

## The prediction of mineral solubilities in natural waters: The Na-K-Mg-Ca-H-Cl-SO<sub>4</sub>-OH-HCO<sub>3</sub>-CO<sub>3</sub>-CO<sub>2</sub>-H<sub>2</sub>O system to high ionic strengths at 25°C

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**Abstract**—The mineral solubility model of HARVIE and WEARE (1980) is extended to the eight component system, Na-K-Mg-Ca-H-Cl-SO<sub>4</sub>-OH-HCO<sub>3</sub>-CO<sub>3</sub>-CO<sub>2</sub>-H<sub>2</sub>O at 25°C to high concentrations. The model is based on the semi-empirical equations of PITZER (1973) and co-workers for the thermodynamics of aqueous electrolyte solutions. The model is parameterized using many of the available isopiestic, electromotive force, and solubility data available for many of the subsystems. The predictive abilities of the model are demonstrated by comparison to experimental data in systems more complex than those used in parameterization. The essential features of a chemical model for aqueous electrolyte solutions and the relationship between pH and the equilibrium properties of a solution are discussed.

### I. INTRODUCTION

GEOCHEMICAL MODELS based on equilibrium thermodynamics have been widely used to interpret field data and to provide theoretical descriptions for the origin and evolution of natural systems. GARRELS and THOMPSON (1962) introduced general equilibrium models to analyze rock-water environments. Their approach has been adopted by many workers and has been successfully applied to a broad range of geochemical systems. The most comprehensive effort to model equilibrium properties has been that of HELGESON (1978) and co-workers. Other aqueous solution models for a large number of components have been developed. These models have been described and compared in a recent review (NORDSTROM *et al.*, 1979; KERRISK, 1981). Because of the inherently complicated nature of concentrated aqueous solutions, these models are limited in their application primarily to the dilute solution range ( $I < .1$ ). Such limitations have been discussed earlier (HARVIE and WEARE, 1980; KERRISK, 1981).

Recently HARVIE and WEARE (1980) (cited hereafter as HW) developed a chemical equilibrium model for calculating mineral solubilities in the Na-K-Mg-Ca-Cl-SO<sub>4</sub>-H<sub>2</sub>O system at 25°C. This model, which was based on the PITZER (1973) equations for aqueous electrolyte solutions, is accurate to high ionic strengths (20 m).

In this article, we extend the HW model to include the carbonate system and acid-base equilibria. This generalized model accurately predicts mineral solubilities in the Na-K-Mg-Ca-H-Cl-SO<sub>4</sub>-OH-HCO<sub>3</sub>-CO<sub>3</sub>-CO<sub>2</sub>-H<sub>2</sub>O system at 25°C to high concentration and variable CO<sub>2</sub> pressure.

In Appendix A, we define the phenomenological equations used for mineral solubility prediction, and discuss several extensions to the equations used by HW. In sections II and III details related to the construction of models for concentrated aqueous solutions are discussed. When necessary, ion complex species are included (*e.g.* HCO<sub>3</sub><sup>-</sup>, HSO<sub>4</sub><sup>-</sup>) within the virial expansion model to describe the observed solution behavior. Guidelines for incorporating these species are discussed in section II. In section III, the approximations in calculating the pH are assessed, and the method for utilizing pH data in the parameterization is discussed.

In section IV, we describe the parameterization of the model. In this section, model calculations are compared to experimental data in numerous systems including seawater. The prediction of data not utilized in the parameterization suggests that mineral solubilities can be calculated to within 10% of the experimental results in concentrated multicomponent systems. For some systems where a large amount of experimental data is available (*e.g.* gypsum) solubility predictions are more accurate.

### II. THE PHENOMENOLOGICAL DESCRIPTION OF AQUEOUS ELECTROLYTE SOLUTIONS—ION ASSOCIATION AND IONIC STRENGTH DEPENDENT VIRIAL COEFFICIENTS

A specific interaction model based on a virial expansion with ionic strength dependent virial coefficients correctly represents the thermodynamic behavior of many mixed electrolyte solutions to high concentration. With this type of model the explicit definition of ion complex species is not normally required. However, the observed concentration dependence of solution properties for certain electrolytes which exhibit strong attractive interactions can only be described with the use of ion complex species (*e.g.* HCO<sub>3</sub><sup>-</sup>). The dilute solution behavior may indicate when complex species are required in a model. We believe that a virial expansion model which includes strongly bound ion complex species is both convenient and sufficiently general to accurately describe the observed behavior of most multicomponent electrolyte solutions to high concentration.

Many aqueous solution models have relied exclusively on

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ion pairing to account for the thermodynamic behavior resulting from the specific interactions among the dissolved ions in solution. In such models ion complexes, such as  $\text{NaSO}_4^-$  or  $\text{NaHCO}_3^0$ , are defined explicitly and the component activities are calculated from the activity coefficients and the equilibrium distributions of mass among the various species. Characteristically, the activity coefficients for all solute species are defined to be universal functions of ionic strength, and therefore, do not depend explicitly on the relative concentrations of the various species in solution. The dependence of the component activities on the solute composition is described totally in terms of the association equilibria and the resulting decrease in the apparent ionic strength. While this model can be accurate in dilute solutions, or over a limited solute concentration range, it cannot be extended to concentrated electrolyte solutions of arbitrary composition. The failure of this ion pairing model stems from the use of activity coefficients which depend only on ionic strength. It is an experimental fact that above the dilute range, the activity coefficients depend on the relative concentrations of the major solutes present in solution. The upper two curves in Fig. 1 illustrate that the mean activity coefficient for HCl,  $\gamma_{\text{HCl}}^{\pm}$ , depends strongly on whether the major solute is HCl or KCl (the  $\gamma_{\text{HCl}}^{\pm 0}$  or  $\gamma_{\text{HCl}}^{\pm \text{tr}}$  curve). Similar plots of  $\gamma_{\text{HCl}}^{\pm}$  measured in other electrolyte solutions (see HARNED and OWEN, 1958, Fig. 14-2-2) also reveal this compositional dependence. Under the reasonable assumption that HCl, KCl, NaCl, etc., are highly dissociated in solution, a model activity coefficient for HCl which depends only on ionic strength cannot explain this behavior. (See HARVIE, 1981 for details concerning the significant problems in fitting the data in Fig. 1 when HCl or KCl are assumed to be strongly associating electrolytes.)

Advances in electrolyte solution theory have suggested new phenomenological approaches which emphasize an excess free energy virial expansion with ionic strength dependent virial coefficients. This form of expansion is obtained from the statistical mechanical treatment of electrolyte solutions given by MAYER (1950), and is incorporated into the semi-empirical approach of PITZER (1973), described in Appendix A. The

success of this approach is illustrated in the following simplified example related to Fig. 1. Neglecting typically less important terms proportional to  $\Phi_{\text{HK}}$ ,  $C_{\text{HCl}}$ ,  $C_{\text{KCl}}$  and  $\psi_{\text{HKCl}}$ , Eqn. (A.3) for  $\gamma_{\text{HCl}}^{\pm}$  and  $\gamma_{\text{KCl}}^{\pm}$  in a HCl-KCl-H<sub>2</sub>O system are simplified to give

$$\ln \gamma_{\text{HCl}}^{\pm} = \ln \gamma_{\text{DH}}(I) + B_{\text{HCl}}(I)m_{\text{H}} + B_{\text{KCl}}(I)m_{\text{K}} + B_{\text{HCl}}(I)m_{\text{Cl}} \quad (1a)$$

$$\ln \gamma_{\text{KCl}}^{\pm} = \ln \gamma_{\text{DH}}(I) + B_{\text{HCl}}(I)m_{\text{H}} + B_{\text{KCl}}(I)m_{\text{K}} + B_{\text{KCl}}(I)m_{\text{Cl}} \quad (1b)$$

In  $\gamma_{\text{DH}}$  represents an extended Debye-Hückel function common to all ions.  $B_{\text{HCl}}$  and  $B_{\text{KCl}}$  are the ionic strength dependent second virial coefficients.

The ionic strength dependent interaction functions,  $B_{\text{HCl}}$  and  $B_{\text{KCl}}$ , may be evaluated from the data in the single electrolyte solutions, HCl-H<sub>2</sub>O and KCl-H<sub>2</sub>O. The following formula, which is obtained from Eqn. (1), can be used to calculate the activity of a trace amount of HCl in a KCl solution

$$\ln \gamma_{\text{HCl}}^{\pm \text{tr}} = \frac{\ln \gamma_{\text{HCl}}^{\pm 0}(I) + \ln \gamma_{\text{KCl}}^{\pm 0}(I)}{2} \quad (2)$$

The superscript zero denotes the experimental mean activity coefficients in single electrolyte solutions (e.g. HCl-H<sub>2</sub>O or KCl-H<sub>2</sub>O). Since no ion association is assumed,  $I$  equals the total concentration of the electrolytes in the respective solutions. Equation (2) gives a relationship between the independently observable values of  $\gamma_{\text{HCl}}^{\pm \text{tr}}$ ,  $\gamma_{\text{HCl}}^{\pm 0}$ , and  $\gamma_{\text{KCl}}^{\pm 0}$  (at the same ionic strength) which is in good agreement with the experimental data (Fig. 1, dashed line).

In the model discussed in this article, our use of ion complex species is dictated by their importance in representing the experimentally determined thermodynamic properties. The virial expansion approach accurately represents the compositional dependence of the thermodynamic properties in most multicomponent electrolyte solutions to high ionic strengths.

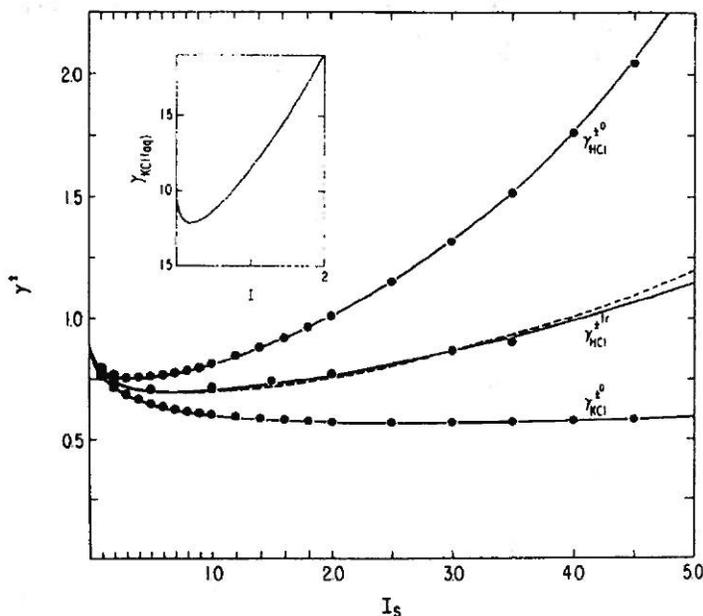


FIG. 1. The mean activity coefficient of HCl in an HCl-H<sub>2</sub>O system, ( $\gamma_{\text{HCl}}^{\pm 0}$ ), the mean activity coefficient of HCl in a KCl-H<sub>2</sub>O system ( $\gamma_{\text{HCl}}^{\pm \text{tr}}$ ), and the mean activity coefficient for KCl in a KCl-H<sub>2</sub>O solution ( $\gamma_{\text{KCl}}^{\pm 0}$ ) versus the stoichiometric ionic strength ( $I_s$ ). The data points are from ROBINSON and STOKES (1968) and HARNED and OWEN (1958). The dashed curve is calculated from the literature data using Eqn. (2). The solid curves are calculated using Eqn. (A.3).

When an accurate description of the data is possible without the addition of ion complex species, this model is preferred due to its computational simplicity. The complete dissociation description appears possible, when the dilute solution activity coefficients are moderately less than or exceed those given by the limiting law in dilute solutions. However, for certain strongly associating or even covalently bound pairs of ions (e.g.,  $H^+$  and  $SO_4^{2-}$  or  $H^+$  and  $CO_3^{2-}$ ), the activity coefficients in dilute solutions are significantly smaller than those predicted by the limiting law assuming complete dissociation (i.e.,  $\ln \gamma^{\pm} \ll -|z^+z^-|A\sqrt{I}$ ). In such cases, the observed solution behavior cannot be conveniently represented by Eqn. (A.3) unless ion complex species are assumed in the model (e.g.,  $HSO_4^-$  and  $HCO_3^-$ ). Even in these cases, it should be emphasized, the virial expansion activity coefficients are necessary for a correct representation of the thermodynamic properties at high concentration.

A hypothetical system,  $A^{+2}B^{-}C^+D^-H_2O$ , was selected for investigating the different thermodynamic behavior predicted using a virial expansion model with or without an  $AB^+$  ion complex. Model solutions were selected evenly spaced between solutions rich in A to solutions rich in B. The salt, CD, was added to many test solutions to increase the ionic strength without increasing the A or B concentration. The  $AB_2$  activity was calculated in each of test solutions using the model with the ion complex. The activities at all points were then used as data to be fit by adjusting parameters in Eqn. (A.3) without the ion complex. A parameter in these calculations is the dissociation constant,  $K_d$ , for the ion complex. As  $K_d$  is increased the agreement between the two models improves. A critical value for  $K_d$  may be defined. For any  $K_d$  above this value the thermodynamic behavior predicted by the model with the ion complex can be fit to within some specified tolerance by the model without the ion pair. This feature is illustrated for dilute single electrolyte solutions in Fig. 2. For  $K_d \geq .05$ , it is always possible to fit the thermodynamic properties given by the model with the ion complex (solid lines) using Eqn. (A.3) and  $\beta_{AB}^0 = \beta_{AB}^1 = C_{AB}^0 = 0$ . For  $K_d$  somewhat below this value, the two models differ significantly, regardless of the parameter value of  $\beta_{AB}^2$  chosen in

Eqn. (A.3). The critical value for  $K_d$  depends on the activity coefficient expression used. When a typical extended Debye-Hückel activity coefficient (fit to  $\gamma_{MgCO_3}$ ),

$$\log \gamma_i = \frac{-z_i^2 A \sqrt{I}}{1 + 1.85 \sqrt{I}} \quad (3)$$

is used to evaluate  $K_d$  from experimental data in dilute solutions, the critical value of  $K_d = .05$  appears to be reliable for 2-1 electrolytes. A similar analysis is possible for 2-2 electrolytes. Comparison of the results of PITZER and MAYORGA (1974) to that of PITZER (1972) suggests that the critical  $K_d$  value is less than .002 for these electrolytes.

Our experience in parameterizing the various subsystems of the complete model (section IV) supports the use of the ion pair model when large negative deviations from the limiting law behavior are observed. In these cases, the dilute solution properties appear to be better represented by the ion complex form. The additional flexibility provided by the virial expansion of the ionic complex activity coefficients is generally required to fit the high concentration behavior. For example, the data in the single electrolyte system,  $H_2SO_4-H_2O$ , cannot be accurately represented using Eqn. (A.3) without an  $HSO_4^-$  complex.  $K_d$  for this species is about .01 (PITZER *et al.*, 1977). The data in mixed electrolyte solutions containing  $H_2SO_4$  also cannot be fit accurately without the use of this complex. In contrast to the  $H_2SO_4-H_2O$  system, the model for  $Ca(OH)_2$  does not require a  $CaOH^+$  ion pair. The activity coefficients for  $Ca(OH)_2$  calculated with Eqn. (A.3) deviate by less than 2% from the  $K_d = .05$  curve depicted in Fig. 2. These calculated activity coefficients for  $Ca(OH)_2$  are in good agreement with precise cmf data in dilute  $Ca(OH)_2-CaCl_2-H_2O$  and  $Ca(OH)_2-KCl-H_2O$  solutions. Moreover, Portlandite solubilities in various mixed electrolyte solutions are accurately represented by the model (Fig. 11). The  $Ca(OH)_2$  model exhibits good predictability in mixed electrolyte solutions to high ionic strengths without the  $CaOH^+$  species.

In parameterizing the model in section IV we have first evaluated virial coefficients assuming no complex species. When, by this analysis, the virial coefficients,  $B_{MX}(I)$ , were

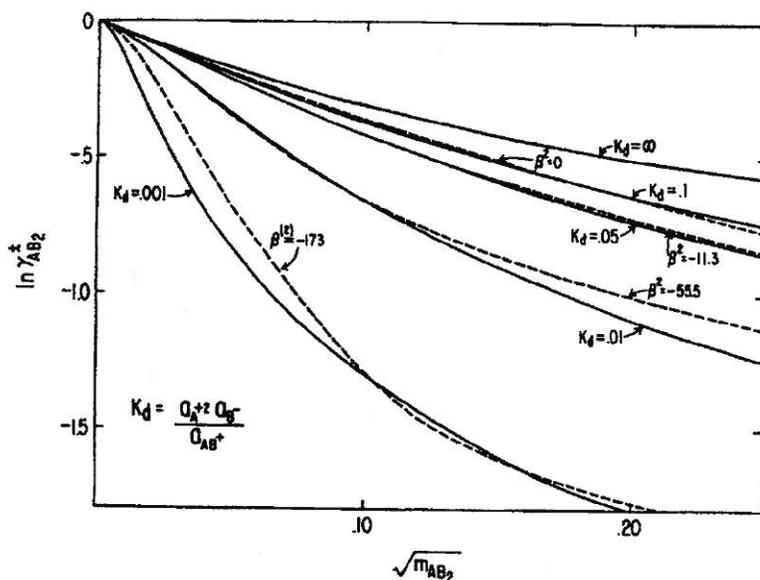


FIG. 2. The calculated dilute solution behavior of the thermodynamic mean activity coefficient for a hypothetical 2-1 electrolyte,  $AB_2$ . A typical ion pair model with activity coefficients given by Eqn. (3) is used to calculate the solid curves for particular values of dissociation constant,  $K_d$ . The dashed curves are calculated using Eqn. (A.3) with  $\beta_{AB}^0 = \beta_{AB}^1 = C_{AB}^0 = 0$ , and particular values for  $\beta_{AB}^2$ . The results are plotted versus the square root of the total  $AB_2$  concentration.

found to be large and negative an ion complex model was defined. There is a strong correlation between negative virial coefficients and the formation of ion complex species (PITZER and SILVESTER, 1976).

### III. THERMODYNAMIC INTERPRETATION OF pH

The only laboratory cell measurements which we have found for a few aqueous electrolyte systems are pH data. pH is one of the most common chemical measurements made in the field. It may also be the only practical cell measurement in some natural waters due to experimental difficulties. Therefore, it is of interest for parameterization and for comparison to field data that a method relating pH to the thermodynamic properties of a solution be defined if possible.

The pH is a semi-quantitative indicator of the acid-base equilibrium properties of aqueous solutions. However, since the emf of a cell with a liquid junction depends on the irreversible as well as the reversible properties of the system, any interpretation of pH in terms of purely reversible (equilibrium) properties is approximate. In this section we attempt to quantitatively assess the approximations involved in equating the operational definition of pH with an equilibrium property of the system.

Consider the following cell which may be used in a pH measurement:



The cell potential,  $E$ , may be calculated by the equation (see Appendix B):

$$E = E_0 - \frac{RT}{F} \ln a_{\text{H}}(\text{X}) - E_{\text{LJ}}(\text{X}). \quad (4)$$

$E_0$  is independent of the composition of solution X and is a constant for fixed hydrogen fugacity.  $E_{\text{LJ}}(\text{X})$  is the liquid junction potential between the KCl-saturated solution and the unknown solution, X. Since absolute single ion activities cannot be measured,  $a_{\text{H}}$  is a conventionally defined hydrogen ion activity in solution X. It is useful to define conventional single ion activities in terms of the measurable mean activities. Such a definition requires that one reference ion activity or ion activity coefficient is specified arbitrarily. The observable emf cannot depend upon the convention used to define the ion activities. However, each of the component terms in Eqn. (4) is a function of this definition. Therefore, a different choice of convention will alter the relative magnitudes of  $E_0$ ,  $E_{\text{LJ}}$  and the term involving  $a_{\text{H}}$ , while the sum of all three terms is invariant. (Appendix B).

