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CARBONATE CHEMISTRY IN HIGH SALINITY WATERS

by

R E Loewenthal

University of Cape Town

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Department of Civil Engineering
University of Cape Town

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R E Loewenthal

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The primary objective of this investigation was to develop phase equilibrium diagrams for the carbonate system in high salinity waters, i.e. for single aqueous phase, solid-aqueous phase, gas-aqueous phase and solid-aqueous-gas phases. Such diagrams have been developed for low salinity waters, viz. Deffeyes and Caldwell-Lawrence diagrams and modifications of these.

The difficulty in developing phase equilibrium diagrams for high salinity waters arises from the factors affecting the equilibria in these waters. For example, in low salinity waters ($\mu < 0{,}1$) the mean activity of a salt and the activity of a single ion species can be determined with acceptable accuracy by means of the Debye-Hückel equation or variations of this equation; ion pairing usually is negligible and, the hydrogen ion activity, (H^+), linked to the true pH, can be found quite accurately from the operational pH (pH_o) reading using a glass-calomel electrode system calibrated against NBS buffers. In contrast, in high salinity waters ($\mu > 0{,}1$) the mean activity of a salt and that of a single ion species no longer can be estimated reliably by means of the Debye-Hückel equation; ion pairing effects may become significant and, pH no longer equals pH_o due to residual liquid junction potential effects. Evidently a general solution to phase equilibria in high salinity waters demands identification of the factors influencing the system and devising methods to incorporate these in a theoretical description of an electrolyte solution - a major portion of this investigation accordingly was devoted to this endeavour.

A number of physico-chemical models, incorporating a greater or lesser number of factors affecting the mean and single ion activities have been proposed for binary and mixed electrolytes, for example, the ionic strength principle approach for mean ionic activity coefficients used with the MacInnes assumption for single ion species; extension of the Debye-Hückel theory using the

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Brønsted-Guggenheim approach for mean activity coefficients with the Whitfield extension for single ions, and, the Robinson-Stokes extension of the Debye-Hückel equation incorporating hydration effects.

The first two approaches above give rise to inconsistencies when applied to single ion activities, and, comparisons between observed and predicted mean activity coefficients for a salt in a mixed electrolyte showed large differences. Robinson and Stokes set out from the fact that the activity coefficient of a species as given by the Debye-Hückel theory relates to *hydrated* species and free water, whereas the concentration unit obtained from analyses is linked to *anhydrous* species and the total water. In low salinity waters this difference in scales is negligible and the Debye-Hückel theory forms a satisfactory approximation. In high salinity water, however, the hydration effect may be so large that a significant difference arises between the free and total water components, and it is necessary to reformulate the Debye-Hückel theory to give activity coefficients on the anhydrous scale (to be consistent with concentration measurement). This they achieved by equating the free energies of the hydrated species and free water to the free energies of the anhydrous species and the total water using mole fraction statistics. For binary systems the approach allowed estimation of the mean activity coefficient of a salt in terms of a mean hydration number for the salt and a distance of closest approach between hydrated anion and cation ($\mathring{a}$) as required in the Debye-Hückel equation. These parameters were estimated by calibration against observed mean activity coefficients for the binary system and the approach gave close prediction over a wide range of ionic strengths.

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Difficulties with the Robinson-Stokes approach were as follows:

(i) The trends in the hydration numbers of chloride, bromide and iodide salts of any particular cation were inconsistent with that expected from the sizes of these anions.

(ii) When applied to determine the mean activity coefficient of a salt in a ternary system, the estimate deviated considerably from that observed experimentally.

Despite these inconsistencies, Robinson and Stokes, using the Gibbs-Duhem equation and the non-thermodynamic assumption that Cl^- has zero primary hydration, formulated equations for single ion activities in binary systems. (This development forms a basis for standardization of specific ion electrodes).

A significant advance in the hydration approach was made by Glueckauf (1955) who followed the approach of Robinson and Stokes but reformulated the free energy equations in terms of volume fraction statistics. This allowed incorporation of volume changes in the formulation thereby removing the inconsistencies in the Robinson-Stokes approach to binary systems mentioned above. Glueckauf applied his approach to mean activity coefficients in binary systems only.

Although Glueckauf incorporated volumetric and hydration effects, he accepted that partial molal volumes behaved ideally (i.e. he used the values at infinite dilution), and that the hydration number did not change with ionic strength. As partial molal volumes certainly are concentration dependant, and the hydration number also is likely to decrease with increased concentration, Glueckauf's equation was reformulated to incorporate these two effects on the assumption that $\mathring{a}$ remains constant. Data on non-ideality of partial molal volumes in binary systems are available, and the changes in hydration numbers, assuming $\mathring{a}$ remains constant, can be found by calibration of the theory against activity coefficient observations in the high salt concentration region. With these changes, close agreement was obtained between predicted and observed activity coefficients for binary systems. Furthermore, the distance of closest approach between hydrated ions should be limited by the hydration layers. One consequently would expect

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the $\mathring{a}$ value from the fit to be at least equal to or greater than that indicated by crystal radii and hydration numbers (because in reality the hydration layers are not held with uniform strength onto an ion as assumed by a mean hydration number). In the extended model $\mathring{a}$ was indeed always equal to or greater than the value indicated by the mean hydration numbers and crystal radii of the ions, but in the Glueckauf model it was always less than the minimum value.

The form of the extended Glueckauf theory (and the Glueckauf theory) was such that it could be readily decomposed to model single ion activity coefficients in binary systems provided the non-thermodynamic assumption was made that Cl^- has zero primary hydration - a conclusion strongly suggested from the hydration numbers from 1-1 chloride salts as determined from the extended Glueckauf theory.

These developments provided the basis for extending the theory to mixed electrolytes. This was possible only by accepting that the non-ideality of partial molal volumes and hydration numbers conform to the ionic strength principle (i.e. that the values for these parameters be accepted as equal to their values in binary systems at the same ionic strength). Experimental data on partial molal volumes showed that this is not an unreasonable assumption. On application to ternary systems the predictions of activity coefficients followed the same trends as the observations, but clearly secondary effects were operative. These secondary effects were incorporated in a lump parameter fashion by addition of terms to the total free energy equation involving a constant multiplied by the product of the concentrations of two salts at a time. Each of these constants were determined by calibration against ternary systems. (This analyses was applied also to the water component through the total free energy equation). A check on the predictions of the theory against observations on mean activity

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coefficients in mixed electrolytes, from data reported in the literature, showed excellent agreement. Of importance, it is to be noted that the formulations are such that the system is internally consistent.

With regard to single ion activities, the form of the equations for mean activity coefficients were such that these could be readily decomposed to give equations for the single ion activity coefficients provided the non-thermodynamic assumptions were made that Cl^- has zero primary hydration and that hydration numbers are additive.

The analyses above considered non-associative salts only. When the theory was applied to binary systems of sulphate and hydroxide salts, it was found that the non-associative theory only held for aqueous systems of Cs_2SO_4 and CsOH. From this it was concluded that cesium does not ion pair with these anionic species and allowed estimation of the hydration numbers and hydrated radii of SO_4^{2-} and OH^-. Using published data on the mean stoichiometric activity coefficients in binary systems of $MgSO_4$, Na_2SO_4 and K_2SO_4 and assuming Cs^+ at a trace concentration in each of these solutions it was possible to determine thermodynamic ion pairing constants between both SO_4^{2-} and OH^- and the cations Mg^{2+}, Na^+ and K^+. Using this approach for determining ion pairing constants, it was found that the resulting stoichiometric mean activity coefficients thus derived closely equalled those observed in both binary and mixed systems.

For the carbonate species, the approach was applied as follows: Based on the hydration number for SO_4^{2-} (which the extended theory indicated to be near zero) and the crystal radii for SO_4^{2-}, CO_3^{2-} and HCO_3^- (from Millero, 1969), it was concluded that the free carbonate species similarly have very little primary hydration, and, assuming (i) low hydration numbers for these species, (ii) that Cs^+ does not ion pair with these species, (iii) that neutral ion paired species have activity coefficients equal to unity, and (iv) that singly

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charged ion pairs have activity coefficients equal to that for Na^+, it was possible to estimate the free ion activity coefficients of the carbonate species.

Application of the extended approach to trace HCl in binary and mixed systems (for both the associated and unassociated electrolyte species listed above) allowed determination of the activity coefficient for H^+. This together with the use of Gran titrations allowed (i) the experimental determination of residual liquid junction potential effects on pH (using low salinity NBS buffers), i.e. the relationship between operational and actual pH could be established. (ii) Using Gran titrations on the carbonate system it was possible to measure the operational apparent stoichiometric equilibrium constants, and, accepting the theoretical values for the activity coefficients of the free carbonate species (described above), to estimate ion pairing constants for the metal carbonates and bicarbonates.

To check the validity of this approach to the carbonate system, operational stoichiometric equilibrium constants for the carbonate weak acid-base system were determined from the extended theory (and residual liquid junction potential effects as described above) and compared with experimental measurements reported in the literature - the values showed excellent agreement.

For the purposes of analyses and/or graphical exposition of the carbonate system, the most convenient approach is to formulate the equilibrium equations in the stoichiometric apparent form (with the associated stoichiometric apparent equilibrium constants), the weak acid-base species expressed as stoichiometric concentrations and the hydrogen ion as an activity (or operational activity). Theoretically it was shown that the apparent stoichiometric equilibrium constants could be formulated in terms of the concentrations of principal cation species which ion pair with the carbonate species, the activity coefficients of the free and ion paired species and

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the thermodynamic equilibrium constants for ion pairing. Using the apparent equilibrium form the solution procedure for the carbonate system in high salinity waters reduces to that for low salinity waters except that it is now necessary to establish by experiment the residual liquid junction potential effects to establish the link between pH and pH_o.

The developments outlined above provided the theoretical basis for utilizing equilibrium chemistry for attaining the objective of developing inter-phase equilibrium diagrams. The calculation procedures to plot these diagrams was carried out along similar lines to those employed by Loewenthal and Marais (1976) for low salinity waters, except that species concentrations are now formulated as stoichiometric entities and equilibrium equations in the stoichiometric apparent form as described above. The theory was utilized for developing three types of equilibrium diagrams:

(i) Single aqueous phase equilibrium diagram in which a family of curves representing either pH or pH_o are plotted within the ordinate parameters Alkalinity and Acidity, i.e. a modified Deffeyes type diagram.

(ii) Aqueous-gas phase equilibrium diagram incorporating families of curves representing both pH and pCO_2 (partial pressure of CO_2 in the gas phase) within the ordinate parameters Alkalinity and Acidity.

(iii) Aqueous-solid phase equilibrium diagram in which families of curves representing Alkalinity, total calcium and either pH or pH_o (and if required pCO_2) are plotted within the co-ordinate system Acidity and (Alkalinity-$2[Ca]_T$) for a solid phase of either calcite, aragonite or magnesian calcite, and brucite.

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Chapter 2
NON-ASSOCIATED BINARY ELECTROLYTES

1. *Introduction*

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Chapter 3
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INTRODUCTION

The carbonate system is a weak acid-base system which exists in aqueous solutions as dissolved carbon dioxide, carbonic acid, bicarbonate and carbonate ions and complexes of these ions. Basically the system is derived from the dissolution of carbon dioxide gas and carbonate minerals into the water. Addition of an acid or a base to an aqueous solution of carbonate species gives rise to changes in pH and concomitant changes in the concentrations of all the species that constitute the system.

A distinguishing feature of the carbonate system is that the gas phase forms an integral part of it. For a system initially in equilibrium, any change in the partial pressure of CO_2 in the gas phase induces a state of non-equilibrium between gas and aqueous phases. This causes, with time, an exchange of CO_2 between the phases resulting in a shift in pH and the species concentrations until equilibrium between the phases is re-established. A further feature is the relative insolubility of many carbonate minerals; the precipitation and dissolution of these minerals have a significant effect on the system behaviour. As a consequence of these two features it is often necessary to consider all three phases, aqueous, gas and solid, in order to describe the response of the systems to external influences.

In the literature, mathematical descriptions of the behaviour of the carbonate system tend to be divided into two categories - low and high ionic strength waters respectively. The reason for this division becomes clear when one considers the two categories in detail.

In low ionic strength descriptions ($\lesssim$ 0,025) it can be assumed that:

(1) The selection of a concentration scale (i.e. molar or molal)

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is immaterial and concentrations and activity coefficients expressed in terms of the two scales differ insignificantly numerically; concentrations and activities on the mole fraction (i.e. rational) scale are proportionally related to the first two scales.

(2) Activity coefficients of charged ionic species in binary and mixed electrolytes can be estimated closely by the Debye-Hückel equation or variants of it; in these equations the activity coefficient of an ionic species is formulated as being dependant only on the charge of the ion, the ionic strength of the solution and a mean hydrated ionic radius. That is, at a particular ionic strength the activity coefficients of an ionic species can be taken as independent of the specific ionic types and their concentrations.

(3) Activity coefficients of neutral species and water itself can be taken as unity.

(4) Ion pairing effects usually can be assumed as negligible.

(5) For ionic strengths $0{,}01 < \mu < 0{,}1$, measurement of pH by means of conventional glass-calomel electrodes gives a reliable measure of the conventional activity of H^+, i.e. pH = -log(activity of H^+), provided the electrode system is standardized against low salinity aqueous NBS buffers. Outside this range of ionic strengths, an error is inherent in the pH readings due to residual liquid junction effects.

The assumptions above greatly simplify computations of intra- and inter-phase equilibrium states.

In high salinity waters a number of factors become significant which greatly increase the complexity of the mathematical description of the system when compared with that of low salinity waters:

(1) Stoichiometric concentrations of principal species on the molar

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scale no longer can be equated to those on the molal scale nor do both of these remain proportional to those on the mole fraction scale; furthermore, the ionic activity coefficients differ between scales. Hence, the concentration scale adopted becomes important in expressing both the concentrations of dissolved substances and their activities.

(2) Whatever the concentration scale adopted, the stoichiometric concentration-activity relationship for a particular ionic species in a solution becomes complex. This is because the activity coefficient becomes significantly dependant on the matrix of the ions and the ionic strength of the solution, consequently, it is no longer possible to retain the general expression for the activity coefficients of an ionic species as done for low ionic strength waters. Instead, the activity coefficient of each ionic species must be formulated separately.

(3) Neutral dissolved species and the water itself may have activity coefficients other than unity.

(4) Ion pairing can become highly significant.

(5) pH measurements by means of glass-calomel electrode systems standardized against NBS buffers no longer form a reliable measure of H^+ activity - principally due to residual liquid junction effects.

(6) Rarely do pure minerals precipitate from mixed electrolytes at high ionic strength. The degree of impurity of a precipitated mineral, and its solubility, become dependant, *inter alia*, on the ionic matrix.

In high salinity waters, in order to overcome the problems listed above, one approach has been to accept the system as a constant ionic medium in which the principal species in the ionic matrix are fixed, to regard this solution as a 'normal' water and to accept

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the glass-calomel electrode standardized against NBS buffer standards as the basis for pH measurement called the operational pH, pH_o (Dyrssen and Sillén, 1965). This approach is specific to the ionic medium and therefore of value only where the ionic medium is one subject to extensive investigation - for example, the approach has been widely used in investigations into seawater. The dissociation constants for this 'normal' water now incorporate all deviations from ideality plus residual liquid junction effects and are designated "operational stoichiometric apparent constants". The values of these apparent constants can be accurately determined experimentally, but it must be remembered that their values are, *inter alia*, dependent on the pH measurement system employed, for example, the glass saturated calomel electrode system; the pH is now, in effect, a parameter which can be measured consistently, but its value only approximates the hydrogen ion activity.

Advantages of the approach above are that (1) the system can be readily depicted graphically by a log (stoichiometric species)-pH plot in the same fashion as for low salinity waters, except that the apparent dissociation constants must be used; (2) the mass parameters alkalinity and acidity (being independent of deviations from ideality and residual liquid junction potential effects) are defined in this plot in the same fashion as the low salinity plot, similarly buffer capacity. The properties of the system provide the means for very simple solutions of some types of problems of an otherwise extremely complex system.

The disadvantage of this approach is that only stoichiometric species concentrations can be determined, consequently, the standard solubility products cannot be applied. Because pH is no longer linked directly to H^+ activity, neither the OH^- activity nor its stoichiometric concentration can be determined unless K_w is redefined for the particular ionic medium, then, from a logical

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point of view, solubility products also should be defined for this medium.

In order to overcome the residual liquid junction potential effects for seawater, Bates and Macaskill (1975) proposed that specific pH standards be established for this medium based on the molality of H^+, i.e. $p[H] = -\log_{10}$ (molality of H^+). This would allow measurement of stoichiometric apparent weak acid dissociation constants in terms of the molalities of H^+ and hence each of the stoichiometric weak acid species concentrations, as in the operational pH approach.

With regard to the two approaches above, from a practical point of view invariably the final objective for establishing stoichiometric apparent equilibrium constants is to estimate each of the weak acid-base species concentrations at some observed pH on the scale selected. For this purpose, each of the species concentrations can be determined unambiguously from pH observations on any of the two pH scales, provided the weak acid equilibrium constants are expressed in terms of the selected pH scale and provided the principal ionic matrix of the solution remains invariant with pH. These approaches therefore are restricted to waters with a specified principal ionic matrix constitution and demand extensive experimentation to fix the various constants defining equilibrium in the medium.

A general solution to high salinity waters would be obtained if one could express the equilibrium state in terms of thermodynamic equilibrium constants and activity coefficients relative to infinite dilution, and through theoretical consideration, develop procedures to determine the distribution of free and ion paired species concentrations and activities in the test solution, whatever its stoichiometric ionic constitution. Such an approach should allow theoretical determination of the stoichiometric weak acid equilibrium constants in the two approaches reviewed above.

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Establishment of such a general model requires providing a structure within which

(1) mean activity coefficients of the various salts in a mixed electrolyte can be determined,

(2) single ion activity coefficients can be estimated,

(3) ion pairing can be identified and the appropriate ion pairing constants can be derived, and

(4) operational pH, pH_o, can be linked to true pH if pH_o is to be used as an independent measureable parameter.

Solutions to each of these factors present formidable problems with many issues to be resolved. The literature records numerous proposals in this regard,

1. Mean activity coefficients: Present day practice for estimating mean activity coefficients in *mixed* electrolytes is to use one of the following approaches (i) the ionic strength principle for the mean activity coefficient of *free* species, or (ii) the specific interaction approach of Brønsted-Guggenheim for the *stoichiometric* mean activity coefficients, or (iii) the Pitzer extension to the specific interaction approach for stoichiometric mean activity coefficients, and, (iv) the hydration approach of Robinson and Stokes for the mean activity coefficients of *free* species (Glueckauf modified the Robinson-Stokes approach but this modification extended only to mean activity coefficients in binary systems). Each of these four approaches are reviewed in some detail in the introduction to Chapter 3. Suffice here to briefly enumerate some of their respective deficiencies in general application in mixed systems.

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(i) Application of the ionic strength principle approach to ternary non-associated electrolytes (i.e. where free and stoichiometric mean activity coefficients are equal) at ionic strengths greater than about $\mu = 0{,}1$, invariably the predictions of mean activity coefficients of the free species are significantly different from experimentally determined values.

(ii) Application of the Brønsted-Guggenheim approach to determine stoichiometric mean activity coefficients in ternary systems in both associated and unassociated electrolytes indicate that only sometimes does it predict values in agreement with experimentally measured stoichiometric mean activity coefficients, depending on the salts in the mixture. Furthermore, where sulphates are present the approach cannot be applied for the estimation of the stoichiometric mean activity coefficient of HCl because of the pH dependency of the interactions between H^+ and SO_4^{2-}.

(iii) The Pitzer extension to the specific interaction approach incorporates data from ternary systems, and appears to predict satisfactorily stoichiometric mean activity coefficients in quaternary systems in both associated and unassociated electrolytes. However, the theory suffers from the same deficiency as the Brønsted-Guggenheim approach for the estimation of the stoichiometric mean activity coefficient for HCl when sulphates are present in solution. Furthermore, the theory for mean activity coefficients gives no lead to single ion activity coefficient determination.

(iv) The Robinson-Stokes hydration theory determines mean activity coefficients of *free* species. Application in ternary non-associated electrolytes indicates that the approach only sometimes gives acceptable agreement with experimental measurements. Furthermore, the theory exhibits an internal

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inconsistency: in its application to binary systems the theory predicts the hydration numbers for the Cl^-, Br^- and I^- salts of any particular cation to increase with increase in anion crystal radius, a prediction contrary to expectation based on the theory of ionic hydration.

2. Single ion activity coefficients: With regard to single ion activity coefficients these entities neither can be measured nor determined from theoretical considerations alone - mean ionic activity (and its associated activity coefficient) is the only entity that has thermodynamic significance and is amenable to experimental measurement. Estimation of single ion activities (and activity coefficients) from a particular theory defining mean activity coefficients requires a non-thermodynamic assumption(s). Although the validity of the assumption(s) cannot be checked absolutely, its utility usually can be assessed in terms of the measure of consistency it offers with regard to other physico-chemical characteristics. Present day practice for estimating single ion activity coefficients in mixed systems is to use one of the following approaches, (i) the MacInnes assumption, (ii) the Brønsted-Guggenheim interaction theory as extended by Whitfield (1973), (iii) the Robinson-Stokes hydration theory.

(i) In the MacInnes assumption it is accepted that the activity coefficient for free K^+ equals that for free Cl^- in both binary and mixed systems, an hypothesis that is contra indicated by the ionic hydration theory. If the mean activity coefficients of free species are known, then using the MacInnes assumption it is possible to estimate the single ion activity coefficients of the free species. However, where ion pairing occurs between K^+ and any of the anionic species, the approach can be used only with a theory giving the mean activity coefficient of free species in the

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associating electrolyte. Now, the most successful approach to date to estimate mean activity coefficients in mixed electrolytes is the extended interaction approach of Pitzer (1973). This approach gives stoichiometric mean activity coefficients and it cannot be extended (as the Brønsted-Guggenheim interaction theory) to single ion activity coefficient estimation. In associated electrolytes the stoichiometric mean activity coefficients incorporate the effects of ion pairing in the activity coefficient, consequently, the MacInnes assumption cannot then be used with this theory for single ion estimation.

(ii) In the Brønsted-Guggenheim specific interaction theory single ion activity coefficient estimation forms part of the theory, Whitfield (1973). However, when applied to aqueous *binary* systems comprised of symmetrical salts, the theory always gives $\gamma(\text{cation}) = \gamma(\text{anion})$; this equality is unacceptable, even more so than the MacInnes assumption. Inadequacy for binary symmetrical salt systems, the simplest of systems, implies inadequacy in the more complex mixed systems.

(iii) The Robinson-Stokes hydration theory has been applied to estimation of single ion activity for Cl^- in mixed system by Robinson and Bates (1979) by making the non-thermodynamic assumption that Cl^- has zero primary hydration, and that each of the cation species Na^+, K^+, Mg^{2+} and Ca^{2+} (which are usually the cation species comprising the principal ionic matrix) each have hydration numbers equal to the values determined from the Robinson-Stokes theory applied to aqueous binary solutions of the chloride salt of each of these cation species. Although the hypothesis of zero primary hydration for Cl^- is acceptable, the incongruity

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arising with the hydration numbers for the Cl^-, Br^- and I^- salts in the theory for mean activity coefficients, makes the predictions less acceptable.

3. Ion pairing equilibrium constants: Where activity coefficients are determined for the free ionic species (i.e. using the ionic strength principle or one of the hydration theories), it is necessary to take cognisance of ion pairing as a separate entity giving rise to deviations in the activities of species from ideality. For those aqueous systems considered in this text (i.e. those with a principal ionic matrix comprising of any combination of the cation species Na^+, K^+, Ca^{2+}, Mg^{2+} and the anion species Cl^- and SO_4^{2-} and with the carbonate weak acid-base species at comparatively low concentrations) it would appear from the literature that (i) Cl^- does not ion pair with any of the cation species above, (ii) SO_4^{2-} ion pairs significantly with each of the cation species above, and (iii) each of the weak acid-base species CO_3^{2-}, HCO_3^- and OH^- ion pair significantly with the cation species above.

The formation of ion pairs in solution in effect removes ions from the system to generate new charged and neutral species. Consequently, where both the anion and cation species of an ion pair constitute part of the principal ionic matrix the actual ionic strength of the solution (μ) may differ significantly from the stoichiometric ionic strength (I), and cognisance must be taken of this difference both in the determination of ion pairing equilibrium constants and where these constants enter into the determination of the distribution of free and ion paired species concentrations and activities. This problem is particularly relevant in solutions containing sulphate. Where ion pairing occurs between a cation (or anion) constituting a principal part of the ionic matrix and an anion (or cation) at a low concentration

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with respect to the principal ionic species, the effects on the principal ionic species, and hence on the ionic strength, will be negligible, but the effect on the minor species can be profound. This problem is particularly relevant in ion pairing of the anionic carbonate and hydroxide weak acid-base species (which are usually at a low concentration) by cations constituting a principal part of the ionic matrix.

Data reported in the literature for the various ion pairing constants (at infinite dilution) show a wide variation in values for a particular ion pair. This variability probably reflects the different experimental and the theoretical approaches used for extrapolating the data back to infinite dilution. For example, Nakayama (1971) determined $pK(MgHCO_3^+) = 1,40$ by estimating $\gamma_{Mg} = 0,54$ in a solution with $\mu \cong 0,04$ using the Debye-Hückel theory with an $\mathring{a}$ value equal to 8,0 from Keilland (1937) for a solution with ionic strength about 0,04; alternatively, if one uses the Davies equation (an approach independent of $\mathring{a}$) one obtains $\gamma_{Mg} = 0,47$ and $pK(MgHCO_3^+) \cong 0,5$. Clearly, in order to maintain consistency, it is necessary to use the same approach for activity coefficient estimation in *both* the determination of ion pairing constants, and, in the utilization of these constants for determining the distribution of species in a particular solution.

4. Operational pH, pH_o, and true pH: Theoretical estimates of residual liquid junction potential effects, giving rise to the difference between pH_o and pH, have been proposed by Plank (1890) and Henderson (1903). However, the accuracy of these estimates is unknown because both approaches neglect non-ideal effects on activity and mobilities of ions, i.e. activities and mobilities of ions are assumed to have their values at infinite dilution. If however the activity coefficient for H^+ can be determined in a particular solution, then (as we shall show in this text) a semi-

experimental method is available for estimating the residual liquid junction potential effect on pH, thereby paving the way for theoretical estimation of operational weak acid-base equilibrium constants.

A thorough study of the approaches set out above eventually led to the conclusion that the hydration approach of Stokes-Robinson-Glueckauf offered the best potential for developing a consistent ionic equilibrium theory for high salinity waters including ion pairing and weak acid-base systems. This demanded extension of the hydration theory for binary systems; for mixed systems, because these can vary from water to water, secondary effects had to be modelled semi-empirically, guided by calibration against experimental data on ternary systems. A brief review of the development of the model is given below.

Robinson and Stokes (1948, 1955) started from the observation that in the Debye-Hückel theory the activity coefficient of a species, in fact, is developed in terms of hydrated species and free water. However the activity coefficient in application is in terms of the anhydrous scale, the scale used for concentrations of the species obtained from analyses of a water, that is, in terms of *anhydrous* species and the total water. In low salinity waters this difference in scales is negligible and the Debye-Hückel theory provides a satisfactory approximation of the anhydrous activity coefficient. In high salinity waters, however, the water hydrated onto the ions may be so substantial that the free water is significantly less than the total water, and, it is necessary to take cognisance of this when reformulating the Debye-Hückel equation to give the activity coefficients directly in terms of the anhydrous scale. This requires hypothesizing on the hydration of ions; here it is accepted that hydration is represented by a mean hydration number in which each molecule is

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held equally strongly about a central ion. This hydrated water is effectively removed from the total water so that for the solvent component, the free water no longer equals the total water.

For non-associated electrolytes, Robinson and Stokes formulated an equation for the activity coefficients of anhydrous species by equating the free energies of the hydrated species and free water to the free energies of the anhydrous species and the total water using mole fraction statistics. For binary systems this approach provides expressions for estimation of the mean activity coefficient of a salt in terms of a mean hydration number for the salt and a distance of closest approach between hydrated anion and cation ($\mathring{a}$), as required in the Debye Hückel equation. The values for these parameters are obtained by calibration against observed mean activity coefficients for the binary system. The approach models the activity coefficients for binary systems very closely over a wide range of ionic strengths. However the approach gives rise to some inconsistencies, as follows:

(i) The trends in the hydration numbers of chloride, bromide and iodide salts of any particular cation are inconsistent with that expected from the sizes of these anions.

(ii) When applied to determine the mean activity coefficient of a salt in a ternary system, the estimate deviates considerably from that observed experimentally.*

A significant advance in the hydration approach was made by Glueckauf (1955). He followed the approach of Robinson and Stokes

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* Despite these inconsistencies the close predictive power of the model led Robinson and Stokes to extend the theory to estimation of single ion activity coefficients in binary systems. This they did by using the Gibbs-Dukem equation and the non-thermodynamic assumption that Cl^- has zero primary hydration. This extension has been used as a basis for standardization of specific ion electrodes.

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but reformulated the free energy equations in terms of volume fraction statistics. This allowed incorporation of volume changes in the formulation thereby removing the inconsistency with regard to the Cl^-, Br^- and I^- salts in the Robinson-Stokes approach to binary systems mentioned above. Glueckauf applied his approach to model mean activity coefficients in binary systems only.

Although Glueckauf incorporated volumetric and hydration effects, he accepted that partial molal volumes behaved ideally (i.e. he used the values at infinite dilution), and that the hydration number did not change with ionic strength. As partial molal volumes certainly are concentration dependant, and the hydration number also is likely to decrease with increased concentration, Glueckauf's equation therefore still was an approximation. Consequently, Glueckauf's equation was redeveloped to incorporate these two effects on the assumption that $\mathring{a}$ remains constant, an assumption which appears to be justified, see below. Data on non ideality of partial molal volumes in binary systems are available, and the changes in hydration numbers, assuming $\mathring{a}$ remains constant, can be found by calibration of the theory against activity coefficient observations in the high salt region ($\mathring{a}$ is determined from calibration in the low salt region - changes in $\mathring{a}$ as ionic strength increases, due to changes in hydration, taken as a secondary effect, is lumped with the terms defining the changes in hydration). With these changes, close agreement, to within 0,002 activity coefficient units (with the exception of CsCl) was obtained between predicted and observed activity coefficients on non-associated binary systems up to an ionic strength of 6, as reported in the literature. The model also appeared to be consistent with other physico-chemical properties. For example the distance of closest approach between hydrated cations and anions should be affected by the hydration layers; one would

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expect the $\mathring{a}$ value from the fit at least to be equal to or greater than that indicated by crystal radii and hydration numbers of the anions and cations of the salt (greater because in reality hydration layers are not held with uniform strength onto an ion as assumed in the mean hydration number hypothesis). In the extended model $\mathring{a}$ indeed was found always to be equal to or greater than the value indicated by the mean hydration numbers and crystal radii of the ions, whereas in the Glueckauf model it was always less than the minimum value.

The developments above provided the basis for extending the mean activity coefficient theory to mixed electrolytes. This was found possible only by accepting that the non-ideality of partial molal volumes and hydration numbers conform to the ionic strength principle (i.e. that the values for these parameters are accepted as equal to their values in binary systems at the same ionic strength). Experimental data on partial molal volumes reported in the literature indicate that this is not an unreasonable assumption. However, on application to ternary systems the predictions of mean activity coefficients followed the same trends as the observations, but could deviate up to five percent. Clearly secondary effects were operative. These secondary effects were incorporated in a lump parameter fashion and modelled, with a view to consistency, by additional terms in the total free energy equation involving a constant multiplied by the product of the concentrations of two salts at a time. Each of these constants could be determined by calibration against ternary systems. This analysis was applied also to the water component through the total free energy equation. A check on the predictions of the theory against observations on mean activity coefficients in mixed electrolytes, from data reported in the literature, shows excellent agreement, to within about 0,5 percent.

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An analysis of the extended Glueckauf theory (and the Glueckauf theory) indicated that the equation for the mean activity coefficient could be readily decomposed to model single ion activity coefficients in both binary and mixed systems provided the non-thermodynamic assumption was made that Cl^- has zero primary hydration and that hydration numbers are additive - a zero value for the primary hydration of Cl^- is strongly supported from the hydration numbers determined for 1-1 chloride salts using the extended Glueckauf theory.

In the analysis above non-associative salts only were considered. When the theory was applied to binary systems of sulphate and hydroxide salts, it was found that the non-associative theory only held for aqueous binary systems of Cs_2SO_4 and CsOH. From this it was concluded that cesium does not ion pair with these anionic species and this allowed estimation of the hydration numbers and hydrated radii of SO_4^{2-} and OH^-. Using published data on the mean stoichiometric activity coefficients in binary systems of $MgSO_4$, Na_2SO_4 and K_2SO_4 and assuming Cs^+ at a trace concentration in each of these solutions it was possible to determine thermodynamic ion pairing constants between both SO_4^{2-} and OH^- and the cations Mg^{2+}, Na^+ and K^+. Using this approach for determining ion pairing constants, it was found that the stoichiometric mean activity coefficients thus derived closely equalled those observed in both binary and mixed systems.

For the carbonate species, the approach above was applied as follows: Based on the hydration number for SO_4^{2-} (which the extended theory indicated to be near zero) and the crystal radii for SO_4^{2-}, CO_3^{2-} and HCO_3^- (from Millero, 1969), it was concluded that the free carbonate species similarly have very little primary hydration, and, assuming

(i) low hydration numbers for these species,

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(ii) that Cs^+ does not ion pair with these species,

(iii) that neutral ion pairs have activity coefficients equal to unity, and

(iv) that single charged ion pairs have activity coefficients equal to that for Na^+,

it was possible to estimate the free ion activity coefficients of the carbonate species.

