}} \right| |\delta m_{02i}| + \left| \frac{\partial m_{1ji}}{\partial \Delta w_i} \right| |\delta \Delta w_i| + \left| \frac{\partial m_{1ji}}{\partial w_{0i}} \right| |\delta w_i|. \quad (24)$$

5. Step (vii)

The osmotic coefficients are calculated from the condition of isopiestic equilibrium, as expressed by the equation

$$(v_{1i}m_{11i} + v_{2i}m_{12i})\phi_i(m_{11i}, m_{12i}) = v_r m_r \phi_r(m_{1r}). \quad (25)$$

The uncertainty in the osmotic coefficient $\phi_i(m_{11i}, m_{12i})$ of the solution in each cup i arises from uncertainties in the reference and sample isopiestic molalities. Therefore, assuming that the error involved in interpolation from the table of reference osmotic coefficient data is negligible,

$$\delta \phi_i = \phi_i(m_{11i}, m_{12i}) \left[\frac{\delta m_{1r}}{m_{1r}} + \frac{v_{1i}\delta m_{11i} + v_{2i}\delta m_{12i}}{v_{1i}m_{11i} + v_{2i}m_{12i}} \right]. \quad (26)$$

The calculations described above assume only that at least two cups containing the reference solution are used.

V. RESULTS AND DISCUSSION

In the initial stages of our work, we were particularly concerned with the precision and accuracy of our results and the extent to which these were determined by the design of the apparatus, and our procedures for carrying out the experiments and analyzing the results. In this section, we describe experiments that were carried out to address these issues, and we present some new data for the osmotic coefficient of NaOH at 353.15 K.

TABLE III. Liquid mass fractions (x), cup contents masses, molalities (m_i), and osmotic coefficients (ϕ) at equilibrium with NaCl as reference electrolyte. Uncertainties in molalities and osmotic coefficients estimated from Eqs. (20)–(24), and (26), respectively.

Cup No.	Solute	x	Liquid mass (g)	Vapor mass (g)	Molality (mol/kg)	Uncertainty (\pm mol/kg)	ϕ	Uncertainty (\pm)
2	NaOH	0.998 93	2.649 87	0.002 83	2.044 24	0.000 37	0.978 56	0.000 37
3	CaCl ₂	0.998 96	2.697 94	0.002 82	1.267 06	0.000 25	1.052 53	0.000 42
5	NaOH	0.998 94	2.652 25	0.002 83	2.042 27	0.000 37	0.979 51	0.000 37
7	CaCl ₂	0.998 97	2.715 35	0.002 81	1.257 71	0.000 25	1.060 35	0.000 42
8	NaOH	0.998 94	2.654 54	0.002 83	2.044 20	0.000 37	0.978 59	0.000 37
9	CaCl ₂	0.998 97	2.725 77	0.002 81	1.258 78	0.000 25	1.059 45	0.000 42
10	NaOH	0.998 94	2.651 94	0.002 83	2.044 00	0.000 37	0.978 68	0.000 37
11	CaCl ₂	0.998 96	2.706 72	0.002 81	1.258 30	0.000 25	1.059 85	0.000 42

A. Precision

The first series of experiments was undertaken to determine the achievable precision in the isopiestic molalities. This involved isopiestic equilibration of small quantities (ca. 2 mL) of NaCl solutions at different concentrations with each other at various temperatures. The conclusions from these trialing experiments are as follows:

- The precision obtainable in the isopiestic molalities is routinely $\pm 0.05\%$ and frequently better than $\pm 0.03\%$;
- there are very few “failures” of individual cups and most of these can be attributed to obvious causes, e.g., premature cup closure, insufficient equilibration time or leakage; and
- three or four days is sufficient for equilibration at temperatures $\geq 40^\circ\text{C}$ under most conditions, although longer times than this are required for the more dilute solutions (< 1 mol/kg) or when the initial concentrations are far removed from the final equilibrium values (Rard and Platford^{3(a)} suggest at least 48 h equilibration time).

B. Accuracy

A second set of trialing experiments was designed to examine the accuracy of osmotic coefficients, derived as described in Sec. IV from isopiestic experiments. To this end, we equilibrated solutions of CaCl₂ (~ 0.8 – 2.2 mol/kg) against NaCl. A typical set of results is shown in Fig. 2, where our data are plotted alongside a curve representing critically assessed osmotic coefficient data for CaCl₂ solutions from Ananthaswamy and Atkinson⁸ based on enthalpies of dilution and heat capacities as well as isopiestic and absolute vapor pressure measurements. The excellent agreement here allows us to conclude that our apparatus and procedures are performing satisfactorily.