Operationally, the pH of solution X is defined by the equation (BATES, 1973):

$$\text{pH}(\text{X}) = \text{pH}(\text{S}) + \frac{(E_{\text{X}} - E_{\text{S}})}{RT(\ln 10)/F}. \quad (5)$$

$E_{\text{X}}$  and  $E_{\text{S}}$  are the measured emf values of the cell of type A with unknown solution X or with standard solution S, respectively. The pH,  $\text{pH}(\text{S})$ , of a standard containing chloride, can be defined in terms of a measurable mean activity, as

$$\text{pH}(\text{S}) = -\log_{10} a_{\text{H}}(\text{S}) = -\log_{10} \left( \frac{a_{\text{HCl}}}{\gamma_{\text{Cl}} m_{\text{Cl}}} \right). \quad (6)$$

$a_{\text{HCl}}$  is the mean activity for hydrochloric acid in solution S determined using a reversible cell (e.g. a cell without a liquid junction).  $\gamma_{\text{Cl}}$  is a specified value for a conventional chloride ion activity coefficient in solution S. The following conventions defining chloride ion activity in a solution of a known ionic strength will be discussed in this and the next section:

$$\ln \gamma_{\text{Cl}} = \ln \gamma_{\text{HCl}}^{\text{H}}(I) \quad \text{Hydrochloric acid convention} \quad (7a)$$

$$\ln \gamma_{\text{Cl}} = \ln \gamma_{\text{NaCl}}^{\text{H}}(I) \quad \text{Sodium chloride convention} \quad (7b)$$

$$\ln \gamma_{\text{Cl}} = \ln \gamma_{\text{KCl}}^{\text{H}}(I) \quad \text{Extended MacInnes convention} \quad (7c)$$

$$\ln \gamma_{\text{Cl}} = -A\sqrt{I}/(1 + 1.5\sqrt{I})$$

$$\text{Extended Bates-Guggenheim convention.} \quad (7d)$$

For the extended MacInnes convention,  $\gamma_{\text{KCl}}^{\text{H}}$  is the mean activity coefficient for KCl in a KCl-H<sub>2</sub>O solution at the same ionic strength as the electrolyte solution in question. Similar definitions are used for the sodium-chloride and hydrochloric acid conventions. The BATES and GUGGENHEIM (1960) convention has been utilized by Bates and co-workers in defining (by interpolation and at low  $I$ ) the pH of N.B.S. standard reference solutions (BATES, 1973). In Eqn. (7d)  $A$  is the Debye-Hückel limiting slope.

In order to relate  $\text{pH}(\text{X})$  to the thermodynamic properties of solution X, some assumption regarding the difference in the liquid junction potentials of the cells with solution X and S must be made. Substituting Eqn. (4) for the cell potentials of Eqn. (5) the following equation can be derived.

$$\begin{aligned} \text{pH}(\text{X}) &= -\log_{10} a_{\text{H}}(\text{X}) - \frac{\Delta E_{\text{LJ}}(\text{X}, \text{S})}{RT(\ln 10)/F} \\ &= -\log_{10} a_{\text{H}}(\text{X}) - \Delta \text{pH}. \end{aligned} \quad (8)$$

$\Delta E_{\text{LJ}}$  represents the difference in the liquid junction potentials between a cell with solution X and a cell with solution S. In deriving Eqn. (8) the terms involving  $\text{pH}(\text{S})$  and  $a_{\text{H}}(\text{S})$  exactly cancel providing that the same ion activity convention was used in Eqn. (4) as was originally used to define the pH of the standard. The value of the term  $\Delta \text{pH}$  reflects this choice of convention. The usual equilibrium interpretation of pH assumes that the irreversible term,  $\Delta E_{\text{LJ}}$ , is negligible; and therefore, that  $\text{pH}(\text{X})$  is approximately equal to  $-\log_{10} a_{\text{H}}(\text{X})$ . Consequently, the magnitude of  $\Delta E_{\text{LJ}}$  is proportional to the error in calculating the thermodynamic property in  $a_{\text{HCl}}(\text{X})$  by this assumption.

The magnitude of  $\Delta E_{\text{LJ}}$  or  $\Delta \text{pH}$  can be determined experimentally by replacing the hydrogen electrode in cell A with an electrode sensitive to the ion whose activity is defined by convention. For the case of chloride the Ag-AgCl electrode may be used in place of the hydrogen electrode. The emf for this modified cell differs from Eqn. (4) in that the conventional activity for chloride appears rather than that for hydrogen and  $E_0$  differs by an additive constant. Since the liquid junction potential does not depend on the electrodes used,  $E_{\text{LJ}}(\text{X})$  is the same for both cells. The difference in the emf between two cells with the AgCl-Ag electrode, one with unknown solution X and the other with standard solution S, can be expressed as:

$$E'_{\text{X}} - E'_{\text{S}} = \frac{RT}{F} \ln \left( \frac{\gamma_{\text{Cl}}(\text{X}) m_{\text{Cl}}(\text{X})}{\gamma_{\text{Cl}}(\text{S}) m_{\text{Cl}}(\text{S})} \right) - \Delta E_{\text{LJ}}(\text{X}, \text{S}). \quad (9)$$

Equation (9) can be used to calculate  $\Delta E_{\text{LJ}}$  with respect to an assumed standard since all other terms can be measured or are defined by convention.

The four curves plotted in Fig. 3 give  $\Delta E_{\text{LJ}}$  in NaCl solutions calculated from the data of SHATKAY and LERMAN (1969). Each curve is defined for a different ion activity convention (also note that the values of  $E_{\text{Cl}}$  reported by SL equal  $-E'$  in Eqn. (9)). In principle any solution could be used as a reference for calculating  $\Delta E_{\text{LJ}}$ . In obtaining Fig. 3, we have defined a .01 m NaCl solution as the standard reference solution. Assuming an ideal glass electrode, this choice of standard is comparable to the  $\Delta E_{\text{LJ}}$  one would expect with standardization using the NBS Scale. (Note that NBS standards contain no chloride and therefore the equation for pH is slightly more complicated than Eqn. (9)). Extrapolation of Eqn. (9) to zero chloride in the standard solution S would provide a consistent definition for  $\Delta E_{\text{LJ}}^{\text{NBS}}$ . In Fig. 3,  $\Delta E_{\text{LJ}}$  is about 3 mv ( $\Delta \text{pH} = .05$ ) using the MacInnes convention for .725 m NaCl solution. Also, using the MacInnes convention,  $\Delta E_{\text{LJ}}$  is computed to be about 3 mv between the NBS standard

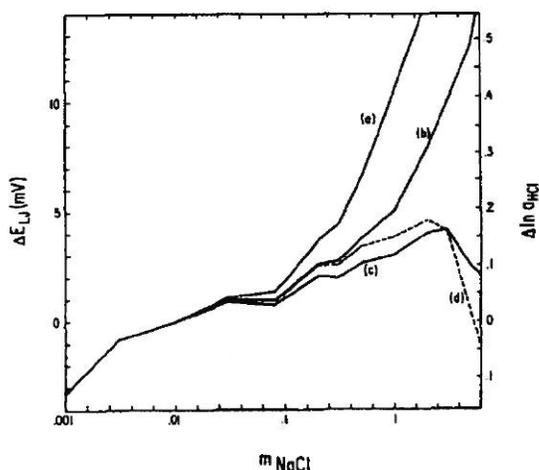


FIG. 3. The value for the liquid junction potential calculated from the data of SHATKAY and LERMAN (1969) using Eqn. (9). Each curve is calculated using one of the ion activity conventions given by Eqn. (7). (Curve a corresponds to convention Eqn. (7a), etc.)

and a .725 m NaCl plus .005 m NaHCO<sub>3</sub> solution (using the data of HAWLEY and PYTKOWICZ, 1973).

Figure 3 emphasizes the conventional nature of the liquid junction. While it has long been recognized that the liquid junction potential between two different solutions cannot be measured (GUGGENHEIM, 1929), once an ion activity convention has been defined the value of the corresponding liquid junction is also defined and measurable by experiment. Conventional ion activities can similarly be measured. From a thermodynamic point of view all ion activity conventions are equivalent and no theoretical value for an ion activity can be verified directly by experiment. That the liquid junction potential is small for a particular convention does not imply that the corresponding  $\gamma_{Cl^-}$  resembles in any way a real ion activity coefficient for the chloride ion. In this article we adopt the MacInnes convention and consistently report ion activities and liquid junction changes with respect to this convention. With a proper choice for  $\omega$ , Eqn. (B.7) in Appendix B can be used to convert Eqn. (A.3) to this convention.

Due to the difficulties associated with the exact interpretation of the pH(X) in terms of the thermodynamic properties of a solution, we utilize reversible cell, isopiestic and solubility data in preference to pH data in the parameterization in section IV. However, pH measurements are the only cell data that we found in certain concentration ranges. In these cases, it is necessary to estimate the change in the liquid junction potential (plus any corrections due to the glass electrode asymmetry potential) using the available data.

To convert pH data into a form which is useful to a thermodynamic model, a constant ionic media assumption often provides a convenient and accurate method to eliminate the  $\Delta pH$  term (see, for example, BATES, 1973 and references therein). Under certain titration conditions, the activity coefficients and  $\Delta pH$  are approximately constant over the entire concentration range resulting from the addition of titrant to solution. Often in such cases, the conventional  $\Delta pH$  can be evaluated from the data in a narrow concentration range of the titration curve. By assuming this  $\Delta pH$  value is constant, the remaining pH data can be corrected to the appropriate ion activity convention and subsequently used to evaluate mean activity coefficients or apparent equilibrium constants.

$\Delta pH$  can often be calculated using the equation,

$$\log_{10} \gamma_H^{NBS} = \log_{10} \gamma_H^M + \Delta pH. \quad (10)$$

$\gamma_H^{NBS}$  is defined by a convention equating  $pH^{NBS}$  to  $-\log_{10}$

$a_H^{NBS}$ , where  $pH^{NBS}$  is determined using the NBS standardization procedure.  $\gamma_H^{NBS}$  can typically be calculated using data on the acid side of a titration curve (see CULBERSON and PYTKOWICZ, 1973 or HANSSON, 1972).  $\gamma_H^M$  is the hydrogen activity coefficient defined within the extended MacInnes convention and may be calculated using  $\gamma_{HCl}^M$  for the same solution. Using the equation,  $\gamma_H^M = \gamma_{HCl}^M / \gamma_{Cl}^M$ , with Eqn. (7c) ( $\gamma_{HCl}^M$  can be measured by experiment or calculated using a suitable model.), reported values of apparent equilibrium constants, such as  $K_1 = a_H^{NBS} m_{HCO_3} / m_{CO_2}$ , can then be corrected to the MacInnes convention once  $\Delta pH$  has been evaluated for the experiment.

#### IV. PARAMETERIZATION AND DATA COMPARISON

In this section, we discuss the extension of our previous solubility model to include acid-base equilibria and the carbonate system at 25°C. Parameters for calculating mineral solubilities in the system Na-K-Ca-Mg-H-Cl-SO<sub>4</sub>-OH-HCO<sub>3</sub>-CO<sub>3</sub>-CO<sub>2</sub>-H<sub>2</sub>O using the model defined in Appendix A are provided in Tables 1, 2, 3 and 4. Since in most cases the model is parameterized from the data in binary and common-ion ternary systems, the following comparisons to data in

Table 1: Single electrolyte solution parameter values.

Cation	Anion	$\beta_{ca}^{(0)}$	$\beta_{ca}^{(1)}$	$\beta_{ca}^{(2)}$	$C_{ca}^{\phi}$
Na	Cl	.0765	.2644	-	.00127
Na	SO <sub>4</sub>	.01958	1.113	-	.00497
Na	HSO <sub>4</sub>	.0454	.398	-	-
Na	OH	.0864	.253	-	.0044
Na	HCO <sub>3</sub>	.0277	.0411	-	-
Na	CO <sub>3</sub>	.039 <sup>a</sup>	1.389	-	.0044
K	Cl	.04835	.2122	-	-.00084
K	SO <sub>4</sub>	.04995	.7793	-	-
K	HSO <sub>4</sub>	-.0003	.1735	-	-
K	OH	.1298	.320	-	.0041
K	HCO <sub>3</sub>	.0296	-.013	-	-.008
K	CO <sub>3</sub>	.1488	1.43	-	-.0015
Ca	Cl	.3159	1.614	-	-.00034
Ca	SO <sub>4</sub>	.20	3.1973	-54.24	-
Ca	HSO <sub>4</sub>	.2145	2.53	-	-
Ca	OH	-.1747	-.2303	-5.72	-
Ca	HCO <sub>3</sub>	.4	2.977	-	-
Ca	CO <sub>3</sub>	-	-	-	-
Mg	Cl	.35235	1.6815	-	.00519
Mg	SO <sub>4</sub>	.2210	3.343	-37.23	.025
Mg	HSO <sub>4</sub>	.4746	1.729	-	-
Mg	OH	-	-	-	-
Mg	HCO <sub>3</sub>	.329	.6072	-	-
Mg	CO <sub>3</sub>	-	-	-	-
MgOH	Cl	-.10	1.658	-	-
MgOH	SO <sub>4</sub>	-	-	-	-
MgOH	HSO <sub>4</sub>	-	-	-	-
MgOH	OH	-	-	-	-
MgOH	HCO <sub>3</sub>	-	-	-	-
MgOH	CO <sub>3</sub>	-	-	-	-
H	Cl	.1775	.2945	-	.0008
H	SO <sub>4</sub>	.0298	-	-	.0438
H	HSO <sub>4</sub>	.2065	.5556	-	-
H	OH	-	-	-	-
H	HCO <sub>3</sub>	-	-	-	-
H	CO <sub>3</sub>	-	-	-	-

For each cation-anion pair there are four model parameters. Up to three  $\beta$  parameters specify the ionic strength dependence of the second virial coefficients,  $\beta_{ca}(I)$ , via Eqs. (A.5). (Dashes indicate zeros.) A constant third virial coefficient is used as a fourth parameter to describe the thermodynamic behavior at high concentrations, when necessary. When Eqs. (A.3) are simplified for single electrolyte solutions, only four model parameters for the particular cation-anion pair remain. When available, data in single electrolyte solutions are used to evaluate these parameters. (See Pitzer and Mayorga (1973, 1974) for details.)

Table 2: Common-ion two electrolyte parameter values.

c'	$\psi_{cc'}^e$	$\psi_{cc'}^{\text{Cl}}$	$\psi_{cc'}^{\text{SO}_4}$	$\psi_{cc'}^{\text{HSO}_4}$	$\psi_{cc'}^{\text{OH}}$	$\psi_{cc'}^{\text{HCO}_3}$	$\psi_{cc'}^{\text{HCO}_2}$
Na	K	-.012	-.0018	-.010	-	-	-.003
Na	Ca	.07	-.007	-.055	-	-	.003
Na	Mg	.07	-.012	-.015	-	-	-
Na	MgOH	-	-	-	-	-	-
Na	H	.036	-.004	-	-.0129	-	-
K	Ca	.032	-.025	-	-	-	-
K	Mg	0.	-.022	-.048	-	-	-
K	MgOH	-	-	-	-	-	-
K	H	.005	-.011	.197	-.0265	-	-
Ca	Mg	.007	-.012	.024	-	-	-
Ca	MgOH	-	-	-	-	-	-
Ca	H	.092	-.015	-	-	-	-
Mg	MgOH	-	.028	-	-	-	-
Mg	H	.10	-.011	-	-.0178	-	-
MgOH	H	-	-	-	-	-	-

a	a'	$\theta_{aa'}$	$\psi_{aa'}^{\text{Na}}$	$\psi_{aa'}^{\text{K}}$	$\psi_{aa'}^{\text{Ca}}$	$\psi_{aa'}^{\text{Mg}}$	$\psi_{aa'}^{\text{MgOH}}$	$\psi_{aa'}^{\text{H}}$
Cl	SO <sub>4</sub>	.02	.0014	-	-.018	-.004	-	-
Cl	HSO <sub>4</sub>	-.006	-.006	-	-	-	-	-.013
Cl	OH	-.050	-.006	-.006	-.025	-	-	-
Cl	HCO <sub>3</sub>	.03	-.015	-	-	-.096	-	-
Cl	CO <sub>2</sub>	-.02	.0085	-.004	-	-	-	-
SO <sub>4</sub>	HSO <sub>4</sub>	-	-.0094	-.0677	-	-.0425	-	-
SO <sub>4</sub>	OH	-.013	-.009	-.050	-	-	-	-
SO <sub>4</sub>	HCO <sub>3</sub>	.01	-.005	-	-	-.161	-	-
SO <sub>4</sub>	CO <sub>2</sub>	.02	-.005	-.009	-	-	-	-
HSO <sub>4</sub>	OH	-	-	-	-	-	-	-
HSO <sub>4</sub>	HCO <sub>3</sub>	-	-	-	-	-	-	-
HSO <sub>4</sub>	CO <sub>2</sub>	-	-	-	-	-	-	-
OH	HCO <sub>3</sub>	-	-	-	-	-	-	-
OH	CO <sub>2</sub>	.10	-.017	-.01	-	-	-	-
HCO <sub>3</sub>	CO <sub>2</sub>	-.04	.002	.012	-	-	-	-

For each cation-cation and each anion-anion pair, a single  $\theta$  parameter is specified, if necessary. (Dashes indicate zeros.) For each anion-anion-cation and each cation-cation-anion triplet a single  $\psi$  parameter is used to describe the high concentration behavior, when necessary. When Eqn. (A.3) are simplified for common ternary solutions (e.g., NaCl-KCl-H<sub>2</sub>O), only one  $\theta$  and one  $\psi$  parameter (in addition to some single electrolyte parameters) remain. The  $\theta$  parameter must be chosen uniquely for all solutions containing the anion-anion or cation-cation pair. When available, these parameters are evaluated from data in common-ion ternary solutions.

more complex systems generally represent predictions by the model. The agreement of the model with the data is good, the model exhibiting good predictability even in complex, mixed electrolyte solutions. While some important qualifications are discussed in this section, we believe that the model defined here is sufficiently accurate for most geological applications. It will calculate accurately mineral solubilities over broad ranges of relative composition and to high ionic strength.

In the following discussion, the model is compared to the experimental data for each of the subsystems. The agreement with isopiestic and electromotive force data is designated by citing standard deviations. For isopiestic data the standard deviation is given in terms of the osmotic coefficient (e.g.,  $\phi_{\text{exp}} - \phi_{\text{calc}}$ ). For emf

Table 3: Neutral-ion parameter values.

	$\lambda^1_{\text{CO}_2, \text{I}}$	$\lambda^2_{\text{CaCO}_3, \text{I}}$	$\lambda^3_{\text{MgCO}_3, \text{I}}$
H	0.0	-	-
Na	.100	-	-
K	.051	-	-
Ca	.183	-	-
Mg	.183	-	-
MgOH	-	-	-
Cl	-.005	-	-
SO <sub>4</sub>	-.097	-	-
HSO <sub>4</sub>	-.003	-	-
OH	-	-	-
HCO <sub>3</sub>	-	-	-
CO <sub>2</sub>	-	-	-

For each neutral-ion pair, one model parameter is used in Eqn. (A.3), when necessary, to describe the experimental data.

Table 4: Values for the standard chemical potentials of the aqueous solution species and minerals.