Application of the extended approach to trace HCl in binary and mixed systems (for both the associated and unassociated electrolyte species listed above) allowed determination of the activity coefficient for H^+. This together with the use of Gran titrations, allowed

(i) experimental determination of residual liquid junction potential effects on pH (using low salinity NBS buffers), i.e. allowed the establishment of the relationship between operational and actual pH,

(ii) measurement of the operational apparent stoichiometric equilibrium constants via Gran titrations,

(iii) estimation of ion pairing equilibrium constants (at infinite dilution) for metal carbonates and bicarbonates by accepting theoretical values for the activity coefficients of the free carbonate species (outlined above).

To check the validity of this approach in its application to the carbonate system, operational stoichiometric apparent weak equilibrium constants for the carbonate weak acid-base system were calculated from the extended theory for seawater together with the residual liquid junction potential effects (as described above). These equilibrium constants were compared with measurements reported in the literature - the values showed excellent agreement,

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to the third significant figure.

For the purposes of analyses and graphical exposition of the carbonate system, the most convenient approach is to formulate equilibrium equations in the stoichiometric apparent form (with the associated stoichiometric apparent equilibrium constants), with the weak acid-base species expressed as stoichiometric concentrations and the hydrogen ion as an activity (or operational activity). Theoretically it was shown that the apparent stoichiometric equilibrium constants could be formulated in terms of the concentrations of principal cation species which ion pair with the carbonate species, the activity coefficients of the free and ion paired species and the thermodynamic equilibrium constants for ion pairing. Using the apparent equilibrium form, the solution procedure for the carbonate system in high salinity waters then reduces to that for low salinity waters except that now it is necessary to determine, by experiment, the residual liquid junction potential effects in order to establish the link between pH and pH_o.

Accepting the scales developed above, inter-phase equilibrium diagrams for the carbonate system were developed. The calculation procedures to plot these diagrams were carried out along similar lines to those employed by Loewenthal and Marais (1976) for low salinity waters, except that species concentrations now were formulated as stoichiometric entities and equilibrium equations in the stoichiometric apparent form. Three types of equilibrium diagrams are presented:

(i) Single aqueous phase equilibrium diagram in which a family of curves representing either pH or pH_o are plotted within the ordinate parameters Alkalinity and Acidity, i.e. a modified Deffeyes type diagram, Deffeyes (1965).

(ii) Aqueous-gas phase equilibrium diagram incorporating families of curves representing both pH and pCO_2 (partial pressure of CO_2 in the gas phase) within the ordinate parameters Alkalinity and Acidity.

(iii) Aqueous-solid phase equilibrium diagram in which families of curves representing Alkalinity, total calcium and either pH or pH_o (and if required pCO_2) are plotted within the co-ordinate system Acidity and (Alkalinity-$2[Ca]_T$) for a solid phase of either calcite, aragonite or magnesian calcite, and brucite, i.e. a modification of the diagram proposed by Caldwell and Lawrence (1952).

To illustrate the utility of these diagrams examples are presented dealing with

(i) The influence of chemical dosage on the aqueous phase equilibrium state.

(ii) Estimation of the masses of calcium carbonate mineral that will dissolve or precipitate from a water with a particular initial state described by measured values for total calcium, pH and Alkalinity, and, tracing the state of the water to the saturated state.

(iii) Effect of inter phase mass exchanges, for example the effects of changes in the partial pressure of CO_2 (in a gas phase) on pH and the solubility of $CaCO_3$ minerals in seawater.

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Chapter 2

NON-ASSOCIATED BINARY ELECTROLYTES

1. INTRODUCTION

Electrolyte solutions in which the ions behave independently of each other are said to be ideal. In ideal solutions the activity of the ionic species equals its concentration. Ideality is approximated only at infinite dilution; at finite dilution deviations from ideality are observed - the activity and concentrations of component species in solution are no longer equal.

From Glueckauf (1955) and Scatchard (1959) the following sources of non ideality can be identified in aqueous electrolyte systems.

(i) Electrostatic interaction between ions of opposite charge, as described by the Debye-Hückel theory.
(ii) Magnitude of the dielectric constant of the solvent.
(iii) Secondary volume changes on mixing solvent and solute (co-volume effects) Flory-Huggins (1941).
(iv) Ionic hydration, Bjerrum (1926), Stokes and Robinson (1948, 1955, 1974) and Glueckauf (1955).
(v) Cation-anion interaction or ion pairing (ionic association), Bjerrum (1926).
(vi) Cation-cation and anion-anion interactions, Scatchard (1959).

The dielectric constant enters into the analysis principally via the Debye-Hückel treatment of the electrostatic effect. Quantitatively, very little is known of the change in the value of this constant with increase in dissolved salt concentration. The usual approach is to accept that the value of the dielectric constant remains unchanged at that of pure water and that effects due to actual changes are absorbed by the values assigned to the constants in the formulation of the electrostatic and other effects.

In low salinity waters generally only the electrostatic effects

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are of importance. However, as the ionic strength of the solution increases, the other effects, i.e. (iii) to (vi), become of increasing importance and eventually dominate over the electrostatic effect.

With the exception possibly of (ii) above, all the sources of non ideality are implicitly bound up with the hydration effect (iv). With hydration, water is effectively removed from the free water mass to form a sheath of hydrated water around each ion, to form an entity, the hydrated ion. The hydrated ion and the free water are the fundamental components in the system, for example, the Debye-Hückel theory for the electrostatic interactions is in terms of the hydrated ions; co-volume changes on adding anhydrous salt to the solvent are due to hydration; ion pairing and cation-cation interactions have been hypothesized as due to interaction effects between the hydration layers of the respective ions.

Hydration introduces two problems, those of (1) scale of measurement and (2) formulation of the activities of species in solution (both salts and water species).

1. With regard to scales of measurement, the two practical ones are the molal and molar scales. These relate the anhydrous moles of salt to the mass of water or volume of solution respectively. The theoretical scale normally is the *mole fraction scale* which expresses the components in solution as fractions, of moles of anhydrous salt (or moles of each ionic specie) or moles of water with respect to the total mole content.

   With hydration, water is effectively removed from the free water mass and hydrated onto the masses of salt entities. Consequently the ratio of moles of anhydrous salt to the moles of *free* water is different from that of the input moles of salt to input moles of water. The theoretical description of electrolytes is in terms of

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the moles of hydrated salt (salt plus hydrated water) and the moles of free water, i.e. in terms of a *"hydrated" mole fraction scale*, hence for theoretical work the anhydrous mole and total water mole fractions need to be converted to "hydrated" mole and free water mole fractions. Similarly quantities made up on the molar and molal scales need to be converted to quantities expressed in terms of the hydrated mole fraction scale.

The link between the hydrated mole fraction scale and the anhydrous scales is established via hydration numbers, i.e. number of moles of water hydrated per mole of salt entity. The magnitudes of the hydration numbers are established by incorporating hydration numbers into the formulations for activity coefficients of salt and water and fitting these equations against observed activity data.

The mole fraction scale has one major drawback; on mixing a salt and water a volume change takes place with respect to that of the pure water before mixing, called a co-volume effect; the change is expressed in terms of the partial molal volume. In high salinity waters, the co-volume effect has significant implications on the activities of species in solution, but this effect cannot be accommodated within the mole fraction scale, either anhydrous or hydrated. For this reason it needs to be replaced by a *volume* fraction scale of "hydrated" salt species and free water called the *hydrated volume fraction scale* which does incorporate co-volume effects.

The link between the hydrated volume fraction scale and the anhydrous scales is established via hydration

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numbers and observed partial molal volumes. The magnitudes of the hydration numbers are established by incorporating both hydration numbers and partial molal volumes in the formulations for activity coefficients of salts and water and fitting these equations against observed activity data.

2. With regard to activities, these are usually expressed in terms of the (anhydrous) molal or molar scale instead of the hydrated fraction scales. It is due to the conversion of the solute activities from the hydrated fraction scales, to say, the anhydrous scales, that the activity coefficient-ionic strength relationship exhibits first a decreasing and than a sharply increasing behaviour with increase in ionic strength; if activity coefficients are expressed in terms of say, the hydrated volume fraction scale, the activity coefficients will show a monotonic decrease with increase in ionic strength.

In the theoretical description of high ionic strength electrolytes a major difficulty is the identification of the effects (i) to (iv) listed above and the estimation of their magnitudes. This can be extremely complex as the effects, although distinctive, may also be interactive. For example, ion pairing "removes" ions from solution to create new species which may or may not be charged, thereby changing the ionic matrix and the ionic strength of the electrolyte.

In order to approach the formulation of activity coefficients in a logical manner, the simplest system should be considered first to form a basis before extension to more complex systems. The simplest system is a binary non-associated electrolyte; Chapter 2 is restricted to this system. In Chapter 3 the theory is extended to

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mixed systems of non-associated electrolytes, and in Chapter 4 to binary and mixed systems having associated (ion pairing) components.

On first sight the presentation may appear to be somewhat confusing. This arises principally because there are a number of preliminary aspects that need to be clarified before the theory of activity coefficients *per se* can be developed. Perhaps the following summary of the sequence of presentation will make the development more clear: (1) Development of model for hydration, in particular the concept of hydration numbers (because hydration enters intimately into virtually every aspect presented). (2) Formulation of hydrated partial molal volumes in terms of partial molal volumes and hydration numbers. (3) Utilization of hydration numbers to link the molal scale to the hydrated mole fraction scale, and utilization of hydration numbers and partial molal volumes to link the molal scale to the hydrated volume fraction scale.

The aspects above complete the groundwork for the principal objective of this chapter namely:(4) Formulation of a model for determining the mean salt, single ion and water activities on the molal scale for binary non-associated electrolytes.

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2. HYDRATION

2.1 Electrolyte structure

The basis of the theory of electrolyte dissociation in aqueous systems is that when an acid, base or salt dissolves in water it splits apart, or dissociates spontaneously into positively and negatively charged species. Dissociation may be complete or partial.

Dissociation involves an interaction between ions and water molecules which give rise to an atmosphere of water molecules surrounding each of the ions, termed a hydration atmosphere. The hydration atmosphere is complex and not well understood. Numerous hypotheses have been proposed to explain this phenomenon. Probably the most widely accepted theory is that proposed by Frank and Evans (1945), and Frank and Wen (1957). They visualize the bare ion in aqueous solution as being surrounded by three zones of water (see Horne, 1970);

(i) An inner zone of tightly bound electrostricted water molecules with a *density greater than that of pure water*,

(ii) an intermediate zone in which the coulombic field of the ion is still strong enough to disrupt the structure of "free water", but insufficient to orientate the molecules into some new configuration; this region is one of disrupted water structure and has a *density less than that of pure water*,

(iii) an outer region with water having the structure of normal water, i.e. free water.

The inner zone of hydration is termed *primary hydration* and the intermediate zone *secondary hydration*

In primary hydration it is considered that a mass of water is abstracted to form an entity separate from the free water, called the hydrated water. It may or may not be present about an ion. The hydrated water has a higher density than that of the free water so that primary hydration induces both volumetric and mass changes within the system. The volumetric effect is important to the development of electrolyte theory because it enters into the activity determination via an entropy term involving hydrated volume fractions. The mass effect is important because it supplies the information linking anhydrous and hydrated masses.

Secondary hydration is always present but the factors affecting it are not clearly understood. Its observable effects appear to be principally a volumetric one and a decrease in viscosity. The volumetric effect is modelled as free water plus a void and enters

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into the activity determination via an entropy term involving volume effects only.

The viscosity effect does not enter explicitly into our analyses. It does however, enter in a qualitative way for it is used as a criterion for sorting binary salts into two categories; structure makers and structure breakers.*

Generally, the degree in which primary and secondary hydration respectively are present around the ions of a particular salt cannot as yet be quantified; only a net effect can be observed - the volumetric changes on mixing a salt and water. This lack, however, does not lead to insurmountable problems in modelling activity coefficients because primary hydration (hydration numbers) can be quantified from observed activity coefficients and partial molal volumes utilizing the hypothesized hydration theory.

2.2 Primary hydration

2.2.1 *Factors affecting primary hydration*

The principal factors affecting primary hydration of ions in aqueous solution are the

1. ionic size,
2. ionic charge, and
3. ionic structure.

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* Structure making ions are classified as those ions in solution which cause an increase in the viscosity of the solution; generally this group includes those ions for which the dominant form of hydration occurs as primary hydration, for example Mg^{++}, Ca^{++}, Sr^{++}, Li^+ and Na^+. Structure breaking ions are classified as those ions which in solution give rise to a decrease in the viscosity of the solution; generally this group includes those ions for which the dominant form of hydration occurs as secondary hydration, for example, Cs^+, Rb^+, Cl^+, Br^- and I^-.

1. *Ionic size:* As the ionic size decreases, the primary hydration tends to increase. For example, due to the small size of the bare lithium ion, there is a strong electrostatic field at its circumference and it attracts a relatively large number of water molecules into its primary hydration layer. In contrast, the bare cesium ion is larger than the lithium ion, although it has the same charge as the lithium ion, due to the weaker field at its circumference it cannot be expected to hold as many water molecules in its primary hydration zone as the smaller lithium ion.

2. *Ionic charge:* The effect of the magnitude of charge of an ion on its hydration is similar to the effect of ionic size; there is a stronger electrostatic field at the circumference of the doubly charged ion than for the single charged ion, consequently one expects the divalent ion to hydrate more water molecules into its primary hydration layer than the singly charged ion.

3. *Ionic structure:* The ionic structures of the bare proton, H^+, and many metal ions are such that these ions can coordinate water molecules covalently. While the proton covalently coordinates only a single water molecule forming the hydronium or hydroxonium ion, H_3O^+, the metal ions Fe^{3+}, Al^{3+} and Mn^{3+}, amongst others can each covalently coordinate up to six water molecules. Besides the covalently bonded water molecules these ions will also exhibit primary hydration due to electrostatic effects.

   The exact number of water molecules covalently coordinated by the central cation depends on the concentrations of bases present in the solution as these bases compete with water molecules for coordination by the

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central ion to form new species. For example, consider addition to pure water of $FeCl_3$. The base in pure water is the hydroxide ion, OH^-. This base competes with the water molecules coordinated by the $Fe(H_2O)_6^{3+}$ ion (usually written simply as Fe^{3+}) to form hydrated species such as $Fe(H_2O)_5OH^{2+}$, $Fe(H_2O)_4(OH)_2{}^+$, $Fe(H_2O)_2(OH)_4^-$ and other polynuclear hydroxo complexes, Stumm and Morgan (1970). Hydration due to covalent bonding is thus pH dependent.

The transition metals, and other metal species forming covalent complexes with water, in trace element concentrations can be of great importance in natural and artificial aqueous systems. Trace elements in ground waters are often utilized as indicators in geological prospecting. Rational incorporation of trace element behaviour into the theory of high salinity waters will be of great utility, but this will be possible only once the behaviour of the principal ions in the solution matrix can be accurately modelled. Trace element behaviour, however, will not be discussed in this text.

2.2.2 *Concept of hydration numbers*

Because the primary hydration atmosphere around an ion is complex and not yet understood quantitatively it is not possible to describe the atmosphere precisely. Nevertheless, a quantitative incorporation of a primary hydration effect, however incomplete, is essential to any rational description of electrolytes. A model that has found support by a number of investigators is that of a mean hydration number for an ion. In this model the *primary hydration atmosphere* around a central ion is replaced by a number of water molecules each regarded as equally strongly hydrated to the ion, Stokes and Robinson (1955), Glueckauf (1955) and Bates, Staples and Robinson (1970). This concept will have value only if by its

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use predictions incorporating the hypothesis give a large measure of consistency with observations on electrolyte solutions.

By accepting a mean hydration number to replace the primary hydration atmosphere, one has created a theoretical entity which for any particular ion will have a numerical value that will depend on the electrolyte theory in which it serves as a parameter. To illustrate this, to date the most widely accepted theories for determining activity coefficients incorporating hydration numbers are those of Stokes and Robinson (1955) and Glueckauf (1955). In their theories the activities of ions are determined from free energy considerations which include, *inter alia*, an entropy term incorporating the primary hydration effect. The hydration number is determined as that value that gives the best correlation between predicted and observed activities, and the hydration number differs significantly between the two theories (see Section 6).

In their respective theories, Stokes and Robinson and Glueckauf accepted that the hydration number is a *constant* for a particular salt, independent of salt concentration, but they recognise that this is a simplification. According to Horne (1970), as the concentration of salt increases from infinite dilution, a stage is reached where appreciable overlapping (or sharing) of the hydration atmospheres around adjacent ions occur. Overlapping can be viewed as causing a decrease in the hydration number for the ion.

Stokes and Robinson (1974) did propose a model incorporating a decrease in hydration number with increase in salt concentration. They hypothesized that each ionic species possesses a finite number of sites onto which a water molecule can be hydrated; in effect they considered a particular ion species as existing as a number of hydrates in equilibrium with each other. At low concentrations the average number of hydration sites per ion occupied is higher than at higher salt concentrations, i.e. equivalently a decrease in the mean hydration number with increase in salt concentration. However, with this approach problems are encountered in attempting

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to extend it to single ion activities and mixed systems. Consequently, in this text an empirical approach is adopted in which a monotonically decreasing functional relationship for the hydration number with increase in salt concentration is assumed. This relationship is incorporated into the theory for determining activity coefficients. By fitting the theory against observed activity coefficient data, the constants in the function defining the decrease in hydration number are determined. The usefulness of this approach is that it allows activity coefficients to be accurately predicted: By applying this approach to binary and ternary systems, it has been found possible to describe quantitatively the effects of other salts on the hydration number of a particular salt and hence to develop a general approach to predicting activity coefficients in mixed systems, Chapter 3. It allows accurate description of salt activities (error less than 0.005 activity coefficient units) in binary, ternary and mixed systems up to an ionic strength of $\mu \simeq 5$ (Section 6 and Chapter 3) and a consistent approach in evaluating single ion activity coefficients in binary and mixed systems (Section 6 and Chapter 3).

2.2.3 *Additivity of hydration numbers*

In Section 2.2.2 the primary hydration number of an ion was defined as some mean number of water molecules equally strongly bound to the ion. A consequence of this definition is that the hydration number of a salt is given by the sum of the hydration numbers of the component ions, i.e. for a salt M_mX_x added to pure water

$$h_{M_mX_x} = d_+h_M + d_-h_X \qquad (1)$$

where

h_Y = hydration number of ionic species Y

d_+ and d_- = number of cations and anions respectively formed by the dissociation of one molecule of salt.

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Consequently, for a 1:2 salt, MX_2, in water

$$h_{MX_2} = h_{M^{++}} + 2h_{X^-}$$

2.2.4 *Mass effect of hydration numbers*

Equations for activity coefficients of species in aqueous solution are formulated in terms of the total free energy of the system, Section 6. To incorporate hydration quantitatively into the theory for activity coefficients, it is necessary to indicate the manner in which primary hydration enters into the relationship for the total free energy of the system. This can be achieved from two considerations. First, with our simplified model of primary hydration, it is possible to divide the total water mass into two distinct components; mass of free water and mass of primary hydrated water. The hydration number is then incorporated by making a mass balance of the water in the system, i.e.

$$n_w = n_{fw} + h_1 n_1 \qquad (2)$$

where

n_{fw} = moles of free water
n_w = total moles of water, both free and hydrated
h_1 = moles of water hydrated by a mole of salt
n_1 = moles of salt in solution.

Second, recognising that the density of pure and hydrated water is different, one can expect secondary volume (co-volume) changes to occur on mixing the anhydrous salt and the water. To incorporate the co-volume effect requires linking the volume fractions of both the hydrated ionic species and free water (the thermodynamic entities in terms of which an equation for free energy is formulated) to volume entities which can be measured or estimated from reported data in the literature. This link can be established by incorporating hydration numbers into the formulations of partial molal volumes of the components in the system.

3. PARTIAL MOLAL VOLUMES*

3.1 Introductory remarks

In the development of a theoretical model for activity coefficients in aqueous electrolyte solutions (Section 6), the theory *inter alia* is in terms of the volume fraction of hydrated salt, V_{hi}, and the volume fraction of free water V_{fw}. These volume fractions are defined as follows for a binary system:

For the salt

$$V_{hi} = n_i \bar{V}_{hi}/V \tag{3a}$$

where

n_i = number of moles of hydrated salt species i

$\bar{V}_{hi}$ = volume of hydrated salt species i in the solution per moles of salt species i, called the partial molal volume of hydrated species i

V = total volume of the system.

For the free water

$$V_{fw} = n_{fw} \bar{V}_{fw}/V \tag{3b}$$

where

n_{fw} = number of moles of free water in the system

$\bar{V}_{fw}$ = volume/mole of free water.

In any particular solution, containing perhaps a number of salts in solution, considering Eqs. (3a and 3b) two problems arise:

1. If the concentration of the salt, species i, in solution is expressed in moles/kg water (i.e. on the molality scale),

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* In terms of SI description the correct terminology is partial *molar* volume. We have retained the conventional description (i.e. partial *molal* volume); the SI designation, in our opinion, creates as much confusion as the conventional one and suffers from being unfamiliar. The SI symbolization for partial molal entities also is rejected for the same reasons.

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the volume V of the system cannot be calculated *ab initio* and must be estimated from some property of the system.

2. The parameters $\bar{V}_{hi}$ and $\bar{V}_{fw}$ are unknown and cannot be measured experimentally.

To overcome the two problems above, an approach is to select some volumetric thermodynamic property which is measurable and can be linked to $\bar{V}_{hi}$, $\bar{V}_{fw}$ and V. A measurable property that satisfies this requirement is the volume change of the system on addition of one mole of the salt (or one mole of water) to an infinite volume of the solution, called the partial molal volume of the salt, $\bar{V}_i$,(or the partial molal volume of the water, $\bar{V}_w$).*

In order to link $\bar{V}_{hi}$ and $\bar{V}_{fw}$ to $\bar{V}_i$ it is necessary to hypothesize a model for the hydrated ionic species in the aqueous solution. The hypothesis that will be used here is that involving the concept of hydration numbers discussed earlier.

A difficulty in developing these links is that the partial molal volumes $\bar{V}_{hi}$, $\bar{V}_i$ and $\bar{V}_{fw}$ are functions of the electrolyte composition of the solution. Consequently, even though it is possible to develop the interrelationship between $\bar{V}_{fw}$, $\bar{V}_{hi}$ and $\bar{V}_i$ for a *specified* solution composition, this is not of much practical use where the objective is to develop a general model of electrolyte behaviour that can accept any solution composition. It will be necessary therefore, also to develop methods whereby the partial molal volume of a particular salt (or the water component) can be estimated in any solution (Chapter 3).

To develop the theory, binary solutions will be considered first, in this chapter; extension to mixed systems is considered in Chapter 3.

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* The objective in adding the component to an infinitely large volume is that essentially the composition of the solution will not change.

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3.2 Definition of partial molal volume, $\bar{V}_i$

In a solution in which the composition is fixed, the partial molal volume of a component (salt or water) is the volume change / mole for an infinitely small mole addition of that component to the solution.

One can illustrate the meaning of a partial molal volume of, say, a salt as follows: Assume the solution is sea water; it is required to determine the partial molal volume of Na_2SO_4 in sea water. The volume change is measured when one mole of Na_2SO_4 is added to such a large mass of sea water that the composition of the sea water *remains essentially unaltered.* The volume change of the solution/mole Na_2SO_4 added is the partial molal volume of Na_2SO_4 in sea water.

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3.3 Partial molal volumes in binary solutions

When a salt is added incrementally to a solution, the associated volume changes can be measured and a volume-salt added curve can be drawn. The slope of the curve at any point gives the partial molal volume of the salt corresponding to the concentration of salt at that point. The volume-salt added curve cannot be established *ab initio*; in order to link the slope of the curve at one point to that at any other point requires additional assumptions regarding the behaviour of ions in solution. To formulate such assumptions it is necessary to obtain an absolute reference point. A convenient one is the partial molal volume of a salt in a binary solution at infinite dilution, termed the *ideal partial molal volume*, $\bar{V}_i^o$. The ideal partial molal volume has the advantage that at infinite dilution long range electrostatic interactions between ions of opposite charge can be neglected and the hydrated water per mole of salt has some fixed value. Consequently, the ideal partial molal volume provides a base-line for separating out the deviations from ideality due to long range electrostatic effects and changes in the nature and mass of the hydrated water.

To develop the concepts set out above, we will proceed as follows:

1. Develop a mathematical formulation for partial molal volume of salt $\bar{V}_i$ in a binary system in terms of the salt and water species. This formulation is valid for any selected concentration.
2. Develop a link between the hydrated partial molal volume of a salt, $\bar{V}_{hi}$, and its partial molal volume $\bar{V}_i$, using the hydration theory.
3. Express the partial molal volumes $\bar{V}_i$, $\bar{V}_{hi}$ and $\bar{V}_w$ at any one concentration in terms of their respective values at infinite dilution (ideal partial molal volumes $\bar{V}^o$, $\bar{V}^o_{hi}$ and $\bar{V}^o_w$) plus deviations from ideality. This allows the partial molal volumes to be calculated at any concentration.
4. Extend the theory to estimation of partial molal volumes of *single ions* in binary solutions at any concentration.

3.3.1 *Partial molal volume* $\bar{V}_i$

Mathematically the partial molal volume, $\bar{V}_i$, of a salt species i in an aqueous *binary* system is defined by the partial derivative of the total volume of solution with respect to moles of the salt species i at constant temperature, T, and pressure, P, and keeping the total moles of water, n_w, in the solution constant, i.e.

$$\bar{V}_i = \left(\frac{\partial V}{\partial n_i}\right)_{T,P,n_w} \tag{4}$$

For the water species

$$\bar{V}_w = \left(\frac{\partial V}{\partial n_w}\right)_{T,P,n_i} \tag{5}$$

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If more than one salt type is present in the solution, say n_1, n_2, n_3 ... moles of salt species, 1, 2, 3 ..., a multicomponent system is formed. The partial molal volume of salt 1, say, is still given by Eq. (4) except that the components n_2, n_3 ... also are kept constant, i.e.

$$V_1 = \left(\frac{\partial V}{\partial n_1}\right)_{T,P,n_2,n_3 \ldots,n_w} \tag{6}$$

In order to formulate an expression for the total volume of the solution in terms of the partial molal quantities defined above, the general expression for the volume of the system is written down that includes all the factors affecting this volume. For a *binary system* for example, these are temperature, T, pressure, P, moles of anhydrous salt species i, n_i, and the total moles of water, n_w, i.e.

$$V = V(T,P,n_i,n_w) \tag{7}$$

If there is a small change in the temperature and pressure of the system and also in the masses of each of the constituents, the change in volume is given by

$$dV = \left(\frac{\partial V}{\partial P}\right)_{T,n_i,n_w} dP + \left(\frac{\partial V}{\partial T}\right)_{P,n_i,n_w} dT + \left(\frac{\partial V}{\partial n_i}\right)_{P,T,n_w} dn_i + \left(\frac{\partial V}{\partial n_w}\right)_{P,T,n_i} dn_w \tag{8}$$

Provided the changes in P, T, n_i and n_w are sufficiently small, the composition of the solution can be taken as remaining constant, and each of the partial differential quantities in Eq. (8) are constants and represent the respective partial molal volumes of the components in the solution with fixed composition. If T and P remain constant, Eq. (8) reduces to

$$dV = \bar{V}_i . dn_i + \bar{V}_w . dn_w \tag{9}$$

The total volume of the solution at some fixed composition (for which

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$\bar{V}_i$ and $\bar{V}_w$ are fixed and defined) is then the integrated form of Eq. (9), i.e.

$$V = n_i.\bar{V}_i + n_w.\bar{V}_w \tag{10}$$

3.3.2 *Partial molal volume of hydrated species $\bar{V}_{hi}$.*

Mathematically the partial molal volume of hydrated salt species i, $\bar{V}_{hi}$, in an aqueous binary system is defined by the partial derivative of the total volume of solution with respect to the moles of hydrated species i at constant temperature T, pressure P and keeping the moles of free water n_{fw}, in the solution constant, i.e.

$$\bar{V}_{hi} = \left(\frac{\partial V}{\partial n_i}\right)_{P,T,n_{fw}} \tag{11}$$

and similarly for the free water component in the system

$$\bar{V}_{fw} = \left(\frac{\partial V}{\partial n_{fw}}\right)_{P,T,n_i} \tag{12}$$

Using a similar approach to that above in the development of Eq.(10), it is possible to develop an equation for the volume of the solution in terms of the partial molal volumes of hydrated species and free water, i.e.

$$V = n_i.\bar{V}_{hi} + n_{fw}.\bar{V}_{fw} \tag{13}$$

3.3.3 *Link between $\bar{V}_i$ and $\bar{V}_{hi}$.*

A relationship between the partial molal volume $\bar{V}_i$ and the hydrated partial molal volume $\bar{V}_{hi}$ can be obtained in two ways. In the first approach both Eq. (10) and Eq. (13) can be differentiated in accordance with Eq. (11) and Eq. (4) respectively, to give two relationships which include terms for which values can be neither measured nor estimated. For example, substituting for n_{fw} from Eq. (2) into

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Eq. (13) and differentiating this expression as in Eq. (4)

$$\bar{V}_i = \bar{V}_{hi} - h_i\bar{V}_{fw} + n_{fw}\left(\frac{\partial \bar{V}_{fw}}{\partial n_i}\right)_{n_w} + n_i\left(\frac{\partial \bar{V}_{hi}}{\partial n_i}\right)_{n_w} - n_i\bar{V}_{fw}\left(\frac{\partial h_i}{\partial n_i}\right)_{n_w} \qquad (14)$$

The value of the sum of the last three terms on the right hand side of Eq. (14) cannot be assessed in the form presented. Consequently, Eq. (14) is not in a useful form for linking $\bar{V}_i$ and $\bar{V}_{hi}$.

In the second approach one can equate the two equations for volume of a particular solution in terms of partial molal volumes and hydrated partial molal volumes of salt species, Eqs. (10) and (13) respectively,

$$n_i\bar{V}_{hi} + n_{fw}\bar{V}_{fw} = n_i\bar{V}_i + n_w\bar{V}_w \qquad (15)$$

Substituting for n_{fw} from Eq. (2) into Eq. (15) and rearranging terms

$$\bar{V}_{hi} = \bar{V}_i + h_i\bar{V}_{fw} + \frac{n_w}{n_i}(\bar{V}_w - \bar{V}_{fw}) \qquad (16a)$$

Alternatively, substituting for n_{fw} from Eq. (2) into Eq. (16a) and rearranging terms

$$\bar{V}_{hi} = \bar{V}_i + h_i\bar{V}_w + \frac{n_{fw}}{n_i}(\bar{V}_w - \bar{V}_{fw}) \qquad (16b)$$

In Eqs. (16a and 16b), if $\bar{V}_w$ can be assumed equal to $\bar{V}_{fw}$, the required link between $\bar{V}_i$ and $\bar{V}_{hi}$ is

$$\bar{V}_{hi} = \bar{V}_i + h_i\bar{V}_w \qquad (17)$$

The assumption in Eq. (17) that $\bar{V}_w$ equals $\bar{V}_{fw}$ can be rationalized as follows: If salt is added to an infinite volume of water then each molecule of salt in the solution can be considered as completely hydrated, long range electrostatic effects between ions of opposite charge are completely negligible and no overlapping occurs of the

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hydration atmospheres about adjacent ions, i.e. the solution is ideal (see later). If pure water is now added to this ideal solution, none of the water added will be abstracted for hydration because hydration is already complete and hence, the partial molal volume of the water in the solution, $\bar{V}_w$, will be equal to that for pure water, and, equal to the partial molal volume of the free water, $\bar{V}_{fw}$. For a solution at finite ionic strength, at any specific salt concentration the hydration is complete for that solution although there is a change in the value of the hydration number from its value at infinite dilution. An infinitesimal addition of water will not change the hydration number (except to the second order of magnitude) and hence one can expect that the partial molal volume of the water in the solution remains equal to that in pure water except insofar as long range electrostatic effects will influence the partial molal volume of the water in the solution. Consequently, again the $\bar{V}_w = \bar{V}_{fw}$. The reasoning above is supported by noting that the partial molal volume of water changes from 18,06 in a one molal solution of LiCl to 17,95 in a six molal solution and the major fraction of this small change can be accounted for by long range electrostatic effects.

Measurement of partial molal volume of salts in aqueous binary systems is obtained in an indirect way from experimental data as follows: At constant temperature and pressure, keeping the total moles of water constant, salt is added incrementally and a plot is made of the total volume of the solution, V, versus the moles of salt, n_i, added. At a selected value of n_i, from Eq. (4) the slope $(\partial V/\partial n_i)_{n_w}$ is determined to give $\bar{V}_i$ at n_i. In order to estimate the slope of the curve at a selected salt concentration with any accuracy, the experimental data must be fitted to some empirical functional relationship for V in terms of n_i (or salt concentration). Differentiation of this relationship gives an equation for determining $\bar{V}_i$ at a particular salt concentration. This method leads to inaccuracies in extrapolating to infinite dilution, V_i^o, Millero (1970).