C. Osmotic coefficient of NaOH at 353.15 K

The normal operation of our apparatus and procedures is best illustrated by considering the results of an experiment in which NaOH solutions were equilibrated simultaneously with NaCl and CaCl₂. The comparison of osmotic coefficients for NaOH obtained by use of either NaCl or CaCl₂ as reference provides a double check that equilibrium has been

TABLE IV. Liquid mass fractions (x), molalities (m_1), and osmotic coefficients (ϕ) at equilibrium with CaCl_2 as reference electrolyte. Uncertainties in molalities and osmotic coefficients estimated from Eqs. (20)–(24) and 26, respectively.

Cup No.	Solute	x	Liquid mass (g)	Vapor mass (g)	Molality (mol/kg)	Uncertainty (\pm mol/kg)	ϕ	Uncertainty \pm
1	NaOH	0.998 98	2.738 89	0.002 81	2.008 68	0.000 33	0.995 37	0.003 65
2	NaOH	0.998 93	2.649 87	0.002 83	2.044 24	0.000 37	0.978 05	0.003 61
4	NaCl	0.998 98	2.736 39	0.002 81	2.008 85	0.000 33	0.995 28	0.003 65
5	NaOH	0.998 94	2.652 25	0.002 83	2.042 27	0.000 37	0.979 00	0.003 61
6	NaCl	0.998 98	2.744 40	0.002 81	2.008 09	0.000 33	0.995 66	0.003 66
8	NaOH	0.998 94	2.654 54	0.002 83	2.044 20	0.000 37	0.978 07	0.003 61
10	NaOH	0.998 94	2.651 94	0.002 83	2.044 00	0.000 37	0.978 68	0.003 70

reached and that the calculations are being performed correctly. The initial masses, molalities, and mass changes of the solutions resulting from isopiestic equilibration for 83.5 h at 353.15 K are given in Table I.

For purposes of illustration, we regard NaCl as the reference electrolyte (cups 1, 4, and 6). The procedures described above enable the composition and amounts of vapor and liquid in each reference cup to be determined [cf. Eqs. (15)–(18)]. These are shown in Table II, from which it is seen that the vapor-phase mass is approximately 2.7 mg, or about 0.1% of the total material in the cups. The concordance of these reference molalities can be examined by application of the Dixon Q statistic;¹⁵ since the corresponding probabilities are less than 0.95, the data are accepted and averaged, and the uncertainty is set equal to the standard deviation. After appropriate adjustment of the vapor density, the contents of the reference electrolyte cups at this average composition can be characterized as follows:

Reference molality	(2.008 46 \pm 0.000 40) mol/kg
Reference osmotic coefficient, ϕ_r	0.996 00
Water activity, a_w	0.930 46
Vapor density ρ_g	0.273 mg cm ⁻³

The values in hand for the vapor density and reference osmotic coefficient can now be used to determine the liquid and vapor masses in the sample cups, which in turn result in the isopiestic molalities [Eqs. (19)–(24)] and osmotic coefficients [Eqs. (25) and (26)]. The resulting data are shown in Table III. If CaCl_2 is assumed to be the reference electrolyte (cups 3, 7, 9, and 11), the osmotic coefficients of NaCl and

NaOH are as shown in Table IV. From Tables III and IV it is seen that the osmotic coefficients for NaOH determined with respect to the two references agree to well within the estimated uncertainties.

The water activities of NaOH solutions at superambient temperatures are required as part of our current investigation of the chemical speciation in synthetic Bayer liquors (concentrated alkaline aluminate solutions). Since few such data appear in the literature, and those that do lack the high precision needed for our purpose, a series of isopiestic experiments of the type just described was carried out to measure water activity in NaOH solutions (ca. 0.5–13 mol/kg) at 353.15 K. Results are summarized in Table V.

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TABLE V. Osmotic coefficient of aqueous NaOH at 353.15 K.

Molality mol/kg	Osmotic coefficient
0.5039	0.9131
1.0458	0.9220
2.0437	0.9786
2.9708	1.0411
5.7110	1.2197
7.1014	1.3239
8.2975	1.4128
9.7839	1.5166
11.609	1.6217
13.168	1.6516

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