Species or Mineral	Chemical Formula	$\mu^\circ$
Water	H <sub>2</sub> O	-91.83
Sodium Ion	Na <sup>+</sup>	-129.25
Potassium Ion	K <sup>+</sup>	-119.90
Calcium Ion	Ca <sup>2+</sup>	-129.60
Magnesium Ion	Mg <sup>2+</sup>	-120.168
Magnesium Hydroxide Ion	MgOH <sup>+</sup>	-27.702
Hydrogen Ion	H <sup>+</sup>	0.
Chloride Ion	Cl <sup>-</sup>	-131.23
Sulfate Ion	SO <sub>4</sub> <sup>2-</sup>	-309.386
Bisulfate Ion	HSO <sub>4</sub> <sup>-</sup>	-302.942
Hydroxide Ion	OH <sup>-</sup>	-191.825
Bicarbonate Ion	HCO <sub>3</sub> <sup>-</sup>	-146.231
Carbonate Ion	CO <sub>3</sub> <sup>2-</sup>	-147.260
Aq. Calcium Carbonate	CaCO <sub>3</sub>	-689.17
Aq. Magnesium Carbonate	MgCO <sub>3</sub>	-561.155
Aq. Carbon Dioxide	CO <sub>2</sub>	-151.88
Carbon Dioxide Gas	CO <sub>2</sub> (gas)	-150.702
Anhydrite	CaSO <sub>4</sub>	-581.73
Aphthitalite (Glaserite)	Na <sub>2</sub> Ca(SO <sub>4</sub> ) <sub>2</sub>	-195.713
Antarcticite	CaCl <sub>2</sub> ·6H <sub>2</sub> O	-893.65
Aragonite	CaCO <sub>3</sub>	-689.17
Arcanite	K <sub>2</sub> SO <sub>4</sub>	-512.39
Bischofite	MgCl <sub>2</sub> ·6H <sub>2</sub> O	-852.3
Bloedite	Mg <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	-1483.0
Brucite	Mg(OH) <sub>2</sub>	-135.0
Burkeite	Ca <sub>2</sub> CO <sub>3</sub> (SO <sub>4</sub> ) <sub>2</sub>	-1442.0
Calcite	CaCO <sub>3</sub>	-689.17
Calcium Chloride Tetrahydrate	CaCl <sub>2</sub> ·4H <sub>2</sub> O	-698.7
Calcium Oxochloride A	Ca <sub>2</sub> Cl <sub>2</sub> (OH) <sub>2</sub> ·1.5H <sub>2</sub> O	-2658.25
Calcium Oxochloride B	Ca <sub>2</sub> Cl <sub>2</sub> (OH) <sub>2</sub> ·H <sub>2</sub> O	-278.21
Carnallite	K <sub>2</sub> MgCl <sub>4</sub> ·6H <sub>2</sub> O	-1020.3
Dolomite	CaMg(CO <sub>3</sub> ) <sub>2</sub>	-871.99
Epsomite	MgSO <sub>4</sub> ·7H <sub>2</sub> O	-1157.83
Gavlussite	CaNa <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> ·5H <sub>2</sub> O	-166.5
Glauberite	Ca <sub>2</sub> Ca(SO <sub>4</sub> ) <sub>2</sub>	-1047.25
Gypsum	CaSO <sub>4</sub> ·2H <sub>2</sub> O	-725.36
Halite	NaCl	-131.23
Hexahydrite	MgSO <sub>4</sub> ·6H <sub>2</sub> O	-1061.60
Kainite	EMgClSO <sub>4</sub> ·3H <sub>2</sub> O	-938.2
Kalicinite	KHSO <sub>4</sub>	-350.06
Kieserite	MgSO <sub>4</sub> ·H <sub>2</sub> O	-579.80
Labile Salt	Na <sub>2</sub> Ca(SO <sub>4</sub> ) <sub>2</sub> ·2H <sub>2</sub> O	-1751.15
Leonite	K <sub>2</sub> Mg(SO <sub>4</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	-1403.97
Magnesite	MgCO <sub>3</sub>	-514.25
Magnesium Oxochloride	Mg <sub>2</sub> Cl(OH) <sub>2</sub> ·4H <sub>2</sub> O	-2029.6
Merrillite	KHSO <sub>4</sub>	-417.57
Mirabilite	Na <sub>2</sub> SO <sub>4</sub> ·10H <sub>2</sub> O	-1411.15
Misonite	K <sub>4</sub> H <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	-1029.24
Nahcolite	NaHCO <sub>3</sub>	-363.33
Natron	Na <sub>2</sub> CO <sub>3</sub> ·10H <sub>2</sub> O	-382.78
Nesquehonite	MgCO <sub>3</sub> ·3H <sub>2</sub> O	-695.3
Picromerite (Schoenite)	K <sub>2</sub> Mg(SO <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	-1596.1
Pirssonite	Na <sub>2</sub> Ca(CO <sub>3</sub> ) <sub>2</sub> ·2H <sub>2</sub> O	-1073.1
Polyhalite	K <sub>2</sub> MgCa <sub>2</sub> (SO <sub>4</sub> ) <sub>4</sub> ·2H <sub>2</sub> O	-2282.5
Portlandite	Ca(OH) <sub>2</sub>	-362.12
Potassium Carbonate	K <sub>2</sub> CO <sub>3</sub> ·1/2 H <sub>2</sub> O	-77.37
Potassium Sesquicarbonate	K <sub>2</sub> H <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub> ·3H <sub>2</sub> O	-2555.4
Potassium Sodium Carbonate	KNaCO <sub>3</sub> ·6H <sub>2</sub> O	-1006.8
Potassium Trona	K <sub>2</sub> NaH(CO <sub>3</sub> ) <sub>2</sub> ·2H <sub>2</sub> O	-971.74
Sesquipotassium Sulfate	K <sub>3</sub> H(SO <sub>4</sub> ) <sub>2</sub>	-950.8
Sesquiosodium Sulfate	Na <sub>3</sub> H(SO <sub>4</sub> ) <sub>2</sub>	-919.6
Sodium Carbonate Heptahydrate	Na <sub>2</sub> CO <sub>3</sub> ·7H <sub>2</sub> O	-1094.95
Solvite	KCl	-164.84
Songonite	K <sub>2</sub> Ca(SO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O	-1164.8
Tachyhydrite	Mg <sub>2</sub> CaCl <sub>4</sub> ·12H <sub>2</sub> O	-2015.9
Tenardite	Na <sub>2</sub> SO <sub>4</sub>	-512.35
Thermomannite	Na <sub>2</sub> CO <sub>3</sub> ·H <sub>2</sub> O	-318.8
Trona	Na <sub>2</sub> H(CO <sub>3</sub> ) <sub>2</sub> ·2H <sub>2</sub> O	-960.78

A single (unitless) parameter is specified for each model species and mineral. Many salt chemical potentials had to be evaluated in systems more complex than common-ion ternary (e.g. polyhalite). However, the composition dependence of such a salt's solubility depends on the trends predicted by the solution model which is parameterized in simple systems (i.e., one parameter,  $\mu^\circ/RT$ , must fit many solubility data points). Equilibrium constants may be calculated from these data using the equation  $\ln K = -\sum \nu_i (\mu^\circ_i/RT)$ , where  $\nu_i$  are the stoichiometric coefficients for the reaction.

data, unless otherwise indicated, the standard deviation is given in terms of the natural logarithm of the activity coefficient for the cell. For example, the standard deviation for the data determined from a cell utilizing a hydrogen electrode and a silver-silver chloride electrode is reported in terms of  $\ln \gamma_{\text{HCl}}^{\text{exp}} - \ln \gamma_{\text{HCl}}^{\text{calc}}$ . The comparison to the solubility data is made graphically.

The parameter values for each system are determined by minimizing a weighted standard deviation of all the data for the system. In general, low weights are assigned to solubility data in comparison to the

typically more accurate isopiestic and cell data. This approach represents an improvement over the methods used by HW where parameter values were determined using various graphical methods. The parameter values given in Tables 1-4, are usually cited to higher accuracy than is warranted by the data fit. The choice of different weights can change parameter values significantly. We have attempted to select weights which give the solubilities within 5% of their observed values. A brief discussion of the numerical method used to evaluate parameters is given by HARVIE (1981). Many parameters in the tables are set equal to zero (denoted by dashes). For some cases, these parameters are approximately redundant with other parameters (see following discussion of  $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$  and PITZER *et al.*, 1977). In other cases, no data are available to evaluate a parameter.

In light of new data, the  $\text{CaSO}_4$  parameters of the original Harvie-Weare model have been revised to improve the calculated dilute solution solubility of gypsum. Recently, ROGERS (1981) fit the  $\text{CaSO}_4$  system using the Pitzer model. We utilize her parameters when they are internally consistent with our model. The revised  $\text{CaSO}_4$  model has been discussed in HARVIE *et al.* (1982) and HARVIE (1981).

In Fig. 4a the calculated solubilities of halite, sylvite, bischofite, antarcticite and  $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$  in aqueous HCl solutions are plotted together with the experimental data. The experimental data usually are those summarized in LINKE (1965). The data for bischofite in hydrochloric acid solutions are given by BEREZ and BADER (1973). The parameters values for  $\beta_{\text{HCl}}^{(0)}$ ,  $\beta_{\text{HCl}}^{(1)}$ , and  $C_{\text{HCl}}^*$  are given by PITZER and MAYORGA (1973). The values for  $\theta_{\text{K,H}}$ ,  $\theta_{\text{Na,H}}$ , and  $\psi_{\text{Na,H,Cl}}$  are taken from PITZER and KIM (1974). The value for  $\psi_{\text{K,H,Cl}}$  is adjusted slightly from the Pitzer value to improve the agreement of the model with the solubility data in the KCl-HCl- $\text{H}_2\text{O}$  system.

The values for  $\theta_{\text{Mg,H}}$  and  $\psi_{\text{Mg,H,Cl}}$  are obtained by refitting the emf results of KHOO *et al.* (1977b) together with the solubility data for the  $\text{MgCl}_2\text{-HCl-}\text{H}_2\text{O}$  system. Unlike the model used by Khoo *et al.* the equations we use contain terms to account for electrostatic forces in unsymmetrical mixtures (PITZER, 1975). Hence, it was necessary to reevaluate the parameters given by Khoo *et al.* The standard deviation of our fit to the Khoo *et al.* data is  $\sigma = .0021$  in  $\ln \gamma^\pm$ . When the emf results are fit without the solubility data,  $\sigma = .0016$ . In evaluating  $\theta_{\text{Ca,H}}$  and  $\psi_{\text{Ca,H,Cl}}$ , a similar analysis was carried out using the emf results of KHOO *et al.* (1977a) and the solubility data in the  $\text{CaCl}_2\text{-HCl-}\text{H}_2\text{O}$  system. The standard chemical potential of  $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$  is treated as an adjustable parameter in the fit. Our standard deviation to the emf data in the  $\text{CaCl}_2\text{-HCl-}\text{H}_2\text{O}$  system is  $\sigma = .0027$ . The activity coefficients for  $\text{CaCl}_2$  at high  $\text{CaCl}_2$  concentrations are not in good agreement with experiment. To fit the solubility data we have made small changes in the chemical potentials for salts like antarcticite. When third virial coefficients are treated as adjustable parameters, it is possible to obtain

agreement (10%) with the observed trends in solubility at high concentrations. This is probably related to the rapidly increasing activity coefficient for  $\text{CaCl}_2$ , in which case small changes in concentration produce pronounced changes in the activity.

PITZER *et al.* (1977) have accurately fit the data for the sulfuric acid-water system, incorporating the species  $\text{HSO}_4^-$ . We found that it is not possible to accurately fit the data for the  $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$  system, without a  $\text{HSO}_4^-$  ion pair, using Eqn. (A.3). Since we are using the unsymmetrical electrolyte theory the parameters given by Pitzer *et al.* are re-evaluated. This is accomplished by fitting the unsymmetrical mixing equations to the interpolated activity and osmotic coefficients given by Pitzer *et al.* In agreement with Pitzer *et al.* an approximate redundancy among the parameters is noted. For example, the standard deviation of a least squares fit when adjusting the parameters,  $\beta_{\text{H}_2\text{SO}_4}^{(0)}$ ,  $C_{\text{H}_2\text{SO}_4}^*$ ,  $\beta_{\text{H}_2\text{SO}_4}^{(1)}$ , and  $\beta_{\text{H}_2\text{SO}_4}^{(2)}$ , is essentially independent of the value of  $\beta_{\text{H}_2\text{SO}_4}^{(1)}$ . Within a broad range of  $\beta_{\text{H}_2\text{SO}_4}^{(1)}$  values the optimal value for any of the adjustable parameters changes but the standard deviation of the fit remains the same. Thus, the parameters for the  $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$  system could not be uniquely determined. Nevertheless, the thermodynamic properties of the system are accurately described by any set of these four parameter values corresponding to a given  $\beta_{\text{H}_2\text{SO}_4}^{(1)}$ . We have adopted Pitzer's convention of setting the redundant parameters,  $\beta_{\text{H}_2\text{SO}_4}^{(1)}$ ,  $C_{\text{H}_2\text{SO}_4}^*$ ,  $\theta_{\text{H}_2\text{SO}_4}$ , and  $\psi_{\text{SO}_4,\text{HSO}_4,\text{H}}$ , equal to zero. As should be expected, we agree with the tabulated activity and osmotic coefficients of Pitzer *et al.* The standard deviation of the overall fit to  $\phi$  and  $\ln \gamma^\pm$  is  $\sigma = .0007$ .

The agreement of the model with the data for the HCl- $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$  system is good. The data for this system are the emf data of NAIR and NANCOLLAS (1958), DAVIES *et al.* (1952) and STORONKIN *et al.* (1967). The first two sets of experiments are confined to low concentrations,  $I \ll 1$ . The data of Storonkin apply to systems up to ionic strengths of almost 4. The standard deviation of the Nair and the Davies data is  $\sigma = .0008$  in  $\gamma^\pm$ . For the Storonkin data, the standard deviation is  $\sigma = .015$ . All of the data are insensitive to reasonable variations in the parameter  $\psi_{\text{H}_2\text{SO}_4,\text{Cl}}$ . Consequently, this parameter is set equal to zero.

The parameters,  $\beta_{\text{Na}_2\text{HSO}_4}^{(0)}$ ,  $\beta_{\text{Na}_2\text{HSO}_4}^{(1)}$ ,  $\psi_{\text{Na}_2\text{HSO}_4}$ , and  $\psi_{\text{Na}_2\text{HSO}_4,\text{SO}_4}$ , and the standard chemical potential for  $\text{Na}_3\text{H}(\text{SO}_4)_2$  are evaluated simultaneously by a least squares fit of the emf data of HARNED and STURGIS (HS) (1925), RANDALL and LANGFORD (1927), and COVINGTON *et al.* (CDW) (1965), together with the solubility data (LINKE, 1965). The parameters,  $\psi_{\text{Na}_2\text{HSO}_4}$  and  $C_{\text{Na}_2\text{HSO}_4}^*$ , are approximately redundant with the above parameters; therefore, they are set equal to zero. The standard emf,  $E^\circ$ , values of Randall and Covington are also treated as adjustable parameters, while the standard emf for the HS data is fixed so that the activity coefficient in 0.1 m  $\text{H}_2\text{SO}_4$  solution agrees with PITZER *et al.* (1977). As noted by Pitzer *et al.* the interpolated  $E^\circ$  value for the Randall data does

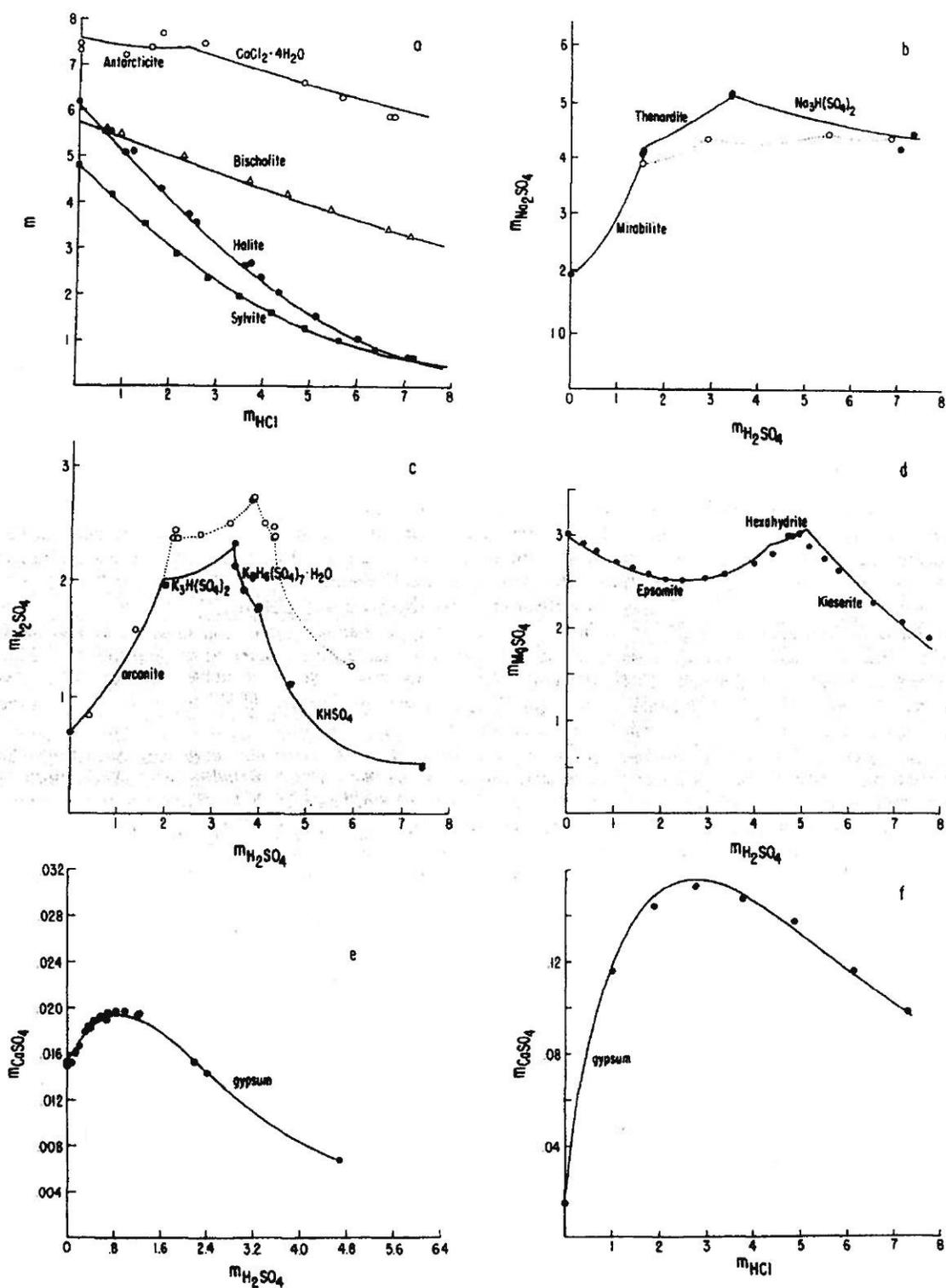


FIG. 4. The calculated and experimental solubilities of salts in acidic solutions. The model is also in agreement with various emf and isopiestic measurements (see text). Curves a-e were used in parameterization. Curve f was predicted using fully parameterized model for acidic solutions.

not agree well with the accepted value for similar cells. As usual in fitting the parameters, the weights on the solubility data are increased until good agreement with

these data is obtained. This procedure tends to minimize the standard deviation of the emf data while insuring good agreement with the solubility measure-

ments. The resulting standard deviations are  $\sigma = .018$ ,  $\sigma = .013$ ,  $\sigma = .006$  for the Harned, Randall and Covington data, respectively. Additional emf measurements at concentrations which will define the Na-HSO<sub>4</sub> interaction are desirable for this system. The resulting solubility curve is given in Fig. 4b. The data defined by the closed circles are that of FOOTE (1919) and LUK'YANOVA (1953). The open circles and dashed line denote the data of KORF and SHCHATROVSKAYA (1940). The Korf experiments observed an additional monohydrate salt separating the thenardite, and Na<sub>3</sub>H(SO<sub>4</sub>)<sub>2</sub> fields. We have parameterized the equations to the Foote and Luk'yanova data since these authors are in good agreement, and the Na<sub>3</sub>H(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O salt has not been observed above 0°C by other authors (see LINKE, 1965).

The data for the system, K<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O, are fit in much the same way as the corresponding sodium system, except that the parameter,  $\psi_{K,H,SO_4}$ , is allowed to vary. The cell data of HARNED and STURGIS (1925) are fit with a standard deviation of .018. The calculated solubilities are compared in Fig. 4c to the data of D'ANS (1913) (solid circles) and of STOROZHENKO and SHEVCHUK (1971) (open circles). The difference between these two sets of data is sizeable. The major difference in the parameters fit with either set of data is in the chemical potentials of the acid salts. We have parameterized the model to the D'Ans data.

A similar analysis for the MgSO<sub>4</sub>-H<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O system yields a standard deviation of  $\sigma = .02$  to the emf data of HARNED and STURGIS (1925). The solubility data predicted in Fig. 4d are that of FILIPOV and ANTONOVA (1978).

The parameters,  $\beta_{Ca,HSO_4}^{(0)}$  and  $\beta_{Ca,HSO_4}^{(1)}$ , are evaluated directly from the solubility data of MARSHALL and JONES (1966) depicted in Fig. 4e. These data are insensitive to reasonable adjustments in all other pa-

rameters for the system. Hence,  $\psi_{Ca,H,HSO_4}$ ,  $\psi_{SO_4,HSO_4}$ ,  $\psi_{SO_4,HSO_4,Ca}$  and  $C_{Ca,HSO_4}^*$  are all set equal to zero. In Fig. 4f the calculated solubility of gypsum in hydrochloric acid solutions is in good agreement with the experimental data summarized in LINKE (1965).