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For this reason a further partial molal volume parameter has been introduced, called the *apparent partial molal volume* Φ_i, which is amenable to direct experimental determination, and for which there are reliable extrapolation procedures for estimating the apparent partial molal volume at infinite dilution, Φ_i^o, Redlich and Meyer (1963). Most experimentally determined volume/mole data in the literature are reported in terms of the apparent partial molal volume. This does not create a problem insofar as the basic theory is affected because the apparent partial molal volume, Φ_i, is linked to the partial molal volume, $\bar{V}_i$, and hence to the hydrated partial molal volume, $\bar{V}_{hi}$.

3.3.4 *Apparent partial molal volume,* Φ_i

The apparent partial molal volume, Φ_i, originally was introduced as a useful measurable parameter for binary systems by Lewis and Randall (1921). Mathematically they defined Φ_i for a binary system containing n_i moles of salt and n_w moles of water at a known temperature and pressure as

$$\Phi_i = \frac{V - n_w.\bar{V}_w^o}{n_i} \tag{18}$$

where $\bar{V}_w^o$ = partial molal volume of pure water.

Solving for V in Eq. (18)

$$V = n_i.\Phi_i + n_w.\bar{V}_w^o \tag{19}$$

From Eq. (19) the partial molal volume of the water component, $\bar{V}_w$, enters into the equation with its value at infinite dilution, $\bar{V}_w^o$, even though the solution is at finite ionic strength. This means that all the factors giving rise to non ideal behaviour of the volume have been incorporated into the partial molal volume parameter for the salt, i.e. Φ_i. One therefore can consider Φ_i as an *apparent* partial molal volume (of salt i) given by the total volume

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change per unit mole of salt added.

/ The relationship linking the partial molal volume, $\bar{V}_i$, and the apparent partial molal volume, Φ_i, is obtained by differentiating Eq. (19) in accordance with Eq. (4), i.e.

$$\left(\frac{\partial V}{\partial n_i}\right)_{n_w} = \bar{V}_i = \Phi_i + n_i\left(\frac{\partial \Phi_i}{\partial n_i}\right) \qquad (20a)$$

and writing Eq. (20a) in terms of concentration units, say molality m_i,

$$\bar{V}_i = \Phi_i + m_i\left(\frac{\partial \Phi_i}{\partial m_i}\right) \qquad (20b)$$

Using Eq. (20b), if a curve of Φ_i versus molality of salt is determined experimentally, then $\bar{V}_i$ can be determined. This is the usual manner for determining $\bar{V}_i$.

In Eq. (20b), as $m_i \to 0$, $m_i(\partial\Phi_i/\partial m_i) \to 0$, hence $\bar{V}_i \to \Phi_i$, i.e. at infinite dilution,

$$\bar{V}_i^o = \Phi_i^o \qquad (21)$$

That is, at infinite dilution the partial molal volume is equal to the apparent partial molal volume. At finite ionic strengths Φ_i always differs from Φ_i^o (and $\bar{V}_i$ differs from $\bar{V}_i^o$). These respective difference arise due to long range electrostatic effects (modelled by the Debye-Hückel Theory) and hydration effects.

On rare occasions one may want to determine Φ_i from $\bar{V}_i$, then from Eq. (20b)

$$\frac{\partial}{\partial m_i}(m_i\Phi_i) = \bar{V}_i$$

i.e.

$$\Phi_i = \frac{1}{m_i}\int_0^{m_i} \bar{V}_i dm_i \qquad (22)$$

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3.4 Deviations from ideality of partial molal volumes - theoretical considerations

3.4.1 *General considerations*

Our principal interest in the non ideality of partial molal volumes arises from the fact that these deviations affect the partial molal free energy and hence the activity and activity coefficients of the various components in aqueous electrolyte solutions (see Section 6.4). For the purposes of estimating the mean activity coefficient of a salt in aqueous solution it is necessary only to have a quantitative estimate of $\bar{V}_i$ and Φ_i for the salt; it is not necessary to consider the factors that give rise to this deviation. Consequently, an empirical functional relationship linking $\bar{V}_i$ or Φ_i to salt concentration is sufficient, provided it allows accurate evaluation of $\bar{V}_i$ or Φ_i. When estimating activity coefficients of individual ionic species, direct experimental measurements of partial molal volumes for these species are not possible. Ionic species partial molal volumes must be estimated by hypothesizing on the structure and behaviour of electrolytes, i.e. on the factors affecting partial molal volumes both at infinite and finite dilutions. It should be noted that in principle the partial molal volume, $\bar{V}_i$, can be separated into ionic components; this however, is not possible for the apparent partial molal volume at finite dilution, Φ_i, because the latter is not a thermodynamic entity.

In terms of the hydration theory and the Debye-Hückel theory it is possible, theoretically at least, to identify factors giving rise to observed deviations at finite ionic strength. Such an analysis however, does not lead to quantitative expression for the deviation due to hydration effects, but most important, it does provide a framework within which non-thermodynamic assumptions can be made to allow assessment of each factor.

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In order to isolate the factors giving rise to partial molal volumes at infinite and finite concentrations, first an equation must be written for the total volume of the system in terms of the component volumes. The volume of an aqueous binary system is considered to be the sum of the volumes of three components: (1) the unhydrated or intrinsic volume of salt species, i, (2) free water, and (3) water hydrated by the salt species i*(i.e. primary hydrated water) designated by the subscript hwi, i.e.

$$V = n_i.\bar{V}_{INTi} + n_{fw}.\bar{V}_{fw} + n_{hwi}.\bar{V}_{hwi} \tag{24}$$

where

$\bar{V}_{INTi}$ = volume/mole of unhydrated salt species i

$\bar{V}_{hwi}$ = volume/mole of hydrated water on salt species i in the primary hydration zone at some specified solution composition. For a particular salt species a specific value can be assigned to $\bar{V}_{hwi}$.

Substituting for $\bar{V}_{INTi}$ from Eq. (23) into Eq. (24) and putting n_{hwi} equal to $n_i h_i$ (from the definition of h_i, see Eq. (2))

$$V = n_i(\bar{V}_{xi} + \bar{V}_{DISi}) + n_{fw}.\bar{V}_{fw} + n_i h_i.\bar{V}_{hwi} \tag{25}$$

The values for $\bar{V}_{DISi}$, $\bar{V}_{fw}$, $\bar{V}_{hwi}$ and h_i in Eq. (25) are for a particular composition of solution. In general these values will be different from their respective values at infinite dilution due to long range electrostatic and hydration effects.

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* The intrinsic volume/mole of an ionic species includes both the bare ion volume (i.e. the crystal volume/mole, V_{xi}) and the volumetric effects due to the disordered water (secondary hydration) $\bar{V}_{DIS}$, Millero (1970), (secondary hydration is considered to have no mass effect, see Section 2), i.e.

$$\bar{V}_{INTi} = \bar{V}_{xi} + \bar{V}_{DISi} \tag{23}$$

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Long range electrostatic effects of the Debye-Hückel type between oppositely charged ions cause changes in the various $\bar{V}$ parameters with change in ionic strength. At this stage in the development it is sufficient to lump the long range electrostatic effects into some total effect on volume, V^{DH}. By including V^{DH} as a separate parameter, Eq. (25) can be rewritten with the values for the parameters $\bar{V}_{xi}$ and $\bar{V}_{fw}$ as those at infinite dilution, $\bar{V}^{o}_{xi}$ and $\bar{V}^{o}_{fw}$ respectively. Because the deviations from ideality of $\bar{V}_{DISi}$ and $\bar{V}_{hwi}$ are due to *both* Debye-Hückel electrostatic effects and interference effects between hydration atmospheres of adjacent ions (see below), once the Debye-Hückel effect has been taken out, $\bar{V}_{DISi}$ and $\bar{V}_{hwi}$ will have different values to $\bar{V}'_{DISi}$ and $\bar{V}'_{hwi}$ respectively, i.e.

$$V = n_i(\bar{V}^{o}_{xi} + \bar{V}'_{DISi}) + n_{fw}.\bar{V}^{o}_{fw} + n_i h_i.\bar{V}'_{hwi} + V^{DH} \qquad (26)$$

With regard to the hydration effect, the values for the partial molal volumes of the disordered water, $\bar{V}'_{DISi}$, (void effects which account for the secondary hydration) change due to increased overlapping, or interference of secondary hydration atmospheres of adjacent ions with increased salt concentration. Also, the values for the hydration number, h_i and, consequently, the partial molal volume of hydrated water $\bar{V}'_{hwi}$, change due to increased competition for free water molecules with increased ionic strength (see Section 2.1).

The factors giving rise to deviations from ideality of $\bar{V}_i$ for species i can now be isolated as follows: Differentiating Eq.(26) in accordance with Eq. (10) gives an expression for $\bar{V}_i$ in terms of $\bar{V}^{o}_i$ plus terms accounting for non ideality, i.e. from Eq. (10)

$$(\partial V/\partial n_i)_{n_w} = \bar{V}_i \qquad (10)$$

Substituting for n_{fw} from Eq. (2) into Eq. (26) and differentiating this equation in accordance with Eq. (10)

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$$\overline{V}_i = \frac{\partial}{\partial n_i}(n_i\overline{V}^o_{Xi} + n_i\overline{V}'_{DISi}) + \frac{\partial}{\partial n_i}\{n_ih_i(\overline{V}'_{hwi} - \overline{V}^o_{fw})\} + \frac{\partial V^{DH}}{\partial n_i}$$

$$= \overline{V}^o_{Xi} + \overline{V}'_{DISi} + h_i(\overline{V}'_{hwi} - \overline{V}^o_{fw}) + n_i\frac{\partial\overline{V}'_{DISi}}{\partial n_i} + n_i\frac{\partial}{\partial n_i}(h_i\overline{V}'_{hwi} - h_i\overline{V}^o_{fw})$$

$$+ \frac{\partial V^{DH}}{\partial n_i} \qquad (27)$$

At infinite dilution $V_i = V^o_i$, $n_i \to 0$ and $\partial V^{DH}/\partial n_i \to 0$, $h = h^o_i$, i.e.

$$\overline{V}^o_i = \overline{V}^o_{Xi} + \overline{V}^o_{DISi} + h^o_i(\overline{V}^o_{hwi} - \overline{V}^o{}_{fw}) \qquad (28)$$

Solving for $\overline{V}^o_{Xi}$ from Eq. (28), substituting into Eq. (27) and rearranging terms gives the required expression for $\overline{V}_i$ in terms of $\overline{V}^o_i$ and terms to account for the deviations from ideality, i.e.

$$\overline{V}_i = \overline{V}^o_i + \{\overline{V}'_{DISi} - \overline{V}^o_{DISi} + n_i\frac{\partial\overline{V}'_{DISi}}{\partial n_i}\} + \{h_i(\overline{V}'_{hwi} - \overline{V}^o_{fw})$$

$$- h^o(\overline{V}^o_{hw} - \overline{V}^o_{fw}) + n_i\frac{\partial}{\partial n_i}(h_i\overline{V}'_{hwi} - h_i\overline{V}^o_{fw})\} + \{\frac{\partial V^{DH}}{\partial n_i}\} \qquad (29)$$

Simplifying this expression and rearranging terms

$$\overline{V}_i - \overline{V}^o_i = \{\overline{V}'_{DISi} - \overline{V}^o_{DISi} + n_i\frac{\partial\overline{V}'_{DISi}}{\partial n_i}\} + \{h^o(\overline{V}^o_{fw} - \overline{V}^o_{hwi})$$

$$- (h_i + n_i\frac{\partial h_i}{\partial n_i})(\overline{V}^o_{fw} - \overline{V}'_{hwi}) + n_ih_i\frac{\partial\overline{V}'_{hwi}}{\partial n_i}\}$$

$$+ \{\frac{\partial V^{DH}}{\partial n_i}\} \qquad (30)$$

The left hand side of Eq. (30) represents the total deviation from ideality of $\overline{V}_i$, $\Delta\overline{V}_i$. Each of the three terms in curly brackets on the right hand side of Eq. (30) accounts for a separate factor in the deviation of $\overline{V}_i$ from ideality. The first term accounts for the effects of secondary hydrated water with change in salt concentration

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and can be depicted as $\Delta\bar{V}_{SH}$; the second for the effects of change in primary hydrated water with change in salt concentration, $\Delta\bar{V}_{PH}$; the third for long range Debye-Hückel electrostatic effects, $\Delta\bar{V}^{DH}$, i.e.

$$\Delta\bar{V}_i = \Delta\bar{V}_{SH} + \Delta\bar{V}_{PH} + \Delta\bar{V}^{DH} \tag{31}$$

The corresponding equations for Φ_i and $\Delta\Phi_i$ are formulated from Eqs. (22 and 27). From Eq. (22)

$$\Phi_i = \frac{1}{m_i}\int_0^{m_i} \bar{V}_i\,dm_i$$

Integrating Eq. (27) in accordance with Eq. (22)

$$\Phi_i = \bar{V}^{\circ}_{xi} + \bar{V}'_{DISi} + h_i(\bar{V}'_{hwi} - \bar{V}^{\circ}_{fw}) + \frac{V^{DH}}{n_i} \tag{32}$$

Substituting for $\bar{V}^{\circ}_{xi}$ from Eq. (28) into Eq. (32), rearranging terms and putting $\bar{V}^{\circ}_i = \Phi^{\circ}_i$

$$\Phi_i = \Phi^{\circ}_i + \{\bar{V}_{DISi} - \bar{V}^{\circ}_{DISi}\} + \{h^{\circ}_i(\bar{V}^{\circ}_{fw} - \bar{V}^{\circ}_{hwi}) - h_i(\bar{V}^{\circ}_{fw} - \bar{V}'_{hwi})\} + \{\bar{V}^{DH}/n_i\} \tag{33}$$

i.e.

$$\Phi_i - \Phi^{\circ}_i = \{\bar{V}_{DISi} - \bar{V}^{\circ}_{DISi}\} + \{h^{\circ}_i(\bar{V}^{\circ}_{fw} - \bar{V}^{\circ}_{hwi}) - h_i(\bar{V}^{\circ}_{fw} - \bar{V}'_{hwi})\} + \{\bar{V}^{DH}/n_i\} \tag{34}$$

i.e.

$$\Delta\Phi_i = \Delta\Phi_{SH} + \Delta\Phi_{PH} + \Delta\Phi^{DH} \tag{35}$$

where $\Delta\Phi_{SH}$, $\Delta\Phi_{PH}$ and $\Delta\Phi^{DH}$ account for the deviation from ideality of Φ_i due to the effects of secondary hydration, primary hydration and long range electrostatic effects respectively.

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Although the three effects above have been separated out qualitatively, there is no independent means available for determining quantitatively the changes in $\bar{V}_i$ due to primary and secondary hydration effects with salt addition (i.e. $\bar{V}_{hwi} - \bar{V}^o_{hwi}$ and $\bar{V}_{DISi} - \bar{V}^o_{DISi}$) either theoretically or experimentally. Consequently, one can only separate out and estimate these effects by making some assumptions on the behaviour of the electrolyte.

One commences with the electrostatic effect and assumes that this effect can be described in terms of the Debye-Hückel theory. The secondary hydration effect is then considered. Here it is assumed that at relatively low ionic strengths the secondary hydration effect dominates over the primary hydration effect. This assumption is based on the behavioural characteristics of the equation for fitting the curves for activity coefficients, Eq. (189), against observed data, and it is apparent that up to ionic strengths of about unity changes in primary hydration are negligible except for the heavily hydrated salts of H^+ and Li^+ where primary hydration effects become significant in the region $\mu > 0,5$ (see Section 6). In this manner the secondary hydration effect is isolated in the lower ionic strength region. In the higher ionic strength region the assumption is made that the secondary hydration effect can be estimated by extrapolation of the behavioural characteristics from the lower ionic strength region. Thus, having an estimate of the secondary hydration effect in the higher region, the primary hydration effect is hypothesized to account for the difference between the total deviation and the sum of the electrostatic and secondary hydration effects. Each of these deviations is now considered in detail.

Electrostatic effects on partial molal volumes

Considering the long range electrostatic effects, Redlich and Rosenfeld (1931), Redlich and Meyer (1963), Owen and Brinkley (1949)

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and Millero (1970) utilized the Debye-Hückel theory and the thermodynamic relationship between partial molal volume and partial molal free energy to obtain expressions for $\Delta\bar{V}^{DH}$ and $\Delta\Phi^{DH}$ in Eqs. (31 and 35) respectively. From Millero (1970)

$$\Delta\bar{V}^{DH} \simeq \frac{A(d_+z_+^2 + d_-z_-^2)\, 2^{\frac{1}{2}} \sqrt{\mu}}{1 + B\mathring{a}\sqrt{\mu}} \tag{36a}$$

and, for $\Delta\Phi^{DH}$, from Millero (1970)

$$\Delta\Phi^{DH} \simeq \frac{0{,}66(d_+z_+^2 + d_-z_-^2)\, 2^{\frac{1}{2}} \sqrt{\mu}}{1 + B\mathring{a}\sqrt{\mu}} \tag{36b}$$

where

μ = ionic strength*

A = a constant varying with the dielectric constant and compressibility of the solution
= 0,99 at 25°C for water

B = a constant varying with temperature and the dielectric constant for the solution
= 0,328 at 25°C for water

$\mathring{a}$ = distance of closest approach between oppositely charged ions in the solution in Ångstrom units

then knowing $\mathring{a}_1$**, the Debye-Hückel effect, $\Delta\bar{V}_i^{DH}$ (or $\Delta\Phi_i^{DH}$), can be calculated and is shown plotted versus $\mu^{\frac{1}{2}}$ in Figure 1(a) for NaCl and $MgCl_2$; also shown are the observed deviations of $\bar{V}_i$, i.e. $\Delta\bar{V}_i$ and the limiting law Debye-Huckel effect, $\Delta\bar{V}_{LL}^{DH}$, for each of the two salts.

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* See Appendix 2B to this chapter for definition.

** The distance of closest approach parameter $\mathring{a}_i$ can be estimated from the theory of activity coefficients (see Section 6).

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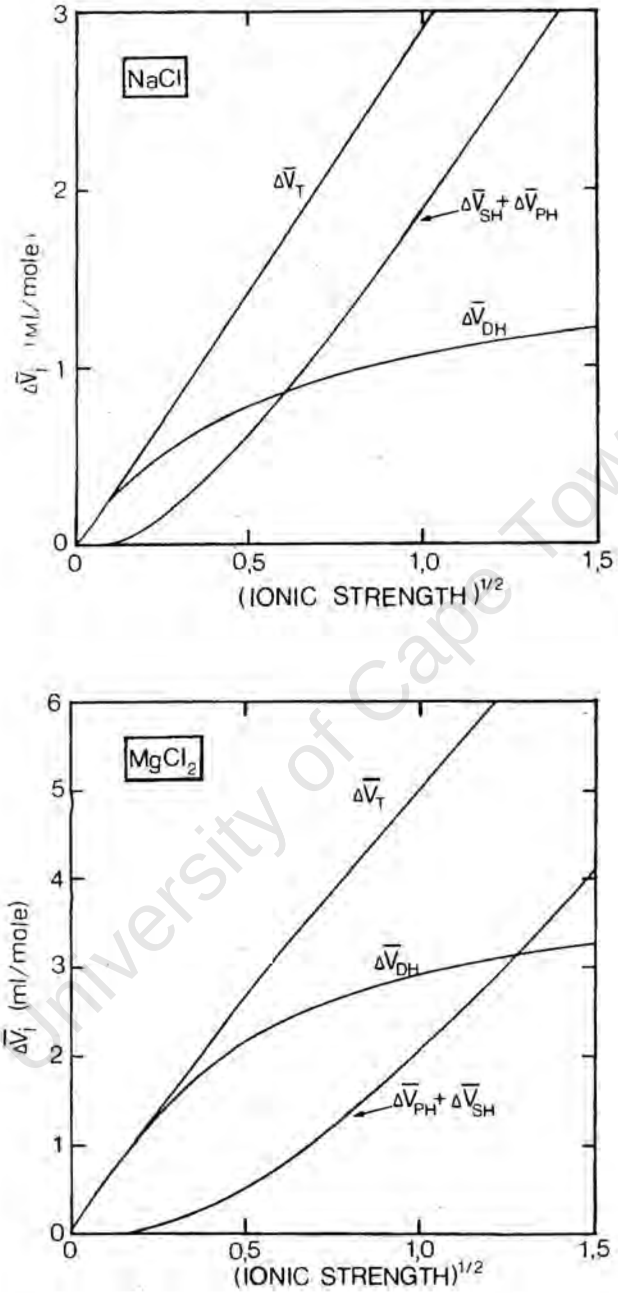

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Figure 1(a). Observed deviations from ideality of partial molal volumes for NaCl *and* $MgCl_2$ *versus* $\mu^{\frac{1}{2}}$ *for* $MgCl_2$ *and* NaCl. *(Values for* $\Delta\bar{V}_T$ *determined from data reported by Wirth and Bangert,1972).*

Secondary and primary hydration effects on partial molal volumes

From Figure 1(a), for both NaCl and $MgCl_2$, with increase in μ the observed deviation $\Delta\bar{V}_i$ becomes increasingly greater than that due to the Debye-Hückel effect alone, $\Delta\bar{V}^{DH}$, determined using Eq. (36a). In terms of what was stated above, we can ascribe this difference, quantitatively, to the effects of changes in the primary and secondary hydrated water from the values at infinite dilution, i.e. to the sum of $\Delta\bar{V}_{PH}$ and $\Delta\bar{V}_{SH}$. The sum of these two hydration effects is shown plotted in Figure 1(a); for both NaCl and $MgCl_2$ the total hydration effect is to increase $\bar{V}_i$ with increased salt concentration.

Some quantitative estimate can be made of the separate effects of primary and secondary hydration, $\Delta\bar{V}_{PH}$ and $\Delta\bar{V}_{SH}$, by using the activity coefficient theory developed in Section 6. From the activity coefficient theory it appears that changes in the primary hydration atmosphere become significant only at ionic strengths greater than about unity. Hence, in the region $\mu < 1$, the hydration effects on $\bar{V}_i$, $\Delta\bar{V}_{SH} + \Delta\bar{V}_{PH}$, can be ascribed to be totally due to secondary hydration, i.e. in the region $\mu < 1$ $\Delta\bar{V}_{SH}$ can be determined as the difference between $\Delta\bar{V}_i$ and $\Delta\bar{V}^{DH}$ (see Eq. 31). In the region $\mu > 1$ the deviation due to hydration effects is assumed to be the sum of the deviations due to primary and secondary hydration effects. In Figure 1(b) the total deviation observed, $\Delta\bar{V}_i$, and the Debye-Hückel effect $\Delta\bar{V}^{DH}$ are shown plotted versus μ for the salts $MgCl_2$ and NaCl. Hence, the balance of the deviation can be calculated as the difference between $\Delta\bar{V}_i$ and $\Delta\bar{V}^{DH}$ and is also shown plotted as $(\Delta\bar{V}_{PH} + \Delta\bar{V}_{SH})$. Accepting the assumption that in the region $\mu < 1$ secondary hydration effects and electrostatic effects only are present, and accepting that the secondary hydration effect can be extrapolated into the region $\mu > 1$ (see dotted line in Figure 1(b)), the balance of the deviation can be ascribed to primary hydration effects.

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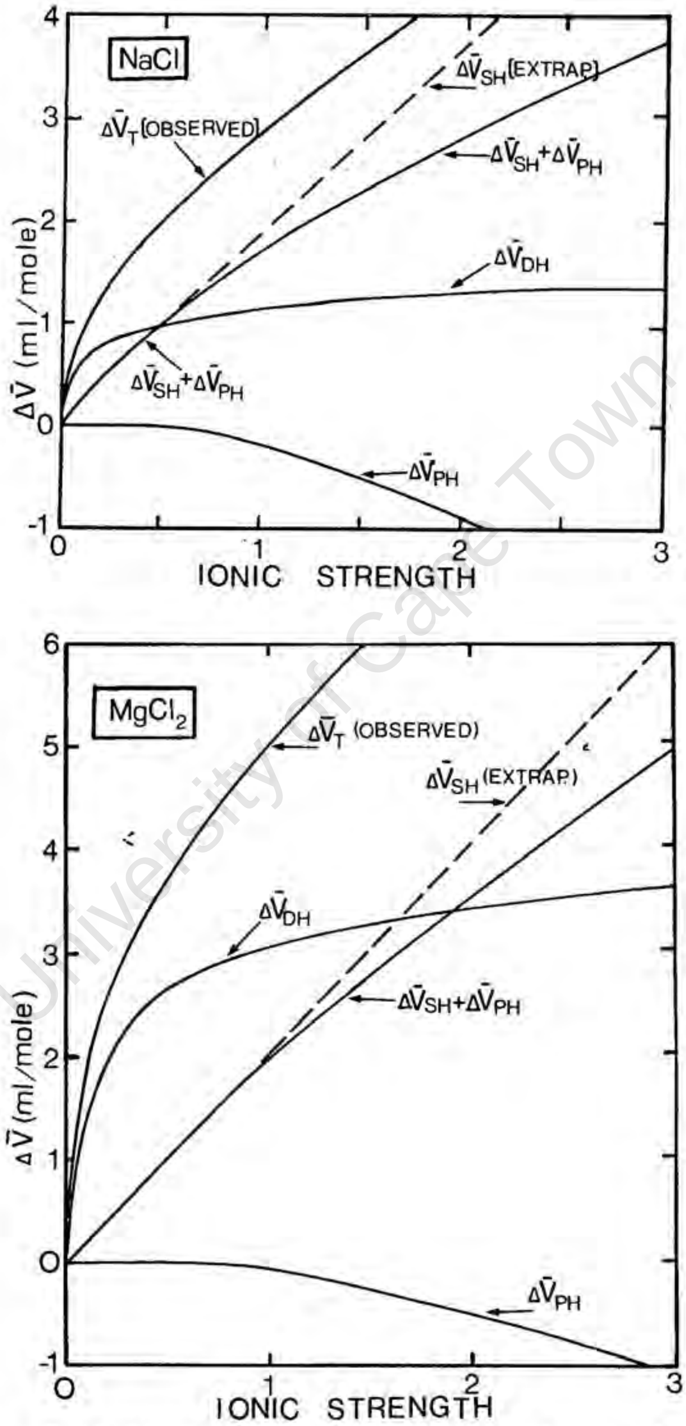

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Figure 1(b). Deviations from ideality of partial molal volumes for NaCl *and* $MgCl_2$. *(Values determined from data reported by Wirth and Bangert, 1972).*

Referring to Figure 1(b), in the region $\mu < 1$ (i.e. where $\Delta\bar{V}_{PH}$ is assumed zero) the plots for ($\bar{V}_{PH}$ + $\bar{V}_{SH}$) are positive and closely linear. That is, in terms of our theory the secondary hydration effects on $\bar{V}_i$ are positive and linear with μ.In the region $\mu > 1$ (i.e. where $\Delta\bar{V}_{PH} \neq$ zero) the sum ($\Delta\bar{V}_{PH} + \Delta\bar{V}_{SH}$) is no longer linear and has a decreasing slope. By assuming that the change in slope of ($\Delta\bar{V}_{PH} + \Delta\bar{V}_{SH}$) versus μ is due to primary hydration effects, $\Delta\bar{V}_{PH}$is estimated as the difference between ($\Delta\bar{V}_{PH} + \Delta\bar{V}_{SH}$) and the value of $\Delta\bar{V}_{SH}$ determined by extrapolating the linear relationship between $\bar{V}_{SH}$ and μ established in the region $\mu < 1$. Each effect, i.e. $\Delta\bar{V}^{DH}$, $\Delta\bar{V}_{SH}$ and $\Delta\bar{V}_{PH}$, can now be plotted separately as shown in Figure 1(b) for the salts NaCl and $MgCl_2$. For both these salts $\Delta\bar{V}_{PH}$ is negative and closely linear in μ but small in volume compared with the positive effects of $\Delta\bar{V}_{SH}$.

The negative but comparatively small effect of changes in primary hydration on $\bar{V}_i$ shown in Figure 1(b) is not inconsistent with the hydration theory utilized in the development of Eqs. (30 and 34) for $\Delta\bar{V}_i$ and $\Delta\Phi_i$ respectively. This is illustrated as follows for $\Delta\Phi_{PH}$: In Eq. (34) the primary hydration effect on Φ_i, $\Delta\Phi_{PH}$, is formulated as

$$\Delta\Phi_{PH} = \{h_i^o(\bar{V}^o_{fw} - \bar{V}^o_{hwi}) - h_i(\bar{V}^o_{fw} - \bar{V}'_{hwi})\} \qquad (37)$$

Now the hydration number h_i decreases with increase in ionic strength, due to the loss of less strongly bound water molecules about a central ion, i.e. $h_i^o > h_i$; referring to Eq. (37) this effect alone will give rise to a positive value for $\Delta\Phi_{PH}$ (because for the electrostricted water $\bar{V}_{hwi} < \bar{V}^{o}_{fw}$). However, because it is the less strongly hydrated water that is lost, the mean density of the primary hydrated water will increase (i.e. $\bar{V}'_{hwi} < \bar{V}^o_{hwi}$) and consequently it is not possible to state explicitly whether the product h_i^o ($\bar{V}^o_{fw} - \bar{V}^o_{hwi}$) will be greater or less than $h_i^o(\bar{V}^o_{fw} - \bar{V}'_{hwi})$, i.e. $\Delta\Phi_{PH}$ (and $\Delta\bar{V}_{PH}$) may have a positive or negative value depending on the magnitudes of h_i and $\bar{V}'_{hwi}$. The same analysis can be repeated

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for $\Delta\bar{V}_{PH}$ but the corresponding equation to Eq.(37) is more complex and not so explicit.

> Desnoyers, Arel, Perron and Jolicoeur (1969) have ascribed the effects of hydration on deviations in $\bar{V}_i$ from ideality in part as being due to structural interactions between the hydrated atmospheres of adjacent ions. They appear to relate these structural interactions to the secondary hydrated water for they specifically mention that the effects of removal of water molecules from the free water component and the consequent alteration of the solvent rôle (as set out by Stokes and Robinson, 1948) i.e. the primary hydrated water, was not considered. In this respect their approach is similar to that set out above.
>
> Millero (1970) ascribes the hydration effects on the deviation from ideality of $\bar{V}_i$ for NaCl (and by implication for most of the alkali halides) as possibly due to the formation of ion pairs. He states that the formation of an ion pair is accompanied by the release of electrostricted water (primary hydrated water) causing an increase in the free water mass and an apparent increase in $\bar{V}_i$ with increase in salt concentration. Millero's interpretation is contrary to that of Desnoyers *et al.* The situation however, is not clear cut for it depends on the meaning one attaches to structural interactions. Padova (1970) states that ion pairing can be viewed as any of a number of interactions between hydration atmospheres of adjacent ions. This would implicate ion pairing in a much broader context than, for example, accepted in this exposition. In the absence of direct experimental evidence on ion pairing, one approach is to accept ion pairing as occurring when, by its inclusion, it is possible to obtain a rational predictive theory otherwise not possible. For example, for the chloride, bromide and iodide salts, it is possible to obtain consistency in the theory without invoking ion pairing; from free energy considerations (activity coefficients), the hydration numbers for ions of these salts appear to be additive which is consistent with the theory of hydration numbers, see Section 6. In contrast, sulphate salts can be described by this approach only if ion pairing is assumed (Chapter 4), this is further supported by direct experimental evidence that appears to indicate that ion pairing does occur for many sulphate salts (Pytkowicz and Kester, 1971). Hence, Millero's hypothesis for ion pairing cannot be supported.

3.4.2 *Semi-empirical approach*

It was stated earlier that our principal interest in the non ideality of partial molal volumes arises from the fact that these deviations affect the partial molal free energy and hence the activity and activity coefficients of species in aqueous electrolyte solutions,see Section 6.4. For the purposes of estimating *mean* activity coefficients of a salt in an aqueous solution, provided one has a quantitative estimate of $(\bar{V}_i - \bar{V}_i^\circ)$ or $(\Phi_i - \Phi_i^\circ)$ for that salt, the factors which gave rise to this deviation are unimportant. Consequently, an empirical functional relationship linking $\bar{V}_i$ to concentration is sufficient, provided it allows accurate evaluation of $(\bar{V}_i - \bar{V}_i^\circ)$ and $(\Phi_i - \Phi_i^\circ)$.

Empirical and semi-empirical relationships for the deviations from ideality of Φ_i and $\bar{V}_i$, i.e. $(\Phi_i - \Phi_i^\circ)$ and $(\bar{V}_i - \bar{V}_i^\circ)$, have been proposed by a number of research workers. Often the formulation of these relationships was for the purpose of estimating $\bar{V}_i^\circ$ by extrapolating experimental data to infinite dilution and simply expressed the relationship in terms of the square root of concentration, i.e. a completely empirical approach was adopted. Others attempted a semi-empirical approach by incorporating the limiting law Debye-Hückel theory as one of the parameters; for estimations at high concentrations the limiting law term was then retained and fits to the data obtained by adding power series terms with concentration as the basic parameter.

Some investigators have used the fact that because the extended Debye-Hückel equation, Eq. (36a), requires empirical adjustment to fit the observed deviation in $\bar{V}_i$, the Debye-Hückel theory does not apply. However, this argument cannot be supported because it would appear from our analyses (in Section 3.4.1) of the various factors influencing $(\bar{V}_i - \bar{V}_i^\circ)$ that hydration effects are significant and, conceptually at least, can be demonstrated to account for the lack of conformity of $(\bar{V}_i - \bar{V}_i^\circ)$ to the extended Debye-Hückel effect.

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The equation of Masson (1930) is an example of a completely empirical equation. He found that the apparent partial molal volumes of electrolytes, Φ_i, often vary linearly with the square root of the molarity, C, as follows:

$$\Phi_i = \Phi_i^o + S_v^* \sqrt{C}_i \tag{38}$$

where

S_v^* = experimental constant obtained from the slope of the plot Φ_i versus $\sqrt{C}$; the value for this constant is temperature dependent and varies between salts.

Although Eq. (38) can be employed as a means of presenting *measured* experimental data, the work of Redlich and Rosenfeld (1931) indicates that extrapolation using this formulation does not allow an accurate estimate of Φ_i^o. To overcome this difficulty Redlich and Rosenfeld developed an explicit solution for isolating the long range electrostatic effect on $\bar{V}_i$, $(\partial V^{DH}/\partial n_i)_{n_w}$ in Eq. (30) for *dilute* binary systems. They utilized the Debye-Hückel theory and the thermodynamic relationship between partial molal volumes and partial molal free energy to obtain the limiting law equation for the long range electrostatic effect on $\bar{V}_i$,

$$\left(\frac{\partial V^{DH}}{\partial n_i}\right)_{n_w} = A(d_+ z_+^2 + d_- z_-^2)^{\frac{3}{2}} \sqrt{C}_i \tag{39a}$$

where

A = a constant varying with the dielectric constant and compressibility of the solution
= 0,99 at 25°C for water.

or, writing Eq. (39a) in terms of ionic strength, μ,

$$\left(\frac{\partial V^{DH}}{\partial n_i}\right)_{n_w} = A(d_+ z_+^2 + d_- z_-^2) \sqrt{2\mu} \tag{39b}$$

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and the equation for $\bar{V}_i$ is

$$\bar{V}_i = \bar{V}_i^o + A(d_+z_+{}^2 + d_-z_-{}^2)^{\frac{3}{2}} \sqrt{C} \tag{40}$$

Using Eq. (40), Redlich and Rosenfeld showed that an explicit theoretical solution can be obtained also for the long range electrostatic deviation from ideality for Φ_i(i.e. $\bar{V}^{DH}/n_i$ in Eq. (33) at low *ionic strength* as follows

From Eq. (22)

$$\Phi_i = \frac{1}{m_i} \int_o^{m_i} \bar{V}_i dm_i$$

$$= \frac{1}{m_i} \int_o^{m_i} (\bar{V}_i^o + \frac{\partial V^{DH}}{\partial n_i}) dm_i$$

Substituting for $(\partial V^{DH}/\partial n_i)_{n_w}$ from Eq. (39a) and noting that

$$V_i^o = \Phi_i^o$$

$$\Phi_i = \Phi_i^o + \frac{1}{m_i} \int_o^{m_i} A(d_+z_+^2 + d_-z_-^2)^{\frac{3}{2}} \sqrt{C}_i dm_i \tag{41}$$

At low ionic strengths the molality, m_i, can be replaced by the molarity, C_i, in Eq. (41) i.e.

$$\Phi_i = \Phi_i^o + \frac{1}{C_i} \int_o^{C_i} A(d_+z_+^2 + d_-z_-^2)^{\frac{3}{2}} \sqrt{C} dC_i$$

Integrating between the limits and simplifying

$$\Phi_i = \Phi_i^o + (2/3)A(d_+z_+^2 + d_-z_-^2)^{\frac{3}{2}}. \sqrt{C}_i$$

$$= \Phi_i^o + S_v \sqrt{C}_i \tag{42}$$

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where

S_v = a constant independent of the nature of the electrolyte except for the valency type. For 1:1, 1:2 and 2:2 electrolytes, S_v has the values 1,86; 9,71 and 14,84 respectively at 25°C.

Equations (39, 40 and 42) are valid only for very dilute solutions.

For higher salt concentrations Redlich and Meyer (1963) have suggested a term linear in C be added to Eq. (42), i.e.

$$\Phi_i = \Phi_i^o + S_v \sqrt{C_i} + b_i C_i \tag{43}$$

where

b_i = an empirical constant for a particular salt, the value of which is temperature dependent and is determined experimentally.

Equation (43) is more rational than Eq. (38) because the former at least separates out the Debye-Hückel effect at low concentrations (i.e. $S_v \sqrt{C}$), whereas the latter incorporates the Debye-Hückel and other effects in a single term, in $S_v^* \sqrt{C}$. In Eq. (43) the Debye-Hückel term becomes the only term of significance at low concentrations allowing Φ_i^o to be determined accurately and thereafter b_i from data at higher concentrations.

Experimental data for partial molal volumes usually is reported in terms of the apparent partial molal volume (which is the parameter measured by experiment). Millero (1970) has listed comprehensive data for determining Φ_i for numerous salts in the temperature range 0 to 200 degrees C. In Table 1 are listed Φ_i^o and b_i values extracted from data listed by Millero for determining Φ_i at 25°C using Eq.(43) for a number of salts of common interest. Some of these values were determined from data at relatively low ionic strength and consequently are possibly unreliable for extrapolation to higher ionic strengths. For many of these salts the Φ_i values have also been formulated independently in terms of the

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Table 1. Data for determining Partial Molal Volumes

Salt	$\bar{V}_i^o = \phi_i^o$ cm³/mole	b_i † cm³ℓ mole⁻²	S_v^* †† cm³ℓ½ mole $^{-\frac{3}{2}}$
HCl	17,82 17,83 (18,07)#	-0,91 ($\mu < 0,6$) -1,15	($\mu > 0,6$) 0,95
LiCl	16,91 (17,0)#	($\mu < 0,6$) -0,36	(" 0,6) 1,49
LiBr	23,76 23,80	-0,60 -0,51	
LiI	35,37	-0,76	
NaCl	16,62 16,62	-0,03 0,048	
NaBr	23,48	-0,26	
NaI	34,82	-0,38	
$NaHCO_3$	22		
$NaHSO_4$	34,5		
Na_2SO_4	11,62 11,64	2,96	12,16
Na_2CO_3	-6,74		11,30
KCl	26,81 26,84	0,16 0,08	
KBr	33,73 33,75	-0,16 0,032	
KI	45,06 45,21	-0,39 -0,22	
$KHCO_3$	32,7		2,6
K_2CO_3	14		
K_2SO_4	31,99	5,17	
RbCl	31,94	0,17	
RbBr	38,84 38,71	-0,36**	2,038
RbI	50,16	-0,05	
CsCl	39,17	0,12	
CsBr	46,04	0,09	
CsI	57,39	0,11	
$MgCl_2$	14,5		5,15
$CaCl_2$	(18,25)# 17,78	-1,8	6,0 7,57
$SrCl_2$	17,94 (18,10)#		7,07
$BaCl_2$	23,15 (23,8)#	-3,027	6,505

† $\Phi_i = \Phi_i + S_v\sqrt{C} + b_iC$

†† $\Phi_i = \Phi_i + S_v^*\sqrt{C}$

\# Where Φ_i is given in brackets its value (determined by extrapolation) is regarded as unreliable (see text), however the Φ_i value at finite ionic strength is regarded as acceptable.

** In the original work the authors question this value, because the extrapolated V_i does not follow the additivity principle.

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Masson equation, Eq. (38), and invariably the fit in terms of Eq. (38) was obtained from data that extended into the high ionic region. Where the Masson equation and Eq. (43) give closely the same prediction of $(\Phi_i - \Phi_i^o)$ in the low ionic strength region but very different in the high ionic strength region, the prediction of Φ_i and $(\Phi_i - \Phi_i^o)$ utilizing the Masson equation obviously is preferable. For such salts, in Table 1 the upper ionic strength limits for the validity of Eq. (43) are noted and the observed constants for the Masson equation (i.e. S_v^*) are added.

From the values for b_i listed in Table 1 it is possible to compare values for the two terms $S_v\sqrt{C}$ and b_iC in Eq. (43). For the alkali halide salts, in the region $\mu <$ unity the term $S_v\sqrt{C}$ is generally very much greater than b_iC. This observation is often interpreted as indicating that the deviation from ideality of Φ_i and $\bar{V}_i$, $\Delta\Phi_i$ and $\Delta\bar{V}_i$ respectively, are due totally to long range electrostatic effects and that these effects can be closely estimated using the Debye-Hückel limiting law theory. If this were indeed so, one would expect that the extended Debye-Hückel theory would give a closer fit of $\Delta\Phi_i$ (or $\Delta\bar{V}_i$) against observed data than the limiting low expression. However, this is not so, and as shown in Figure 1(a) for NaCl and $MgCl_2$, the extended Debye-Hückel equation generally predicts $\Delta\bar{V}_i$ values significantly below both observed data and values predicted using the limiting law equation at 25°C. This observation would indicate that the term b_iC in Eq. (43) accounts for a number of compensating effects on $\Delta\bar{V}_i$ of which one factor is an electrostatic effect to account for the difference between the Debye-Hückel limiting law and its extended counterpart. This is illustrated as follows: In the region $\mu < 1$ the extended Debye-Hückel equation can be expanded to give closely an expression in terms of the limiting law equation plus a term linear in μ, i.e. from Millero (1970)

$$\Delta\Phi^{DH} \simeq \frac{S_v\sqrt{\mu}}{1 + B\mathring{a}\sqrt{\mu}} \qquad (44a)$$

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and in the region $\mu < 1$

$$\Delta\Phi^{DH} \simeq S_v\sqrt{\mu} + (-S_v B\mathring{a})\mu \tag{44b}$$

Equation (44b) is in the same form as the terms for the total deviation of Φ_i from ideality in Eq. (43), i.e. for a 1:1 salt $\Delta\Phi_i$ Eq. (43) becomes

$$\Delta\Phi_i = S_v\sqrt{\mu} + b_i\mu \tag{45}$$

Comparing Eqs. (44b and 45), if the Debye-Hückel effects alone accounted for $\Delta\Phi_i$ then one would expect that the second terms on the right hand side of these two equations to be closely equal. However, generally $b_i >> (-S_v B\mathring{a}_i)$. Consequently, to fit Eq. (44b) to observed data for $\Delta\Phi_i$ an extra term (also linear in μ) must be added to Eq. (44b), i.e.

$$\Delta\Phi_i = S_v\sqrt{\mu} - S_v Ba_i\mu + C_i\mu \tag{46a}$$

$$= S_v\sqrt{\mu} + (C_i - S_v Ba_i)\mu \tag{46b}$$

Now, comparing Eqs. (45 and 46b) and considering b_i values determined from experiment for say the 1:1 alkali halides, there should be a linear relationship between b_i and $\mathring{a}_i$ if the extended Debye-Hückel equation, Eq. (44a), is closely the correct expression to be used to account for long range electrostatic effects on $\Delta\Phi_i$, and provided that the constant C_i is independent of $\mathring{a}_i$. In Figure 2 are plotted b_i values versus $\mathring{a}_i$ (determined using the hydration theory, Eq. 189) for the alkali halides. The plot is closely linear and reinforces the hypothesis that the extended Debye-Hückel theory gives a better description of the long range electrostatic effects on $\Delta\Phi_i$ and $\Delta\bar{V}_i$. Furthermore, the analysis above reinforces the earlier hypothesis that in the ionic strength region $\mu > 0{,}1$ there is some extra positive effect on $\Delta\Phi_i$ and $\Delta\bar{V}_i$ which we attribute to primary and secondary hydration effects.

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3.4.3 *Relationships linking* $\bar{V}_i$ *and* $\bar{V}_w$ *to* Φ_i

Where $\bar{V}_i$ and $\bar{V}_w$ are to be determined from reported data for Φ_i, these can be estimated as follows:

Assume that for the selected salt the relationship linking Φ_i to molarity (C_i) is known and that this information is in terms of either the Masson equation, Eq. (38), the Redlich-Meyer equation, Eq. (43), or some other formulation in terms of C_i, that is, assume:

$$\Phi_i = f_i\ (C_i) \tag{47}$$

To determine $\bar{V}_i$, the relationship linking $\bar{V}_i$ to Φ_i (Eq. 20b) is in terms of molality, m_i,

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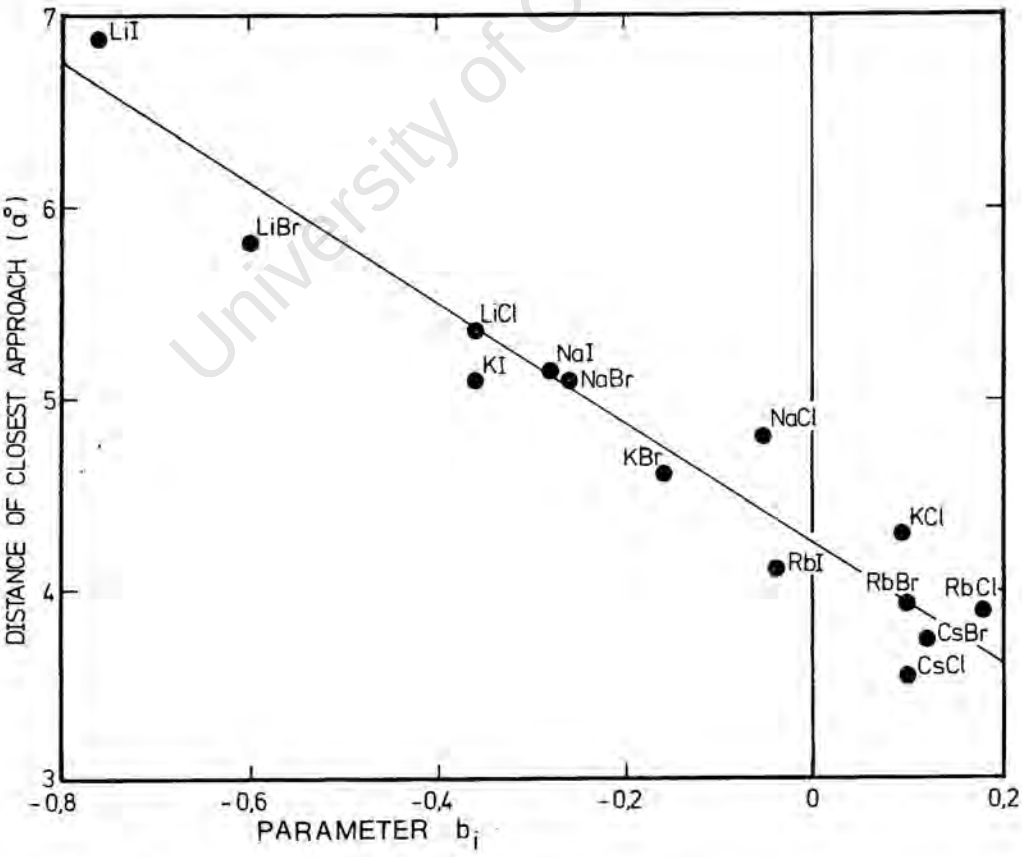

Figure 2. å versus b_i *for the alkali halides.*

$$\bar{V}_i = \Phi_i + m_i \frac{d\Phi_i}{dm_i} \tag{20b}$$

and in Eq. (20b) neither m_i nor $d\Phi_i/dm_i$ are known. However, from Section 4, m_i can be determined if Φ_i and C_i are known, i.e.

$$m_i = \frac{1000\ C_i}{1000\ \rho_o - \Phi_i C_i \rho_o} \tag{48a}$$

where

ρ_o = density of pure water, g/cc.

From Eq. (48a), m_i is a function of C_i and Φ_i, i.e.

$$m_i = f_2(C_i, \Phi_i) \tag{48b}$$

The term $d\Phi_i/dm_i$ in Eq. (20b) can be formulated in terms of the known quantities Φ_i, C_i and $d\Phi_i/dC_i$ as follows:

From Eqs. (47 and 48b)

$$\frac{dm_i}{d\Phi_i} = \frac{\partial m_i}{\partial \Phi_i} + \frac{\partial m_i}{\partial C_i}\frac{dC_i}{d\Phi_i} \tag{49}$$

$$= 1/(d\Phi_i/dm_i)$$

i.e.

$$\bar{V}_i = \Phi_i + m_i \left(\frac{\partial m_i}{\partial \Phi_i} + \frac{\partial m_i}{\partial C_i}\frac{dC_i}{d\Phi_i}\right. \tag{50}$$

Partial differentiation of Eq. (48a) with respect to Φ_i and C_i gives the $\partial m_i/\partial\Phi_i$ and $\partial_{mi}/\partial C_i$ terms. Substituting these into Eq. (50) and inserting m_i from Eq. (48a) gives the required relationship linking $\bar{V}_i$ to parameters Φ_i, C_i and $d\Phi_i/dC_i$ which are known or can be derived, i.e.

$$\bar{V}_i = \Phi_i + \frac{(1000 - \Phi_i C_i) C_i\, d\Phi_i/dC_i}{(1000 + C_i^2 d\Phi_i/dC_i)} \tag{51}$$

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To determine $\bar{V}_w$ in terms of the known entities Φ_i and C_i, equate Eqs. (10 and 19) and substitute for $\bar{V}_i$ from Eq. (20b) giving

$$\bar{V}_w = \bar{V}^o_w + \frac{n_i}{n_w} \left(- m_i \frac{d\Phi_i}{dm_i} \right)$$

$$= \bar{V}^o_w - \frac{M_w m_i^2}{1000} \frac{d\Phi_i}{dm_i} \tag{52}$$

where

$\bar{V}^o_w$ = partial molal volume of pure water, equal to 18 cc/mole at 25°C

M_w = molecular mass of pure water.

Substituting for m_i and $d\Phi_i/d_{mi}$ from Eqs. (48a and 49) respectively into Eq. (52) and re-arranging terms

$$\bar{V}_w = \frac{1000\ \bar{V}^o_w}{(1000 + C_i^2) d\Phi_i/dC_i} \tag{53}$$

Example:

For a solution of NaCl salt in water, determine $\bar{V}_i$ and $\bar{V}_w$ at a salt molality, $m_i = 2{,}0$ and temperature 25°C. To determine the values of $\bar{V}_i$ and $\bar{V}_w$ (from Eqs. 51 and 53) respectively, first determine the values for Φ_i, C_i and $d\Phi_i/dC_i$ for NaCl at molality $m_i = 2{,}0$. From Table 1 for NaCl in water at 25°C, $\Phi^o_i = 16{,}62$ cc/mole; $b_i = 0{,}048$. Now C_i is initially unknown and must be determined. In Eq. (48a) solving for C_i in terms of m_i and Φ_i,

$$C_i = \frac{1000\ m_i \rho_o}{1000 + \Phi_i m_i \rho_o} \tag{54}$$

The most rapid solution procedure for determining the values of C_i and Φ_i from Eqs. (43 and 54) is by successive approximation. That is, first assume $\Phi_i = \Phi^o_i$ in Eq. (54) and determine a value for C_i;

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for this calculated value of C_i determine Φ_i from Eq. (43). The procedure is repeated until successive determinations of Φ_i differ by less than 0,005 cm^3/mole, usually three iterations are required. This procedure, for NaCl at molality $m_i = 2{,}0$ gives $C_i = 1{,}926$ mole/ℓ and $\Phi_i = 19{,}29$ cm^3/mole. For $d\Phi_i/dC_i$ differentiate Eq. (43)

$$\delta\Phi_i/\delta C_i = 0{,}93\ C_i^{-\frac{1}{2}} + b_i \tag{55}$$

and inserting $C_i = 1{,}926$ and $b_i = 0{,}048$ in Eq. (55); $d\Phi_i/dC_i =$ 0,719.

To determine V_i, insert $\Phi_i = 19{,}29$, $C_i = 1{,}926$ and $d\Phi_i/dC_i =$ 0,718 in Eq. (51)

$\bar{V}_i = 20{,}62$ cm^3/mole.

To determine $\bar{V}_w$, insert $C_i = 1{,}926$, $d\Phi_i/dC_i = 0{,}718$ and $\bar{V}^o_w =$ 18,0 in Eq. (53):

$\bar{V}_w = 17{,}95$.

3.5 Partial molal volumes of single ion species

The reason for developing the theory for partial molal volumes of salts is that the volumetric effect influences the mean activity coefficients of salts (Section 6.5). Similarly, the activity of single ion species is affected by the partial molal volume of that species (Section 6.6). Whereas the partial molal volume of a salt is directly determinable, that of a single ion species is not; this is because it is not possible to add a single ion species alone to a solution.

To obtain estimates of partial molal volume of single ion species it is necessary to make some assumption of the division of the partial molal volume of the salt into its ionic components. Such a division requires an hypothesis which, although essentially empirical, usually must be justified by (i) some physical characteristic between component ions of a salt (for example, it is sometimes

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assumed that for 1:1 salts, the partial molal volume of cation and anion species will be equal if these species have equal crystal radii), and (ii) the consistency in the prediction when applied to a number of salts.

Bearing in mind the observations made above, one can develop a technique whereby it is possible to make a consistent estimate of single ion partial molal volumes. The analysis is completely in terms of partial molal quantities, as stated earlier apparent partial molal volumes are not thermodynamic quantities.

3.5.1 *Additivity of single ion partial molal volumes*

The first statement one can make for strong binary electrolytes is that the sum of the partial molal volumes of the component ions of a salt is equal to the partial molal volume of the salt in the solution, i.e. for salt M_mA_a in water:

$$\bar{V}_{M_mA_a} = m\bar{V}_{M^+} + a\bar{V}_{A^-} \tag{56}$$

where

m,a = moles of cation and anion formed by the dissociation of one mole of salt type M_mA_a.

We may describe this behaviour by saying that the *additivity rule* applies.*

The form of Eq. (56) does not give any indication as to what the division of $\bar{V}_{M^+}$ and $\bar{V}_{A^-}$ will be.

At infinite dilution, comparing the partial molal volumes of salts having a common ion, the partial molal volume of the common ion will have the same value in each solution at the same temperature and pressure. This is in conformity with the concept of

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* The *additivity* rule differs from the *additivity principle*. The additivity rule as expressed by Eq. (56) applies to single electrolytes; the additivity principle applies between electrolytes at infinite dilution, see Section 2.4.

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ideal solutions. Consequently, if the partial molal volume of one ion species can be estimated at infinite dilution, the partial molal volumes of all other ionic species theoretically can be estimated provided the values are known for the partial molal volumes for the relevant salts at infinite dilution. Hence the *principle of additivity* holds at infinite dilution.

In solutions at finite ionic strength deviations from ideality occur. The magnitudes of these deviations from ideality will depend *inter alia* on the particular species of cation and anion in the solution. Consequently, even though for a particular binary solution Eq. (56) continues to hold, it is no longer possible to determine the partial molal volume of a particular ion species from the estimated value for this ion species in another binary salt solution at the same ionic strength by applying the procedure applicable at infinite dilution. That is, for solutions at finite dilution the partial molal volumes of component ions are additive, i.e. an additivity rule applies but the additivity principle no longer holds rigorously.

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3.5.2 *Infinite dilution*

At infinite dilution, once the value for the partial molal volume of a particular ion species (i.e. $\bar{V}_{i}+$ or $\bar{V}^{o}_{i}$) has been estimated on the basis of some non thermodynamic assumption, the values for all other ion species can be determined using the additivity principle. The values for all the single ion species at infinite dilution are then relative to this reference $\bar{V}^{o}$ (single ion) value. Wirth (1940), for example, estimates single ion partial molal volumes utilizing the assumption that $\bar{V}^{o}_{K^+} = \bar{V}^{o}_{F^-}$ because these two ions have closely equal Pauling crystal radii, i.e. in terms of this assumption, $\bar{V}^{o}_{K^+} = \bar{V}^{o}_{F^-} = \bar{V}^{o}_{KF}/2 = 3{,}9\ cm^3/mole$ at 25°C; other single ion partial molal volumes then are estimated from experimentally determined $\bar{V}^{o}$ values for relevant salts (see Table 1) and Eq.(56) as follows:

For Cl^- : $\bar{V}^o_{Cl} = \bar{V}^o_{KCl} - \bar{V}^o_{K^+} = 26{,}8 - 3{,}9 = 22{,}9\ cm^3/mole$

For H^+ : $\bar{V}^o_{H^+} = \bar{V}^o_{HCl} - \bar{V}^o_{Cl} = 17{,}8 - 22{,}9 = -\ 5{,}1\ cm^3/mole$

For Ca^{++} : $\bar{V}^o_{Ca^{++}} = \bar{V}^o_{CaCl_2} - 2\bar{V}^o_{Cl^-} = 17{,}8 - 48{,}8 = -\ 28\ cm^3/mole$

Many non thermodynamic assumptions have been proposed for estimating single ion partial molal volumes at infinite dilution. These have been critically reviewed by Millero (1970). In order to compare quantitatively the results obtained using these assumptions, Millero took $\bar{V}^o_{H^+}$ at 25°C as his basis of comparison. For each assumption he determined the value for $\bar{V}^o_{H^+}$ using the additivity principle. The various assumptions give a range of values for $\bar{V}^o_{H^+}$ from -7,6 to -0,2 cm^3/mole. Based on the assumptions alone, it is not possible to evaluate these values in an absolute sense. However, the choice of a particular assumption may be influenced by the consistency achieved within the theory for which the $\bar{V}^o$ (single ion) will be used.

For our purpose, single ion $\bar{V}^o$ values are required for estimating single ion activity coefficients and our approach has been to develop the estimations utilizing the hydration theory, and in particular the hydration number assigned to single ions, as follows: The activity coefficient theory applied to *salts* indicates that hydration numbers follow the additivity principle and that Cl^-, Br^- and I^- all have the same hydration number, equal to zero, Section 6.5. Hydration numbers for all other ions, and hence activity coefficients for all the single ion species, are determined using this observation. Consequently, to be consistent, single ion partial molal volumes should also be based on this conclusion. For ions with no primary hydration (i.e. hydration numbers equal to zero), there will be no electrostricted water about these ions, and from Eq. (29), at infinite dilution their partial molal volumes will equal their respective intrinsic volumes/mole, i.e. for Cl^-, Br^- and I^- :

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$$\bar{V}^o_i = \bar{V}^o_{INTi} \tag{57}$$

To determine the intrinsic volume/mole, many research workers assume that $\bar{V}^o_{INT}$ is directly proportional to the ionic crystal volume Millero (1970), i.e. for a single ion species

$$\bar{V}^o_{INTi} = Ar^3_i \tag{58}$$

where

A = constant independent of the ion type but varying with pressure and temperature

r_i = crystal radius of ionic species i in Ångstrom units.

Equating Eqs. (57 and 58) for the Cl^-, Br^- and I^- species and simplifying:

$$\bar{V}^o_{Cl^-}/\bar{V}^o_{I^-} = r^3_{Cl^-}/r^3_{I^-} \tag{59a}$$

$$\bar{V}^o_{Br^-}/\bar{V}^o_{I^-} = r^3_{Br^-}/r^3_{I^-} \tag{59b}$$

$$\bar{V}^o_{Cl^-}/\bar{V}^o_{Br^-} = r^3_{Cl^-}/r^3_{Br^-} \tag{59c}$$

Equations (59a to 59c) provide three independent means of estimating a single ion partial molal value and hence a means for evaluating the consistency of the approach. Considering first Eq.(59a), the equations for the partial molal volumes for the Cl^- and I^- salts of any particular cation species (say K^+) from Eq. (56) are:

$$\bar{V}^o_{KCl} = \bar{V}^o_{K^+} + \bar{V}^o_{Cl^-} \tag{60a}$$

$$\bar{V}^o_{KI} = \bar{V}^o_{K^+} + \bar{V}^o_{I^-} \tag{60b}$$

To formulate an equation for $\bar{V}^o_{I^-}$ in terms of parameters whose values are known, subtract Eq. (60a) from Eq. (60b) and solve for $\bar{V}^o_{I^-}$

$$\bar{V}^o_{I^-} = \bar{V}^o_{KI} - \bar{V}^o_{KCl} - \bar{V}^o_{Cl^-} \tag{61}$$

Solve for $\bar{V}^o_{Cl^-}$ from Eq. (59a), sibstitute into Eq. (61) and solve for $\bar{V}^o_{I^-}$

$$\bar{V}^o_{I^-} = \frac{\bar{V}^o_{KI} - \bar{V}^o_{KCl}}{\{1 - (r_{Cl^-}/r_{I^-})^3\}} = 44,7 \text{ cm}^3/\text{mole}$$

The corresponding value for $\bar{V}^o_{H^+}$ is then determined using the additivity principle, i.e.

$$\bar{V}^o_{H^+} = \bar{V}^o_{KI} + \bar{V}^o_{HCl} - \bar{V}^o_{KCl} - \bar{V}^o_{I}$$

$$= 8,4 \text{ cm}^3/\text{mole}$$

Comparing the $\bar{V}^o_{H^+}$ values listed in Table 2(a), the values are all within 1 cm^3/mole which indicates that the $C-^-$, Br^- and I^- ions probably all have primary hydration close to zero. However, in both cases where the assumption is used that Cl^- has zero primary hydration, one obtains a $\bar{V}^o_{H^+}$ value 1 cm^3/mole lower than that obtained assuming that Br^- and I^- have zero primary hydration (-8,4 as against -7,4 cm^3/mole). Although this difference is small, it is consistent and indicates that possibly there is a small electrostriction effect associated with Cl^-, that is, Cl^- probably has some very small hydration number; the assumption $\bar{V}^o_{Cl^-} = \bar{V}^o_{INT(Cl^-)}$ therefore constitutes an approximation, albeit a close one. When estimating single ion activity coefficients this small primary hydration of Cl^- is negligible (see Section 6.7), but for consistency, single ion partial molal volumes will be based on the assumption $\bar{V}^o_{XBr}/\bar{V}^o_{XI} = r^3_{Br^-}/r^3_{I^-}$, i.e. $\bar{V}^o_{H^+} = -7,4$ cm^3/mole.

In Table 2(b) which follows are listed single ion $\bar{V}^o$ values based on $\bar{V}^o_{XBr}/\bar{V}^o_{XI} = r^3_{Br^-}/r^3_{I^-}$ and utilizing the additivity principle.

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Table 2(a). Estimation of $\bar{V}^o_{H^+}$ at 25°C assuming Cl^-, Br^- and I^- each have zero primary hydration

$\bar{V}^o_{H^+}$ $cm^3/mole$	Method used
- 8,4	$\bar{V}^o_{Cl^-}/\bar{V}^o_{I^-} = r^3_{Cl}/r^3_{I}$
-7,4	$\bar{V}^o_{Br^-}/\bar{V}^o_{I^-} = r^3_{Br^-}/r^3_{I^-}$
-8,4	$\bar{V}^o_{Cl^-}/\bar{V}^o_{Br^-} = r^3_{Br^-}/r^3_{Br^-}$

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Table 2(b). Single ion partial molal volumes at infinite dilution and 25°C from salt values listed in Table 1 and based on the assumption $\bar{V}^o_{Br^-}/\bar{V}^o_{I^-} = r^3_{Br^-}/r^3_{I^-}$ and no primary hydration of Br^- and I^-.

Cation species	$\bar{V}^o$ $cm^3/mole$	Anion species	$\bar{V}^o$ $cm^3/mole$
H^+	-7,4	Cl^-	25,2
Li^+	-8,3	Br^-	32,1
Na^+	-8,6	I^-	43,6
K^+	1,6	HCO_3^-	28,6
Rb^+	6,7	HSO_4^-	43,1
Cs^+	13,9	$SO_4^=$	28,8
Ca^{++}	-32,6	$CO_3^=$	10,5
Mg^{++}	-36,0		
Ba^{++}	-27,3		
Sr^{++}	-33,0		

3.5.3 *Finite dilution*

Whereas the partial molal volume of a salt and its deviation from ideality can be measured, this is not possible for the component ionic species of the salt. At infinite dilution it was shown, in Section 3.5.2, that single ion partial molal volumes can be estimated with a fair degree of consistency utilizing the observation from activity coefficient theory that Cl^-, Br^- and I^- species have no primary hydration. The problem now to be considered is the formulation of single ion partial molal volumes at finite concentration.

To formulate an equation for the partial molal volume of a single ionic species one commences by expressing the partial molal volume of the salt in terms of its value at infinite dilution plus a deviation from ideality, i.e.

$$\bar{V}_i = \bar{V}_i^o + \Delta\bar{V}_i \tag{62}$$

The partial molal volume of the salt is then expressed in terms of its ionic compounds

$$\bar{V}_i = d_+\bar{V}_{i+} + d_-\bar{V}_{i-}$$

where

$$\bar{V}_{i+} = \bar{V}_{i+}^o + \Delta\bar{V}_{i+} \tag{63a}$$

and

$$\bar{V}_{i-} = \bar{V}_{i-}^o + \Delta\bar{V}_{i-} \tag{63b}$$

i.e.

$$\bar{V}_i = d_+(\bar{V}_{i+}^o + \Delta\bar{V}_{i+}+ + d_-(\bar{V}_{i-}^o + \Delta\bar{V}_{i-}) \tag{64}$$

Equating Eqs. (62 and 64)

$$\Delta\bar{V}_i = d_+\Delta\bar{V}_{i+} + d_-\Delta\bar{V}_{i-} \tag{65}$$

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Now it was shown in Section 3.4.1 that the partial molal volume of a salt species, i, $\bar{V}_i$, can be written in terms of an ideal value $\bar{V}_i^o$ and three terms each of which accounts for a particular factor giving rise to the deviation of $\bar{V}_i$ from ideality: a Debye-Hückel electrostatic terms $\Delta\bar{V}^{DH}$; a primary hydration term $\Delta\bar{V}_{PH}$; a secondary hydration term $\Delta\bar{V}_{SH}$, i.e.

$$\bar{V}_i = \bar{V}_i^o + \Delta\bar{V}^{DH} + \Delta\bar{V}_{PH} + \Delta\bar{V}_{SH} \tag{66}$$

$$= d_+(\bar{V}_{i+}^o + \Delta\bar{V}_+^{DH} + \Delta\bar{V}_{PH+} + \Delta\bar{V}_{SH+}) + d_-(\bar{V}_{i-}^o + \Delta\bar{V}_-^{DH} + \Delta\bar{V}_{PH-} + \Delta\bar{V}_{SH-}) \tag{67}$$

Comparing Eqs. (66 and 67), if the terms $\bar{V}_i^o$, $\Delta\bar{V}^{DH}$, $\Delta\bar{V}_{PH}$ and $\Delta\bar{V}_{SH}$ could be decomposed into cationic and anionic components by some means, then the individual components to $\bar{V}_i$, $\bar{V}_{i+}$ and $\bar{V}_{i-}$, could be estimated. For the ideal components $\bar{V}_{i+}^o$ and $\bar{V}_{i-}^o$, it was shown in Section 3.5.2 that single ion ideal partial molal volumes can be estimated if the assumption is made that Cl^- has no primary hydration. Based on this assumption, $\bar{V}_{Cl-}^o$ was determined. Knowing the ideal partial molal volume for one ionic species the ideal partial molal volumes for other ionic species could be determined using the additivity principle (see Table 2(b)).