In Figs. 5a and 5b the calculated solubility of CO<sub>2</sub> in different aqueous electrolyte solutions is compared to experiment. Each curve is labelled with the salt present in the solution. As previously discussed, the parameterization includes the evaluation of a single parameter,  $\lambda_{CO_2,i}$ , for each ion *i* present in the system. Since measurements can only be made in neutral solutions, one of the parameters must be assigned arbitrarily. We use the convention of setting  $\lambda_{CO_2,H}$  equal to zero. The remaining parameters, evaluated directly from the solubility data, are given in Table 3. The standard chemical potential for CO<sub>2</sub> (gas), given in Table 4, is that of ROBIE *et al.* (1978).  $\mu_{CO_2(aq)}^0$  is evaluated, together with the  $\lambda$ 's, from the solubility data. The calculated CO<sub>2</sub> solubility in pure water is about 3% low. This is probably the result of a deficiency of the linear theory. However, since deviations in the entire concentration range are usually within 5%, the increased complication of higher order terms for neutral species does not seem warranted. (This is particularly true in the context of the geochemical applications for which the model is intended.) The solubility data given in Fig. 5 are primarily those of YASUNISKI and YOSHIDA (1979) and MARKHAM and KOBE (1941). The data of GEFFCHEN (1904) are given for the CO<sub>2</sub>-HCl-H<sub>2</sub>O system. The HARNED and DAVIS (1943) data are included in the figure for the NaCl-HCl-H<sub>2</sub>O system. The parameter,  $\lambda_{CO_2,Cl}$ , is determined from the data in the HCl-CO<sub>2</sub>-H<sub>2</sub>O system. Using this parameter, the value of  $\lambda$  for each of the cations (except H<sup>+</sup>) is obtained by fitting the data in the chloride systems. The parameter,  $\lambda_{SO_4,CO_2}$ , is then evaluated from the

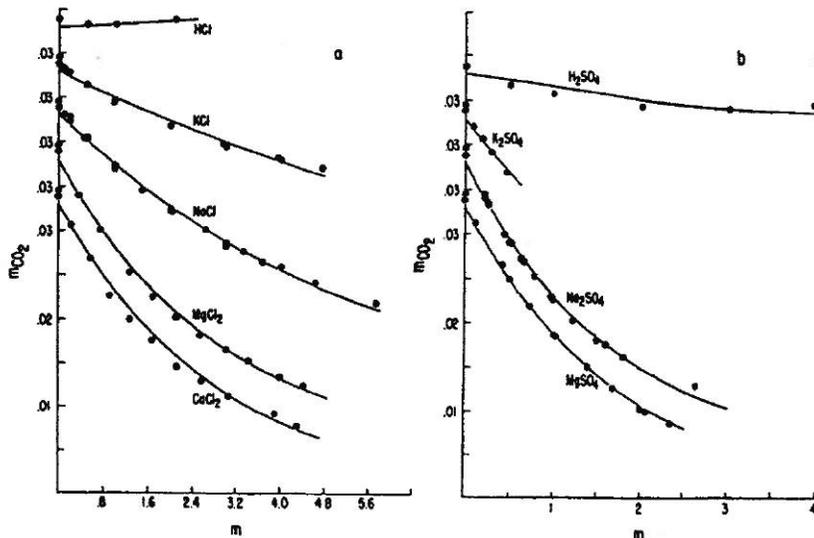


FIG. 5. The solubility of carbon dioxide in single electrolyte solutions. The curves in MgSO<sub>4</sub> and K<sub>2</sub>SO<sub>4</sub> solutions were predicted using the model fully parameterized from the other data.

data in the  $\text{Na}_2\text{SO}_4\text{-CO}_2\text{-H}_2\text{O}$  system. Lastly,  $\lambda_{\text{H}_2\text{SO}_4\text{-CO}_2}$  is evaluated from the  $\text{H}_2\text{SO}_4\text{-CO}_2\text{-H}_2\text{O}$  system. The data in the  $\text{K}_2\text{SO}_4$  and  $\text{MgSO}_4$  systems in Fig. 5b test the specific interaction model, since all the parameters for these systems are evaluated from other data.

The Na-OH and K-OH interaction parameters are obtained from PITZER and MAYORGA (1973). The values for  $\theta_{\text{OH,Cl}}$  and  $\psi_{\text{OH,Cl,Na}}$  of PITZER and KIM (1974) are retained, while  $\psi_{\text{OH,Cl,K}}$  is slightly adjusted to improve the fit with the solubility data. The calculated solubility curves for these hydroxide systems are plotted together with the solubility data of AKERLOF and SHORT (1937) in Fig. 6a. The parameters,  $\theta_{\text{OH,SO}_4}$ ,  $\psi_{\text{OH,SO}_4\text{Na}}$  and  $\psi_{\text{OH,SO}_4\text{K}}$ , are evaluated solely from the solubility data in these systems. For the Na-OH- $\text{SO}_4$  system the data of WINDMAISSER and STOCKL (1950) are used exclusively (Fig. 6b). For the K-OH- $\text{SO}_4$  system the data of D'ANS and SCHREINER (1910) were used (Fig. 6d). (It is noteworthy that the data of D'ANS

and SCHREINER (1910) for the Na-OH- $\text{SO}_4$  system are not in good agreement with that of Windmaisser (LINKE, 1965)).

The parameters representing the Na- $\text{HCO}_3$  interaction and  $\theta_{\text{HCO}_3\text{Cl}}$  are from PITZER and PEIPER (1980). (At the time of publication improved parameter values have been evaluated by PEIPER and PITZER, 1982.) The chemical potential for bicarbonate is evaluated from the equilibrium constant given by PITZER and PEIPER (1980). The Na- $\text{CO}_3$  interaction parameters, together with  $\mu_{\text{CO}_3}^0$ , are evaluated from the isopiestic results of ROBINSON and MACASKILL (1979) and the emf results of HARNED and SCHOLES (1941). Parameters for Na,  $\text{CO}_3$  listed in Table 2 differ from those given by Robinson and Macaskill because we account for the hydrolysis of carbonate to bicarbonate. The standard deviation of the isopiestic data remains at  $\sigma = .002$  in the osmotic coefficient. The standard deviation of the Harned and Scholes emf data equals .004.

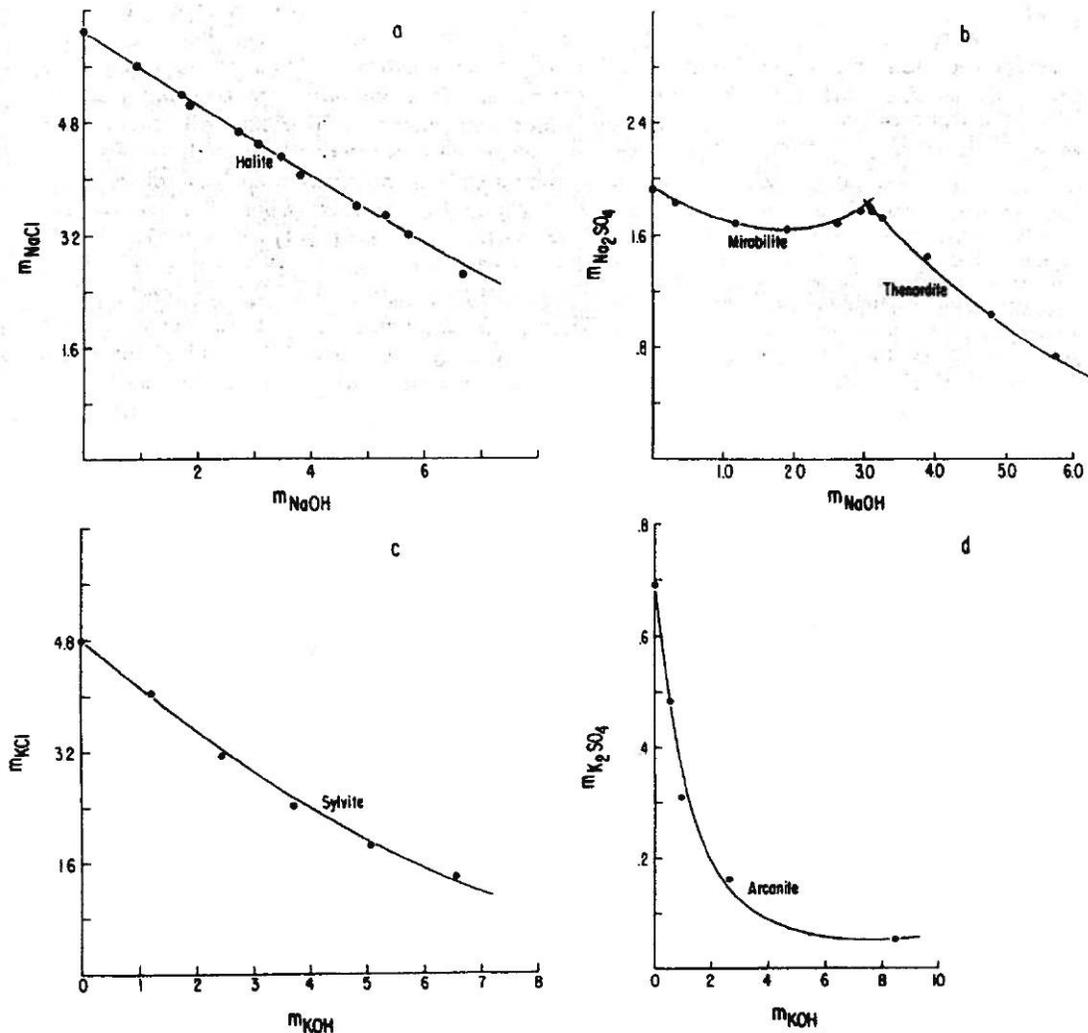


FIG. 6. The solubilities of sodium and potassium salts in hydroxide solutions. The model is also in agreement with emf data at lower concentrations.

The remainder of the Na-CO<sub>3</sub>-HCO<sub>3</sub>-Cl-SO<sub>4</sub>-OH-H<sub>2</sub>O system is parameterized exclusively from solubility data in common ion systems. The chemical potentials of nahcolite and natron are obtained from the solubility data of HILL and BACON (1927) and ROBINSON and MACASKILL (1979), respectively. The parameters,  $\theta_{\text{CO}_3, \text{HCO}_3}$  and  $\psi_{\text{CO}_3, \text{HCO}_3, \text{Na}}$  and the standard chemical potential for trona are based on the solubility data of HILL and BACON (1927) and FREETH (1922) (Fig. 7a). Several of the Freeth points are in poor agreement with the Hill data and the model. The parameter,  $\psi_{\text{Cl, HCO}_3, \text{Na}}$ , is evaluated from the data of BOGOYAVLENSKII and MANANNIKOVA (1955) and FREETH (1922).  $\theta_{\text{HCO}_3, \text{SO}_4}$  and  $\psi_{\text{HCO}_3, \text{SO}_4, \text{Na}}$  are evaluated primarily from the data of MAKAROV and JAKIMOV (1933). In the Na-SO<sub>4</sub>-HCO<sub>3</sub> system  $\theta_{\text{SO}_4, \text{HCO}_3}$  and  $\psi_{\text{SO}_4, \text{HCO}_3, \text{Na}}$  are nearly redundant, hence these parameters cannot be determined uniquely. Acceptable values which are in good agreement with the majority of the data in the more complex systems are given in Table 2. (See Fig. 7b.) Additional experiments are required to refine these values.

The solubility data of FREETH (1922) are used in evaluating the parameters,  $\theta_{\text{Cl, CO}_3}$  and  $\psi_{\text{Cl, CO}_3, \text{Na}}$ , as well as the standard chemical potential for sodium carbonate heptahydrate (Fig. 7d). The parameters,  $\theta_{\text{SO}_4, \text{CO}_3}$  and  $\psi_{\text{SO}_4, \text{CO}_3, \text{Na}}$ , are evaluated primarily from the data of MAKAROV and KRASNIKOV (1956) and CASPARI (1924). Given the data available there is redundancy between these parameters. The values chosen are consistent with the data (Figs. 7 and 8).

The parameters,  $\theta_{\text{OH, HCO}_3}$  and  $\psi_{\text{OH, HCO}_3, \text{Na}}$ , are unnecessary since the concentrations of OH and HCO<sub>3</sub> cannot simultaneously be large. The small effects of these parameters are redundant with the more important parameters,  $\theta_{\text{CO}_3, \text{OH}}$  and  $\psi_{\text{CO}_3, \text{OH, Na}}$ . The parameter,  $\theta_{\text{OH, HCO}_3}$ , and all  $\psi$ 's for OH, HCO<sub>3</sub> and a cation are set equal to zero.  $\theta_{\text{CO}_3, \text{OH}}$  and  $\psi_{\text{CO}_3, \text{OH, Na}}$  are evaluated from the data of FREETH (1922) and HOSTALEK (1956). The chemical potential of thermonatrite is also determined from these data.

Data from more complex systems are used to test the model. The Na-CO<sub>3</sub>-SO<sub>4</sub>-OH-H<sub>2</sub>O system was studied by ITKINA and KOKHOVA (1953). From their data the burkeite chemical potential is evaluated. Comparison of our solubility calculations with these experimental data is given in Fig. 8a. In general the agreement is quite good. With the exception of burkeite, 70% of the calculated activity products for each salt at each of the points (Fig. 8b) are within 5% of the corresponding equilibrium constant. 90% of the activity products are within 10% of the equilibrium constant. An exception is the natron-Na<sub>2</sub>CO<sub>3</sub>·7H<sub>2</sub>O-burkeite point which appears from calculation to be undersaturated by about 12% in the calculated equilibrium constant for natron. In Fig. 8, the burkeite fields are assumed to be in equilibrium with the mineral having a sulfate to carbonate ratio of 2 to 1. The agreement of the data with this model is somewhat surprising, since Na<sub>2</sub>CO<sub>3</sub>-Na<sub>2</sub>SO<sub>4</sub> solid solutions of the

burkeite type are known to occur (see JONES, 1963). In Fig. 8f, the model activity of Na<sub>2</sub>CO<sub>3</sub> in aqueous solution is plotted versus the model activity for Na<sub>2</sub>SO<sub>4</sub> in aqueous solution. Each point represents the Na<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>SO<sub>4</sub> activities calculated for each solution composition reported by ITKINA and KOKHOVA (1953) to be in equilibrium with a burkeite phase. A curve resembling that of a Na<sub>2</sub>CO<sub>3</sub>·2Na<sub>2</sub>SO<sub>4</sub> mineral (solid curve) is suggested. In contrast, an ideal solid solution would satisfy linear behavior (e.g. dashed curve). The mineral approximation for the burkeite phase gives relatively good results. The Na<sub>2</sub>CO<sub>3</sub>-Na<sub>2</sub>SO<sub>4</sub> diagram indicates that burkeite is only slightly unstable at 25°C in this system. This is consistent with the 25.5°C invariant point for burkeite-natron-mirabilite-solution coexistence in Na<sub>2</sub>CO<sub>3</sub>-Na<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O solution (MAKAROV and BLEIDEN, 1938).

Further comparisons of the model with experiment are given for the Na-CO<sub>3</sub>-Cl-OH-H<sub>2</sub>O, Na-CO<sub>3</sub>-Cl-SO<sub>4</sub>-H<sub>2</sub>O, Na-CO<sub>3</sub>-HCO<sub>3</sub>-Cl-H<sub>2</sub>O and Na-CO<sub>3</sub>-HCO<sub>3</sub>-SO<sub>4</sub>-H<sub>2</sub>O systems (Fig. 8). With the exception of the Na-CO<sub>3</sub>-SO<sub>4</sub>-Cl-H<sub>2</sub>O data of MAKAROV and BLEIDEN (1938), all of the calculated diagrams are in good agreement with the experiments. In the Na-CO<sub>3</sub>-SO<sub>4</sub>-Cl system (Fig. 8e) the experimental natron-mirabilite-burkeite invariant point (triangle) is not in good agreement with the model or the experimental 25.5°C invariant point on the CO<sub>3</sub>-SO<sub>4</sub> edge.

In Table 5, the calculated activities of water and the equilibrium carbon dioxide partial pressures are compared to the experimental determinations of HATCH (1972) and EUGSTER (1966) in the Na-CO<sub>3</sub>-HCO<sub>3</sub>-Cl-H<sub>2</sub>O system. These experiments were performed by saturating aqueous solutions with the various minerals listed in Table 5 and measuring the activity of water and/or carbon dioxide pressure. Agreement with the activity of water measurements is within 3% and often better. The calculated CO<sub>2</sub> pressures are within the scatter of the data for the Eugster measurements, and within about 10% of the Hatch measurements.

The data available for the K-CO<sub>3</sub>-HCO<sub>3</sub>-OH-Cl-SO<sub>4</sub>-H<sub>2</sub>O system are more sparse than for the corresponding sodium system. In particular, emf data in the moderate concentration appear to be absent. Consequently, a parameterization procedure using more complicated data is used. The value for  $\beta_{\text{K, HCO}_3}^{\text{I}}$  is estimated by PITZER and PEIPER (1980).  $\beta_{\text{K, CO}_3}^{\text{I}}$  is estimated from the data of MACINNES and BELCHER (1933). The extensive solubility data in the Na-K-CO<sub>3</sub>-HCO<sub>3</sub>-H<sub>2</sub>O system are used in a nonlinear least square evaluation of the parameters:  $\beta_{\text{K, HCO}_3}^{\text{II}}$ ,  $\beta_{\text{K, CO}_3}^{\text{II}}$ ,  $C_{\text{K, HCO}_3}$ ,  $C_{\text{K, CO}_3}$ ,  $\psi_{\text{Na, K, HCO}_3}$ ,  $\psi_{\text{Na, K, CO}_3}$ , and  $\psi_{\text{HCO}_3, \text{CO}_3, \text{K}}$ . The standard chemical potentials for the carbonate salts with potassium are also adjusted in an eleven parameter fit. The data used are those of HILL and HILL (1927) for the KHCO<sub>3</sub>-K<sub>2</sub>CO<sub>3</sub>-H<sub>2</sub>O system; HILL and MILLER (1927) for the K<sub>2</sub>CO<sub>3</sub>-Na<sub>2</sub>CO<sub>3</sub>-H<sub>2</sub>O system; HILL and SMITH (1929) and OGLESBY (1929) for the KHCO<sub>3</sub>-

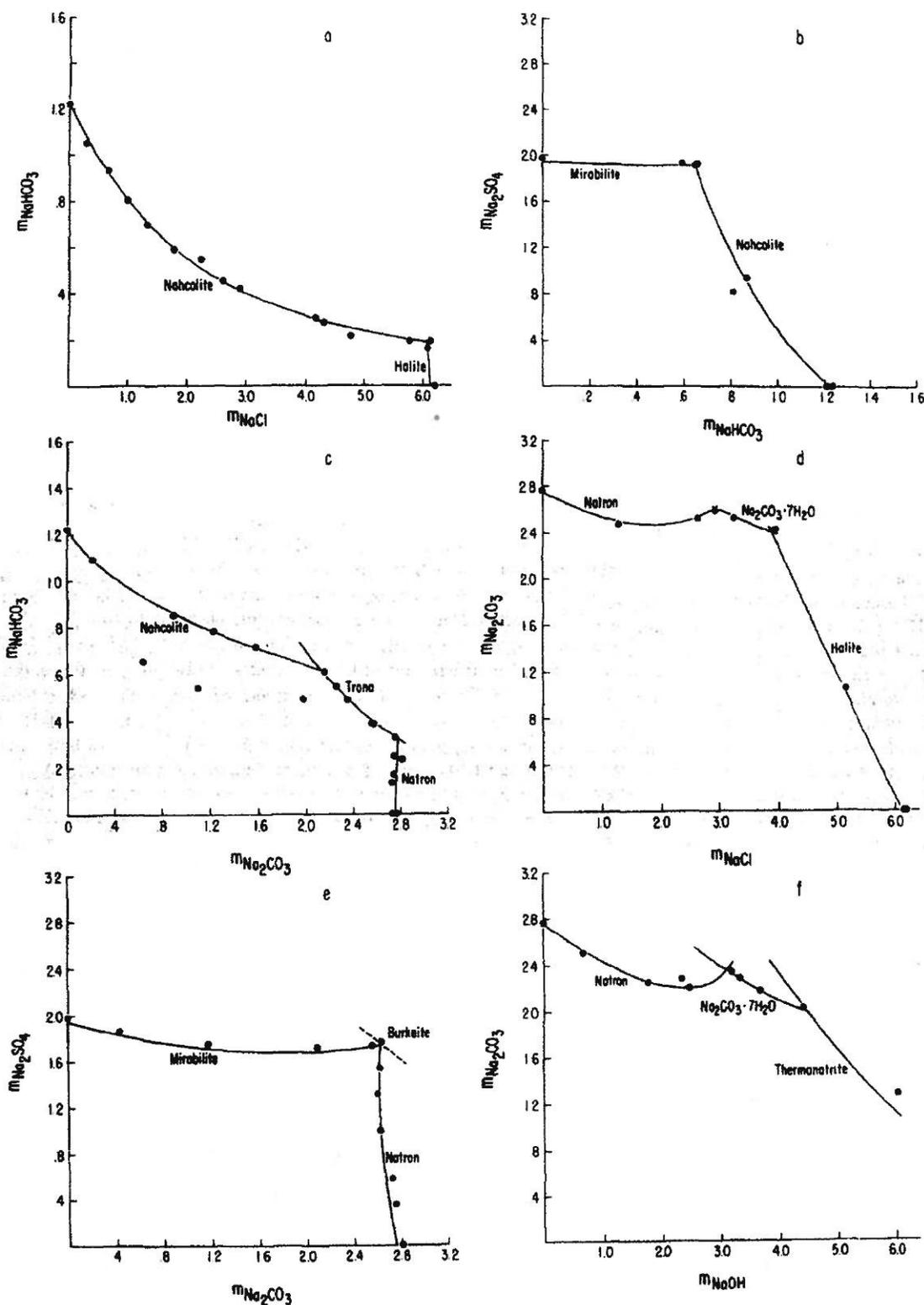


FIG. 7. Salt solubilities in the Na-Cl-SO<sub>4</sub>-HCO<sub>3</sub>-CO<sub>3</sub>-OH-H<sub>2</sub>O system. Closed systems.