For the Debye-Huckel deviation, $\Delta\bar{V}^{DH}$, it was shown in Section 3.4.1 that *inter alia* this term depends on the sum of the charges on the component ionic species and consequently can be decomposed in accordance with the charges, i.e. from Eq. (36a):

$$\Delta\bar{V}^{DH} = \frac{(d_+z_+^2 + d_-z_-^2)\ 2^{\frac{1}{2}}\sqrt{\mu}}{1 + B\mathring{a}\sqrt{\mu}}$$

$$= \frac{(d_+z_+^2)\ 2^{\frac{1}{2}}\sqrt{\mu}}{1 + B\mathring{a}\sqrt{\mu}} + \frac{(d_-z_-^2\ 2^{\frac{1}{2}}\sqrt{\mu}}{1 + B\mathring{a}\sqrt{\mu}} \tag{68a}$$

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$$= d_+\Delta\bar{V}_+^{DH} + d_-\Delta\bar{V}_-^{DH} \tag{68b}$$

The problem remaining is to decompose the terms for primary and secondary hydration effects, $\Delta\bar{V}_{PH}$ and $\Delta\bar{V}_{SH}$ respectively, in Eq. (66), into cationic and anionic components. In Section 3.4.1 it was postulated that secondary hydration effects, $\Delta\bar{V}_{SH}$, be estimated in the low ionic strength region (i.e. in the region where primary hydration effects are negligible) as the difference between the observed deviation $\Delta\bar{V}_i$ and the Debye-Hückel effect $\Delta\bar{V}^{DH}$. For all the alkali and alkaline earth halides (except for the lithium salts) $\Delta\bar{V}_{SH}$ was found to increase closely linearly with μ up to ionic strength of about unity, see Figure 1(b) for NaCl and $MgCl_2$ (for the lithium salts the linearity holds only up to ionic strength of about 0,5). To estimate $\Delta\bar{V}_{SH}$ for each salt in the region $\mu > 1$ it was assumed that the linear relationship established in the range $\mu < 1$ can be extrapolated into the higher ionic strength region. Because k appears to be independent of the salt type (see below), the effects of $\Delta\bar{V}_{SH}$ on the individual species are assumed to arise from the number and charge of ionic species present, i.e. again the decomposition into component ionic species is in accordance with the charges, i.e.

$$\Delta\bar{V}_{SHi} = k_i\ \mu \tag{69}$$

$$= \tfrac{1}{2}(d_+z_+^{\,2} + d_-z_-^{\,2})\ k_iC_i$$

and, as k_i is common the equation can be written

$$\Delta\bar{V}_{SH} = \tfrac{1}{2}\ d_+z_+^{\,2}k_iC_i + \tfrac{1}{2}\ d_-z_-^{\,2}k_iC_i \tag{70a}$$

i.e.

$$= d_+\Delta\bar{V}_{SH+} + d_-\Delta\bar{V}_{SH-} \tag{70b}$$

where

k_i = a constant, the value of which is determined from the slope of $\bar{V}_{SH}$ versus μ in the region $\mu < 1$ (i.e. from the slope of the plot $(\bar{V}_i - \bar{V}^{DH})$ versus μ).

C_i = molarity of salt species i.

A list of values for k_i for various salts determined from plots of $(\bar{V}_i - \bar{V}^{DH})$ versus μ in the region $\mu < 1$ is given in Table 3. It is of interest to note that the values of the constants k_i are all closely equal to 2,1 cm^3/mole/mole. This equality is of significance when formulating a consistent equation for estimating single ion partial molal volumes and activities in mixed electrolyte systems, see Chapter 3.

For the single ion primary hydration effects, $\Delta\bar{V}_{PH+}$ and $\Delta\bar{V}_{PH-}$ these are estimated using the assumption that the halides Cl^-, Br^- and I^- have zero primary hydration, see Section 6.6. Consequently, the salt primary hydration effect, $\Delta\bar{V}_{PHi}$, is allocated totally to the cation, i.e.

$$\Delta\bar{V}_{PHi} = d_+\Delta\bar{V}_{PH+} + d_-\Delta\bar{V}_{PH-} \qquad (71)$$

$$= d_+\Delta\bar{V}_{PH+} + 0 \qquad (72)$$

Substituting for $\Delta\bar{V}^{DH}$, $\Delta\bar{V}_{SH}$ and $\Delta\bar{V}_{PH}$ from Eqs. (68, 70 and 72) respectively into Eq. (66) gives $\bar{V}_i$ in terms of a cationic and an anionic component, i.e.

$$\bar{V}_i = d_+\left(\bar{V}^o_{i+} + \frac{z_+^{\,2}\, 2^{\frac{1}{2}}\sqrt{\mu}}{1 + B\mathring{a}_i\sqrt{\mu}} + \tfrac{1}{2}z_+^{\,2}\, k_i C + \Delta\bar{V}_{PH+}\right)$$

$$+ d_-\left(\bar{V}^o_{i-} + \frac{z_-^{\,2}\, 2^{\frac{1}{2}}\sqrt{\mu}}{1 + B\mathring{a}_i\sqrt{\mu}} + \tfrac{1}{2}z_-^{\,2}\, k_i C\right) \qquad (73)$$

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Table 3. k_i values in Eq. (60) determined from the slope of the plot $(\bar{V}_i - \bar{V}^{DH})$ versus μ in the region $\mu <$ unity.

Salt	k_i
$MgCl_2$	2,13
$CaCl_2$	2,18
NaCl	2,18
KCl	2,14
RbCl	2,18
CsCl	2,12
LiCl	1,70

Equating Eqs. (64 and 73) and decomposing:

$$\bar{V}_{i+} = \bar{V}^o_{i+} + \frac{z_+^2\, 2^{\frac{1}{2}} \sqrt{\mu}}{1 + B\overset{o}{a}_i\sqrt{\mu}} + \tfrac{1}{2} z_+^2\, k_i C_i + \frac{\Delta\bar{V}_{PHi}}{d+} \qquad (74a)$$

and

$$\bar{V}_{i-} = \bar{V}^o_{i-} + \frac{z_-^2\, 2^{\frac{1}{2}} \sqrt{\mu}}{1 + B\overset{o}{a}_i\sqrt{\mu}} + \tfrac{1}{2} z_-^2\, k_i C_i \qquad (74b)$$

Generally, in determining single ion partial molal volumes, the anion value is determined first using Eq. (74b), and the cation value is then determined as follows:

$$\bar{V}_{i+} = \frac{\bar{V}_i - d_- \bar{V}_{i-}}{d+} \qquad (75)$$

Example:

Estimate the single ion partial molal volumes for Na^+ and Cl^+ in a 2,0 molal aqueous solution of NaCl at 25°C, ($\overset{o}{a}_{NaCl}$ = 4,95 Ångstrom units).

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The approach will be first to determine $\bar{V}_{Cl^-}$ and $\bar{V}_{NaCl}$ and then to determine $\bar{V}_{Na}$ using the additivity rule (see Section 3.5.1).

For $\bar{V}_{Cl}$: Because Cl^- has no primary hydration, the deviations from ideality for $\bar{V}_{Cl^-}$ arise due to two effects only, long range electrostatic effects and secondary hydration effects, i.e. $\bar{V}^{DH}_{Cl^-}$ and $\bar{V}_{SH-}$ respectively, i.e. from Eq. (74b)

$$\bar{V}_{Cl^-} = \bar{V}^{o}_{Cl} + \bar{V}^{DH}_{-} + \bar{V}_{SH-}$$

$$= \bar{V}^{o}_{Cl^-} + \frac{z_-^{\,2}\, 2^{\frac{1}{2}} \sqrt{\mu}}{1 + B\mathring{a}\sqrt{\mu}} + \tfrac{1}{2} z_-^{\,2}\, k\, C_i \qquad (76)$$

Substituting for $\bar{V}^{o}_{Cl}$ from Table 2(b), i.e. $\bar{V}^{o}_{Cl^-} = 25{,}2$ cm^3/mole, for μ and C_i from the example set out in Section 3.4.3, i.e. $\mu = C = 1{,}926$, and for k from Table 3, i.e. $k = 2{,}10$

$$\bar{V}_{Cl^-} = 25{,}20 + 0{,}60 + 2{,}02$$

$$= 27{,}82 \text{ cm}^3\text{/mole.}$$

For $\bar{V}_{NaCl}$: From the example set out in Section 3.4.3

$$\bar{V}_{NaCl} = 20{,}62 \text{ cm}^3\text{/mole.}$$

For $\bar{V}_{Na^+}$: From Eq. (75)

$$\bar{V}_{Na^+} = \bar{V}_{NaCl} - \bar{V}_{Cl^-}$$

$$= 20{,}62 - 27{,}82 = -7{,}20 \text{ cm}^3\text{/mole.}$$

4. UNITS OF CONCENTRATION

In the previous section the different molal volumes and their interrelationships were analysed in detail. With this background it is possible to discuss quantitatively the different units of concentration and their interrelationships.

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The basic chemical unit of quantity of substance is the mole: A gram mole of a salt (or simply a mole of salt) is defined as the molecular mass of the salt in grams; a mole of water is the molecular mass of water in grams. The solute is the salt in solution; there may be more than one solute species in solution. The solvent is the liquid into which the salt is dissolved; the solution constitutes the solute and solvent.

In aqueous electrolyte chemistry, units of concentration are usually expressed in one of three ways: molality, m; molarity, c; mole fraction, N; defined as follows:

(i) *Molality, m_i*

Molality is defined as the moles of anhydrous salt per kilogram of water. The molality can be expressed in terms of moles of salt and water as follows: Say a solution contains n_a moles of salt A (molecular mass in grams = M_a) and n_w moles of water (molecular mass in grams = M_w); the molality of salt A, m_a is given by

$$m_a = \frac{n_a}{n_w M_w/1000} \qquad (77)$$

where $n_w M_w$ equals mass of water in grams and $n_w M_w/1000$ equals mass of water in kilograms.

Putting Eq. (77) into words

$$m_a = \frac{\text{mass of anhydrous solute species A in grams}}{(\text{molecular mass of solute species A})(\text{mass of water in grams}/1000)}$$

(ii) *Molarity, c_i*

Molarity is defined as the moles of solute per litre of solution. If a solution has volume V_ℓ litres and contains n_a moles of salt A, then the molarity of salt A, c_a, is

$$c_a = n_a/V_\ell \qquad (78a)$$

If volume is expressed in ml, say V_{ml}, then

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$$c_a = n_a/(V_{ml}/1000) \tag{78b}$$

(iii) *Mole fraction, N_i*

$$\text{Mole fraction of species 'a'} = N_a = \frac{\text{moles of solute a}}{\text{moles of solute + moles of water}}$$

When considering electrolyte solutions, a problem arises in defining the mole fraction of salt species. This is because mole fraction of salt in solution, say species 'a', can be defined logically in two ways. First, it can be defined as the ratio of the total numbers of *ions* of salt species 'a' to the total number of ions plus water molecules in the solution, i.e. for a binary system:

$$N'_a = \frac{d_a n_a}{d_a n_a + n_w} \tag{79}$$

where

d_a = moles of ions produced by one mole of salt species 'a'.

Second, mole fraction can be defined as the ratio of the moles of salt species 'a' in solution to the total moles of ions plus moles of water in solution, i.e.

$$N_a = \frac{n_a}{d_a n_a + n_w} \tag{80}$$

Fortunately, from a practical point of view it does not matter which definition is used. This is because the relationships linking activity coefficient on the mole fraction scale to activity coefficients on molar and molal scales are unaffected by the choice, see later. With regard to ionic species, the mole fraction scale is unambiguous.

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4.1 Interrelationships between concentration units

Molarity, molality and mole fraction of species in solution are interlinked as follows:

(i) *Molality (m) and molarity (c)*

Given the molarity of solute species A in aqueous solution is c_a, its molality m_a, is determined as follows:
Solving for n_a from Eq. (78b) and substituting into Eq. (77)

$$m_a = \frac{c_a V_{ml}}{n_w M_w} \tag{81}$$

The mass of water in solution, $n_w M_w$, can be expressed in terms of the total volume, V in ml, density of the pure water, ρ_o in g/ml, and the apparent partial molal volume of solute species, A, Φ_A in ml/mole, as follows:
From Eq. (19), for an aqueous binary system

$$V_{ml} = n_a \Phi_a + n_w \bar{V}^o_w \tag{82}$$

Rearranging Eq. (82)

$$n_w M_w = \frac{V_{ml} M_w}{\bar{V}^o_w} - \frac{n_a \Phi_a M_w}{\bar{V}^o_w} \tag{83}$$

Substituting for $n_w M_w$ from Eq. (83) into Eq. (81) and simplifying

$$m_a = \frac{c_a}{(M_w/\bar{V}^o_w)(1 - n_a \Phi_a / V_{ml})}$$

By definition $M_w/\bar{V}^o_w = \rho_o$ the density of pure water; and $n_a/V_{ml} = c_a/1000$, see Eq. (78b), i.e.

$$m_a = \frac{c_a}{\rho_o(1 - c_a \Phi_a/1000)} \tag{84}$$

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Conversion from c_a to m_a (and vice versa) provides no problems in binary systems as Φ_a values for salts in binary systems with respect to their concentration are well documented, Millero (1970).

Difficulties are encountered, however, when more than one salt is present in the solution. If the solution contains n_a moles of salt species A, n_b moles of species B, ..., and n_w moles of water, then from Chapter 3

$$V_{ml} = n_a\Phi_a + n_b\Phi_b + \dots n_w\bar{V}^o_w$$

Following the same procedure as for the binary system,

$$m_a = c_a/(\rho_o(1 - \sum_i c_i\Phi_i/1000)) \tag{85}$$

where

c_i = molarity of salt species 'i' in solution.

The difficulty in Eq. (85) lies in the determination of Φ_i in a mixed system. The apparent partial molal volume of a particular salt in a multi-component system is certainly not even approximated by its apparent partial molal volume at the same concentration for that salt in a binary solution. However, the experimental findings of Young and Smith (1954) provide an excellent approximation for the Φ_i value of a particular salt, i, in a solution made up of several salts: They found *that Φ_i is very closely equal to its value in a binary solution at an ionic strength equal to that of the solution made up of the several salts*. The Young and Smith approximation is very close to the true value and is of the greatest utility when dealing with mixed electrolytes. The approximation is considered in greater detail in Chapter 3.

(ii) *Molarity, m_i, and mole fraction, N_i*

The molarity of a salt in solution can be linked to the mole fraction for the salt through the density of the solution, ρ in g/ml, as follows:

$$\rho = \frac{\sum_i n_i M_i}{V_{ml}} \tag{86}$$

where

$n_i M_i$ = mass in grams of salt species i

V_{ml} = volume of solution in ml

Solving for V from Eq. (86) and rewriting volume in terms of litres, V_ℓ,

$$V_\ell = \frac{\sum_i n_i M_i}{\rho 1000} \text{ litres}$$

Substituting for V_ℓ from the equation above into Eq. (78b)

$$c_a = \frac{n_a \rho 1000}{\sum_i n_i M_i} \tag{87}$$

Solving for n_a from Eq. (80) and substituting into Eq. (87), gives

$$c_a = \frac{N_a(\sum_i d_i n_i + n_w)\rho 1000}{\sum_i n_i M_i}$$

and solving for N_a, the mole fraction of species A,

$$N_a = \frac{c_a}{1000\rho} \frac{\sum_i n_i M_i}{\sum_i d_i n_i + n_w} \tag{88}$$

Considering a binary system with a total volume of solution of one litre, the moles of salt, n_a, and water, n_w are as follows:

For the salt species:

$n_a = c_a$

For the water:

From Eq. (86)

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$$\rho = \frac{c_a M_a + n_w M_w}{1000}$$

where the units of density are g/ml.

Solving for n_w in the above equation,

$$n_w = (1000\rho - c_a M_a)/M_w \qquad (89)$$

Substituting for n_w from Eq. (89) into Eq. (88) and putting $c_a = n_a$ in Eq. (88) gives

$$N_a = \frac{M_w c_a}{1000\rho + c_a(dM_w - M_a)} \qquad (90a)$$

For a system with more than one salt specie in solution, say species B, C, D ...

$$N_a = \frac{M_w c_a}{1000 + c_a(d_a M_w - M_a) + c_b(d_b M_w - M_B) + \ldots} \qquad (90b)$$

(iii) *Molality, m_i, and mole fraction, N_i*

The mole fraction of a salt in solution can be linked to the molality using Eqs. (77 and 80) as follows:

Solving for the moles of salt species A in solution, n_a, from Eq. (77),

$$n_a = m_a(n_w M_w/1000) \qquad (91)$$

Substituting for n_a from Eq. (91) into Eq. (80) and simplifying gives the required relationship for a binary system;

$$N_a = \frac{m_a}{(1000/M_w) + d_a m_a} \qquad (92)$$

For a solution with more than one salt species in solution, Eq.(92) becomes:

$$n_a = \frac{m_a}{(1000/M_w) + d_a m_a + d_b m_b + \ldots} \qquad (93)$$

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With increasing dilution the term $(1000/M_w) + m_a + m_b$ ... in Eq. (88) tends to $(1000/M_w)$, i.e.

$$N_a = \frac{m_a}{(1000/M_w)}$$

That is, for a very dilute solution mole fraction is proportional to molality and hence also to the molarity.

Molarity is the concentration scale on which species concentrations are most easily measured analytically, but it is temperature dependent through the volume term. Molality does not vary with temperature but gives rise to problems when determining concentration by titration if the density of the test solution is not known. The mole fraction scale is an impractical unit for general use, but of basic theoretical importance as it is a consistent thermodynamic unit.

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4.2 Hydrated species concentrations

Though the definitions above are unambiguous, a characteristic of each of the definitions is that they are in terms of the anhydrous solute species. In solution all the salt species hydrate water molecules to a lesser or greater extent. The result of this hydration is that the moles of free water differs from the moles of total water in the solution.

For example, considering the mole fraction of a salt in a binary system, from Eq. (80)

$$N_a = \frac{n_a}{dn_a + n_w} \quad \text{i.e. anhydrous scale} \qquad (94a)$$

$$N_a^h = \frac{n_a}{dn_a + n_{fw}} \quad \text{i.e. hydrated scale} \qquad (94b)$$

where

n_{fw} = moles of free or unhydrated water in the solution.

The theory describing the behaviour of solutes in solution is explicitly in terms of hydrated species on the mole fraction scale. There are two hydrated scales, the *hydrated mole fraction scale* and the *hydrated volume fraction scale*. Both have been used to model the entropy changes of mixing solute and solvent. If one uses the hydrated volume fraction scale the effect of co-volume changes can be directly incorporated into the entropy term, a procedure not possible using the mole fraction scale. To convert from the hydrated scale to any of the anhydrous scales, in particular the molal scale,* requires linking the mass of free water to the total mass of water. Using the hydration theory this link is established through the hydration number, the hydrated mole fraction scale is expressed in terms of molality and the hydration number, the hydrated volume fraction scale in terms of molality, partial molal volumes and the hydration number.

4.2.1 *Molality and hydrated mole fraction scales*

Expression for the hydrated mole fraction of salt species 'a', N_a^h, above is written in terms of molality and hydration number as follows:

$$N_a^h = \frac{n_a}{dn_a + n_{fw}}$$

Substituting for n_{fw} from Eq. (2) in the equation above, and dividing through by n_w

---

* Investigations into high salinity waters usually are done in terms of the molal scale; virtually all the data collected have been reported in terms of this scale. This is a fact of history and probably stems from the ease with which the molality of a solution can be increased by simply adding more salt. In contrast, investigation, on the molar scale will require the making up of a new solution for every concentration. Unless a major effort is made to convert the useful data collected in the past to a different scale, it is unlikely that the molal scale will be replaced by another.

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$$N_a^h = \frac{n_a/n_w}{dn_a/n_w + 1 - hn_a/n_w}$$

and

$$n_a/n_w = ma/m_w$$

where

m_w = molality of water, 1000/18

i.e.

$$N_a^h = \frac{0{,}018\ m_a}{0{,}018\ dm_a + 1 - 0{,}018\ hm_a} \qquad (95)$$

4.2.2 *Molality and the hydrated volume fraction scale*

The hydrated volume fraction of salt species 'a', V_a^h, is written in terms of molality, partial molal volumes and a hydration number as follows:

$$V_a^h = \frac{n_a\bar{V}_a^h}{V}$$

$$= \frac{n_a\bar{V}_a^h}{n_a\bar{V}_a + n_w\bar{V}_w}$$

Substituting for $\bar{V}_a^h$ from Eq. (17) into the above equation, dividing through by n_w and putting n_a/n_w equal to 0,018 m_a (as shown above) gives the required expression

$$V_a^h = \frac{0{,}018\ m_a(\bar{V}_a + h\bar{V}_w)}{0{,}018\ m_a\bar{V}_a + \bar{V}_w} \qquad (96)$$

Example:

2,0 moles of anhydrous NaCl is added to 1 kg of pure water at 25°C. Estimate (i) the anhydrous and hydrated mole fractions, and (ii) the anhydrous and hydrated volume fractions of NaCl and water. (Hydration number of NaCl = 2,40, see Section 6.5).

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(i) Anhydrous mole fraction of NaCl, N_{NaCl}: From Eq. (94a)

$N_{NaCl} = n/(dn + n_w)$

and for the mole fraction of water, N_w,

$N_w = n_w/(dn + n_w)$.

For 1 kg of water: $n_w = 1000/18$ and $n = m$ (by definition)

i.e.

$N_{NaCl} = 0{,}018\ m/(0{,}018\ dm + 1) = 0{,}0336$

and

$N_w = 1/(0{,}018\ dn + 1) = 0{,}933$.

Hydrated mole fraction of NaCl, N^h_{NaCl}, and mole fraction of free water, N_{fw}: From Eq. (95)

$N^h_{NaCl} = 0{,}018\ m/(1 + 0{,}018\ dm - 0{,}018\ hm) = 0{,}0365$

and

$$N_{fw} = (n_w - n_1 h)/(n_w + dn_1 - n_1 h_1)$$
$$= (1 - 0{,}018\ mh)/(1 + 0{,}018\ dm - 0{,}018\ hm) = 0{,}927.$$

(ii) Anhydrous volume fraction of NaCl, V_{NaCl}; and volume fraction of water, V_w:

$V_{NaCl} = 0{,}018\ m\bar{V}_{NaCl}/(0{,}018\ m\bar{V}_{NaCl} + \bar{V}_w)$

$V_w = n_w\bar{V}_w/(n\bar{V}_{NaCl} + n_w\bar{V}_w)$

From the example set out in Section 3.4.3

$\bar{V}_{NaCl} = 20{,}62\ cm^3/mole$, $\bar{V}_w = 17{,}95\ cm^3/mole$, i.e

$V_{NaCl} = 0{,}0397$

$V_w = 0{,}960$.

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Hydrated volume fraction of NaCl, V^h_{NaCl}, and volume fraction of free water, V_{fw}: From Eq. (96)

$$V^h_{NaCl} = 0{,}018\ m(\bar{V}_{NaCl} + h\bar{V}_w)/(0{,}018\ m\bar{V}_{NaCl} + \bar{V}_w)$$
$$= 0{,}123$$

and

$$V_{fw} = (n_w - nh)\bar{V}_{fw}/(n\bar{V}_{NaCl} + n_w\bar{V}_w)$$
$$= (1 - 0{,}018\ mh)\bar{V}_{fw}/(0{,}018\ m\bar{V}_{NaCl} + \bar{V}_w)$$
$$= 0{,}877.$$

In the calculation above if it is accepted that the partial molal volume for the water equals its value at infinite dilution, i.e. 18,0 cm^3/mole, then $V_w = 0{,}963$, $V^h_{NaCl} = 0{,}123$ and $V_{fw} = 0{,}879$. That is, non ideality of $\bar{V}_w$ has very little effect on volume fractions of species.

5. ACTIVITY AND ACTIVITY COEFFICIENTS

5.1 Activity scales

The chemical behaviour of solvent and solute components in aqueous solutions is expressed in terms of the activities of the components. Activity is an idealized concentration relative to some reference state. At the reference state the concentration (on some selected scale) is equal to the activity. At any other state, the activity of a species is linked to its concentration through an activity coefficient, for example, for a salt component 'i' with molality m_1

$$a_{m_i} = \gamma_{m_i} m_i \tag{97}$$

where

a_{m_i} = activity of salt species 'i' on the molal scale

γ_{m_i} = activity coefficient of salt species 'i' on the molal scale and, in terms of the molarity and mole fraction scales

$$a_{c_i} = \gamma_{c_i} c_i \tag{98}$$

$$a_{N_i} = \gamma_{N_i} N_i \tag{99}$$

where

γ_{c_i} and γ_{N_i}	are the activity coefficients of salt species 'i' on the molar and mole fraction scales respectively
a_{c_i} and a_{N_i}	are the activities of the salt species 'i' on the molar and mole fraction scales respectively.

The activity and activity coefficient of a component in a solution will differ depending on the concentration scale adopted, i.e. for species 'i' in solution

$$a_{m_i} \neq a_{c_i} \neq a_{N_i} \quad \text{and} \quad \gamma_{m_i} \neq \gamma_{ci} \neq \gamma_{N_i}$$

Before linking activity and activity coefficients on the various concentration scales, first it is necessary to introduce a convention for defining activity coefficients quantitatively. This can be done from free energy considerations.

5.1.1 *Free energy*

Free energy, G, is a measure of the capacity to do work. The partial molal free energy component, i, $\bar{G}_i$, is the free energy per mole of component i. Hence, the free energy of component i is $n_i\bar{G}_i$ where n_i is the number of moles of component i present in the system. The free energy of the system, G, is therefore

$$G = n_i\bar{G}_1 + n_2\bar{G}_2 + \ldots n_i\bar{G}_i \tag{100}$$

The partial molal free energy $\bar{G}_i$ is also called the chemical potential of component i. Like partial molal volume, $\bar{V}_i$, $\bar{G}_i$ is also a partial molal entity. An equation for $\bar{G}_i$, which is analogous to Eq. (4) for $\bar{V}_i$, is thus

$$\bar{G}_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j} \tag{101}$$

Now, the partial molal free energy of component 'i', $\bar{G}_i$ (i.e. the chemical potential of component i) is a parameter that can be measured. Consequently, Lewis (1909) defined activity of a component i in terms of the measurable parameter $\bar{G}_i$, i.e.

$$\bar{G}_i = \bar{G}_i^{\circ} + RT\mathit{ln}(a_i) \tag{102}$$

The parameter $\bar{G}_i^{\circ}$ in Eq. (102) is a constant of integration which arises in the development of this equation from basic theory and is termed the *standard partial molal free energy* of component i; for a particular component, this constant varies with temperature, pressure and the units of concentration in which activity a_i is expressed. The dependence of $\bar{G}_i^{\circ}$ on concentration scale can be appreciated from the following:

The partial molal free energy of a component 'i', $\bar{G}_i$, in a particular solution has some fixed finite value which is independent of the concentration scale adopted for a_i, i.e.

On the molal scale:

$$\bar{G}_i = \bar{G}_{m_i}^{\circ} + RT\mathit{ln}(a_{m_i}) \tag{103}$$

i.e. from Eq. (97)

$$\bar{G}_i = \bar{G}_{m_i}^{\circ} + RT\mathit{ln}(\gamma_{m_i} m_i) \tag{104}$$

On the molar scale:

$$\bar{G}_i = \bar{G}_{c_i}^{\circ} + RT\mathit{ln}(a_{c_i}) \tag{105}$$

i.e. from Eq. (98)

$$\bar{G}_i = \bar{G}^o_{c_i} + RT\ln(\gamma_{c_i} c_i) \tag{106}$$

On the mole fraction scale:

$$\bar{G}_i = \bar{G}^o_{N_i} + RT\ln(a_{N_i}) \tag{107}$$

i.e. from Eq. (99)

$$\bar{G}_i = \bar{G}^o_{N_i} + RT\ln(\gamma_{N_i} N_i) \tag{108}$$

Referring to Eqs. (103 to 108) above, $\bar{G}_i$ is given unambiguously by any of these equations; the parameters a_i, γ_i and concentrations c, N or m, will have different values in the respective equations depending on the concentration scale selected. Consequently, the value for $\bar{G}^o_i$ will also vary between the equations; however, the sum $\bar{G}_i$ will be the same in all cases.

5.1.2 *Standard and reference states*

A consequence of Eqs. (103 to 108) is that the parameter activity, a_i, can be defined unambiguously in terms of a *standard state and a reference state.*

In the standard state : activity = 1 and $\bar{G}_i = \bar{G}^o_i$
In the reference state: activity=concentration and $\gamma_i = 1$

With regard to the reference state, two conventions can be used for defining activity coefficients: (i) the infinite dilution convention and (ii) the constant ionic medium convention.

(i) *Infinite dilution convention*

This convention is defined in such a way that the activity coefficient tends to unity as the concentrations of all solute species tend to zero, i.e. for the molal scale

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$\gamma_{m_i} \to 1$ as $\sum_i m_i \to 0$

where

m_i = molality of solute species i.

With this convention activity approaches concentration with increasing dilution. It is the convention that will be followed in this monograph.

(ii) *Constant ionic medium convention*

This convention is defined in such a way that the *activity coefficient of a particular component in a mixed system* tends to unity as the concentration of this component tends to zero while the concentrations of all other components (termed the medium ions) remain at some constant finite value. For example, consider water containing a salt species MA with molality m_{MA} and 'i' other salt species, NX_i, with molalities m_{NX_i}. The salts, i, constitute the medium ions. In this medium

$\gamma_{MA} \to 1$ as $m_{MA} \to 0$, i.e. $m_{MA} + \sum_i m_{NX_i} \to \sum_i m_{NX_i}$

This convention has proved most useful for high salinity aqueous systems when considering individual species at low concentration with respect to the medium ions, for example weak acid species in sea water. Where the concentration of the medium ions is more than about ten times the concentration of the species under consideration, then the medium ions 'swamp' the ionic strength effects of the species under consideration and activity coefficients of these species remain virtually constant and very close to unity for that system.

From the structure of the system the thermodynamic equilibrium constants determined in this approach apply to a specific ionic medium at a particular temperature. Consequently, the approach is not amenable to generalization, i.e. to analyzing situations where different ionic media need to be considered.

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5.2 Interrelationships between activity coefficients on different scales

Returning to the infinite dilution scale, the activity coefficients on the molal, molar and mole fraction scales can be linked very simply by noting that (1) when the concentration of salt in solution tends to zero each of the activity coefficients γ_m, γ_c and γ_N tends to unity, and (2) on any particular concentration scale the ratio of the activity of a species at finite dilution to its activity at infinite dilution is a measure of the free energy change between the two states, Eqs. (85 to 90). As the free energy change is independent of the scale adopted, the free energy change must be equal irrespective of the concentration scale selected, i.e.

$$\frac{a_m}{a^*_m} = \frac{a_c}{a^*_c} = \frac{a_N}{a^*_N} \quad , \quad \text{i.e.}$$

$$\frac{\gamma_m m}{m^*} = \frac{\gamma_c c}{c^*} = \frac{\gamma_N N}{N^*} \tag{109}$$

where

superscript '*' refers to the species parameter at infinite dilution, and

$\gamma^*_x = 1$ in Eq. (109)

The independence of free energy change from the concentration scale allows the activities on the different scales to be readily linked: At infinite dilution from Eq. (90a)

$$N^* = \frac{c^* M_w}{\rho_o 1000} \tag{110}$$

and from Eq. (93)

$$N^* = \frac{m^* M_w}{1000} \tag{111}$$

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γ_N and γ_m:

A relationship linking γ_N and γ_m is now obtained by substituting for N* and N in Eqs. (111 and 93) respectively into Eq. (109) and rearranging,

$$\gamma_N = \gamma_m(1 + \frac{dmM_w}{1000}) \tag{112}$$

where

d = number of ions formed in the dissociation of one molecule of salt.

γ_N and γ_c:

Substituting for N* and N from Eqs. (110 and 90a) respectively into Eq. (109) and rearranging,

$$\gamma_N = \frac{\gamma_c}{\rho_o}\rho + c\ (\frac{dM_w - M_a}{1000}) \tag{113}$$

γ_m and γ_c:

Equating Eqs. (110 and 111),

$$m^* = c^*/\rho_o \tag{114}$$

Substituting for m* and m from Eqs. (114 and 85) respectively into Eq. (109) and rearranging,

$$\gamma_m = \gamma_c(1 - \frac{c\Phi}{1000}) \tag{115}$$

From Eqs. (112, 113 and 115), as the concentration of salt decreases, γ_m, γ_c and γ_N approach the same value. Consequently, at low ionic strength, $\mu < 0{,}1$, these activity coefficients are closely equal.

5.3 *Single ion activities*

For electrolyte solutions, one is usually interested in the activities and activity coefficients for single ion species, i.e.

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$$a_+ = \gamma_+ m_+, \quad \text{and} \tag{116a}$$

$$a_- = \gamma_- m_- \tag{116b}$$

where

a_+, a_- = activities of cation and anion

γ_+, γ_- = activity coefficients for cation and anion

m_+, m_- = molalities of cation and anion, respectively.

The link between the single ion activities for a salt in solution and the activity of the salt, a_i, (see Eq. 102), is best developed from free energy principles. Consider the partial molal free energies (chemical potentials) of the cation and anion species of the salt,

$\bar{G}_{i+}$ and $\bar{G}_{i-}$, i.e.

$$\bar{G}_{i+} = \bar{G}^\circ_{i+} + RT\ln\gamma_{i+}m_{i+} \tag{117a}$$

and

$$\bar{G}_{i-} = \bar{G}^\circ_{i-} + RT\ln\gamma_{i-}m_{i-} \tag{117b}$$

These individual ion partial molal free energies are linked to the partial molal free energy of the salt species i as follows

$$\bar{G}_i = d_+\bar{G}_{i+} + d_-\bar{G}_{i-} \tag{118}$$

where

d_+,d_- = moles of cation and anion respectively formed by the dissolution of 1 mole of salt.

Substituting for $\bar{G}_{i+}$ and $\bar{G}_{i-}$ from Eqs. (117a and 117b) into Eq. (118) and simplifying,

$$\bar{G}_i = d_+\bar{G}^\circ_{i+} + d_-\bar{G}^\circ_{i-} + RT\ln(a_i^{d_+} \cdot a_{i-}^{d_-})$$

$$= \bar{G}^\circ_i + RT\ln(a_{i+}^{d_+} \cdot a_{i-}^{d_-}) \tag{119}$$

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5.4 Salt activity and mean ionic activity

Equation (102) forms the basic definition for the activity of a species in solution. If the salt species as a whole is considered as a single entity, then the activity of the salt, a_i, is linked to the single ion activities (the actual entities in the solution) by equating Eqs. (102 and 119), i.e.

$$a_i = a_{i+}^{d_+} \cdot a_{i-}^{d_-} \tag{120}$$

Although this relationship between the salt activity and the component ion activities is basic to the theory, for the purposes of developing a theoretical description of activities for *strong electrolytes*, a more useful form of expressing the salt activity is in terms of the mean ionic activity, $a_{i\pm}$. The mean ionic activity of a salt is defined as the geometric mean of the activities of the component ions, i.e. for a molecule of salt which dissociates giving rise to d ions (d_+ cations and d_- anions)

$$a_{i\pm} = (a_+^{d_+} \cdot a_-^{d_-})^{1/d} \tag{121}$$

and, for $\bar{G}_i$ in terms of $a_{i\pm}$, substitute for a_i from Eq. (122) into Eq. (102)

$$\bar{G}_i = \bar{G}_i^o + dRT\mathit{ln}a_{i\pm} \tag{123}$$

that is, for a specific electrolyte solution, $\bar{G}_i$ and $\bar{G}_i^o$ will have the same value whether the salt activity is considered in terms of a_i or $a_{i\pm}$ *provided* both these activities are on the same concentration scale.

The mean ionic activity (or simply the *mean activity*) is used generally in the description of strong electrolyte behaviour, only rarely (and then only with particular reference) is the salt activity utilized.

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5.5 Mean ionic activity coefficients and molalities

To introduce the mean ionic activity coefficient, $\gamma_{\pm}$, first it is necessary to define the mean ionic molality, $m_{i\pm}$, for a strong electrolyte: the mean ionic molality of a salt is defined as the geometric mean of the molalities of the component ions, i.e.

$$m_{i\pm} = (m_{i+}^{d_+} \cdot m_{i-}^{d_-})^{1/d} \tag{124}$$

The mean ionic activity coefficient, $\gamma_{i\pm}$, is then defined through the general relationship linking activity and concentration, i.e.

$$a_{i\pm} = \gamma_{i\pm} \cdot m_{i\pm} \tag{125}$$

The consistency of this approach is shown by substituting for the single ion activities from Eqs. (116a and 116b) into the equation for the mean ionic activity, Eq. (121), i.e.

$$\begin{aligned} a_{i\pm} &= (a_{i+}^{d_+} \cdot a_{i-}^{d_-})^{1/d} \\ &= \{(\gamma_{i+} \cdot m_{i+})^{d_+} \cdot (\gamma_{i-} \cdot m_{i-})^{d_-}\}^{1/d} \\ &= \{(\gamma_{i+}^{d_+} \cdot \gamma_{i-}^{d_-})^{1/d} \cdot (m_{i+}^{d_+} \cdot m_{i-}^{d_-})^{1/d}\} \\ &= \gamma_{i\pm} \cdot m_{i\pm} \end{aligned}$$

Generally, data for activity coefficients of strong electrolytes is reported in terms for the *mean ionic activity coefficient*, $\gamma_{i\pm}$ (unless otherwise explicitly stated). However, for concentration, the input data for experiments is invariably in terms of concentration (*not* mean ionic concentration) so that it is useful (and usual) to retain salt concentration explicitly in electrolyte description. If $a_{i\pm}$ is to be determined from reported data for $\gamma_{i\pm}$ at a particular concentration (in terms of say molality) the

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mean ionic molality must first be determined. The mean ionic molality, $m_{i\pm}$, is linked to the salt molality, m_i, as follows: From Eq. (124)

$$m_{i\pm} = \{m_{i+}^{d_+} \,.\, m_{i-}^{d_-}\}^{1/d}$$

where $m_{i+} = d_+ m_i$ and $m_{i-} = d_- m_i$, i.e.

$$m_{i\pm} = \{(d_+ m_i)^{d_+} \,.\, (d_- m_i)^{d_-}\}^{1/d}$$

$$= m_i \{d_+^{d_+} \,.\, d_-^{d_-}\}^{1/d} \qquad (126)$$

Equations (122, 125 and 126) are general in the sense that these equations have the same form for each of the concentration scales. For example, on the mole fraction scale the activity a_{N_i} and the mean ionic activity, $a_{N_{i\pm}}$, are linked as follows: From Eq. (122)

$$a_{N_i} = a_{N_{i\pm}}^{d} \,,$$

and from Eq. (125)

$$a_{N_{i\pm}} = \gamma_{N_{i\pm}} N_{i\pm} \qquad (127a)$$

and from Eq (126)

$$N_{i\pm} = N_i (d_+^{d_+} \; d_-^{d_-})^{1/d}$$

where

$$N_i = n_i/(dn_i + n_w).$$

In general, the mean ionic activity, $a_{i\pm}$, can be measured and $m_{i\pm}$ can be calculated for the particular salt, consequently one can calculate the activity coefficient $\gamma_\pm$. The mean ionic activity coefficients $\gamma_\pm$ have been determined over a wide concentration range for most salts of interest to aquatic chemists and are well documented in the literature, Stokes and Robinson (1955).

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Example:

2,0 moles of anhydrous $MgCl_2$ is added to 1 kg of pure water at 25°C, the mean ionic activity(on the molality scale) of $MgCl_2$ is measured as $a_{MgCl_2\pm} = 3{,}343$. Determine the salt activity of $MgCl_2$ (on the molality scale) a_i, the mean ionic molality of $MgCl_2$ and hence, the mean ionic activity coefficient, $\gamma_{MgCl_2\pm}$

For $MgCl_2$:

$d = 3, \;\; d_+ = 1$ and $d_- = 2$

To determine the salt activity a_{MgCl_2}, from Eq. (122)

$$a_i = (a_{i\pm})^d = (3{,}343)^3$$

$$= 37{,}360.$$

To determine the mean ionic molality, from Eq. (126)

$$m_{i\pm} = m_i(d_i^{d_+} \cdot d_-^{d_-})^{1/d} = 2(1.2^2)^{1/d}$$

$$= 3{,}175$$

To determine the mean ionic activity coefficient, from Eq. (125)

$$\gamma_\pm = a_\pm/m_\pm = 3{,}343/3{,}175$$

$$= 1{,}053.$$

In contrast to mean ionic activities, there is no explicit experimental process by means of which single ion activities can be measured. Single ion activities can be calculated from mean ionic activities only by making some non thermodynamic assumption(s). The validity of the assumptions cannot be tested unequivocably.The usefulness of an assumption or set of assumptions can be gauged only by comparing the consequences with as many observable characteristics as possible that are influenced by the assumption(s) and to accept that, or those, assumption(s) resulting in the best overall correlation.

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Our final objective is development of procedures to calculate single ion activities. But in order to do this it is necessary to examine in some detail the factors that give rise to deviations from the ideal activity of a salt. Once a reasonable model has been formulated to explain the deviation, one then has the basic framework to attack the more formidable problems of estimating (i) single ion activities in binary systems and (ii) mean and single ion activities in mixed systems.

6. MODELLING OF MEAN IONIC AND SINGLE ION ACTIVITY COEFFICIENTS IN BINARY SYSTEMS

6.1 Preliminary considerations

Whereas it is possible to measure mean ionic activities, the problem which arises is that it is necessary in any particular situation to assign activity coefficients to single ion species. To assign values to these coefficients it is necessary first to know what are the factors affecting the coefficient, and second to have a model to quantify these effects.

In the introduction to this Chapter a list was given of six factors which affect the non-ideal behaviour of ions in aqueous solutions:

(i) electrostatic interactions
(ii) dielectric constant for the solution
(iii) ionic hydration
(iv) co-volume effects
(v) ion pairing
(vi) ion-ion interactions.

In the historical development of modelling mean and single ion activity coefficients these factors were identified and incorporated sequentially, approximately in the sequence set out above. The development of a model incorporating all these effects is perhaps

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best approached by also following the same sequence.

To develop a rational approach to modelling the deviation from ideality for a component in solution, it is necessary to return to the equation for mean ionic activity in terms of partial free energy, i.e. on the molal scale:

$$\bar{G}_i = \bar{G}_i^o + dRT\ln\gamma_{\pm}m_{\pm} \tag{128}$$

Considering a binary system in which hydration of the salt species occurs, Eq. (128) can be formulated in two ways. First, if we assume no hydration, all the parameters in Eq. (128) are on the anhydrous scale, i.e. $m_{\pm}$ refers to an analytical mass of salt added to the solution and $\bar{G}_i$ is the partial molal free energy of anhydrous species, i. Second, if we assume that hydration occurs, all the parameters in Eq. (128) are in terms of the hydrated scale, i.e.

$$\bar{G}_i^h = \bar{G}_i^{oh} + dRT\ln\gamma_{\pm}^h m_{\pm}^h \tag{129}$$

Now, in practice, all mean ionic activity coefficient data determined by experiment and tabulated in the literature are in terms of the anhydrous species, i.e. the anhydrous scale, so that from a practical point of view the form expressed by Eq. (129) is of no interest. Consequently, our principal interest will be in determining $\bar{G}_i$ and hence $\gamma_{\pm}$ values on the anhydrous scale.
The anhydrous partial molal free energy, $\bar{G}_i$, is defined by Eq. (101) as the partial differential of free energy, G, with respect to moles of salt species i keeping the total moles of water, n_w, constant, i.e.

$$\bar{G}_i = \left(\frac{\partial G}{\partial n_i}\right)_{n_w} \tag{130}$$

Consequently, *if we can formulate an equation for G incorporating all the deviations from ideality, then on differentiating this* *expression in accordance with Eq. (130) the differential will give an equation for $\bar{G}_i$ that includes both ideal and non-ideal terms.** Equating this expression for $\bar{G}_i$ to $(\bar{G}_i^o + dRT\ln\gamma_\pm m_\pm)$, and solving for $\gamma_\pm$ will give an expression for $\gamma_\pm$. The problem lies in formulating the expression for the total free energy, G.

An expression for the total free energy, G, can be formulated by first considering an ideal solution and then 'switching in' each of the sources of non-ideality, i.e. (i), (ii), (iv) and (vi) in the list above.

Ideal solutions

In an ideal binary system the effects of (i) to (vi) above on the free energy are all negligible, hence from Eq.(100) for a binary system

$$G = n_i\bar{G}_i + n_w\bar{G}_w \tag{131}$$

where

$$\bar{G}_i = \bar{G}_i^o + dRT\ln N_{i\pm}, \text{ for the ideal case, and}$$

$$\bar{G}_w = \bar{G}_w^o + RT\ln N_w$$

Ideality plus hydration effects

Switching in the non-ideal solute-solvent interaction effects, i.e. hydration effects, then the two components in the system in effect become n_i moles of hydrated solute species and n_{fw} moles of free water, i.e. from Eq. (100)

$$G = n_i\bar{G}_i^h + n_{fw}\bar{G}_{fw} \tag{132}$$

where

$$\bar{G}_i^h = \bar{G}_i^{oh} + dRT\ln N_{i\pm}^h \tag{132a}$$

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* In this chapter subscript 'i' is restricted to i = 1 to denote the particular salt species in the binary system, except where mixed electrolytes are considered.

$$\bar{G}_{fw} = \bar{G}^{o}_{fw} + RT\ln N_{fw} \qquad (132b)$$

$$N^{h}_{i\pm} = \frac{n_i}{dn_i + n_{fw}} \left(d_+^{d_+} d_-^{d_-}\right)^{1/d} \qquad (132c)$$

$$N_{fw} = \frac{n_{fw}}{dn_i + n_{fw}} \qquad (132d)$$

In Eqs. (132) the number of moles of free water, n_{fw}, is unknown, and consequently the mole fraction quantities $N^{h}_{i\pm}$ and N_{fw} are also unknown. However, by hypothesizing that a particular solute species hydrates a specific mass of water per mass of solute (i.e. by assigning a hydration number, h_i, to the solute) the unknown parameters in Eq. (132), n_{fw}, $N^{h}_{i\pm}$ and N_{fw} are linked to the known ones n_w, $N_{i\pm}$ and N_w respectively, as follows:

$$n_{fw} = n_w - n_i h_i \qquad (133a)$$

$$N^{h}_{i\pm} = \frac{n_i}{dn_i + n_w - n_i h_i} \left(d_+^{d_+} d_-^{d_-}\right)^{1/d} \qquad (133b)$$

and

$$N_{fw} = \frac{n_w - n_i h_i}{dn_i + n_w - n_i h_i} \qquad (133c)$$

Equations (133a, 133b and 133c) can be substituted into Eqs. (132, 132c and 132d) respectively, to give an equation for free energy, G, containing only one unknown parameter, the hydration number, h_i, i.e.

$$G = n_i \bar{G}^{h}_{i} + (n_w - n_i h_i)\bar{G}_{fw} \qquad (134)$$

where $\bar{G}^{h}_{i} = \bar{G}^{oh}_{i} + dRT\ln N^{h}_{i\pm}$, see Eq. (133b) for $N^{h}_{i\pm}$

$\bar{G}_{fw} = \bar{G}^{o}_{fw} + RT\ln N_{fw}$, see Eq. (133c) for N_{fw}.

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Ideality plus hydration and electrostatic effects

Switching in the electrostatic effects between the hydrated ions, the total free energy of the system must also include a term G^{el} to account for this effect, i.e.

$$G = n_i\bar{G}_i^h + n_f\bar{G}_{fw} + G^{el} \tag{135}$$

that is,

$$G = n_i[\bar{G}_i^{oh} + dRT\ln N_{i\pm}^h] + n_{fw}[\bar{G}^o_{fw} + RT\ln N_{fw}] + G^{el} \tag{136}$$

Ideality plus hydration, electrostatic and co-volume effects

In the development above, the total free energy of the system, G, cannot include deviations from ideality arising from volume changes (co-volume effects) due to interactions between solute and solvent species because the entropy terms are in terms of mole fraction statistics. To include co-volume effects, the equation for the ideal free energy of the system (Eq. 131) must be formulated in terms of volume fractions rather than mole fractions. The *ideal free energy* of the binary system utilizing volume fraction statistics for the co-volume effects and considering the ions as hydrated is then

$$G = n_i\left(\bar{G}_i^{oh} + d_+RT\ln\frac{d_+n_i\bar{V}_i^+}{V} + d_-RT\ln\frac{d_-n_i\bar{V}_i^-}{V}\right)$$

$$+ n_{fw}\left(\bar{G}^o_{fw} + RT\ln\frac{n_{fw}\bar{V}^o_w}{V}\right) + G^{el}$$

where

$\bar{V}_i$ = partial molal volume of hydrated species, i

V = total volume of the system.

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Ideality plus hydration, electrostatic, co-volume and ion-ion effects

Deviations due to ion-ion interactions as the salt concentration increases will be manifested by changes in primary and secondary hydration, that is, by changes in salt hydration number and co-volume - changes in hydration number due to competition between ions for free water, changes in co-volume in the non-ideality of partial molal volumes due to changes in secondary hydrated water. From this point of view ion-ion interaction effects are absorbed in the hydration and co-volume effects on free energy as set out above. By taking this approach it is readily possible to extend ion-ion interaction effects to mixed electrolytes (Chapter 3).

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The exposition above is given with the objective of showing how in principle the main sources of deviation from ideality of partial molal free energies may be incorporated into the theory.

With respect to quantitative expression in low salinity waters, $\mu < 0{,}01$, some effects are negligible and need not be considered, in fact, only the electrostatic effects are of significance. In high salinity waters by using mole fraction statistics it is possible to incorporate only electrostatic and hydration effects but not co-volume and ion-ion effects. Using volume fraction statistics all the effects can be considered for inclusion. These approaches will now be considered under the headings:

(i) Low salinity approach (electrostatic effects only)

(ii) Stokes-Robinson approach (electrostatic and hydration effects)

(iii) Glueckauf approach (electrostatic, hydration and co-volume effects)

(iv) Extended approach (electrostatic, hydration, co-volume and ion-ion effects).

6.2 Low salinity approximation

6.2.1 *Mean activity coefficients*

In low salinity water, $\mu < 0{,}01$, the effects of hydration and co-volume on deviations from ideality are negligible. Consequently, in the development of an equation for total free energy, G, one can make the following simplifying assumptions:
(i) The effect of hydration on the moles of free water in solution is negligible, i.e. $n_{fw} = n_w$, and (ii) Mole fractions can replace volume fractions in the partial molal free energy equations. Utilizing these two assumptions Eq. (136) reduces to

$$G = n_i(\bar{G}_i^{oh} + dRTlnN_{i\pm}) + n_w(\bar{G}_w^{o} + RTlnN_w) + G^{el}$$

i.e.

$$G = n_i\{\bar{G}_i^{oh} + d_+RTln\,(\frac{d_+n_i}{dn_i + n_w}) + d_-RTln\,(\frac{d_-n_i}{dn_i + n_w})\}$$

$$+ n_w\{\bar{G}_w^{o} + RTln\,(\frac{n_w}{dn_i + n_w})\} + G^{el} \qquad (138)$$

Now, the mean activity coefficient on the mole fraction scale, $\gamma_{N_{i\pm}}$, is defined by Eq. (123) as

$$\bar{G}_i = \bar{G}_i^{o} + dRTln\gamma_{N_{i\pm}}N_{i\pm} \qquad (139)$$

and, from Eq. (101)

$$\bar{G}_i = (\frac{\partial G}{\partial n_i})_{n_w} \qquad (140)$$

Consequently, differentiating Eq. (138) in accordance with Eq.(140)

gives an equation for $\bar{G}_i$. Equating this equation with Eq. (139) and solving for $\gamma_{N_{i\pm}}$ gives the required expression for $\gamma_{N_{i\pm}}$. From Eqs. (138 and 140)

$$\bar{G}_i = \left(\frac{\partial G}{\partial n_i}\right)_{n_w}$$

$$= \bar{G}_i^{oh} + dRT\,ln N_{i\pm} + \left(\frac{\partial G^{el}}{\partial n_i}\right)_{n_w} \tag{141}$$

Equating Eqs. (139 and 141) and simplifying

$$ln\gamma_{N_{i\pm}} = (\bar{G}_i^{oh} - \bar{G}_i^{o})/dRT + \frac{1}{dRT}\left(\frac{\partial G^{el}}{\partial n_i}\right)_{n_w} \tag{142}$$

The constant in Eq. (142), $(\bar{G}_i^{oh} - \bar{G}_i^{o})/dRT$, is determined by putting $n_i = 0$. For $n_i = 0$ in Eq. (142), the electrostatic term is zero, and by definition $\gamma_{N_{i\pm}} = 1$, i.e. at finite but low ionic strengths Eq. (142) reduces to

$$ln\gamma_{N_{i\pm}} = \frac{1}{dRT}\left(\frac{G^{el}}{\partial n_i}\right)_{n_w} \tag{143}$$

From the Debye-Hückel theory, the right hand side of Eq. (143) can be resolved as follows: From Fowler and Guggenheim (1939), Eq. (918,9) and Stokes and Robinson (1957)

$$\frac{1}{dRT}\left(\frac{\partial G^{el}}{\partial n_i}\right)_{n_{fw}} = \frac{2{,}303\ Az_+z_-\sqrt{\mu}}{1 + B\mathring{a}_{\pm}\sqrt{\mu}} \tag{144a}$$

and, in the ionic strength range $\mu < 6$ (Glueckauf, 1957)

$$\left(\frac{\partial G^{el}}{\partial n_i}\right)_{n_w} \simeq \left(\frac{\partial G^{el}}{\partial n_i}\right)_{n_{fw}} \tag{144b}$$

i.e. substituting Eqs. (144a and 144b) into Eq. (143)

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$$ln\gamma_{N_{i\pm}} = \frac{2,303\ Az_+z_-\sqrt{\mu}}{1 + B\mathring{a}\sqrt{\mu}} \qquad (145)$$

or

$$\log\ \gamma_{N_{i\pm}} = \frac{Az_+z_-\sqrt{\mu}}{1 + B\mathring{a}\sqrt{\mu}} \qquad (146)$$

where

A = constant which depends on absolute temperature and dielectric constant ε of pure water
= 0,511 at 25°C in pure water

B = constant which is a function of absolute temperature and the dielectric constant for the water
= 0,328 at 25°C in pure water

$\mathring{a}$ = distance of closest approach between hydrated ions in Ångstrom units.

The development of Eq. (146) indicates that strictly speaking this equation can be used to estimate activity coefficients only on the mole fraction scale (i.e. $\gamma_{N_{i\pm}}$) in solutions where ion pairing, hydration and co-volume effects are negligible.

On the molarity and molality scales the equations for $\gamma_\pm$ that correspond to Eq. (146) are developed from the relationships linking $\gamma_{N\pm}$ to $\gamma_{C\pm}$ and $\gamma_{m\pm}$, i.e.

Substituting for $\gamma_{N\pm}$ from Eq. (113) in Eq. (146) and rearranging terms:

$$ln\gamma_{C\pm} = \frac{-2,303\ Az_+z_-\sqrt{\mu}}{1 + B\mathring{a}\sqrt{\mu}} - ln\ [\frac{1}{\rho_o}\ \{\rho + \frac{(dM_w - M_i)}{1000}\ c_i\}] \qquad (147a)$$

and, similarly from Eq. (94)

$$ln\gamma_{m\pm} = \frac{-2,303\ Az_+z_-\sqrt{\mu}}{1 + B\mathring{a}\sqrt{\mu}} - ln\ (1 + 0,001\ dm_iM_w) \qquad (147b)$$

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At low ionic strengths the scale factor terms in Eqs.(147a and 147b) are negligible and Eq. (146) can be used equally well for $\gamma_{N_{i\pm}}$, $\gamma_{c_{i\pm}}$ and $\gamma_{m_{i\pm}}$.

6.2.2 *Single ion activity coefficients*

Considering single ions, equations for their activity coefficients in binary systems at low ionic strength are developed from Eq.(146) simply by decomposing this equation, i.e. from Eq. (125)

$$\log\gamma_{\pm} = \log\left(\gamma_{+}^{d_+}\,\gamma_{-}^{d_-}\right)^{1/d} \quad , \quad \text{i.e.}$$

$$d\,\log\gamma_{\pm} = d_{+}\,\log\gamma_{+} + d_{-}\,\log\gamma_{-} \tag{148a}$$

Equating Eqs. (146 and 148a) and simplifying

$$d_{+}\,\log\gamma_{+} + d_{-}\,\log\gamma_{-} = \frac{-Ad_{+}z_{+}z_{-}\sqrt{\mu}}{1 + B\mathring{a}\sqrt{\mu}} - \frac{Ad_{-}z_{+}z_{-}\sqrt{\mu}}{1 + B\mathring{a}\sqrt{\mu}} \tag{148b}$$

and making the substitutions $d_{+}z_{+} = d_{-}z_{-}$ in the two terms on the right hand side of Eq. (148) and rearranging

$$d_{+}\,\log\gamma_{+} + d_{-}\,\log\gamma_{-} = \frac{-Ad_{+}z_{+}^{2}\sqrt{\mu}}{1 + B\mathring{a}\sqrt{\mu}} - \frac{Ad_{-}z_{-}^{2}\sqrt{\mu}}{1 + B\mathring{a}\sqrt{\mu}} \tag{149a}$$

i.e.

$$\log\gamma_{-} = \frac{-Az_{-}^{2}\sqrt{\mu}}{1 + B\mathring{a}\sqrt{\mu}} \tag{149b}$$

and

$$\log\gamma_{+} = \frac{-Az_{+}^{2}\sqrt{\mu}}{1 + B\mathring{a}\sqrt{\mu}} \tag{149c}$$

That is, for a particular binary system at low ionic strength, the activity coefficients for the cationic and anionic species of the salt will differ depending only on their charges, i.e. for a 1:1 salt, $\gamma_{+} = \gamma_{-}$.

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With increase in ionic strength, Eq. (146) no longer can be used to fit observed $\gamma_\pm$ data. Invariably the reason for the failure of Eq. (146) is as follows: Equation (146) predicts that with an increase in ionic strength $\gamma_\pm$ decreases monotonically, and tends to a finite value, i.e. $\ln\gamma_\pm \rightarrow -2{,}303\ Az_+z_-/B\mathring{a}$, for $\mu >> 1$.

However, observed data in strong electrolytes invariably show $\gamma_\pm$ to decrease initially then pass through a minimum and thereafter increase with increased ionic strength. The failure of Eq. (146) to model observed $\gamma_\pm$ data in part reflects the inadequacies of the assumptions in setting up the free energy equation (i.e. Eq. 138) in which hydration and co-volume effects are neglected. Cognizant of these inadequacies, Stokes and Robinson (1955) introduced the effects of hydration into the theoretical modelling of mean ionic activities.

6.3 Stokes and Robinson approach

6.3.1 *Mean ionic activity coefficients*

Stokes and Robinson hypothesized that at higher ionic strengths ($\mu > 0{,}1$) the effects of hydration cannot be neglected in the development of an equation to model $\gamma_\pm$. To include the hydration effects they proposed in effect* that the free energy equation for the system should be formulated in terms of hydrated solute species and free water (see Eq. 150), i.e.

$$G = n_i(\bar{G}_i^{oh} + dRT\ln N_{i\pm}^h) + n_{fw}(\bar{G}_{fw}^o + RT\ln N_{fw}) + G^{el} \tag{150}$$

and linked the unknown mass parameter n_{fw}, to the known mass

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* Though Stokes and Robinson formulated their equation for $\gamma_\pm$ utilizing free energy considerations, their development is slightly different to that given above. The treatment above is carried out in such a way as to maintain a common framework between the various approaches to determining $\gamma_\pm$ and thereby to highlight the fundamental differences between these approaches.

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parameter n_w using a hydration number of the salt, h_i, *which they assumed independent of concentration*, i.e. from Eq. (133a)

$$n_{fw} = n_w - n_i h_i \tag{133a}$$

Substituting for n_{fw} from Eq. (133a) into Eq. (136) and rearranging

$$G = n_i\{\bar{G}_i^{oh} + d_+ RT\mathit{ln}\,(\frac{d_+ n_i}{dn_i + n_w - n_i h_i}) + d_- RT\mathit{ln}(\frac{d_- n_i}{dn_i + n_w - n_i h_i})\}$$

$$+ (n_w - n_i h_i)\{\bar{G}_{fw}^o + RT\mathit{ln}(\frac{n_w - n_i h_i}{dn_i + n_w - n_i h_i})\} + G^{el} \tag{151}$$

The corresponding equation for $\gamma_\pm$ is obtained by first differentiating Eq. (151) in accordance with Eq. (152) (i.e. assuming h_i independent of n_i) to give $\bar{G}_i$, i.e.

$$\bar{G}_i = (\frac{\partial G}{\partial n_i})_{n_w, h} \tag{152}$$

$$= \bar{G}_i^{oh} - h_i \bar{G}_{fw}^o + RT[\mathit{ln}(d_+^{d_+} \,.\, d_-^{d_-}) + d\mathit{ln}(\frac{n_i}{dn_i + n_w - n_i h_i})$$

$$+ h_i \mathit{ln}(\frac{dn_i + n_w - n_i h_i}{n_w - n_i h_i})] + (\frac{\partial G^{el}}{\partial n_i})_{n_w} \tag{153}$$

Converting concentration units in this equation to the molality scale, i.e. putting $m_i = n_i/(n_w M_w/1000)$ with $M_w = 18$g/mole, gives

$$\bar{G}_i = \bar{G}_i^{oh} - h_i \bar{G}_{fw}^o + RT[\mathit{ln}(d_+^{d_+} \,.\, d_-^{d_-}) + d\mathit{ln}(\frac{0{,}018\ m_i}{1 + 0{,}018\ m_i(d - h_i)})$$

$$+ h_i \mathit{ln}(\frac{1 + 0{,}018(d - h_i)}{1 - 0{,}018\ m_i h_i})] + (\frac{\partial G^{el}}{\partial n_i})_{n_w} \tag{154}$$

An equation for $\gamma_\pm$ is now formulated by equating Eq. (154) to the

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equation for the basic definition of $\gamma_\pm$, Eq. (123), i.e. on the molal scale

$$\bar{G}_i = \bar{G}^\circ_{m_i} + dRT\,ln\{\gamma_\pm m_i (d_+^{d_+} . d_-^{d_-})^{1/d}\} \tag{155}$$

Equating Eqs. (154 and 155) and rearranging

$$dRT\,ln\gamma_\pm = (\bar{G}_i^{\circ h} - h_i\bar{G}^\circ_{fw} - \bar{G}^\circ_{m_i}) + RT[d\,ln \frac{0,018}{1 + 0,018\; m_i(d - h_i)} + h_i\,ln(\frac{1 + 0,018\; m_i(d - h_i)}{1 - 0,018\; m_i h_i})] + (\frac{\partial G^{el}}{\partial n_i})_{n_w} \tag{156}$$

The constant in Eq. (156), $(\bar{G}_i^{\circ h} - h_i\bar{G}^\circ_{fw} - \bar{G}^\circ_{m_i})$ is determined by putting $m_i = 0$, i.e.

For $m_i = 0$; $ln\gamma_\pm = 0$ and $(\frac{\partial G^{el}}{\partial n_i})_{n_w} = 0$, i.e.

$$\bar{G}_i^{\circ h} - h_i\bar{G}^\circ_{fw} - \bar{G}^\circ_{m_i} = - dRT\,ln\;0,018$$

and making this substitution in Eqs. (156) and rearranging

$$ln\gamma_\pm = \frac{1}{dRT}(\frac{\partial G^{el}}{\partial n_i})_{n_w} - \frac{h_i}{d_i}\,ln(1 - 0,018\; m_i h_i) + \frac{(h_i - d)}{d}\,ln\{1 + 0,018\; m_i(d - h_i)\} \tag{157}$$

Using the assumption set out in Eq. (144b), i.e.

$(\frac{\partial G^{el}}{\partial n_i})_{n_w} \simeq (\frac{\partial G^{el}}{\partial n_i})_{n_{fw}}$, then from Eqs. (144b and 157)

$$ln\gamma_\pm = \frac{- 2,303\; Az_+z_-\sqrt{\mu}}{1 + B\mathring{a}\sqrt{\mu}} - \frac{h_i}{d_i}\,ln(1 - 0,018\; m_i h_i) + \frac{(h_i - d)}{d}\,ln\{1 + 0,018\; m_i(d - h_i)\} \tag{158a}$$

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If the exact Debye-Hückel solution to $(\partial G^{el}/\partial n_i)_{n_w}$ is substituted into Eq. (157), then Eq. (157) becomes (see Stokes and Robinson, 1957)

$$ln\gamma_{\pm} = \frac{-\ 2{,}303\ Az_+z_-\sqrt{\mu}}{1 + B\mathring{a}\sqrt{\mu}} - \frac{h_i}{d}\ ln a_w - ln\{1 + 0{,}018\ m_i(d - h_i)\} \qquad (158b)$$

where a_w = activity of water in the solution.

However, for a particular electrolyte the difference in the values determined for $\mathring{a}$, h_i and $\gamma_{\pm}$ between Eqs. (158a and 158b) are totally negligible in the region $\mu < 6$, Glueckauf (1957).