NaHCO<sub>3</sub>-H<sub>2</sub>O system; and HILL and SMITH (1929) and HILL (1930) for the reciprocal system (Fig. 10). The agreement between the model and the above experimental data is generally good (see Figs. 9 and 10),

except for the nacholite data of OGLESBY (1929) at  $P_{\text{CO}_2} = 1$  atm. (Fig. 9a). However in Fig. 9a, calculation does agree well with the experimental value for the nacholite-KHCO<sub>3</sub> invariant point of HILL and SMITH

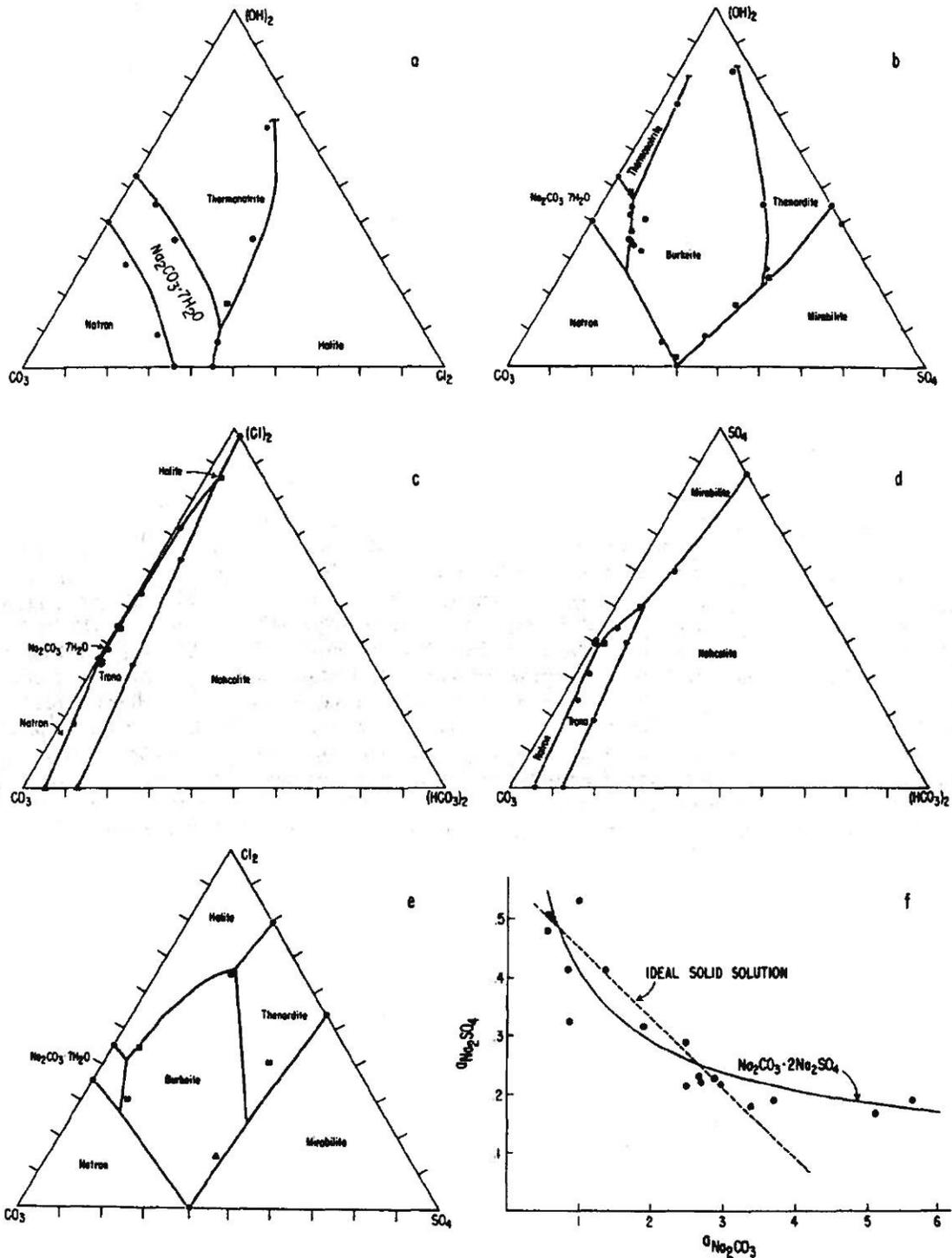


FIG. 8. Predicted Jänecke projections for ternary systems in the Na-Cl-SO<sub>4</sub>-HCO<sub>3</sub>-CO<sub>3</sub>-OH-H<sub>2</sub>O system. Closed systems. See text for discussion of (f). Figures predicted from fully parameterized model using solubility data in Fig. 7, emf and isopiestic data.

(1929) (square point in Fig. 9a), and the KHCO<sub>3</sub> solubility data of Oglesby. We suspect that the Hill and Smith invariant point is probably correct, since the nacholite-KHCO<sub>3</sub> coexistence data of Hill plotted in Fig. 10 extrapolate to this value. The 13% discrepancy

between the Hill and Oglesby data must be resolved experimentally.

The "mineral," KNaCO<sub>3</sub>·6H<sub>2</sub>O, is an approximation for the solid solution (K,Na)CO<sub>3</sub>·6H<sub>2</sub>O (HILL, 1930) (Fig. 9e). As was the case with the burkeite phase,

Table 5: Comparison of the calculated and experimental water activities and equilibrium  $P_{CO_2}$  pressures for solutions in equilibrium with the specified phase assemblages in the Na-Cl-HCO<sub>3</sub>-CO<sub>2</sub>-H<sub>2</sub>O system at 25°C.

	$a_{H_2O}$		$P_{CO_2} \times 10^2$	
	calc	Hatch	calc	Eugster
Na-HCO <sub>3</sub> -CO <sub>2</sub> -H <sub>2</sub> O + Nahcolite + Trona	.906	.89 <sup>a</sup> -.90 <sup>b</sup>	1.87	1.80-1.95
Na-HCO <sub>3</sub> -CO <sub>2</sub> -H <sub>2</sub> O + Natron + Trona	.888	.868-.872	.37	.30-.34
Na-HCO <sub>3</sub> -CO <sub>2</sub> -Cl-H <sub>2</sub> O + Nahcolite + Trona + Halite	.766	.765-.771	1.5 <sup>a</sup>	1.45-1.60
Solution + Natron + Na <sub>2</sub> CO <sub>3</sub> ·7H <sub>2</sub> O	.756	.756*		1.72-1.77
Solution + Thermonstrite + Na <sub>2</sub> CO <sub>3</sub> ·7H <sub>2</sub> O	.697	.705*		

\*Extrapolated to 25°C by Hatch

The data cited are those of Hatch (1972) and Eugster (1966).

data giving the solid phase composition in equilibrium with an aqueous solution are required to model the solid solution behavior. Nevertheless, the experimental

aqueous solution concentrations in equilibrium with the solid solution are adequately calculated using the mineral approximation. (See Figs. 9 and 10.) The data

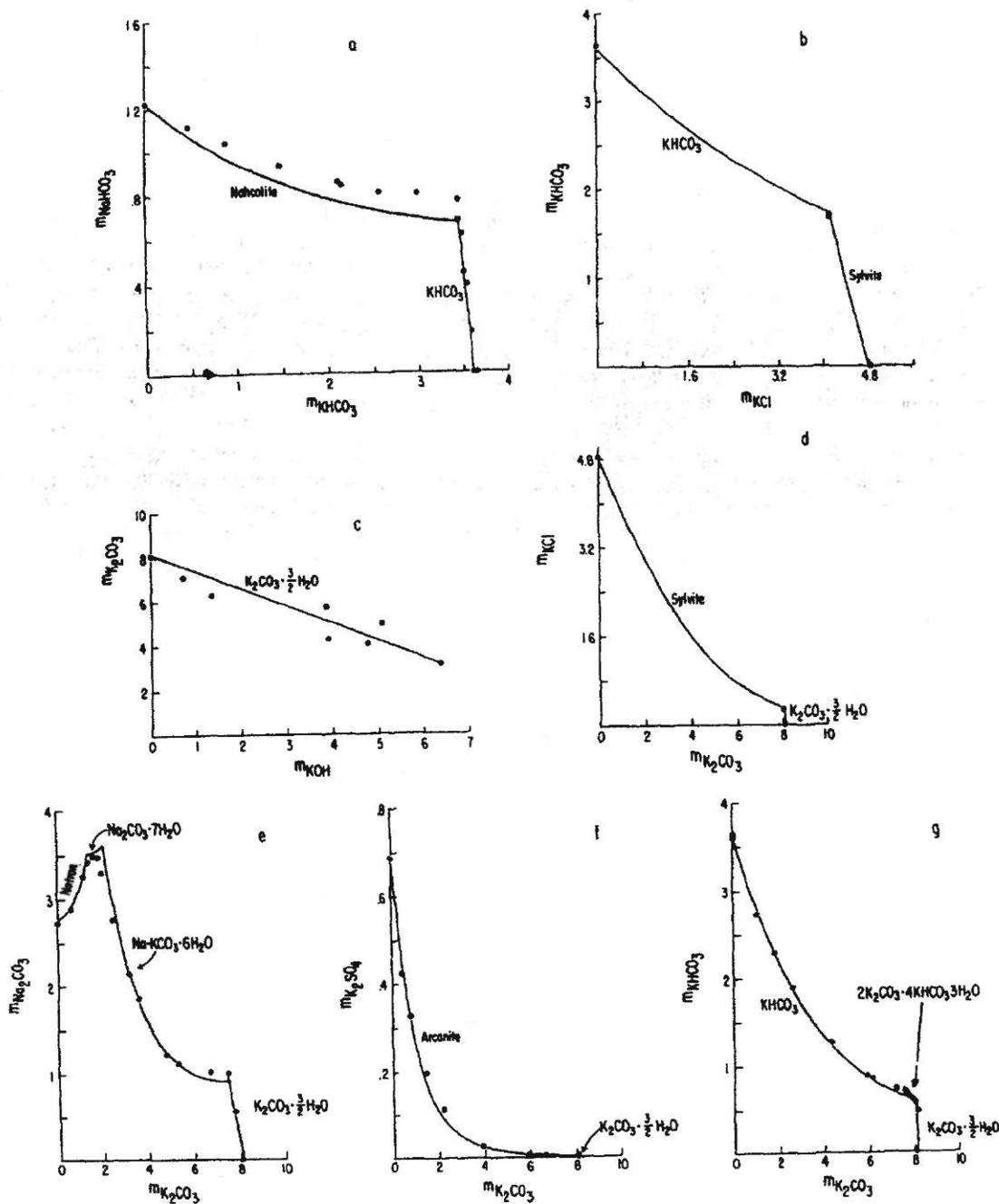


FIG. 9. Salt solubilities in potassium carbonate systems. Closed systems.

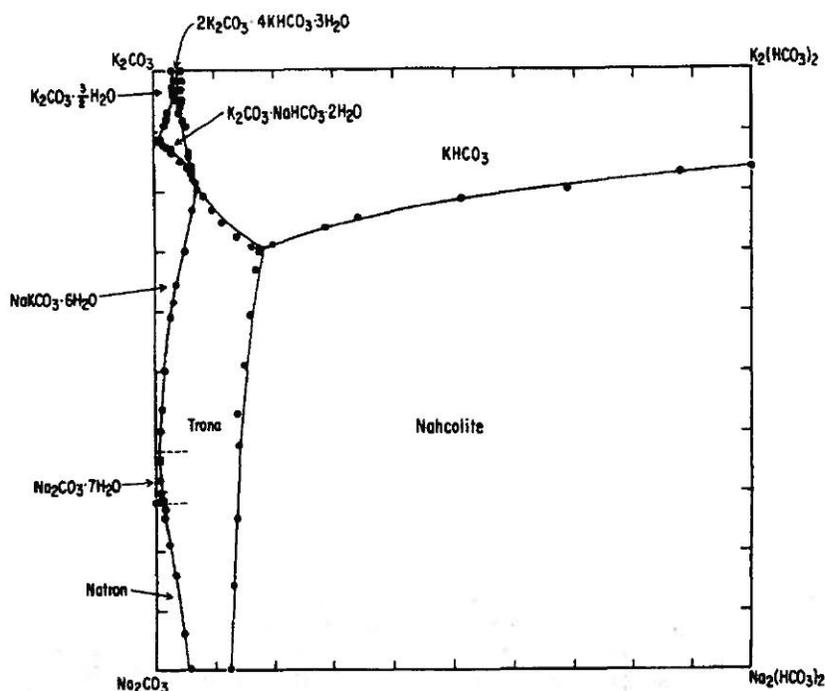


FIG. 10. The reciprocal Na-K-HCO<sub>3</sub>-CO<sub>2</sub> closed system.

for this solid solution are not used in the fit of the potassium carbonate parameters.

The data for the chloride system of potassium carbonate and bicarbonate are sparse. The parameters,  $\psi_{\text{Cl},\text{CO}_3,\text{K}}$  and  $\psi_{\text{Cl},\text{HCO}_3,\text{K}}$ , are evaluated from the solubility data of BLASDALE (1923) and BAYLISS and KOCH (1952). The agreement of the model with the emf data of MACINNES and BELCHER (1933) is good. The standard deviation of the fit to these authors' potassium bicarbonate data is  $\sigma = .006$  in  $\ln(\gamma_{\text{Cl}}/\gamma_{\text{HCO}_3})$  and the standard deviation to their potassium carbonate-bicarbonate data is  $\sigma = .014$  in  $\ln \gamma_{\text{HCl}}$ . The conditions of the MacInnes and Belcher experiments are analogous to the Harned emf experiments in the sodium system. The fit to the BLASDALE (1923) solubility data is good, with the exception of several natron points which correlated quite well with the sodium carbonate heptahydrate salt. Blasdale also does not observe the heptahydrate in the NaCO<sub>3</sub>-NaCl-H<sub>2</sub>O ternary system. The single point in the K<sub>2</sub>CO<sub>3</sub>-KCl diagram (Fig. 9d) is the K<sub>2</sub>CO<sub>3</sub> · 3/2 H<sub>2</sub>O-KCl coexistence point of BLASDALE (1923). The data for the KHCO<sub>3</sub>-KCl system are those of BAYLISS and KOCH (1952) for sylvite-KHCO<sub>3</sub> coexistence.

The value of the parameter,  $\psi_{\text{SO}_4,\text{CO}_3,\text{K}}$ , is based on the data of HILL and MOSKOWITZ (1929) in the K<sub>2</sub>CO<sub>3</sub>-K<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O system (Fig. 9f). No data are found which are sensitive to the parameter,  $\psi_{\text{SO}_4,\text{HCO}_3,\text{K}}$ . Consequently, this parameter is set equal to zero until data become available. In disagreement with the data of BLASDALE (1923) the calculated reciprocal diagram Na-K-SO<sub>4</sub>-CO<sub>2</sub> displays different, perhaps more stable, mineral coexistences than those reported. In particular, apthitalite appears to occupy a large portion of the

phase diagram where a NaKCO<sub>3</sub> · 6H<sub>2</sub>O-apthitalite-arcanite invariant point is stable. Also, a stable zone for burkeite between the apthitalite-mirabilite and natron fields may be present.

The KOH-K<sub>2</sub>CO<sub>3</sub> data (Fig. 9c) used to fit  $\psi_{\text{OH},\text{CO}_3,\text{K}}$  are that of LANG and SUKAVA (1958) (circles) and KLEBANOV and PINCHUK (1967) (squares). These two sets of data are not in good agreement with each other and an average of the two sets is taken.

A CaOH<sup>+</sup> ion pair is not explicitly included in our model (see section II). The aqueous solution parameters for the Ca(OH)<sub>2</sub>-H<sub>2</sub>O system have been evaluated from the emf data of BATES *et al.* (1959) and the solubility data of MILLIKAN (1918) in the Ca(OH)<sub>2</sub>-CaCl<sub>2</sub>-H<sub>2</sub>O system. In Fig. 11 the calculated solubilities for Ca(OH)<sub>2</sub> and other oxychloride salts are plotted vs. experiment. Since the parameterization is based only on the Bates and Millikan data the calculated solubilities in the Ca(OH)<sub>2</sub>-NaCl, Ca(OH)<sub>2</sub>-KCl, Ca(OH)<sub>2</sub>-NaOH and Ca(OH)<sub>2</sub>-KOH aqueous solutions are checks on the model (Figs. 11c-11f). The agreement is for the most part excellent. The data denoted by squares in Fig. 11c and 11d are those of FRATINI (1949) at 20°C. The analytical values of Fratini are consistently higher than the model and higher than the data of other authors in Ca(OH)<sub>2</sub>-H<sub>2</sub>O solutions (circles in the same figures). An increased chemical potential for portlandite brings all of the Fratini data in good agreement with the model. The data in the NaCl and KCl solutions are those of JOHNSTON and GROVE (1931) and YEATTS and MARSHALL (1957). The CaSO<sub>4</sub>-Ca(OH)<sub>2</sub> data are those of CAMERON and BELL (1906) and JONES (1939). The Bates data are for dilute Ca(OH)<sub>2</sub>-KCl and Ca(OH)<sub>2</sub>-CaCl<sub>2</sub> solutions. The

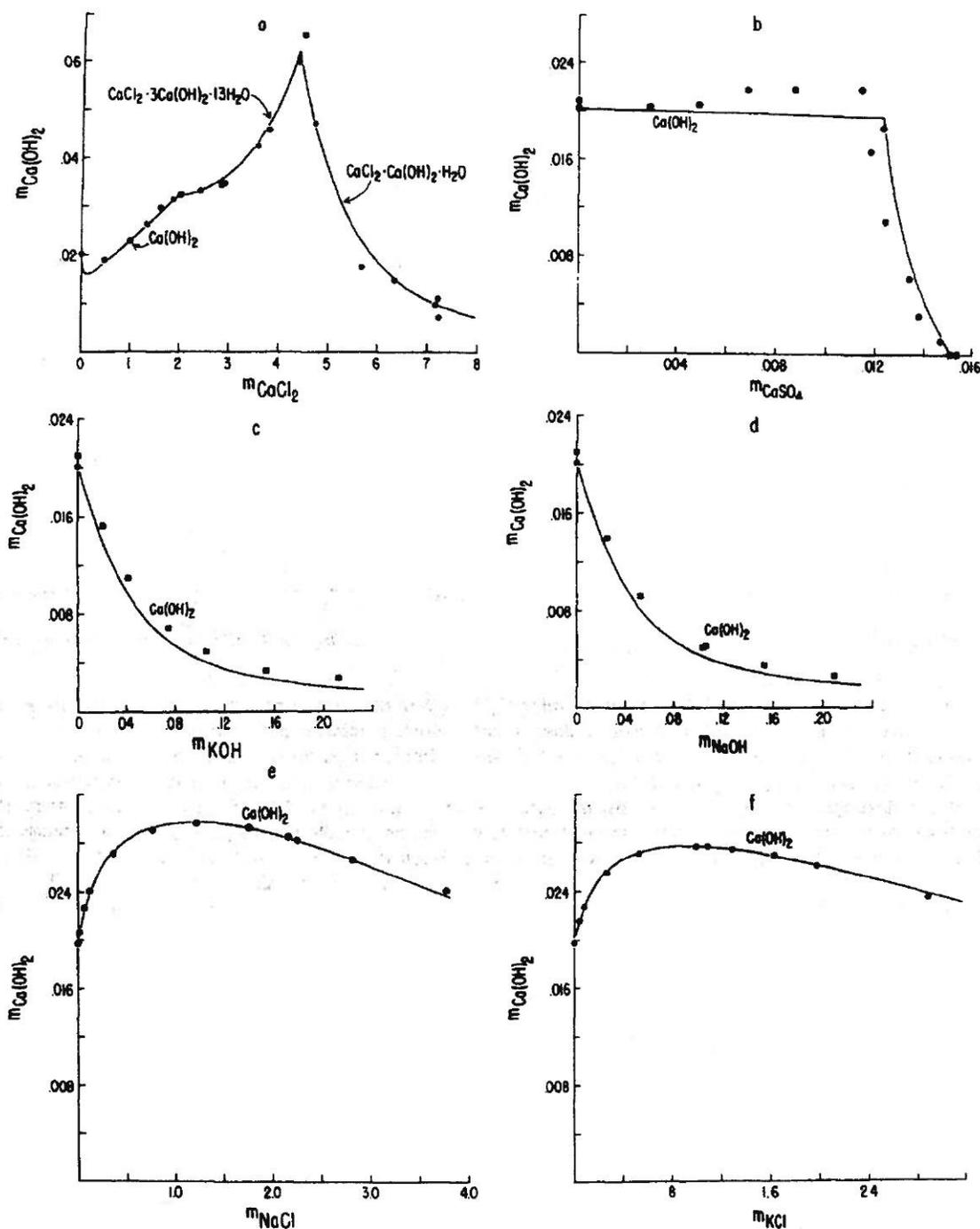


FIG. 11.  $\text{Ca}(\text{OH})_2$  salt solubilities in various salt solutions. In (a) and (b) solubility and emf data are used in parameterization. (c)–(f) are predicted using fully parameterized model.

measurements are at concentrations where significant ion association should be present, yet we did not need to include a  $\text{CaOH}^+$  species to obtain good agreement with the data. The standard deviation of the model to the data is  $\sigma = .003$ .

In Fig. 12a–f the calculated solubilities of calcite (solid curves) in water and NaCl solutions are compared to experiment. The solubilities of aragonite (dashed curves) are also plotted. The experimental data in the

$\text{CaCO}_3\text{-H}_2\text{O-CO}_2$  system (Fig. 12a) are those summarized by JACOBSON and LANGMUIR (1974) to 1 atm. and those of MILLER (1952) (below the curve) and MITCHELL (1923) (above the curve) at higher pressure. For  $\text{CO}_2$  pressures somewhat greater than 1 atm. the fugacity was calculated from the  $\text{CO}_2$  pressure using the real gas virial coefficient summarized in ANGUS *et al.* (1976). Figure 12a compares the calculated and measured solubilities of calcite in pure water as

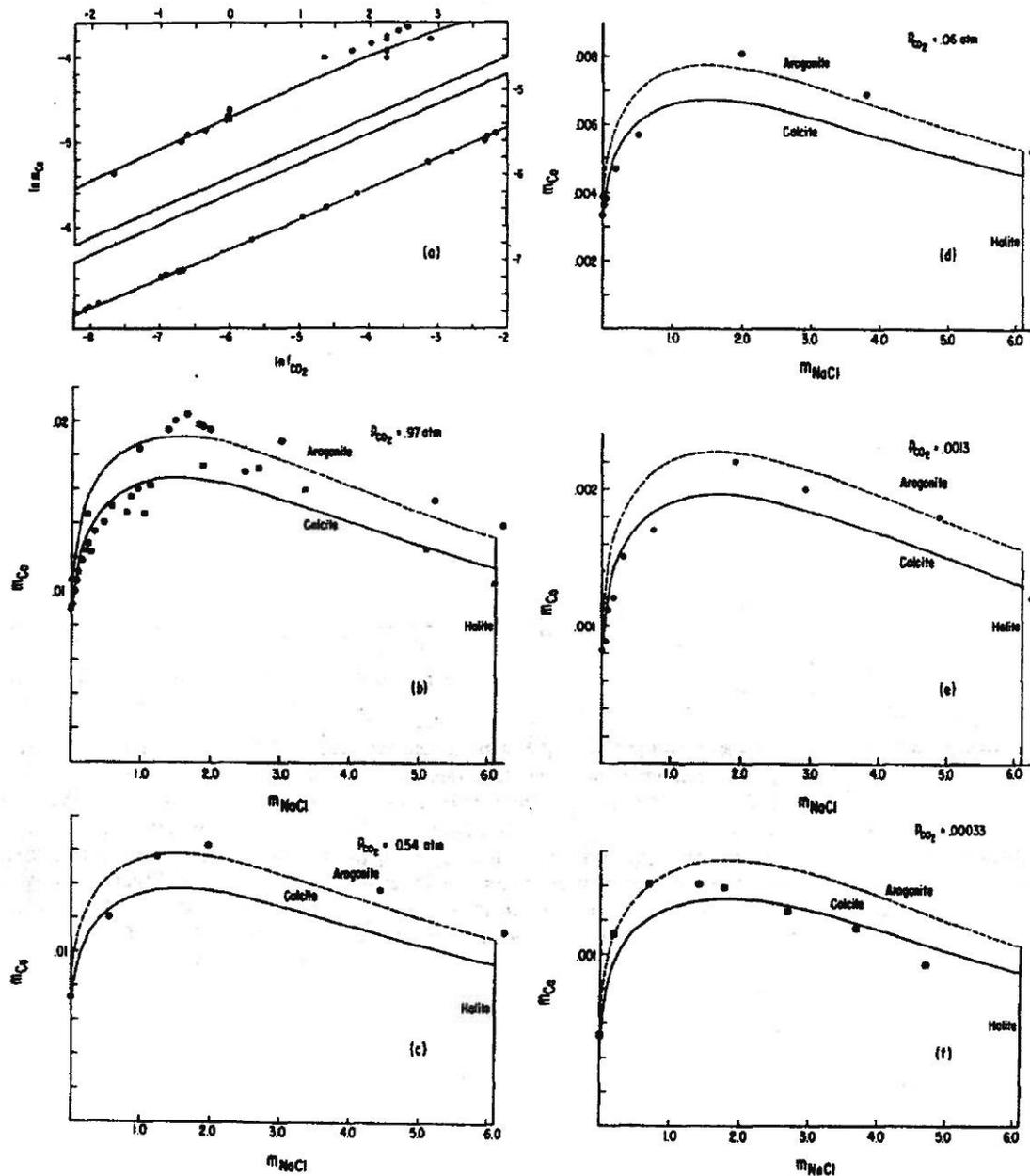


FIG. 12. The solubility of calcite in water (a) and the predicted solubilities of calcite in NaCl solutions (b)-(f).

a function of the fugacity of  $\text{CO}_2$  in the vapor phase. (The lowest and right hand scales depict the lower pressure range, whereas the upper and left hand scales are for higher  $\text{CO}_2$  fugacities.) The calcium carbonate interaction parameters and the chemical potentials for calcite and aragonite are evaluated from these data.  $\mu^0$  for aragonite is evaluated from the data of BACKSTROM (1921).

A neutral ion complex,  $\text{CaCO}_3^0$ , was defined for this system, since the parameter,  $\beta_{\text{CaCO}_3}^{(2)}$ , was extremely large and negative ( $\sim -200$ ) when the pH data of REARDON and LANGMUIR (1974) are fit without this complex. We suspect that the model with the ion com-

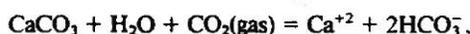
plex is the better model for this system. This is consistent with the conclusions drawn in section II for 2-1 electrolytes. This conclusion is admittedly based on a relatively sparse set of pH data. With or without  $\text{CaCO}_3^0$ , the resulting model is found to be consistent with the  $\text{CaCO}_3\text{-H}_2\text{O-CO}_2$  solubility data when the  $\text{Ca-HCO}_3$  second virial coefficient parameters are adjusted to fit the data.

JACOBSON and LANGMUIR (1974) showed that the  $\text{CO}_2$  pressure dependence of the solubility of calcite in water is not consistent with strong  $\text{Ca}(\text{HCO}_3)_2^+$  ion pair formation. Our calculations agree with this result. Since these solubility data, plotted in Fig. 12, are re-

producible an ion pair is not assumed. Positive coefficients, which are inconsistent with strong association, are obtained when these data are fit without the ion pair,  $\text{CaHCO}_3^+$ . The value for  $\beta_{\text{CaHCO}_3}^{(0)}$  is selected within a range of possible values consistent with the data.  $\beta_{\text{CaHCO}_3}^{(1)}$  is fit to the data given this choice of  $\beta_{\text{CaHCO}_3}^{(0)}$ . More recent data taken by PLUMMER and BUSENBERG (1982) suggest that ion association is important.

In Figs. 12b-f, the predicted solubility of calcite in NaCl solutions is plotted together with the available data. At 0.97 atm. the data are those of SHTERNINA and FROLOVA (1952, 1962), FREAR and JOHNSTON (1929) and CAMERON *et al.* (1907). At lower pressures, the data are primarily those of SHTERNINA and FROLOVA (1952). In Fig. 12f, the results of CAMERON and SEIDELL (1902) are plotted. The Shternina data are consistently designated by circles. All of the data are reported for calcite solubility.

The calculated behavior for the solubility of calcite is constrained by the data in other systems. For  $P_{\text{CO}_2} \geq .06$  atm. the concentrations of  $\text{CO}_3^{2-}$  and  $\text{CaCO}_3^0$  are negligible compared to the solubility of calcite. Consequently, the dominant reaction determining the calcite solubility is:



and the solubility may be calculated to good approximation by the following equation:

$$K = \frac{a_{\text{Ca}}(a_{\text{HCO}_3})^2}{a_{\text{H}_2\text{O}}P_{\text{CO}_2}} \approx 4 \frac{(\gamma_{\text{Ca}^{+2}}^{\text{HCO}_3})^2 m^3}{a_{\text{H}_2\text{O}}P_{\text{CO}_2}}. \quad (11)$$

In the above equation  $m$  is the solubility of calcite. Since the solubility is small, the thermodynamic mean activity coefficient for  $\text{Ca}(\text{HCO}_3)_2$  may be approximated by the trace activity coefficient for  $\text{Ca}(\text{HCO}_3)_2$  in NaCl solutions. This activity coefficient is related to the trace activity coefficients in the  $\text{CaCl}_2$ -NaCl- $\text{H}_2\text{O}$  and  $\text{NaHCO}_3$ - $\text{H}_2\text{O}$  systems by the equation,

$$\gamma_{\text{Ca}(\text{HCO}_3)_2}^{\text{HCO}_3} = \gamma_{\text{CaCl}_2}^{\text{HCO}_3} (\gamma_{\text{HCO}_3}^{\text{HCO}_3} / \gamma_{\text{Cl}})^{2/3}. \quad (12)$$

$\gamma_{\text{CaCl}_2}^{\text{HCO}_3}$  may be determined from the isopiestic data of ROBINSON and BOWER (1966) or from the solubility data of gypsum or portlandite in NaCl solutions. The activity coefficient ratio  $(\gamma_{\text{HCO}_3}^{\text{HCO}_3} / \gamma_{\text{Cl}})$  is measured directly by the emf experiments of HARNED and BONNER (1945) (see also BONNER, 1944) to 1.0 molal NaCl. Our model is in good agreement with all the above data. Substituting Eqn. (12) into Eqn. (11), the following equation is obtained:

$$m = \left( \frac{K a_{\text{H}_2\text{O}}}{4 (\gamma_{\text{CaCl}_2}^{\text{HCO}_3})^2 (\gamma_{\text{HCO}_3}^{\text{HCO}_3} / \gamma_{\text{Cl}})^2} \right)^{1/3} P_{\text{CO}_2}^{1/3}. \quad (13)$$

For relatively large NaCl concentrations the ionic strength,  $a_{\text{H}_2\text{O}}$  and the trace activity coefficients are fixed and the solubility of calcite should depend roughly on the  $\text{CO}_2$  pressure to the  $1/3$  power. As noted by SHTERNINA and FROLOVA (1952), this behavior is satisfied by the data.

Since the solubility of calcite is not negligible, Eqn. (13) is approximate due to the neglect of the Ca- $\text{HCO}_3$  interaction. From other data we have an independent determination of  $\gamma_{\text{Ca}(\text{HCO}_3)_2}^{\text{HCO}_3}$  and we can, therefore, calculate the effects due to this interaction. When the Ca- $\text{HCO}_3$  interaction is positive the observed solubility will be less than that predicted by Eqn. (13) as is the case below 1 m NaCl and for calcite in pure water. When the interaction is negative (*e.g.* ion association) the opposite behavior should be observed. This is consistently the case above 1 m NaCl.

However, there exists an inconsistency between a strong negative interaction and a  $1/3$  power law in the solubility. At 2 m NaCl and  $P_{\text{CO}_2} = .97$  atm. the calculated solubility is about 85% of the experimental value. A  $\text{Ca}(\text{HCO}_3)^+$  ion pair might be introduced to improve the agreement at this pressure and NaCl concentration. However, such a model is inconsistent with other data at lower NaCl concentrations. Furthermore, calculations verify that while agreement can be improved at any given pressure with a  $\text{CaHCO}_3^+$  ion pair, it is not possible to fit the observed pressure dependence of SHTERNINA and FROLOVA (1952) with such a model. As the pressure is reduced, the concentration and the degree of association are also reduced. Further data are needed to understand these discrepancies.

The pH data of STOCK and DAVIES (1948) are used to evaluate the chemical potential for the  $\text{MgOH}^+$  ion pair which is found to have a  $pK_a$  value of 2.19. A liquid junction plus asymmetry potential of .23 pH units is obtained from the acidic region of the titration curve reported by these authors (Table II of SD). While this value is large, our  $K_a$  is also in good agreement with that determined by MCGEE and HOSTETLER (1975) from pH data. With the McGee and Hostetler data, however, the model deviations trend from  $-.029$  at pH = 10.03 to  $.005$  at pH = 10.39. The change in the solution composition for this range is small. If this trend is significant there may be a problem with an  $\text{MgOH}^+$  model. A detailed reversible cell study of the  $\text{Mg}(\text{OH})_2$ - $\text{MgCl}_2$ - $\text{H}_2\text{O}$  system would be useful in precisely characterizing the interactions in this system. Higher concentrations of  $\text{MgCl}_2$  should be possible owing to the increasing solubility of brucite. This study would also be useful due to the importance of the Mg-OH interaction in determining  $pK_w$  in seawater. There is also some evidence that the precipitation of a magnesium oxychloride buffers highly concentrated  $\text{MgCl}_2$  evaporite solutions (BODINE, 1976). Our preliminary calculations support this result.

The solubility data for brucite and magnesium oxychloride in  $\text{MgCl}_2$  solutions are plotted in Fig. 13. Brucite is denoted by the circles and the oxychloride is denoted by squares. Closed points correspond to the data of ROBINSON and WAGGAMAN (1909). Open points are those of D'ANS and KATZ (1941) and D'ANS *et al.* (1955) at 20°C. It is difficult to obtain any definitive information from these data. We, therefore, estimate the intermediate concentration behavior of  $\text{MgOH}^+$  from the CULBERSON and PYTKOWICZ (1973)

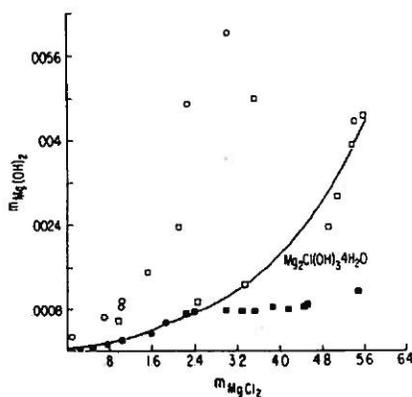


FIG. 13. The predicted solubility of brucite and magnesium oxychloride in Mg-OH-Cl-H<sub>2</sub>O solutions versus the available data.

measurements of  $pK_w$  in artificial seawater. Adjustments in the third virial coefficients,  $\psi_{Mg, MgOH, Cl}$ , are then made so the DBF data are fit at high concentration. We select these over the other data in Fig. 13 since the model fit to the dilute solution and seawater system approximately without the third virial coefficient predicts these data. We also require that the brucite-oxychloride invariant point is less than 2 M MgCl<sub>2</sub> since BODINE (1976) observes conversion of brucite to oxychloride slightly above this concentration. The chemical potential for brucite is evaluated from the equilibrium constant given by MCGEE and HOSTETLER (1973).

In fitting the model to the CULBERSON and PYTKOWICZ (1973) data, the composition of the artificial seawater used in the experiments is also used in the calculations, except that NaF is replaced by NaCl. The presence of F in solution should cause a decrease in the total (stoichiometric) activity coefficient for H due to HF association. The experimentally determined apparent equilibrium constant,  $K'_w = m_H^+ m_{OH}^-$ , should therefore be larger in solutions with traces of fluorine than in solutions without fluorine. However, HANSSON (1972) has determined  $K_w$  in the absence of F, and his values are larger than those in the fluorine containing solutions when corrected to the same units as CP. Our calculations indicate that the difference cannot be explained by the concentration differences of the artificial seawater used in the different studies. For the above reasons, we make no corrections for this effect. The fitted results are compared to the data in Table 6. Values for  $\Delta pH$  (Eqn. 10) calculated from these data and the activity coefficient for H (in molality units) are also given.

The Mg-HCO<sub>3</sub> and Mg-CO<sub>3</sub> interaction parameters are estimated from the HANSSON (1973) data for  $K'_1$  and  $K'_2$  in seawater together with the high pressure nesquehonite solubility data of MITCHELL (1923) and the  $P_{CO_2} \sim 1$  atm result of KLINE (1929). The high pressure (1-10 atm) trend for the solubility has been reproduced at a number of different temperatures and

the .97 atm result is in agreement with these determinations as well as the smoothed temperature dependence (See LINKE, 1965, and LANGMUIR, 1965). In fitting the high pressure results the fugacity-pressure correction is made as in the CaCO<sub>3</sub> system.

In Table 7, reported  $pK'_1$  and  $pK'_2$  values are compared to those calculated. The total hydrogen activity coefficients (in NBS convention), determined by MEHRBACH *et al.* (1973) may be used with the calculated activity coefficients in the MacInnes convention to evaluate the liquid junction potential contribution,  $\Delta pH$ , using Eqn. (10) (section III). The resulting values differ from those calculated with the CULBERSON and PYTKOWICZ (1973) data by about .02 pH units (see Table 6). Since the differences in the concentration are small (as comparison of the calculated  $\gamma_H^M$  suggests), this would appear to reflect a changing liquid junction potential. (MEHRBACH *et al.*, 1973, observe a .011 pH change between "identical" reference electrodes.)

There appear to be some problems with the lower pressure results of KLINE (1929). A solubility product for nesquehonite of  $3.5 \times 10^{-5}$  is consistent with the Kline brucite-nesquehonite equilibrium  $P_{CO_2}$  (.00038 atm.) and the MCGEE and HOSTETLER (1973) brucite solubility product. Using the  $3.5 \times 10^{-5}$  value and the analytic concentrations of Mg and HCO<sub>3</sub> cited by Kline,  $\gamma_{Mg(HCO_3)_2}^{\pm}$  is calculated to be greater than one at lower pressures. Assuming the solubility product of  $1.1 \times 10^{-5}$  cited by Kline,  $\gamma_{Mg(HCO_3)_2}^{\pm} = .76$  at  $P_{CO_2} = .000511$ . The limiting law value of  $\gamma_{Mg(HCO_3)_2}^{\pm}$  is .59. To fit this difference with an extended Debye-Hückel equation requires a very large ionic radius of about 10 Å (for a model without ion pairs). Furthermore, this 10 Å Debye-Hückel model is not consistent with the reproducible (see above) solubility data of nesquehonite at  $P_{CO_2} \approx 1$  atm.

Assuming that the Kline nesquehonite data are accurate, a  $K_{sp} = 1.2 \times 10^{-4}$  may be determined from the Mg and HCO<sub>3</sub> concentrations at low pressures assuming limiting law activity coefficients. To explain the high carbonate concentrations at low pressures a MgCO<sub>3</sub><sup>0</sup> ion pair (or large negative MgCO<sub>3</sub> interaction parameters) may be defined. This model, however, cannot account for the rapidly decreasing total CO<sub>3</sub> concentration observed by Kline at high pressure. (The MgCO<sub>3</sub><sup>0</sup> concentration is fixed when in equilibrium with nesquehonite, neglecting small changes in a<sub>H<sub>2</sub>O</sub>, and the concentration determined from the low

Table 6:  $pK_w$  in seawater at various salinities.

Salinity	19.90	26.87	34.82	44.0
$pK_w^{\pm}$ (exp)	13.31-13.32	13.24-13.25	13.19	13.12
$pK_w$ (calc)	13.32	13.25	13.19	13.12
$\gamma_{H^+}^{NBS}$ (exp)	.695-.698	.694-.696	.702-.704	.719-.723
$\gamma_{H^+}$ (calc)	.630	.623	.624	.632
$\Delta pH$	.043-.044	.047-.048	.051-.052	.056-.058
$*K_w = m_H^+ m_{OH}^-$ (molality) <sup>2</sup>				

The data for  $pK_w$  and  $\gamma_{H^+}^{NBS}$  are those cited by Culberston and Pytkowicz (1973) (converted from molarity to molality units).  $\gamma_{H^+}^{NBS}$  is the total hydrogen ion activity coefficient defined by the convention,  $pH(NBS) = -\log_{10} a_{H^+}$ .  $\gamma_{H^+}$  is the hydrogen ion activity coefficient defined using the extended MacInnes convention, Eq. (7c). pH is calculated using Eq. (10).