For a binary electrolyte system, Eqs. (158a and 158b) each have two unknowns, $\mathring{a}$ and the hydration number, h. Values for these two parameters are established by fitting Eqs. (158) to the observed $\gamma_{\pm}$ data. From experience with the fitting procedure, it is evident that in the low ionic strength range ($\mu < 0{,}1$) h has virtually no effect on the calculated value of $\gamma_{\pm}$ so that $\mathring{a}$ can be fixed in this range. Using this value of $\mathring{a}$, the hydration number is then established by curve fitting in the range $\mu < 1$. This range is used because h is more likely to have a constant value than in a higher ionic strength range. The range of fit of $\gamma_{\pm}$ (calculated) can then be determined by comparing with $\gamma_{\pm}$ data in the region $\mu > 1$. A range of pairs of $\mathring{a}$ and h values can be determined, all of which give good fits up to different upper limits of ionic strength. From the fitting procedure it was established that small differences in $\mathring{a}$ have a disproportionate influence on the range of fit of the calculated $\gamma_{\pm}$ values. If a poorer fit is allowed at $\mu \simeq 0{,}1$ (with its associated $\mathring{a}$ value) one can usually fit $\gamma_{\pm}$ (calculated) up to a very much higher limit in μ. By doing so however, the $\mathring{a}$ value loses its hypothesized significance and the process becomes, in a sense, an empirical fitting technique. In order to reduce this empiricism, $\mathring{a}$ was determined in the region

$\mu < 0{,}1$ to give a fit for $\gamma_{\pm}$ to less than 0,001. The h value was then selected as that value that gives the best possible fit in the region $\mu < 1$. In the higher ionic strength region any deviation could then be ascribed to a deficiency in the theory. Fits obtained by this procedure give rise to $\mathring{a}$ and h values slightly different from those determined by Stokes and Robinson; the ranges of close fit consequently also differed.

Using the above procedure, usually for the heavily hydrated salt species (e.g. HCl and LiCl) a good fit was possible up to $\mu \simeq 1$; similarly for the salts with low hydration (e.g. RbCl and CsCl); for salts with medium hydration good fits up to $\mu \simeq 3$ were obtained. For comparison with the other approaches mean activity coefficients versus μ for HCl, NaCl, CsCl and $MgCl_2$ are listed in Table 5, (Page 2.117).

Although the Stokes-Robinson equation is successful in representing $\gamma_{\pm}$ data for some binary systems up to high ionic strengths its use leads to some contradictions. First, as pointed out by Robinson and Stokes, the hydration numbers determined from their theory (i.e. Eq. 158) for chloride, bromide and iodide salts for a particular cation are in the order h (iodide) > h (bromide) > h (chloride) which follows the same trend as the Pauling crystal radii for these anions where r (iodide) > r (bromide) > r (chloride). This observation is contrary to accepted theory for ionic hydration which is that small ions with a high surface charge will hydrate to a greater extent than larger ions with the same net charge.

Second, it is well established that addition of salts to water results in volume changes occurring for both the solute and the solvent with concomitant free energy changes. The Stokes-Robinson model does not take cognizance of these energy changes. Finally, as pointed out by Robinson and Stokes (1955), any attempt to extend their model to mixed systems gives only very approximate agreement with observations.

6.3.2 *Single ion activity coefficients*

Bates, Staples and Robinson (1970) extended the Stokes-Robinson model to estimate single ion activity coefficients in non-associated binary metal chloride electrolytes. Based on the non thermodynamic assumption that Cl^- remains unhydrated in aqueous solutions, they formulated equations for single ion activity coefficients in binary systems as

$$\log\gamma_{M+} = \log\gamma^{DH} - h\ \log a_w - \log[1 + 0{,}018(d-h)m] \qquad (159a)$$

and

$$\log\gamma_{Cl^-} = \log\gamma^{DH} - \log[1 + 0{,}018(d-h)m] \qquad (159b)$$

where

$\log\gamma^{DH}$ = Debye-Hückel expression for single ion activity coefficient, Eq. (149).

The present day state of the art with regard to single ion activity accepts the Stokes-Robinson equation Eq. (158), as the basis for assigning single ion activity coefficients, Bates *et al.*(1970).

If it is accepted that the Debye-Hückel theory does in fact give a realistic estimate of deviations from ideality due to long range electrostatic effects, then values estimated for single ion activity coefficients using Eqs. (159a and 159b) depend not only on the assumption regarding non hydration of Cl^- in aqueous solutions, but also on the value of the hydration number h determined for the electrolyte. Now, in the formulation of their equation Stokes and Robinson ignored co-volume effects and this omission is reflected in the observation that Eq. (158) gives a hydration number for a particular metal-bromide (or -iodide) salt greater than that for the metal chloride salt even though the Pauling radii for Br^- and I^- are significantly greater than that for Cl^-. Consequently, by placing the total hydration effect on the cation (i.e., assuming $h_{Cl} = 0$) Bates *et al.* in fact also place the co-volume effects on

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the cation. This approach appears to underestimate the activity coefficient of the cation and over-estimate that of the anion (see later).

6.4 Glueckauf's approach

6.4.1 *Mean ionic activity coefficients*

Glueckauf (1955) extended the hydration approach of Stokes and Robinson to include co-volume effects in the development of an equation to model $\gamma_\pm$ in binary systems. In order to incorporate co-volume effects, Glueckauf proposed that the idealized equation for the free energy of the system, Eq. (131), be formulated in terms of volume fraction statistics and not mole fractions, see Eq. (137). An equation for the total free energy of the system, including both ideal and non-ideal terms and analogous to the Stokes-Robinson approach, Eq. (151), is then

$$G = n_i(\bar{G}_i^{oh} + d_+RT\ln\frac{d_+n_i\bar{V}_h^+}{V} + d_-RT\ln\frac{d_-n_i\bar{V}_h^-}{V})$$

$$+ n_{fw}(\bar{G}^o_{fw} + RT\ln\frac{n_{fw}\bar{V}_{fw}}{V}) + G^{el} \qquad (160)$$

where $\bar{V}_h^+$, $\bar{V}_h^-$ = partial molal volumes of hydrated cation and anion

$= \bar{V}_i + h_i\bar{V}_w$ (see Eq. 17) (161a)

V = volume of the system

$= n_i\Phi_i + n_w\bar{V}_w^o$ (see Eq. 19) (161b)

$= n_i\bar{V}_{hi} + n_{fw}\bar{V}_{fw}$ (see Eq. 13) (161c)

To obtain the corresponding equation for $\gamma_\pm$, Glueckauf first determined $\bar{G}_i$ by differentiating Eq. (160) in accordance with Eq. (162) below; that is, that the hydration number, h_i, partial molal volume $\bar{V}_{hi}$ and apparent partial molal volume Φ_i are all independent of

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salt concentration, i.e.

$$\bar{G}_i = \left(\frac{\partial G}{\partial n_i}\right)_{n_w, \bar{V}_{hi}, \Phi_i, h_i} \tag{162}$$

The equation determined for $\bar{G}_i$ using Eqs. (160 and 162) is then equated to the equation defining $\gamma_\pm$, i.e. Eq. (123), where

$$\bar{G}_i = \bar{G}_i^\circ + dRT\,ln\gamma_\pm m_\pm \tag{163}$$

Solving for $\gamma_\pm$ gives the desired expression.

One will have difficulty in following Glueckauf's derivation for the partial molal free energy, $\bar{G}_i$, (using Eqs. 160 and 162) except if the assumption is made that the geometric mean of the *hydrated partial molal volumes* of cation and anion equals the arithmetic mean, i.e.

$$\{(\bar{V}_{hi}^+)^{d_+}(\bar{V}_{hi}^-)^{d_-}\}^{1/d} = (d_+\bar{V}_{hi}^+ + d_-\bar{V}_{hi}^-)/d \tag{164}$$

It would seem that Glueckauf implicitly accepted Eq. (164) in his derivation of the equation for $\bar{G}_i$. However, it is possible to derive Glueckauf's formulation without invoking an equality between geometric and arithmetic means for $\bar{V}_{hi}$, as we shall show below. Nevertheless, Glueckauf's implied assumption can be shown to be a good one, and it is of great utility when developing equations for single ion activity coefficients in both binary and mixed systems,

Derivation of an equation for $\gamma_\pm$ without invoking equality between the geometric and arithmetic means of hydrated partial molal volume is as follows: Differentiating the equation for G (i.e. Eq. 160) in accordance with Eq. (162) and rearranging terms gives

$$\left(\frac{\partial G}{\partial n_i}\right)_{nw} = \bar{G}_i^{\circ h} - h_i\bar{G}_{fw}^\circ + RT[\,ln(d_+^{d_+} \cdot d_-^{d_-}) + d\,ln\left(\frac{n_i}{n_i\Phi_i + n_w\bar{V}_w^\circ}\right)$$

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$$+ \ln\{(\bar{V}_{hi}^{+})^{d_{+}}(\bar{V}_{hi}^{-})^{d_{-}}\} - h_i \ln\frac{(n_w - n_i h_i)\bar{V}_w^{o}}{n_i\Phi_i + n_w\bar{V}_w^{o}}$$

$$- \frac{(n_i\Phi_i - d\, n_w\bar{V}_w^{o} + n_w h_i\bar{V}_w^{o})}{n_i\Phi_i + n_w\bar{V}_w^{o}}\Big] + \left(\frac{\partial G^{el}}{\partial n_i}\right)_{n_w} \qquad (165)$$

Replacing moles of salt species by molality using Eq.(91), i.e. $n_i = 0{,}018\ m_i n_w$ and putting $r_i = \Phi_i/\bar{V}_w^{o}$ in Eq. (165) gives

$$\left(\frac{\partial G}{\partial n_i}\right)_{n_w} = \bar{G}_i^{oh} - h_i\bar{G}_{fw}^{o} + RT\Big[\ln(d_{+}^{d_{+}} \cdot d_{-}^{d_{-}}) + d\ln\Big(\frac{0{,}018\ m_i}{1 + 0{,}018\ m_i r_i}\Big)$$

$$- d\ln\bar{V}_w^{o} + \ln\{(\bar{V}_{hi}^{+})^{d_{+}}(\bar{V}_{hi}^{-})^{d_{-}}\} - h_i\ln\Big(\frac{1 - 0{,}018\ m_i h_i}{1 + 0{,}018\ m_i r_i}\Big) .$$

$$- \frac{(r_i - d + h_i)}{1 + 0{,}018\ m_i r_i}\Big] + \left(\frac{\partial G^{el}}{\partial n_i}\right)_{n_w} \qquad (166)$$

$$= \bar{G}_i \qquad (167)$$

An equation for $\gamma_{\pm}$ is now formulated by equating Eq. (166) to the equation for the basic definition of $\gamma_{\pm}$, Eq. (123), i.e. on the molal scale

$$\bar{G}_i = \bar{G}_{m_i}^{o} + dRT\ln\{\gamma_{\pm} m_i (d_{+}^{d_{+}} \cdot d_{-}^{d_{-}})^{1/d}\} \qquad (168)$$

Equating Eqs. (166 and 168) and rearranging terms

$$dRT\ln\gamma_{\pm} = (\bar{G}_i^{oh} - h_i\bar{G}_{fw}^{o} - \bar{G}_{m_i}^{o}) + RT\Big[d\ln\frac{0{,}018}{1 + 0{,}018\ m_i r_i}$$

$$+ \ln\{(\bar{V}_{h_i}^{+})^{d_{+}}(\bar{V}_{h_i}^{-})^{d_{-}}\} - d\ln\bar{V}_w^{o} - h_i\ln\Big(\frac{1 - 0{,}018\ m_i h_i}{1 + 0{,}018\ m_i r_i}\Big)$$

$$- \Big(\frac{r_i - d + h_i}{1 + 0{,}018\ m_i r_i}\Big)\Big] + \left(\frac{\partial G^{el}}{\partial n_i}\right)_{n_w} \qquad (169)$$

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The constant in Eq. (169), $(\bar{G}_i^{\circ h} - h_i\bar{G}^\circ_{fw} - \bar{G}^\circ_{m_i})$, is determined by putting $m_i = 0$ in the equation, i.e.

For $m_i = 0$; $ln\gamma_\pm = 0$ and $\left(\frac{\partial G^{el}}{\partial n_i}\right)_{n_w} = 0$; i.e.

$$\bar{G}_i^{\circ h} - h_i\bar{G}^\circ_{fw} - \bar{G}^\circ_{m_i} = -[dRT\,ln\,0{,}018 + ln\{(\bar{V}^+_{h_i})^{d_+}(\bar{V}^-_{h_i})^{d_-}\}$$

$$- d\,ln\bar{V}^\circ_w - (r_i - d + h_i)]$$

and making this substitution in Eq. (169) and rearranging

$$ln\gamma_\pm = \frac{1}{dRT}\left(\frac{\partial G^{el}}{\partial n_i}\right)_{n_w} + \frac{0{,}018\ m_i r_i(r_i - d + h_i)}{d(1 + 0{,}018\ m_i r_i)}$$

$$+ \frac{(h_i - d)}{d}\,ln(1 + 0{,}018\ m_i r_i) - \frac{h_i}{d}\,ln(1 - 0{,}018\ m_i h_i) \quad (170)$$

Using the assumption set out in Eq. (144b),

$$ln\gamma_\pm = \frac{-\ 2{,}303\ Az_+z_-\sqrt{\mu}}{1 + B\mathring{a}\sqrt{\mu}} + \frac{0{,}018\ m_i r_i(r_i - d + h_i)}{d(1 + 0{,}018\ m_i r_i)}$$

$$+ \frac{(h_i - d)}{d}\,ln(1 + 0{,}018\ m_i r_i)$$

$$- \frac{h_i}{d}\,ln(1 - 0{,}018\ m_i h_i) \quad (171)$$

Equation (171) is identical to that determined by Glueckauf.

Equation (171) has two variable parameters, å - the mean distance of closest approach between cation and anion in the Debye-Hückel term, and h - the mean hydration number for the salt. Each of these terms is determined in a binary system by curve fitting against observed experimental $\gamma_\pm$ data, as outlined earlier for the Robinson-Stokes equation, Eq. (158).

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Comparison illustrative of fits of $\gamma_{\pm}$ versus μ for binary systems obtained by the Glueckauf approach with that by the Stokes-Robinson approach for HCl, NaCl, CsCl and $MgCl_2$ is given in Table 5. In general, the fits obtained by the Glueckauf approach are not significantly better than those obtained by the Stokes-Robinson approach although the ranges of good fits differ between the two approaches for a particular salt.

In evaluating the overall merits of the two approaches it should be remembered that the hydration number for a salt is estimated by fitting theory against observation. Consequently, the derived hydration number is dependent on the theory. The only way in which the merits of a particular theory can be assessed is to check whether the derived hydration numbers do not show inconsistencies, and the measure in which the derived numbers are reasonably consistent with the trends expected from other physical-chemical considerations.

With regard to the Stokes-Robinson approach, the inconsistencies that arise have been discussed in Section 6.3; indeed it was because of these inconsistencies that the Glueckauf approach was investigated.

With regard to the Glueckauf approach, in terms of the criteria set out above, in assessing the consistency of Glueckauf's approach one expects that the hydration numbers determined for, say, the alkali halide salts should indicate that for a particular anion, say Cl^-, the hydration numbers follow the trend $h_{LiCl} > h_{NaCl} > h_{KCl} > h_{RbCl} > h_{CsCl}$ (see Section 2.2); similarly, for a particular cation, say Li^+, the salt hydration numbers should follow the trend $h_{LiCl} > h_{LiBr} > h_{LiI}$.
Using Eq. (171) and data reported by Millero (1970) for partial molal volumes at infinite dilution, hydration numbers for the alkali halide salts were re-determined. These numbers are shown plotted against cation Pauling Radius in Figure 4. Referring to this figure: With regard to the cation species for a particular

anion, say Y^-, the salt hydration numbers follow the expected trend $h_{LiY} > h_{NaY} > h_{KY} > h_{RbY} > h_{CsY}$; with regard to the anion species for a particular cation, say X^+, the plot indicates $h_{XCl} \simeq h_{XBr} \simeq h_{XI}$, i.e. from the additivity principle for hydration numbers, $h_{Cl} \simeq h_{Br} \simeq h_I$. Now, because Cl^-, Br^- and I^- each have different Pauling Radii (i.e. 1,81, 1,95 and 2,16 Angstrom units respectively) the hydration theory would predict $h_{Cl} > h_{Br} > h_I$. The observation that these hydration numbers are closely equal, therefore, can be explained only by accepting that each of these ions has a hydration number equal to zero. This hypothesis is supported by the plot shown in Figure 4: The plot is closely linear; on the basis of this linearity an extrapolation to h = 0 indicates that the alkali halide salts have a zero hydration number when the cation radius is > 1,65 Å, that is, Cs^+ and Cl^+, Br^-

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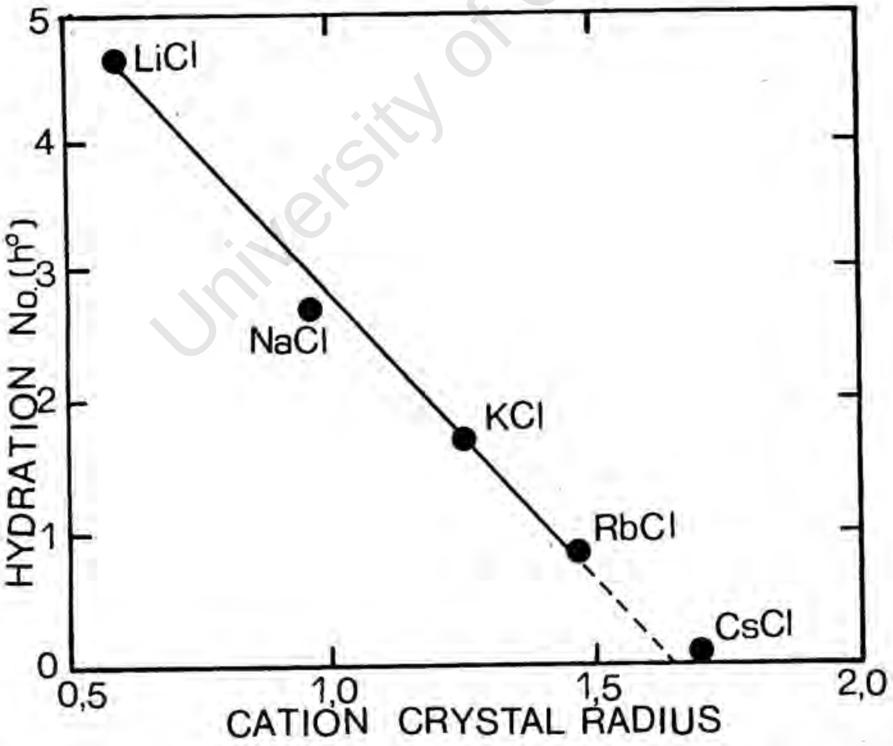

Figure 4 Hydration number from Eq (171) versus cation Pauling radius for alkali chloride salts in aqueous solution.

and I^- each have zero primary hydration. Glueckauf's approach thus eliminates the contradictions mentioned previously for the halide salts that arise with the Stokes-Robinson approach.

Returning to the fit of Glueckauf's equation, Eq. (171) to observed $\gamma_{\pm}$ data: It was stated earlier that $\mathring{a}$ and h values can be selected for a particular salt such that a fit is obtained with observed $\gamma_{\pm}$ data to within about 0,005 activity coefficient units up to an ionic strength of about 3; at higher ionic strengths theory and observation diverge rapidly, the predicted $\gamma_{\pm}$ values falling *below* observed data (except for HCl). If one selects $\mathring{a}$ and h values such that theory and observation agree to within 0,001 activity coefficients units, a fit is obtained only up to an ionic strength of about two; at higher ionic strengths Eq. (171) fails systematically as before (Glueckauf, 1961). One or more of three factors can be hypothesized to give rise to the failure of the theory at $\mu > 2$; (1) The Debye-Hückel theory for electrostatic effects between ions may fail at these higher ionic strengths; however, according to Stokes and Robinson (1973) there appears to be good reason for accepting the theory up to exceptionally high ionic strengths. (2) The assumption that the partial molal volume parameter, r, can be taken as a constant and equal to its value at infinite dilution may be invalid. Glueckauf utilized this assumption for the sake of simplicity in his development of an equation for $\gamma_{\pm}$; however, as discussed earlier in this chapter, both theory and observation show that the partial molal volume changes with concentration. (3) In the theories of both Glueckauf and Stokes and Robinson, the hydration number for a salt is accepted as a constant independent of ionic strength. If this were indeed so, then considering say LiCl for which Glueckauf's equation predicts a hydration number of about 4, one would expect all the free water in the solution to be bound by the salt at a molality of about 14 (i.e. 55,5/4); however, LiCl is soluble at molalities greater than 20, Stokes and Robinson (1973). This behaviour can be explained

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by accepting that the hydration number for LiCl, and indeed all salts, is not a constant but *decreases* with increase in concentration. Glueckauf (1961), however, intimated that a decreasing hydration number will not resolve the problem because he found that in order to obtain satisfactory fits against observed data his equation requires *increasing* the value of the hydration number with increasing concentration. But this conclusion does not necessarily apply, because his equation was developed based on a constant hydration number; if the basis of formulation includes acceptance of a concentration dependent hydration number, the behaviour of the derived equation changes significantly and no longer exhibits this contradiction (see Section 6.5).

6.4.2 *Single ion activity coefficients*

As discussed in Sections 6.3 and 6.4.1, in terms of the hydration theory Glueckauf's approach, Eq. (171), shows greater consistency than that of Stokes-Robinson's, Eq. (158), and consequently the former should serve as a more reliable basis for estimating single ion activities than the latter.

An important consequence of the additive nature of partial molal volumes and hydration numbers of the component ions for a salt is that it is logically possible to decompose Eq. (171) for $\gamma_{\pm}$ into equations for the activity coefficients for each of the constituent ions. The approach is first to formulate an equation for $\gamma_{\pm}$ in a mixed electrolyte of non-associated salts assuming that both partial molal volumes and hydration numbers of the salts are independent of ionic strength (see Chapter 3), i.e. for the mean activity coefficient of salt 'j' in an aqueous solution containing 'i' types of salts,

$$ln\gamma_{j\pm} = ln^{DH}_{j\pm} + \frac{0{,}018r_j(\sum_i m_i r_i + \sum_i m_i h_i - \sum_i m_i d_i)}{d_j(1 + 0{,}018\sum_i m_i r_i)} +$$

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$$+ \frac{h_j - d_j}{d_j} \ln(1 + 0{,}018 \sum_i m_i r_i) - \frac{h_j}{d_j} \ln(1 - 0{,}018 \sum_i m_i h_i) \quad (172)$$

This formulation indicates that irrespective of the salt type (j) for which $\gamma_{j\pm}$ is determined, the terms in brackets are *constants for any particular ionic medium,* i.e.

$$\ln\gamma_{j\pm} = \ln\gamma^{DH}_{j\pm} + \frac{0{,}018 r_j A'}{d_j B} + \frac{(h_j - d_j)}{d_j} \ln B' - \frac{h_j}{d_j} \ln C' \quad (173)$$

where

$$A' = (\sum_i m_i r_i + \sum_i m_i h_i - \sum_i m_i d_i)$$

$$B' = (1 + 0{,}018 \sum_i m_i r_i)$$

$$C' = (1 - 0{,}018 \sum_i m_i h_i)$$

Applying additivity to both the hydration number, h_j, and the partial molal volume parameter, r_j, in Eq. (173) and multiplying both sides of the equation by d_j, gives

$$\begin{aligned} d_j \ln\gamma_{j\pm} = {} & d_j \ln\gamma^{DH}_{j\pm} + \frac{0{,}018(d_{j+} r_{j+} + d_{j-} r_{j-}) A'}{B'} \\ & + (d_{j+} h_{j+} + d_{j-} h_{j-}) \ln B' - (d_{j+} + d_{j-}) \ln B' \\ & - (d_{j+} h_{j+} + d_{j-} h_{j-}) \ln C' \end{aligned} \quad (174)$$

From Eq. (148b), for the Debye-Hückel terms in Eq. (174)

$$d_j \ln\gamma^{DH}_{j\pm} = \frac{-(d_{j+} + d_{j-})\ 2{,}303\ A z_+ z_- \sqrt{\mu}}{1 + B\mathring{a}\sqrt{\mu}} \quad (175)$$

and since $d_+ z_+ = d_- z_-$, Eq. (175) becomes

$$d_j \ln\gamma^{DH}_{j\pm} = \frac{-(d_+ z_+^2 + d_- z_-^2)\ 2{,}303\ A\sqrt{\mu}}{1 + B\mathring{a}\sqrt{\mu}} \quad (176)$$

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Substituting Eq. (176) into Eq. (174) and rearranging terms gives *for a binary system*

$$d\ln\gamma_{\pm} = d_+\ln\gamma_+^{DH} + \frac{0,018\ d_+r_+A'}{B'} + (d_+h_+ - d_+)\ln B' - d_+h_+\ln C'$$

$$+ d_-\ln\gamma_-^{DH} + \frac{0,018\ d_-r_-A'}{B'} + (d_-h_- - d_-)\ln B' - d_-h_-\ln C' \qquad (177)$$

and by definition the left hand side of Eq. (177) is

$$d\ln\gamma_{\pm} = d_+\ln\gamma_+ + d_-\ln\gamma_- \qquad (178)$$

Comparing Eq. (178) with Eqs. (177 and 173), the equations for single ion activity coefficients in a binary system can be written

$$\ln\gamma_+ = \frac{-\ 2,303\ z_+^2A\sqrt{\mu}}{1 + B\mathring{a}\sqrt{\mu}} + \frac{0,018\ r_+(mr+mh-md)}{(1 + 0,018\ mr)} + (h_+ - 1)\ln(1 + 0,018mr)$$

$$- h_+\ln(1 - 0,018\ mh) \qquad (179a)$$

and

$$\ln\gamma_- = \frac{-\ 2,303\ z_-A\sqrt{\mu}}{1 + B\mathring{a}\sqrt{\mu}} + \frac{0,018\ r_-(mr+mh-md)}{(1 + 0,018\ mr)} + (h_- - 1)\ln(1 + 0,018\ mr)$$

$$- h_-\ln(1 - 0,018\ mh) \qquad (179b)$$

Single ion activity coefficients can now be determined using Eqs. (179a and 179b) provided the following parameters are known or can be estimated:

(a) the single ion partial molal volume parameters, r_+ and r_- at infinite dilution,

(b) single ion hydration numbers h_+ and h_- at infinite dilution, and

(c) the distance of closest approach, $\mathring{a}$

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(a) Estimation of single ion partial molal volumes at infinite dilution was discussed in detail earlier in Section 3.5.2; values for ions of common interest were listed in Table 2.

(b) Single ion hydration numbers at infinite dilution, h_+ and h_-, are estimated using the additivity principle and the assumption $h_{Cl} = 0$ discussed in Section 6.4.1.

(c) Distance of closest approach, $\mathring{a}$, is obtained from the fit of Eq. (171) for $\gamma_\pm$ of the salt to observed data over the lower range of ionic strength.

Values estimated for single ion activity coefficients for 1:1 salts using Eqs. (179a and 179b) are generally very close to those determined by Bates *et al.*(1970) using Eqs. (159a and 159b) despite the very large differences in $\mathring{a}$ and h values for a particular salt between the two approaches. However, for 1:2 salts (e.g. $MgCl_2$), the decomposed Glueckauf equation generally predicts significantly higher γ_{++} values (and lower γ_- values) than the values predicted using the Stokes-Robinson equation, see Table 8(a) and 8(b).

Although the decomposition of Glueckauf's equation allows a more consistent approach than that of the Stokes-Robinson equation to single ion activities, there still remain those unsatisfactory aspects pertaining to the Glueckauf equation discussed earlier in Section 6.4.1. Furthermore, extension of Glueckauf's approach to $\gamma_\pm$ in mixed electrolyte systems leads to unsatifactory predictions when compared with observed data. For these reasons, the approach was extended to account for non-ideality of partial molal volumes and a hydration number that is concentration dependent.

6.5 Extended approach

6.5.1 *Mean ionic activity coefficients*

In this approach to the formulation of an equation for $\gamma_\pm$, it is accepted that both the partial molal volume and the degree of

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hydration of ions vary with salt concentration. Initially an equation is developed for $\gamma_{\pm}$ by considering these deviations simply in the differential form, i.e. $\partial\bar{V}_i/\partial m_i$ and $\partial h_i/\partial m_i$. Quantitative aspects are applied to these differentials later.

Development of an equation for $\gamma_{\pm}$ follows a similar procedure to that set out above for Glueckauf's equation, Eq.(171). That is, first an equation is written down for the total free energy of the system utilizing volume fraction statistics in place of the conventional mole fraction statistics, see Eq. (160), i.e.

$$G = n_i(\bar{G}_i^{oh} + d_+RT\mathit{ln}\,\frac{d_+n_i\bar{V}_{hi}^{+}}{V} + d_-RT\mathit{ln}\,\frac{d_-n_i\bar{V}_{hi}^{-}}{V})$$

$$+ n_{fw}(\bar{G}_{fw}^{o} + RT\mathit{ln}\,\frac{n_{fw}\bar{V}_{fw}}{V}) + G^{el} \tag{180a}$$

The partial molal free energy of salt species 'i', $\bar{G}_i$, is then determined by differentiating Eq. (180a) above in accordance with Eq. (180b) below, i.e.

$$\bar{G}_i = (\frac{\partial G}{\partial n_i})_{n_w} \tag{180b}$$

The equation determined for $\bar{G}_i$ using Eqs. (180a and 180b) is then equated to the equation defining $\gamma_{\pm}$, Eq. (123), i.e.

$$\bar{G}_i = \bar{G}_i^{o} + dRT\mathit{ln}\gamma_{i\pm}m_{i\pm} \tag{181}$$

Solving for $\gamma_{\pm}$ gives the desired expression.

Differentiating Eq. (180a) in accord with Eq. (180b), rearranging terms and converting to molality, i.e. putting $m_i = n_i/0{,}018\ n_w$

$$\bar{G}_i = \bar{G}_i^{oh} - h\bar{G}_{fw}^{o} - n_i\,\frac{\partial h}{\partial n_i}\,.\,\bar{G}_{fw}^{o} + RT[\,\mathit{ln}d_+^{d_+}\,.\,d_-^{d_-} - d\,\mathit{ln}d$$

$$+ d\,\mathit{ln}(\frac{0{,}018\ m_in_w}{V}) + d\,\mathit{ln}\bar{V}_{hi} + \frac{dm_i}{\bar{V}_{hi}}\,.\,\frac{\partial\bar{V}_{hi}}{\partial m_i} - h\,\mathit{ln}\{\frac{n_w\bar{v}_w^{o}(1-\ \ 018\ m_ih)}{V}\}$$

$$+ \frac{(d-h)V - n_w\{1 + 0{,}018(md-mh)\}(V/n_i)}{V} + \frac{(n_w - n_i h)}{\bar{V}_{fw}} . \frac{\partial \bar{V}_{fw}}{\partial n_i}$$

$$- m_i \frac{\partial h}{\partial m_i} \{1 + ln \frac{\bar{V}^o_w n_w(1 - 0{,}018 m_i h)}{V}\}] + (\frac{\partial G^{el}}{\partial n_i})_{n_w} \quad (182)$$

As in Glueckauf's development, let $r_i = \Phi_i/\bar{V}^o_w$ and $q_i = \bar{V}_i/\bar{V}_w \simeq \bar{V}_i/\bar{V}^o_w$; equating $\partial V/\partial n_i = \bar{V}_i$ (by definition)

$$\frac{(n_w - n_i h)}{\bar{V}_{fw}} . \frac{\partial \bar{V}_{fw}}{\partial n_i} = -m_i \frac{\partial q_i}{\partial m_i}(1 - 0{,}018\, m_i h) \quad \text{and}$$

$$\frac{dm_i}{\bar{V}_{hi}} . \frac{V_{hi}}{m_i} = \{m_i \frac{\partial q_i}{\partial m_i}(\frac{d - 0{,}018 d m_i h}{q_i + h}) + \frac{dm_i}{q_i + h}\frac{\partial h}{\partial m_i}\}$$

Insert in Eq.(182), rearrange and simplify

$$\bar{G}_i = \bar{G}^{o h}_i - (h + m_i \frac{h}{m_i})\, \bar{G}^o_{fw} + RT\, [ln\, d_+^{d_+} . d_-^{d_-} - d\, ln d$$

$$+ d\, ln \frac{0{,}018 m_i}{1 + 0{,}018 m_i r_i} + d\, ln\, (q_i + h) - h\, ln\, (\frac{1 - 0{,}018 m_i h}{1 + 0{,}018 m_i r_i})$$

$$+ \frac{d - h - q_i}{1 + 0{,}018 m_i q_i} - m_i \frac{\partial h}{\partial m_i} \frac{q_i + h - d}{q_i + h} + ln \frac{1 - 0{,}018 m_i h}{1 + 0{,}018 m_i r_i}$$

$$- m_i \frac{\partial q_i}{\partial m_i} \{\frac{q_i + h - d)(1 - 0{,}018 mh)}{q_i + h}\}] + (\frac{\partial G^{el}}{\partial n_i}) \quad (183)$$

An equation for $\gamma_\pm$ is now formulated by equating Eq.(183) to the equation defining $\gamma_\pm$, Eq.(123), i.e. on the molal scale

$$\bar{G}_i = \bar{G}^o_{m_i} + dRT ln\{\gamma_\pm m_i (d_+^{d_+}\, d_-^{d_-})^{1/d}\} \quad (184)$$

Equating Eqs. (183 and 184) and rearranging terms

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$$dRT\,ln\gamma_{\pm} = \{\bar{G}_i^{\circ h} - \bar{G}^{\circ}_{m_i} - (h + m_i \frac{\partial h}{\partial m_i})\bar{G}^{\circ}_{fw}\} + RT[- d\,ln\,d$$

$$+ d\,ln \frac{0{,}018}{1 + 0{,}018\, m_i r_i} + d\,ln(q_i + h) - h\,ln\,\{\frac{1 - 0{,}018\, m_i h}{1 + 0{,}018\, m_i r_i}\}$$

$$+ \frac{d - h - q_i}{1 + 0{,}018\, m_i q_i} - m_i \frac{\partial h}{\partial m_i}\{X\} - m_i \frac{\partial q_i}{\partial m_i}\{Y\}]$$

$$+ (\frac{\partial G^{el}}{\partial n_i})_{n_w} \qquad (185)$$

where {X} and {Y} are given by the corresponding terms in Eq. (183).