Table 7:  $pK_1'$  and  $pK_2'$  calculated from a fit of Hansson's data (1973).

Salinity (‰)	$\gamma_H$	$pK_1'$ (calc)	$pK_1'$ (Mehrbach)	$pK_1'$ (Hansson)	$pK_2'$ (calc)	$pK_2'$ (Mehrbach)	$pK_2'$ (Hansson)
20	.631	5.893	5.920	5.921	9.133	9.130	9.117
25	.625	5.865	5.882	5.892	9.064	9.060	9.052
30	.624	5.842	5.860	5.866	9.006	9.000	8.987
35	.625	5.823	5.833	5.842	8.956	8.949	8.932
40	.629	5.808	5.810	5.831	8.917	8.896	8.883

$$(a) K_1' = \frac{(H_2CO_3)}{(CO_2, aq.)}; K_2' = \frac{(HCO_3^-)(CO_3^{2-})}{(HCO_3^-)} \quad (\text{concentration products}) \text{ molality units}$$

All  $pK'$ 's are in terms of molality;  $\gamma_H$  is in the MacInnes convention and is in terms of molality. Mehrbach *et al.* (1973) results are interpolated and corrected for HF.

pressure data is significantly larger than the total  $CO_3$  observed at high pressure.)

To explain the Kline data, we must assume that enormous changes in the interactions occur over a very small concentration range. We could not fit the Kline data, using a number of conventional electrolyte solution models including those with and without  $MgHCO_3^+$ , etc. type ion pairs. Kline points to some problems with his  $HCO_3^-$  determination. Also, his solutions may not have equilibrated with the low  $P_{CO_2}$  atmospheres in 3 to 5 days. As nesquehonite dissolves,  $CO_2$  is depleted from solution. If  $CO_2$  were not sufficiently replenished from the atmosphere, the apparent  $CO_2$  pressure could be significantly reduced and brucite would precipitate. This might explain Kline's observation of the nesquehonite to brucite conversion at a seemingly high  $P_{CO_2}$ . Using our model derived from data other than Kline's we calculate the total Mg concentration at nesquehonite-brucite equilibrium to be .0140. This is in agreement with the value of .0136 which Kline extrapolated from his alkalinity measurements, but our calculated transition pressure is  $7.6 \times 10^{-5}$  atm. as compared to Kline's value of  $3.8 \times 10^{-4}$  atm. Further data for this system are needed.

After establishing the parameters  $\beta^0$  and  $\beta^{(1)}$  for the  $MgHCO_3$  and  $MgCO_3$  systems, the parameters  $\psi_{Mg,HCO_3,SO_4}$  and  $\psi_{Mg,HCO_3,Cl}$  were obtained from the nesquehonite solubility data of TRENDAFELOV *et al.* (1981). The low concentration end of these data places a rather strong constraint on the acceptable values of  $\beta^{(1)}$  and  $\beta^{(0)}$ . The predicted solubilities of the model for these systems are compared to experimental data in Fig. 14.

In Fig. 15, the pH for 35‰ salinity seawater in equilibrium with calcite is plotted versus the carbonate alkalinity. The data are those of MORSE *et al.* (1980). These authors determine the calcium concentration, pH, and carbonate alkalinity,  $A_c$ . Calcite equilibrium is approached from supersaturation and undersaturation in a closed apparatus. The supersaturation experiments are performed by adding calcite to natural seawater. For these experiments the relationship,  $2m_{Ca} - A_c = Q$ , (where  $Q$  is a constant for seawater), is approximately satisfied by their data. The curve corresponding to the data from supersaturation is calculated using seawater with composition given in Table 8. In Table 8, the molal concentration of 35‰ salinity seawater are given together with the calculated total MacInnes ion activity coefficients. The seawater con-

centrations are derived from the Appendix Table 2 in RILEY and SKIRROW (1975).

Starting with natural seawater, in contact with calcite crystals, calcite will precipitate from solution under atmospheric conditions. Specification of one additional variable, such as pH,  $P_{CO_2}$  or  $A_c$  is sufficient to completely define chemical equilibrium. For a given value of  $A_c$ , the pH and  $P_{CO_2}$  can be calculated from equilibrium conditions using a model. The data and calculated curve in Fig. 15 represent the dependence of the equilibrium pH as a function of  $A_c$ . The apparent  $P_{CO_2}$  also varies along the curve. By virtue of electrical

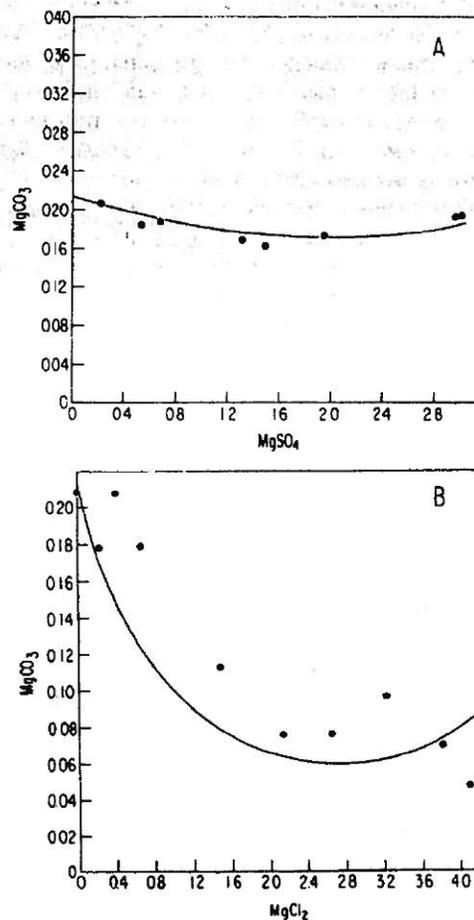


FIG. 14. Predicted solubility of nesquehonite in  $MgSO_4$  (a) and  $MgCl_2$  (b) solutions.

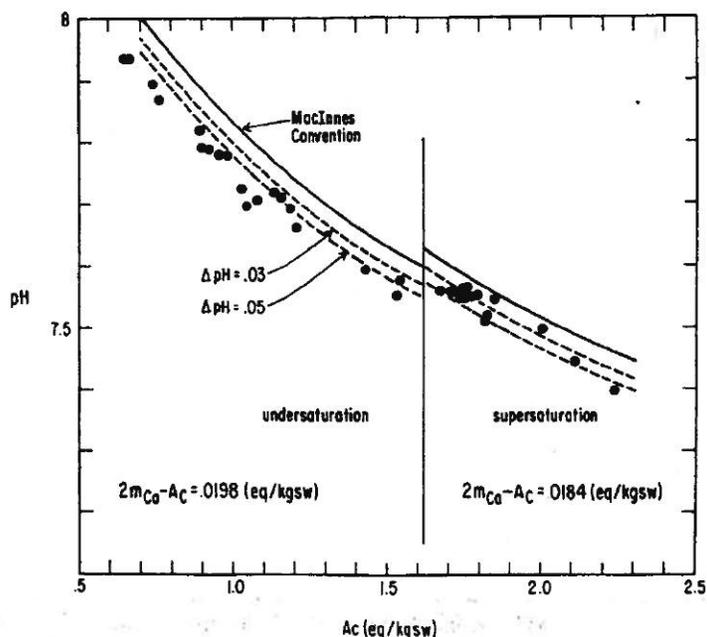


FIG. 15. The predicted relationship between pH and carbonate alkalinity ( $A_c = (\text{HCO}_3^-)_T + 2(\text{CO}_3^{2-})_T$ ) for seawater at 35‰ and 25°C in equilibrium with calcite. Closed circles represent the raw data of MORSE *et al.* (1980).

neutrality constants, the function is independent of the equilibrium values of  $P_{\text{CO}_2}$ , pH or  $A_c$ . For unmodified seawater  $Q = .018$  eq/kg SW.

To approach calcite equilibrium from undersaturation, Morse *et al.* add a small amount of HCl to undersaturate the natural seawater with respect to calcite. From the average value of  $Q$  calculated for the data from undersaturation, the quantity of HCl added has been estimated and added to the synthetic seawater in Table 8. This modified seawater solution was then used to calculate the curve corresponding to the undersaturation approach to equilibrium (leftmost curve in Fig. 15).

Table 8: The composition of artificial 35‰ salinity seawater used in the calculations for this article and the total ion activity coefficients calculated with the extended MacInnes ion activity coefficient convention (Eq. (7c)).

i	$n_i$	$\gamma_i^T$
Na	.48695	.706
K	.01063	.651
Ca	.01073	.229
Mg	.05516	.251
H	-	.622
Cl	.56817	.623
$\text{SO}_4$	.02939	.0864
OH	-	.243
$\text{HCO}_3$	.00185	.547
$\text{CO}_3$	.000276	.0346
$\text{CO}_2$	$9.63 \times 10^{-4}$	1.13
$P_{\text{CO}_2}$	$3.3 \times 10^{-4}$	-
$-\log_{10} a_{\text{H}^+}$	8.31	-
$a_{\text{H}_2\text{O}}$	.981	-

The solution given is in equilibrium with a  $\text{CO}_2$  pressure of  $3.3 \times 10^{-4}$  atm. Units are in moles/kg  $\text{H}_2\text{O}$ . Neutral activity coefficients can be calculated using the formula Eq. (8.6) in Appendix B, i.e.  $\gamma_{\text{CaCO}_3}^T = [(.23)(.035)]^4$ . The concentrations and activity coefficients are cited to high accuracy to facilitate program verification. See Harvie *et al.* (1982) for tables which are also useful in this regard.

The solid curves in Fig. 15 correspond to the calculated "pH" using the conventional hydrogen activity for the MacInnes convention. The two dashed curves are calculated assuming that  $\Delta\text{pH}$  for the Morse *et al.* apparatus equals .03 (Table 6) or .05 (Table 7). The .05 curve is generally above the undersaturated data points and below the supersaturation points. There appears to be little trend in the data with equilibration times or the small variations in  $Q$ . Morse *et al.* also report no statistically significant variation in the solubility with the solid calcite to solution ratio.

The increased solubility due to the precipitation of magnesium-calcite surface layers has recently received careful consideration (WOLLAST *et al.*, 1980; SCHOONMAKER, 1981). The measurements from supersaturation of Morse *et al.* should presumably be sensitive to this effect although undersaturated experiments should not. With the uncertainty due to the liquid junction and the potential formation of magnesium-calcite surface layers, it is not possible to make an exact comparison to the data of Morse *et al.* Pessimistically, the calculation is within 10% of the true solubility. If  $\Delta\text{pH} = .05$  and the data represent true calcite equilibrium the agreement is much better. Using the model, a value of  $K'_{\text{calcite}} = m_{\text{Ca}}^T m_{\text{CO}_3}^T = 4.98 \times 10^{-7}$  (molal)<sup>2</sup> is obtained ( $4.65 \times 10^{-7}$  (moles/kg SW)<sup>2</sup>).

## V. DISCUSSION

In the previous section, we have utilized, for the most part, data in binary and ternary systems to parameterize the solution model. We have tested the

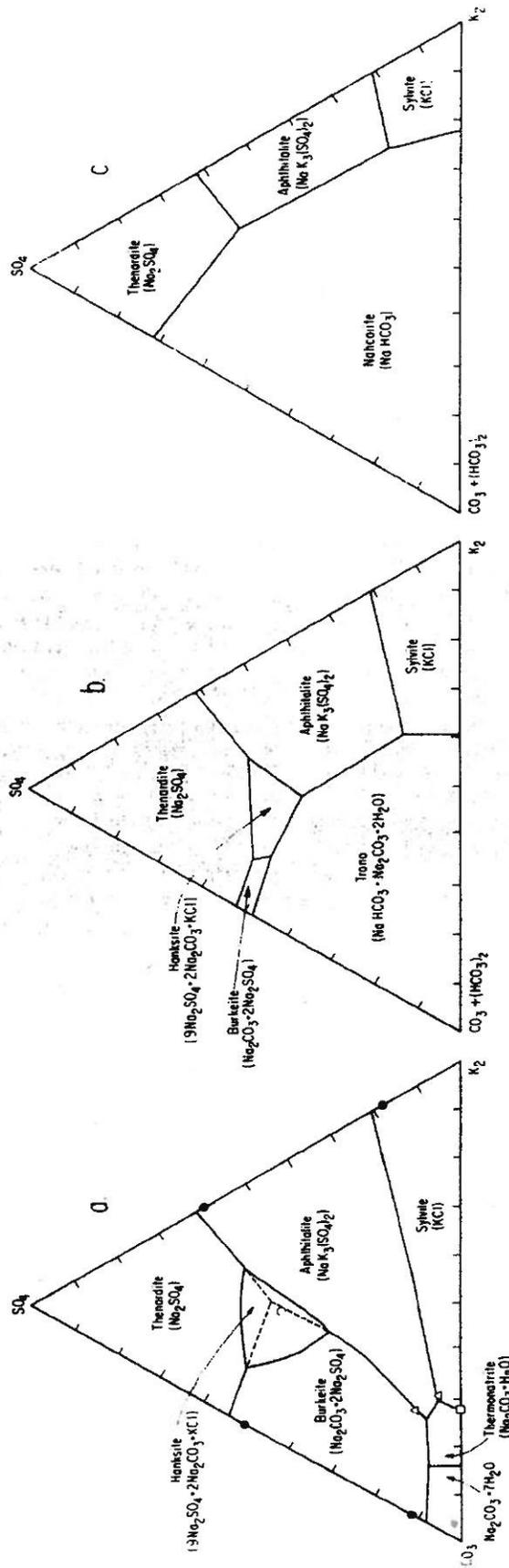


FIG. 16. Predicted mineral solubilities in the Na-K-Cl-SO<sub>4</sub>-CO<sub>2</sub>-H<sub>2</sub>O system at 25°C. All solutions are also saturated with halite (NaCl). (a) Predicted phase equilibria for the closed CO<sub>2</sub> system. The data denoted by closed circles are those of D'ANS (1933) and MAKAROV and BLEIDEN (1938). The open circle (Aph-Bur-Hal-Thern) was interpolated between the 35°C and metastable 20°C data of TEEPLE (1929). The open square was extrapolated from the 35°C and 50°C data of Teple. The open triangles were estimated from the 35°C and 50°C data of Teple and the invariant points at 20°C where Na<sub>2</sub>CO<sub>3</sub> · 7H<sub>2</sub>O replaces thernonitrite. Similar estimates using the Teple data are in good agreement with the closed circles. (b) Predicted phase equilibria at the atmospheric P<sub>CO<sub>2</sub></sub> level of 3.3 × 10<sup>-4</sup> atm. (c) Predicted phase equilibria at 3.3 × 10<sup>-3</sup> P<sub>CO<sub>2</sub></sub>, or 10 times the atmospheric P<sub>CO<sub>2</sub></sub> level.

model by calculating mineral solubilities in different, more complex systems. For example, in Fig. 15, the predicted relationship between the pH and carbonate alkalinity of 35‰ salinity seawater in equilibrium with calcite is shown to be in good agreement with experiment.

The chemistry of seawater has been well measured. While this system provides an excellent test of the model, there are other models which can accurately produce these data over a limited range of composition and concentration. The model, used in calculating Fig. 15, also accurately predicts thermodynamic properties to very high concentration for systems with composition very different from seawater. This capability is unique. To illustrate this flexibility, the predicted halite-saturated Jänecke projection for the Na-K-Cl-SO<sub>4</sub>-CO<sub>2</sub>-H<sub>2</sub>O quinary system is compared to experimental data in Fig. 16a.

The calculations and data depicted in Fig. 16a are confined to a closed system, where CO<sub>2</sub> bearing minerals are dissolved in water and CO<sub>2</sub> transfer between the atmosphere and solution is prevented. For many natural waters, the aqueous CO<sub>2</sub> activity or the effective equilibrium  $P_{\text{CO}_2}$  is controlled by reaction with the atmosphere, photosynthesis, water-rock reactions, etc. Fig. 16b and 16c depict the change in the phase equilibria from that shown in Fig. 16a when the solutions are allowed to equilibrate with a gas phase of constant  $P_{\text{CO}_2}$  ( $3.3 \times 10^{-4}$  and  $3.3 \times 10^{-3}$  atm., respectively).

Comparison of Figs. 16a, 16b and 16c illustrates the strong  $P_{\text{CO}_2}$  dependence of the stable mineral equilibria. It is known that the aqueous CO<sub>2</sub> activity is an important indicator of the chemical processes leading to the formation and subsequent diagenetic evolution of carbonate sediments. However, quantitative interpretation of carbonate sediments in terms of this CO<sub>2</sub> variable has not generally been possible due to the lack of data or of a sufficiently accurate model. The model described here enables accurate prediction of the CO<sub>2</sub> activity for arbitrary fluid composition in the eight-component system. This allows improved analysis of mineral stabilities and directions of diagenetic reactions in carbonate mineral systems by quantitative equilibrium and ion activity product calculations.

It is apparent that we have relied on a diverse set of data, much of which is over half a century old, in our effort to obtain a complete model for the system Na-K-Mg-Ca-H-Cl-SO<sub>4</sub>-OH-HCO<sub>3</sub>-CO<sub>3</sub>-CO<sub>2</sub>-H<sub>2</sub>O. We have attempted to identify compositional ranges where additional data would significantly improve the accuracy of the model. For many systems, it was necessary to estimate parameter values from limited and often unreproduced data. We believe that an increased effort to experimentally characterize the chemical interactions between the various aqueous species by examining the thermodynamics of binary and ternary systems in detail will lead to a significant improvement in the quantitative understanding of the thermodynamics of carbonate natural waters.

We have utilized earlier versions of the Pitzer pa-

rameters, some of which have more recently been improved (see DOWNES and PITZER, 1976; PEIPER and PITZER, 1981). In the future, as refinements of the model are made, we will attempt to incorporate the currently accepted parameter values into the solubility model. The reader is cautioned, however, from modifying parameters in the present model without extensive checking of the calculated solubilities, since the parameters are quite interdependent. The parameter values in Tables 1-4 are a function of the model chosen. The parameters in Table 4 may differ slightly from those of other authors. However in order to obtain consistent solubilities these values must be used.

The most important limitation of the application of this and similar models to natural systems is the inherent equilibrium nature of the predictions. Recently, we have used this model to compare the evolution of seawater in natural evaporation processes with the prediction of chemical equilibrium. The agreement between the results of the equilibrium models and the measured field results is remarkable, emphasizing the value of equilibrium evaporation paths as guidelines for understanding evaporite evolution (MØLLER *et al.*, in preparation).

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## APPENDIX A PHENOMENOLOGICAL EQUATIONS

The theory of calculating multiphase equilibria at fixed temperature and pressure is based on the Gibbs free energy minimization principle (CALLEN, 1960). The solution to the following minimization problem is required.

Minimize

$$G = \sum_{i=1}^N n_i \mu_i \quad (\text{A.1a})$$

subject to

$$\sum_{i=1}^N n_i c_{ij} = b_j \quad j = 1, M + P_E \quad (\text{A.1b})$$

$$n_i \geq 0 \quad i = 1, N$$

In Eqn. (A.1),  $G$  is the Gibbs free energy for the system;  $n_i$  is the number of moles of species  $i$ ;  $\mu_i$  is the chemical potential for species  $i$ ;  $b_j$  is the number of moles of component  $j$ ;  $c_{ij}$  are the coefficients in the linear mass and charge balance equations;  $N$  is the total number of species;  $P_E$  is the number of possible electrolyte aqueous and solid solution phases; and  $M$  is the total number of components. All the variables in Eqn. (A.1) are adequately defined except the chemical potentials, which depend upon the macroscopic chemical properties of the system. Since it is currently impossible to calculate these properties *ab initio*, a phenomenological description of these functions must be provided.

It is conventional to define the activities of the species,  $a_i$ , in electrolyte solutions by the following equation:

$$\left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j} = \mu_i = \mu_i^0 + RT \ln a_i \quad (\text{A.2a})$$

where  $\mu_i^0$  is the standard chemical potential for species  $i$ . The activity and osmotic coefficients are defined by

$$\ln a_i = \ln \gamma_i m_i \quad (\text{A.2b})$$

for each solute species  $i$  and,

$$\ln a_{\text{H}_2\text{O}} = -\frac{W}{1000} \left(\sum_i m_i\right) \phi \quad (\text{A.2c})$$

for the solvent,  $\gamma_i$  and  $m_i$  are the activity coefficient and molality of the solute species. The osmotic coefficient,  $\phi$ , is related to the activity of the solvent by Eqn. (A.2c) where  $W$  is the molecular weight of water (18.016). (The sum over  $i$  in Eqn. (A.2c) represents the sum over all solutes: cations, anions and neutrals.)

The chemical potentials for pure phases, such as minerals, are constants at fixed temperature and pressure. For gases, the fugacity of a gas phase species,  $f_i$ , is defined by the equation.

$$\frac{\mu_i}{RT} = \frac{\mu_i^0}{RT} + \ln f_i \quad (\text{A.2d})$$

For many gases below one atm., the fugacity nearly equals the partial pressure,  $P_i$ .

The remaining variables lacking explicit definition in the theory are the excess functions,  $\gamma_i$  and  $(\phi - 1)$ . We use the semiempirical equations of PITZER (1973) and co-workers to model these functions. These functions have been rewritten in Eqn. (A.3), and resemble those of HW except for the addition of terms for neutral species. The neutral species terms

include new parameters,  $\lambda$ , which account for the interactions between neutral species and ionic species in the solution (see PITZER and SILVESTER, 1976). In the carbonate system, the inclusion of neutral species (e.g.  $\text{CO}_2(\text{aq})$ ) is required to describe observed solution behavior.

$$\begin{aligned} & \sum_i m_i(\phi - 1) \\ &= 2(-A^*I^{3/2}/(1 + 1.2I^{1/2}) + \sum_{c=1}^{N_c} \sum_{a=1}^{N_a} m_c m_a (B_{ca}^* + ZC_{ca}) \\ &+ \sum_{c=1}^{N_c-1} \sum_{c'=c+1}^{N_c} m_c m_{c'} (\Phi_{cc'}^* + \sum_{a=1}^{N_a} m_a \psi_{cca}) \\ &+ \sum_{a=1}^{N_a-1} \sum_{a'=a+1}^{N_a} m_a m_{a'} (\Phi_{aa'}^* + \sum_{c=1}^{N_c} m_c \psi_{aac}) \\ &+ \sum_{a=1}^{N_a} \sum_{a'=1}^{N_a} m_a m_{a'} \lambda_{aa'} + \sum_{a=1}^{N_a} \sum_{c=1}^{N_c} m_a m_c \lambda_{ac} \end{aligned} \quad (\text{A.3a})$$

$$\begin{aligned} \ln \gamma_M &= z_M^2 F + \sum_{a=1}^{N_a} m_a (2B_{Ma} + ZC_{Ma}) \\ &+ \sum_{c=1}^{N_c} m_c (2\Phi_{Mc} + \sum_{a=1}^{N_a} m_a \psi_{Mc a}) \\ &+ \sum_{a=1}^{N_a-1} \sum_{a'=a+1}^{N_a} m_a m_{a'} \psi_{aa'M} + |z_M| \sum_{c=1}^{N_c} \sum_{a=1}^{N_a} m_c m_a C_{ca} \\ &+ \sum_{a=1}^{N_a} m_a (2\lambda_{aM}) \end{aligned} \quad (\text{A.3b})$$

$$\begin{aligned} \ln \gamma_X &= z_X^2 F + \sum_{c=1}^{N_c} m_c (2B_{cX} + ZC_{cX}) \\ &+ \sum_{a=1}^{N_a} m_a (2\Phi_{Xa} + \sum_{c=1}^{N_c} m_c \psi_{Xac}) + \sum_{c=1}^{N_c-1} \sum_{c'=c+1}^{N_c} m_c m_{c'} \psi_{cc'X} \\ &+ |z_X| \sum_{c=1}^{N_c} \sum_{a=1}^{N_a} m_c m_a C_{ca} + \sum_{a=1}^{N_a} m_a (2\lambda_{aX}) \end{aligned} \quad (\text{A.3c})$$

$$\ln \gamma_N = \sum_{c=1}^{N_c} m_c (2\lambda_{nc}) + \sum_{a=1}^{N_a} m_a (2\lambda_{na}) \quad (\text{A.3d})$$

In Eqn. (A.3)  $m_c$  and  $z_c$  are the molality and charge of cation  $c$ .  $N_c$  is the total number of cations. Similar definitions apply for anions,  $a$ , and neutrals,  $n$ . The subscripts M, X and N refer to cations, anions, and neutrals, respectively. For use in Eqn. (A.3), the following terms are defined.

$$\begin{aligned} F &= -A^* \left( \frac{I^{1/2}}{1 + 1.2I^{1/2}} + \frac{2}{1.2} \ln(1 + 1.2I^{1/2}) \right) \\ &+ \sum_{c=1}^{N_c} \sum_{a=1}^{N_a} m_c m_a B_{ca} + \sum_{c=1}^{N_c-1} \sum_{c'=c+1}^{N_c} m_c m_{c'} \Phi_{cc'} \\ &+ \sum_{a=1}^{N_a-1} \sum_{a'=a+1}^{N_a} m_a m_{a'} \Phi_{aa'} \end{aligned} \quad (\text{A.4a})$$

$$C_{MX} = C_{MX}^* / 2 |z_M z_X|^{1/2} \quad (\text{A.4b})$$

$$Z = \sum_i |z_i| m_i \quad (\text{A.4c})$$

$A^*$  is one third the Debye-Hückel limiting slope and equal to .39 at 25°C (BRADLEY and PITZER, 1979).

Equations (A.2b) and (A.3c) are ion activity coefficients which have been defined by convention. In general, the thermodynamic properties of a system do not depend upon the value of any single ion activity (GUGGENHEIM, 1929, 1930a). Consequently, single ion activity cannot be measured, and

Eqn. (A.3) should not be interpreted as having special physical significance as written. Equations (A.3b) and (A.3c) are symmetric for anions and cations, and satisfy Maxwell relationships among all the species in solution. When these equations are used to calculate mean activity coefficients, or any linear combination,  $\sum \nu_i \ln a_i$ , for which  $\sum \nu_i z_i = 0$ , (e.g. solubilities), they are equivalent to the equations given by Pitzer and co-workers.

The second virial coefficients, B, in Eqn. (A.3) are given the following ionic strength dependence. (See PITZER, 1973).

$$B_{MX}^* = \beta_{MX}^{(0)} + \beta_{MX}^{(1)} e^{-\alpha_{MX} \sqrt{I}} + \beta_{MX}^{(2)} e^{-12\sqrt{I}} \quad (\text{A.5a})$$

$$B_{MX} = \beta_{MX}^{(0)} + \beta_{MX}^{(1)} g(\alpha_{MX} \sqrt{I}) + \beta_{MX}^{(2)} g(12\sqrt{I}) \quad (\text{A.5b})$$

$$B_{MX}^* = \beta_{MX}^{(1)} g'(\alpha_{MX} \sqrt{I}) / I + \beta_{MX}^{(2)} g'(12\sqrt{I}) / I \quad (\text{A.5c})$$

The functions,  $g$  and  $g'$ , are defined by the equations,

$$g(x) = 2(1 - (1+x)e^{-x})/x^2 \quad (\text{A.5d})$$

$$g'(x) = -2 \left( 1 - \left( 1 + x + \frac{x^2}{2} \right) e^{-x} \right) / x^2 \quad (\text{A.5e})$$

with  $x = \alpha_{MX} \sqrt{I}$  or  $12\sqrt{I}$ . When either cation M or anion X is univalent  $\alpha_{MX} = 2.0$ . For 2-2 or higher valence pairs  $\alpha_{MX} = 1.4$ . In most cases  $\beta^{(2)}$  equals zero for univalent type pairs. For 2-2 electrolytes a non-zero  $\beta^{(2)}$  is more common. The addition of a  $\beta^{(2)}$  term for univalent electrolytes represents a minor modification of the original Pitzer approach. This term has primarily been utilized to describe small negative deviations from the limiting law which are observed for certain pairs of ions. A more detailed discussion is given in Section II.

The second virial coefficients,  $\Phi$ , which depend on ionic strength, are given the following form (see PITZER, 1975).

$$\Phi_{ij}^* = \theta_{ij} + {}^E\theta_{ij}(I) + I^2 \theta_{ij}^{(2)}(I) \quad (\text{A.6a})$$

$$\Phi_{ij} = \theta_{ij} + {}^E\theta_{ij}(I) \quad (\text{A.6b})$$

$$\Phi_{ij}^* = {}^E\theta_{ij}^{(2)}(I) \quad (\text{A.6c})$$

The functions,  ${}^E\theta_{ij}(I)$  and  $\theta_{ij}^{(2)}(I)$  are functions only of ionic strength and the electrolyte pair type. Integrals defining these terms are given by PITZER (1975) and are summarized in the Appendix of HW. The interested reader is referred to HARVIE (1981) for a useful numerical method for calculating these functions. The constant,  $\theta_{ij}$ , is a parameter of the model.

The second virial coefficients,  $\lambda_{ia}$ , representing the interactions between ions and neutral species are assumed to be constant. The form of Eqn. (A.3) for neutral species follows very closely the treatment of PITZER and SILVESTER (1976). We refer the reader to this article for details concerning the derivation of these equations.

The third virial coefficients,  $C_{MX}^*$  and  $\psi_{ijk}$ , are also assumed to be independent of ionic strength.  $C_{MX}^*$  is a single electrolyte parameter which is related to  $C_{MX}$  in Eqn. (A.3) by Eqn. (A.4b).  $\psi_{ijk}$  are mixed electrolyte parameters which are defined when the indices  $i, j$ , and  $k$  do not all correspond to ions of the same sign. By convention, the first two subscripts are chosen as the like charged ions and the last subscript is chosen as the oppositely charged ion.

The complete set of parameters defining the model for the nonideal behavior of electrolyte solutions are:  $\beta_{MX}^{(0)}$ ,  $\beta_{MX}^{(1)}$ ,  $\beta_{MX}^{(2)}$  and  $C_{MX}^*$  for each cation-anion pair, MX;  $\theta_{ij}$  for each cation-cation and anion-anion pair;  $\psi_{ijk}$  for each cation-cation-anion and anion-anion-cation triplet; and  $\lambda_{ia}$  for ion-neutral pairs. Given a set of mole numbers which satisfy charge balance (Eqn. A.1b), the molalities and, consequently, the functions  $I$ ,  $Z$ ,  $g$ ,  $g'$ ,  ${}^E\theta$  and  $\theta^{(2)}$  can be calculated. The functions  $B_{MX}^*(I)$ ,  $B_{MX}(I)$ ,  $B_{MX}^*(I)$ ,  $\Phi_{ij}^*(I)$ ,  $\Phi_{ij}(I)$ ,  $\Phi_{ij}^{(2)}(I)$  and then  $F$  may be calculated using their defining equations. Given these parameters the free energy may be calculated from Eqns. (A.1)-(A.2). Equilibrium conditions are defined when the assumed set of  $n_i$  minimizes the free energy, Eqn. (A.1). Mathematical

procedures for adjusting the values for the  $n_i$  so that the free energy is minimized are discussed elsewhere (HW). The parameters which completely define the model for the Na-K-Mg-Ca-H-Cl-SO<sub>4</sub>-HCO<sub>3</sub>-CO<sub>3</sub>-OH-CO<sub>2</sub>-H<sub>2</sub>O system are given in Tables 1, 2, 3 and 4. The process of determining these parameters is discussed in some detail in section IV.

### APPENDIX B

As has been discussed in detail by GUGGENHEIM (1929, 1930a) an ion activity or ion chemical potential cannot be measured by experiment; e.g., emf, phase equilibria, diffusion rates or reaction rates. However, ion activities may be defined by convention. In the following discussion, we demonstrate that the emf for a cell with a liquid junction can be calculated using any convention for the ion activities. Similar analyses implying the following results are discussed elsewhere (BATES, 1973; GUGGENHEIM, 1960; and MACINNES, 1961).

Consider the electrochemical cell, discussed in section III,



The emf of the cell is not an equilibrium property of the system. In addition to the reversible electrode potential, the electromotive force,  $E$ , of the cell depends on the electro-potential difference between solution, X, and the KCl-saturated solution. This liquid junction potential develops because of ionic diffusion between the two solution phases, and therefore, depends upon the relative mobilities of the various ionic species in solution. Using the principles of irreversible thermodynamics (see HAASE, 1963, for a general derivation), the following equation is obtained for the emf of cell A:

$$E = E^* - \frac{RT}{F} \left( \ln a_{\text{H}}(\text{X}) + \ln a_{\text{Cl}}(\text{KCl}) + \int_{\text{X}}^{\text{KCl}} \sum_k \frac{t_k}{z_k} d \ln a_k \right). \quad (\text{B.1})$$

$E^*$  is given by,

$$E^* = \frac{1}{2F} (\mu_{\text{H}_2}^0 + RT \ln f_{\text{H}_2} + \mu_{\text{Hg}_2\text{Cl}_2}^0 - 2\mu_{\text{Hg}}^0 - 2\mu_{\text{H}}^0 - 2\mu_{\text{Cl}}^0). \quad (\text{B.2})$$

In Eqn. (B.1),  $t_k$  is the reduced Hittorf transference number of ion  $k$ , and  $z_k$  is the charge on ion  $k$ . By definition, the transference numbers satisfy the relationship,

$$\sum_k t_k = 1. \quad (\text{B.3})$$

The sum in Eqns. (B.1) and (B.3) includes all ionic species in the solution. The integration in Eqn. (B.1) extends over the transition region from solution X to the KCl saturated solution. The ionic activities in Eqn. (B.1) are theoretically defined by a derivative in the free energy (i.e., Eqn. A.2a Appendix A).

Any arbitrary function of composition,  $\omega(x)$ , satisfies the equation,

$$\begin{aligned} \ln \omega(\text{KCl}) - \ln \omega(\text{X}) &= \int_{\text{X}}^{\text{KCl}} d \ln \omega \\ &= \int_{\text{X}}^{\text{KCl}} \sum_k \frac{t_k}{z_k} d(z_k \ln \omega), \end{aligned} \quad (\text{B.4})$$

where Eqn. (B.3) has been used to obtain the last identity. Adding this equality to Eqn. (B.1) and collecting similar terms, the following equation, identical to Eqn. (B.1) is obtained

$$E = E^* - \frac{RT}{F} \left[ \ln a_{\text{H}}(\text{X}) + z_{\text{H}} \ln \omega(\text{X}) + \ln a_{\text{Cl}}(\text{KCl}) + z_{\text{Cl}} \ln \omega(\text{KCl}) + \int_{\text{X}}^{\text{KCl}} \sum_k \frac{t_k}{z_k} d(\ln a_k + z_k \ln \omega) \right]. \quad (\text{B.5})$$

The cell emf is independent of the arbitrary function,  $\omega$ .

The activity coefficient for ion  $k$  is defined by the familiar equation,

$$a_k = \gamma_k m_k. \quad (\text{B.6})$$

Consider the conventional definition for the ion activity coefficients given by the equation,

$$\gamma_k^{\text{C}} = \gamma_k \omega^{z_k}, \quad (\text{B.7})$$

where  $\omega$  is chosen common to all ions in a particular solution. The conventional ion activity coefficients so defined are consistent with the measurable mean activity coefficients since,

$$\begin{aligned} (\gamma_{\text{M}}^{\text{C}})^{\nu_{\text{M}}} (\gamma_{\text{X}}^{\text{C}})^{\nu_{\text{X}}} &= (\gamma_{\text{M}})^{\nu_{\text{M}}} (\gamma_{\text{X}})^{\nu_{\text{X}}} \omega^{(\nu_{\text{M}}\nu_{\text{M}} + \nu_{\text{X}}\nu_{\text{X}})} \\ &= (\gamma_{\text{M}})^{\nu_{\text{M}}} (\gamma_{\text{X}})^{\nu_{\text{X}}} = (\gamma_{\text{MX}}^{\text{C}})^{\nu}. \end{aligned} \quad (\text{B.8})$$

In obtaining Eqn. (B.8), the identities  $z_{\text{M}}\nu_{\text{M}} + z_{\text{X}}\nu_{\text{X}} = 0$  and  $\nu_{\text{M}} + \nu_{\text{X}} = \nu$  have been used. Using the definition for ion activity coefficients in Eqn. (B.6), conventional ion activities are calculated by the equation,

$$a_k^{\text{C}} = \gamma_k^{\text{C}} m_k = \gamma_k m_k \omega^{z_k} = a_k \omega^{z_k}. \quad (\text{B.9})$$

Substituting the natural logarithms of Eqn. (B.9) for terms like  $\ln a_k + z_k \ln \omega$  in Eqn. (B.5), the following equation for the cell emf in terms of the conventional ion activities is obtained:

$$E = E^* - \frac{RT}{F} \left[ \ln a_{\text{H}}^{\text{C}}(\text{X}) + \ln a_{\text{Cl}}^{\text{C}}(\text{KCl}) + \int_{\text{X}}^{\text{KCl}} \sum_k \frac{t_k}{z_k} d \ln a_k^{\text{C}} \right]. \quad (\text{B.10})$$

Comparison of Eqns. (B.1) and (B.10) indicates that any conventional ion activities defined by Eqn. (B.9) may be substituted for the theoretical ion activities in calculating the emf by Eqn. (B.1) without making any approximation. Therefore, it is impossible to distinguish between the various conventional or the theoretical ion activities using the measured values of the emf. Consequently, it is not possible to utilize such data to unambiguously obtain any information regarding real ion activities. This is a general result (TAYLOR, 1927; GUGGENHEIM, 1929, 1930a,b, 1960).

For convenience, Eqn. (B.10) may be written as:

$$E = E_{\text{O}}^{\text{C}} - \frac{RT}{F} \ln a_{\text{H}}^{\text{C}}(\text{X}) - E_{\text{L}}^{\text{C}}(\text{X}). \quad (\text{B.11})$$

$E_{\text{O}}^{\text{C}}$  and  $E_{\text{L}}^{\text{C}}$  are defined by the equations,

$$E_{\text{O}}^{\text{C}} = E^* - \frac{RT}{F} \ln a_{\text{Cl}}^{\text{C}}(\text{KCl}) \quad (\text{B.12})$$

and

$$\begin{aligned} E_{\text{L}}^{\text{C}}(\text{X}) &= \frac{RT}{F} \int_{\text{X}}^{\text{KCl}} \sum_k \frac{t_k}{z_k} d \ln a_k^{\text{C}} \\ &= \frac{RT}{F} \left[ \int_{\text{X}}^{\text{KCl}} \sum_k \frac{t_k}{z_k} d \ln a_k + \ln \frac{\omega(\text{KCl})}{\omega(\text{X})} \right]. \end{aligned} \quad (\text{B.13})$$

In Eqns. (B.11) and (B.13), nomenclature representing the liquid junction potential explicitly denotes the dependence of this term on the composition of solution X.  $E_{\text{L}}^{\text{C}}$  also depends on the KCl reference solution and the nature of the liquid junction. The last equality in Eqn. (B.13) illustrates that the liquid junction potential depends on the ion activity coefficient conventions chosen in solution X and the reference solution. While the observed emf of the cell is not dependent upon the conventional definition of the ion activities, each of the separate terms in Eqn. (B.11) is a function of the convention.

In particular, it is demonstrated in Fig. 3 (section III), that the magnitude of the conventional liquid junction term is a strong function of the convention specified for solution X.

The general definition of an ion activity coefficient convention is given by Eqn. (B.7). These equations are defined in terms of absolute ion activity coefficients which cannot be measured and consequently are not known. It is, therefore, necessary to specify an alternate procedure for calculating the conventional ion activities. The arbitrary nature of  $\omega$  in Eqn. (B.9) permits specifying the conventional value of any ion activity coefficient in a given solution. Defining the value of  $\gamma_k^C$  for a particular ion  $k$  implicitly defines the value for  $\omega$  by Eqn. (B.7). It is common practice to define the ion activity coefficient for  $\text{Cl}^-$  by convention when interpreting the data from cell A (BATES and GUGGENHEIM, 1960). It has been demonstrated in this appendix that the interpretation of the data from a cell utilizing a liquid junction in terms of an ion

activity (e.g. in  $a_{\text{H}^+}$ ) requires the specification of a convention. Once a convention is specified (e.g.,  $\gamma_{\text{Cl}^-}^C$  is designated by an arbitrary value), the conventional ion activities are unambiguously defined in terms of the mean activities of the solution by Eqn. (B.8). Therefore, since mean activities can be obtained using equilibrium measurements (i.e. cells without liquid junctions), it is, in principle, unnecessary to utilize cells with liquid junctions to obtain conventional ion activities. Of course, this fact does not preclude the use of cells with liquid junctions when experimental difficulties exclude the equilibrium approach. However, the interpretation of such data in terms of the equilibrium properties of the system without the use of the cumbersome theory of irreversible thermodynamics is approximate. Figure 3 illustrates that such an approach may lead to non-negligible errors in the reported values of the thermodynamic properties for a system when these values are derived from pH data.