The constant $(\bar{G}_i^{\circ h} - \bar{G}^{\circ}_{m_j})$ on the right hand side of Eq. (185) is solved for by considering the system at infinite dilution, i.e. for $m_i \to 0$. At $m_i = 0$, $ln\gamma_{\pm} = 0$, $(\partial G^{el}/\partial n_i)_{n_w} = 0$, $r_i = r_i^{\circ}$, $q_i = q_i^{\circ}$ and $h = h^{\circ}$; the superscript '°' refers to the value of the parameter at infinite dilution, i.e.

$$\bar{G}_i^{\circ h} - \bar{G}^{\circ}_{m_i} = h^{\circ}\bar{G}^{\circ}_{fw} - RT[- d\,ln\,d + d\,ln\, 0{,}018 + d\,ln(q_i^{\circ} + h^{\circ})$$

$$- (q_i^{\circ} + h^{\circ} - d)] \qquad (186)$$

$$= h^{\circ}\bar{G}^{\circ}_{fw} + RT[d\,ln\,d - d\,ln\, 0{,}018 - d\,ln(q_i^{\circ} + h^{\circ})$$

$$+ (q_i + h - d) - \Delta q_i - \Delta h] \qquad (187)$$

where

$$\Delta q_i = q_i - q_i^{\circ} \qquad (188a)$$

$$\Delta h = h - h^{\circ} \qquad (188b)$$

Substituting Eqs. (187, 188a and 188b) into Eq. (185) and rearranging terms gives the required equation for $\gamma_{\pm}$:

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$$
\begin{aligned}
ln\gamma_{\pm} &= \frac{1}{dRT}\left(\frac{\partial G^{el}}{\partial n_i}\right)_{n_w} + \frac{0{,}018\, q_i(q_i + h - d)}{d\,(1 + 0{,}018\, m_i q_i} \\
&+ \frac{(h - d)}{d}\, ln(1 + 0{,}018\, m_i r_i) - \frac{h}{d}\, ln(1 - 0{,}018\, m_i h) \\
&+ (h^{o} - h - m_i \frac{\partial h}{\partial m_i})\, \frac{\bar{G}^{o}_{fw}}{dRT} - (h - h^{o})/d - (q - q^{o})/d \\
&+ ln\{(q_i + h)/(q_i^{o} + h^{o})\} - \frac{m_i}{d}\,\frac{\partial h}{\partial m_i}\,\{X\} \\
&- \frac{m_i}{d}\,\frac{\partial q_i}{\partial m_i}\,\{Y\} \qquad (189)
\end{aligned}
$$

where

$$\{X\} = \{\frac{q_i + h - d}{q_i + h} + ln\,\frac{1 - 0{,}018\, m_i h}{1 + 0{,}018\, m_i r_i}\}$$

$$\{Y\} = \{\,\frac{(q_i + h - d)(1 - 0{,}018\, m_i h)}{q_i + h}$$

and from Eq (144^{b})

$$\frac{1}{dRT}\left(\frac{\partial G^{el}}{\partial n_i}\right)_{n_w} \simeq -\,\frac{2{,}303A z_+ z_- \sqrt{\mu}}{1 + B\mathring{a}\sqrt{\mu}}$$

Fitting of Eq (189) to observed data of $\gamma_{\pm}$ follows in a similar fashion to that for fitting the Glueckauf equation, that is, å is determined by fitting in the lower ionic strength region ($\mu \leqslant 0{,}1$); the hydration number at infinite dilution, h_o, by fitting in the region $0{,}1 < \mu < 1$ (using the å value) and, the change in hydration with salt concentration, $\partial h/\partial m$, by fitting in the region $\mu > 1$. These aspects are considered in more detail later.

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Examining Eq. (189): The first four terms on the right hand side of the equation correspond to Glueckauf's equation, Eq. (171), except that the parameters q_i and h now refer to the values for these parameters at salt molality m_i; the last six terms on the right hand side of the equation account for changes in partial molal volumes and hydration number with increase in salt concentration.

In order to fit Eq. (189) to observed data for a particular salt requires knowing and determining values for a number of parameters, these are:

(i) the partial molal volume parameters r_i and q_i at both infinite and finite dilutions, and $\partial r_i/\partial m_i$ and $\partial q_i/\partial m_i$,

(ii) the distance of closest approach parameter, å in the Debye-Hückel term,

(iii) the hydration number at infinite dilution, h°, and the change in hydration number with salt concentration.

(i) *Partial molal volume parameters r_i, q_i, $\partial r_i/\partial m_i$ and $\partial q_i/\partial m_i$*

Reliable values for the partial molal volume parameters r_i and q_i at infinite dilution (i.e. $r_i^\circ = q_i^\circ$) are well documented in the literature for most salts of common interest, Horne (1970). With regard to the apparent partial molal volume parameter r_i (i.e. $\Phi_i/\bar{V}_w^\circ$) at finite ionic strengths, it was shown earlier in this chapter that the change in r with concentration can be modelled using the Redlich-Meyer formulation (Eq. 43) for Φ_i, then

$$r_i = \frac{\Phi_i}{\bar{V}_w^\circ} = \frac{1}{\bar{V}_w^\circ}\left(\Phi_i^\circ + S_v\sqrt{c_i} + b_i c_i\right) \qquad (190)$$

where

$$S_v = 0{,}66\ (d_+ z_+{}^2 + d_- z_-{}^2)^{\frac{3}{2}}$$

b_i = an experimentally determined constant.

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Consequently,

$$\frac{\partial r_i}{\partial m_i} = \frac{1}{\bar{V}_w^o}\left(\frac{0{,}5S_v}{\sqrt{c}} + b_i\right)\frac{dc_i}{dm_i}$$

The term dc_i/dm_i can be put equal to unity in the ionic strength range where Eq. (189) is assumed valid, i.e. $\mu \leq 6$. For example, for NaCl at molality 3, $dc/dm = 0{,}995$, i.e.

$$\frac{\partial r_i}{\partial m_i} = \frac{1}{\bar{V}_w^o}\left(\frac{0{,}5S_v}{\sqrt{c}} + b_i\right) \qquad (191)$$

With regard to the partial molal volume parameter q_i (i.e. $\bar{V}_i/\bar{V}_w^o$) and $\partial q_i/\partial m_i$ from Eq.(22)

$$\bar{V}_i = \frac{1}{c}\int \Phi_i dc_i$$

i.e. substituting for Φ_i from Eq. (43) and noting that $\Phi_i^o = \bar{V}_i^o$,

$$\bar{V}_i = \bar{V}_i^o + 1{,}5S_v\sqrt{c_i} + 2b_i c \qquad (192)$$

Putting $q_i = \bar{V}_i/\bar{V}_w^o$ in Eq. (192), and using the assumption derived above, i.e. $dc_i/dm_i \simeq 1$,

$$\frac{\partial q_i}{\partial m_i} = \frac{1}{\bar{V}_w^o}\left(\frac{0{,}75S_v}{\sqrt{c_i}} + 2b_i\right) \qquad (193)$$

(ii) *$\overset{o}{a}$ and h_i^o*

If it is accepted that the hydration number, h_i, decreases slowly with salt concentration, then in the ionic strength region $\mu < 1$ the terms involving $m_i(\partial h_i/\partial m_i)$ are very small and initially can be assumed zero. Within this range, values for $\overset{o}{a}$ and h_i^o can be established in exactly the same fashion as outlined earlier for the determination of these two constants using the Stokes-Robinson

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equation - except that the ionic strength limit is now set at about unity. (An important point here is that within this range the fit against observed $\gamma_\pm$ data to determine a and h^o must now be to within 0,001 activity coefficient units because at the high ionic strength the determination of $\gamma_\pm$ is sensitive to h_i and $\partial h_i/\partial m_i$ both of which depend on h^o).

(iii) *Hydration number h, the function $(\partial h_i/\partial m_i)$ and $\bar{G}^o_w$*

If one maintains the assumption that $(\partial h_i/\partial m_i) = 0$ in Eq. (189) at ionic strengths greater than the region in which å and h^o_i were established, then it is found that there is an increasing divergence between the predicted value for $\gamma_\pm$ and observed data. Invariably the predicted value for $\gamma_\pm$ is less than the observed value. Now, as discussed earlier, one expects the hydration number of a salt to decrease slowly as the salt concentration increases. Consequently, at higher ionic strengths, in addition to the arbitrary constant $\bar{G}^o_w$, there are two unknowns in Eq. (189) - the hydration number h_i and the function linking h_i to the salt molality. However, we have no theory for predicting the form of this function. Our approach here simply is to accept that h_i decreases monotonically with m_i in the region $\mu < 6$ and to assume a function of the form

$$h_i = h^o_i - y_i m^{x_i} \qquad (194)$$

i.e.

$$\frac{\partial h_i}{\partial m_i} = - y_i x_i m^{x_i - 1} \qquad (195)$$

Values for y_i and x_i for a particular salt species, i, are estimated by first assuming a value for the constant $\bar{G}^o_{fw}$ and then fitting Eq. (189) to observed $\gamma_\pm$ data in the ionic strength region

TABLE 4

Values for the various parameters to fit the extended equation, Eq (189) to observed $\gamma_\pm$ data
[$(\bar{G}^\circ_{fw}/RT) = 30$]

SALT	$\overset{\circ}{a}$	$\overset{\circ}{h}$	f(h) i.e. h = f(h)	$\bar{V}^\circ_i$ cc/mole	*			Upper limit of μ	Max. deviation in activity co-efficient
					$\bar{V}^\circ_i$ cc/mole	S_v or S^*_v	b_i		
Li Cℓ	5,34	4,20	$h^\circ - 1,8.10^{-4}m^{1,5}$	16,99	16,99	1,49		4,0	0,001
Li Br	5,70	4,00		23,76	23,76	1,867	-0,60		
Li I	6,90	4,20		35,37	35,37	1,867	-0,76		
Na Cℓ	4,95	2,40	$h^\circ - 1,4.10^{-4}m^2$	16,61	16,61	1,867	0,048	6,0	0,002
Na Br	5,15	2,45		23,48	23,51	1,76	-		
Na I	5,70	2,65		34,82	34,82	1,867	-0,38		
K Cℓ	4,35	1,01	$h^\circ - 1,7.10^{-4}m^2$	26,80	26,80	1,867	0,1	4,5	0,001
K Br	4,60	1,05		33,73	33,73	1,867	-0,16		
K I	5,10	1,05		45,06	45,06	1,867	-0,39		
Rb Cℓ	3,90	0,6	$h^\circ - 1,7.10^{-4}m^2$	31,94	31,94	1,867	0,17	5,0	0,002
Rb Br	3,95	0,6		38,84	38,71	2,04	-		
Rb I	4,10	0,4		50,16	50,16	1,867	-0,05		
Cs Cℓ	3,42 (3,55)**	0,3	$h^\circ - 1,5.10^{-4}m^2$	39,17	39,17	1,867	0,12		
H Cℓ	5,60	4,09	$h^\circ - 9.10^{-4}m^{1,5}+1,5.10^{-5}m^3$	17,82	18,07	0,95	-	5,0	0,002
Mg Cℓ$_2$	5,70	8,12	$h^\circ - 18,5.10^{-4}m^2$	14,49	14,49	5,15	-	6	0,001
Ca Cℓ$_2$	5,65	7,05	$h^\circ - 18.10^{-4}m^2$	17,78	17,78	6,0	-	6	0,001
Sr Cℓ$_2$	5,55	6,43	$h^\circ - 16.10^{-4}m^2$	18,10	18,10	7,07	-	6	0,001
Ba Cℓ$_2$	5,00	5,00	$h^\circ - 7.10^{-4}m2$	23,15	23,15			5	0,001

(*) In this column V°, S_v(or S^*_v) and b values are those values to be used with the Masson or Redlich-Meyer equations.

(**) Best fit at m = 0,1

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Table 5.

Fits of the Stokes-Robinson equation, Eq. (158a), Glueckauf equation, Eq. (171), and the extended equation, Eq. (189), against observed $\gamma_{\pm}$ data for NaCl, HCl, RbCl, $MgCl_2$ and CsCl at 25°C.

(a) NaCl

$m^{\dagger}$	μ	$\gamma_{\pm}$ Stokes-Robinson $\overset{\circ}{a} = 4{,}07$ $h = 3{,}20$	$\gamma_{\pm}$ Glueckauf $\overset{\circ}{a} = 4{,}12$ $h = 2{,}55$	$\gamma_{\pm}$ Extended* $\overset{\circ}{a} = 4{,}95$ $h^{\circ} = 2{,}40$	$\gamma_{\pm}$ (Observed)
0,0016	0,0016	0,957	0,956	0,956	0,957
0,1	0,1	0,778	0,778	0,778	0,778
0,5	0,496	0,680	0,681	0,681	0,681
1,0	0,98	0,658	0,658	0,658	0,657
1,4	1,36	0,658	0,654	0,657	0,655
2,0	1,92	0,670	0,664	0,669	0,668
3,0	2,83	0,709	0,693	0,713	0,714
4,0	3,70	0,766	0,738	0,781	0,783
5,0	4,56	0,840	0,793	0,873	0,874
6,0	5,32	0,935	0,857	0,989	0,986

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* Data used in Extended equation, Eq. (189), is listed in Table 4.

† m = Molality.

Table 5 (continued)

(b) HCl

$m^{\dagger}$	μ	$\gamma_{\pm}$ Stokes-Robinson $\mathring{a} = 4,47$ $h = 7,70$	$\gamma_{\pm}$ Glueckauf $\mathring{a} = 4,45$ $h = 4,68$	$\gamma_{\pm}$ Extended* $\mathring{a} = 5,60$ $h^{o} = 4,09$	$\gamma_{\pm}$ (Observed)
0,001	0,001	0,965	0,965	0,965	0,966
0,01	0,01	0,905	0,905	0,905	0,905
0,1	0,1	0,796	0,796	0,796	0,796
0,5	0,495	0,756	0,757	0,758	0,757
1,0	0,98	0,813	0,809	0,808	0,809
2,0	1,93	1,061	1,005	1,007	1,009
3,0	2,84	1,572	1,316	1,316	1,316
4,0	3,73	2,76	1,793	1,762	1,762
5,0	4,54	6,63	2,55	2,38	2,38
6,0	5,45	33,64	3,82	3,25	3,22

(c) RbCl

$m^{\dagger}$	μ	$\gamma_{\pm}$ Stokes-Robinson $\mathring{a} = 3,50$ $h = 1,20$	$\gamma_{\pm}$ Glueckauf $\mathring{a} = 3,60$ $h = 0,7$	$\gamma_{\pm}$ Extended* $\mathring{a} = 3,90$ $h^{o} = 0,60$	$\gamma_{\pm}$ (Observed)
0,1	0,1	0,763	0,763	0,764	0,764
0,5	0,49	0,637	0,635	0,634	0,634
1	0,97	0,586	0,582	0,584	0,583
2	1,87	0,544	0,533	0,544	0,546
3	2,71	0,525	0,507	0,533	0,536
4	3,49	0,514	0,489	0,537	0,538
5	4,22	0,508	0,476	0,550	0,546

* Data used in Extended equation, Eq. (189), is listed in Table 4.

† m = Molality.

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Table 5 (continued)

(d) $MgCl_2$

m[†]	μ	$\gamma_\pm$ Stokes-Robinson $\mathring{a}$ = 4,95 h° = 13,1	$\gamma_\pm$ Glueckauf $\mathring{a}$ = 5,02 h° = 7,80	$\gamma_\pm$ Extended[*] $\mathring{a}$ = 5,60 h° = 8,12	$\gamma_\pm$ (Observed)
0,1	0,3	0,529	0,530	0,529	0,529
0,2	0,6	,490	0,490	0,489	0,489
0,3	0,895	0,476	0,477	0,477	0,477
0,5	1,49	0,481	0,478	0,480	0,481
1,0	2,94	0,570	0,544	0,570	0,570
2,0	5,75	1,124	0,835	1,052	1,053

(e) CsCl

m[†]	μ	$\gamma_\pm$ Stokes-Robinson $\mathring{a}$ = 3,25 h° = 0	$\gamma_\pm$ Glueckauf $\mathring{a}$ = 3,20 h° = 0	$\gamma_\pm$ Extended[*] $\mathring{a}$ = 3,42 h° = 0,3	$\gamma_\pm$ (Observed)
0,1	0,1	0,755	0,755	0,755	0,756
0,5	0,49	0,614	0,613	0,612	0,606
1,0	0,96	0,551	0,549	0,551	0,544
2,0	1,85	0,487	0,484	0,496	0,496
3,0	2,66	0,449	0,447	0,479	0,479
4,0	3,41	0,422	0,419	0,469	0,474
5,0	4,1	0,400	0,397	0,469	0,475
6,0	4,74	0,382	0,379	0,471	0,480

[*] Data used in Extended equation, Eq.(189), is listed in Table 4.

[†] m = Molality

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Considering the consistency of the extended and Glueckauf approaches, the following comparisons can be made: (i) In general, the h^{o} values from the extended approach closely equal the h values determined using the Glueckauf approach, compare h^{o} (extended) and h (Glueckauf) in Table 5; (ii) the trend between h^{o} (extended) approach) and the cation Pauling crystal radius, Figure 5, is also very similar to that of h (from the Glueckauf approach), Figure 4; (iii) the å values for any particular salt determined using the two approaches, differ significantly for all the alkali and alkaline earth halides and HCl. The å values from the extended approach are much greater than those from the Glueckauf approach (and the Stokes-Robinson approach). The å (extended approach) values, however, exhibit greater consistency than the å (Glueckauf): Considering salts with very low hydration for example, CsCl, because both Cs^{+} and Cl^{-} have hydration numbers close to zero (see Section 6.6.2), one would expect that the å value for CsCl would be equal to, or greater than, the sum of the Pauling crystal radii of the component ions, Σr_x. In the extended approach å $\simeq$ 3,50 and Σr_x = 3,50; in both the Glueckauf and Stokes-Robinson approaches å $\simeq$ 3,20, that is, å is smaller than Σr_x.

Considering salts with significant hydration, for example HCl, the alkali halide salts (excluding cesium salts) and all the alkaline earth salts, one would expect that the distance of closest approach å would be greater than the sum of the crystal radii, Σr_x. Knowing the hydration number at infinite dilution, it is possible to form an estimate of the *minimum* radius of a primary *hydrated* ion (see Appendix 2A). The basis of such an estimate is that all the primary hydrated water is equally strongly held about a particular ion, i.e. there is no gradient in density in the sheath of hydrated water. As this is not likely, the primary hydrated radius can be expected to be larger than the estimate using the constant density hypothesis.

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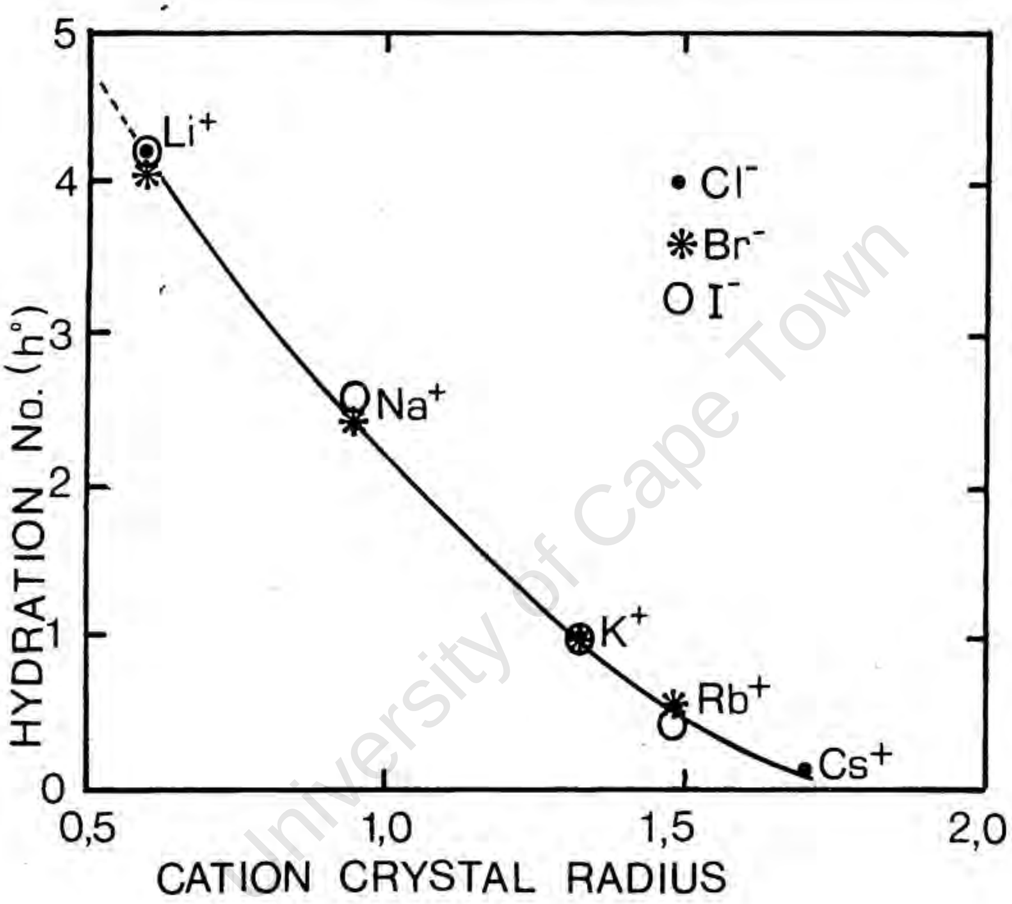

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Figure 5. Plot of hydration number at infinite dilution h_i° *from extended Eq.(189) versus cation Pauling radius for alkali and alkaline earth halides.*

In Table 6 the theoretical minima for the distance of closest approach, $\overset{o}{a}_{min}$, estimated as the sum of the primary hydrated radii of cation and anion (using Eq.(E), Appendix 2A) together with the hydration numbers from the respective theories (assuming that Cl^- has a hydration number equal to zero, see Section 6.5.2) are compared with the $\mathring{a}$ values determined by fitting the respective theories against observed data for $\gamma_\pm$. For the Glueckauf approach the majority of salts give $\mathring{a} < \mathring{a}_{min}$, whereas the extended approach gives $\mathring{a} > \mathring{a}_{min}$ for all salts except CsCl (not hydrated) where $\mathring{a} \simeq \mathring{a}_{min}$.

The differences in values between the two approaches arise as follows: In the extended approach $\mathring{a}$ is determined in the ionic strength region $\mu \simeq 0{,}1$ where the effects of deviation in partial molal volume from ideality are significant (but the effects of changes in primary hydration are negligible) and the formulation for determining $\mathring{a}$ takes cognizance of this effect. In the Glueckauf approach $\mathring{a}$ is also determined near $\mu = 0{,}1$, but the non-ideality of the partial molal volumes is not recognised and consequently this effect is included in $\mathring{a}$.

A comment on the change in hydration with salt molality: Essentially the formulation of this change is empiric, the constants in the formulation being selected such that good fits can be obtained between the observed and calculated mean activity coefficients. There is no surety that the change in the hydration is the only effect to be considered or whether other effects (as yet unknown) also contribute to the observed deviations. Consequently, all the unknown effects, in fact, are absorbed in the change in hydration.

Example:

Determine the mean molal activity coefficient for NaCl in a binary aqueous solution at molality m = 2,0 and temperature 25°C using the extended equation, Eq. (189).

In order to utilize Eq. (189), the following parameters (for NaCl) must be known or determined: h^o, r^o, q^o, μ, r, q, h, $\partial h/\partial m$ and $\partial q/\partial m$. Quantitative values of the parameters $\mathring{a}$, h^o, r^o and q^o for NaCl are listed in Table 4, as $\mathring{a} = 4{,}95$, $h^o = 2{,}40$, $r^o = q^o = \bar{V}^o/\bar{V}^o_w = 0{,}923$. The ionic strength, μ, of a 2M NaCl solution

Table 6.

Comparison of $\overset{\circ}{a}$ determined from Glueckauf and extended equations respectively (i.e. by fitting Eqs. (171 and 189) with observed data for $\gamma_{\pm}$) with $\overset{\circ}{a}_{min}$ (from Appendix 2A, Eq. (E)).

Salt	Glueckauf approach		Extended approach	
	$\overset{\circ}{a}$ From fit of Eq. (171)	$\overset{\circ}{a}_{min} = r_+^h + h_-^h$ Appendix 2A Eq. (E)	$\overset{\circ}{a}$ From fit of Eq. (189)	$\overset{\circ}{a}_{min} = r_+^h + r_-^h$ Appendix 2A Eq. (E)
$MgCl_2$	5,02	5,21	5,70	5,31
$CaCl_2$	4,85	5,11	5,65	5,08
$SrCl_2$	4,62	5,01	5,55	4,97
$BaCl_2$	4,43	4,72	5,23	4,80
HCl	4,50	4,92	5,60	4,81
LiCl	4,30	4,84	5,34	4,79
NaCl	4,10	4,23	4,95	4,16
KCl	3,96	3,71	4,35	3,67
RbCl	3,60	3,56	3,90	3,48
CsCl	3,20	3,50	3,46	3,50

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already has been determined in the example set out in Section 3.4.3 as $\mu = C_i = 1{,}926$.

The parameters r and q are determined from Eqs. (190 and 192) respectively,

$$r = \frac{1}{\bar{V}_w^\circ} (\Phi^\circ + 1{,}868 \sqrt{C_i} + 0{,}048\, C_i)$$

$$= 1{,}072$$

$$q = \frac{1}{\bar{V}^\circ_w} (\bar{V}^\circ + 1,5.1,868\sqrt{c} + 0,096\ c)$$

$$= 1,146$$

The parameters h and $\partial h/\partial m$ are determined from data listed in Table 4 as follows:

$$h = h^\circ - 0,00012\ m^2$$

$$= 2,3995$$

Differentiating the expression above with respect to m gives $\partial h/\partial m$,

$$\partial h/\partial m = -\ 2,4.10^{-4}.m$$

$$= -0,00048$$

To determine $\partial q/\partial m$, from Eq. (193)

$$\partial q/\partial m = \frac{1}{\bar{V}^\circ_w} \left(\frac{0,75\ S_v}{\sqrt{c}} + 2b_i\right) \qquad (196)$$

and, from Table 4, $S_v = 1,868$ and $b_i = 0,048$, i.e.

$$\partial q/\partial m = 0,0614$$

Substituting the values above for å, h°, r°, q°, μ, r, q, h, $\partial h/\partial m$ and $\partial q/\partial m$ in Eq. (189) and putting d = 2 and m = 2 gives $\gamma_\pm$ (NaCl) = 0,669.

6.5.2 *Single ion activity coefficients*

It was shown in Section 6.4.2 that because of the additive nature of partial molal volumes and hydration numbers, Glueckauf's equation, Eq. (171) can be decomposed to give equations for the activity coefficients of single ion species in binary systems. The extended equation, Eq. (189), is similar to Glueckauf's equation except that it contains six extra terms to account for the effects of change in partial molal volume and hydration number with salt concentration, but each of these terms also can be decomposed into the ionic components. Consequently, the approach in formulating

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the equations for single ion activity coefficients using the extended equation can follow on lines similar to that for decomposing Glueckauf's equation. The approach is first to formulate an equation for the mean activity coefficient of a salt in a mixed system of non-associated salts, see Chapter 3, i.e. the mean activity coefficient of salt 'j' in an aqueous solution containing 'i' salt types:

$$
\begin{aligned}
\ln\gamma_{j\pm} = {} & \ln\gamma_{j\pm}^{DH} + \frac{0{,}018q_jA'}{d_jB''} + \frac{(h_j - d_j)}{d_j}\ln B' - \frac{h_j}{d_j}\ln C' \\
& + (h_j^{\circ} - h_j - \sum_i m_i \frac{\partial h_i}{\partial m_j})\frac{\bar{G}^{\circ\prime}_{fw}}{d_j} - (h_j - h_j^{\circ})/d_j - (q_j - q_j^{\circ})/d \\
& + \ln\{(q_j + h_j)/(q_j^{\circ} + h_j^{\circ})\} - \frac{1}{d_j}\sum_i m_i . \frac{\partial h_i}{\partial m_j}\{X\} - \frac{1}{d_j}\sum_i m_i \frac{\partial q_i}{\partial m_j}\{Y\}
\end{aligned}
\tag{197a}
$$

where

$$A' = \sum_i m_iq_i + \sum_i m_ih_i - \sum_i m_id_i$$

$$B'' = (1 + 0{,}018 \sum_i m_iq_i)$$

$$B' = (1 + 0{,}018 \sum_i m_ir_i)$$

$$C' = (1 - 0{,}018 \sum_i m_ih_i)$$

$$X = \{\frac{q_i + h_i - d_i}{q_i + h_i} + C'/B'\}$$

$$Y = \{1 - (0{,}018\ A'/B'') - d_i/(q_i + h_i)\}$$

$$\bar{G}^{\circ\prime}_{fw} = \bar{G}^{\circ}_{fw}/RT = 30 \text{ (by convention)}$$

To decompose this equation, first multiply by d_j. The terms on the left hand side of the equation then becomes

$$d_j\ln\gamma_{j\pm} = d_j\ln(\gamma_{j+}^{d_+}\ \gamma_{j-}^{d_-})^{1/d_j}$$

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$$= d_{j+} ln\, \gamma_{j+} + d_{j-} ln\, \gamma_{j-} \qquad (197b)$$

On the right hand side of Eq. (197a), the first four terms are decomposed in exactly the same fashion as in Eq. (174); the remaining problem involves decomposing the term $d_j ln(q_j + h_j)/q_j^o + h_j^o$ and the parameters $\partial h_i/\partial m_j$ and $\partial q_i/\partial m_j$.

Considering the term $d_j ln(q_j + h_j/q_j^o + h_j^o)$: From Eq. (197a), this term can be written as the ratio of the hydrated partial molal volume of salt j at finite dilution to its value at infinite dilution, i.e.

$$d_j ln \frac{q_j + h_j}{q_j^o - h_j^o} = d_j ln \frac{\bar{V}_{hj}}{\bar{V}^o_{hj}} = d_j ln\bar{V}_{hj} - d_j ln\bar{V}^o_{hj} \qquad (198a)$$

i.e.

$$d_j ln\bar{V}_{hj} - d_j ln\bar{V}^o_{hj} = d_j ln[(d_{j+}\bar{V}_{hj+} + d_{j-}\bar{V}_{hj-})/d_j]$$
$$- d_j ln[(d_{j+}\bar{V}^o_{hj+} + d_{j-}\bar{V}^o_{hj-})/d_j] \qquad (198b)$$

Now, in Eq. (198b), because the hydrated partial molal volumes are all positive and not greatly different in value, the arithmetic mean of $\bar{V}_{h+}$ and $\bar{V}_{h-}$ will be very close to the geometric mean. Utilizing this assumption in the right hand side of Eq. (198b)

$$\text{RHS} = d_j ln[\bar{V}_{hj+}^{d_{j+}} \cdot \bar{V}_{hj-}^{d_{j-}}]^{1/d_j} - d_j ln[\bar{V}^{o\,d_{j+}}_{hj+} \cdot \bar{V}^{o\,d_{j-}}_{hj-}]^{1/d_j}$$

$$= ln[\bar{V}_{hj+}^{d_{j+}}/\bar{V}^{o\,d_{j+}}_{hj+}] + ln[\bar{V}_{hj-}^{d_{j-}}/\bar{V}^{o\,d_{j-}}_{hj-}]$$

$$= d_{j+} ln[\frac{q_{j+} + h_{j+}}{q^o_{j+} + h^o_{j+}}] + d_{j-} ln[\frac{q_{j-} + h_{j-}}{q^o_{j-} + h^o_{j-}}] \qquad (198c)$$

i.e.

$$d_j ln[\frac{q_j + h_j}{q^o_j + h^o_j}] = d_{j+} ln[\frac{q_{j+} + h_{j+}}{q^o_{j+} + h^o_{j+}}] + d_{j-} ln[\frac{q_{j-} + h_{j-}}{q^o_{j-} + h^o_{j-}}] \qquad (199)$$

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For the decomposition of the parameter $\partial h_i/\partial m_j$:

$$\frac{\partial h_i}{\partial m_j} = \frac{\partial h_i}{\partial m_{j+}}\frac{\partial m_{j+}}{\partial m_j} + \frac{\partial h_i}{\partial m_{j-}}\frac{\partial m_{j-}}{\partial m_j} \qquad (200)$$

and, noting that $m_{j+} = d_{j+}m_j$ and $m_{j-} = d_{j-}m_j$

$$\frac{dm_{j+}}{dm_j} = d_{j+} \ ; \quad \frac{dm_{j-}}{dm_j} = d_{j-} \qquad (201)$$

Substituting Eq.(201) into Eq.(200) gives the required results,i.e.

$$\frac{\partial h_i}{\partial m_j} = d_{j+}\frac{\partial h_i}{\partial m_{j+}} + d_{j-}\frac{\partial h_i}{\partial m_{j-}} \qquad (202)$$

For the decomposition of the parameter $\partial q_i/\partial m_j$:
A similar approach to that utilized above in decomposing the parameter $\partial h_i/\partial m_j$ gives,

$$\frac{\partial q_i}{\partial m_j} = d_{j+}\frac{\partial q_i}{\partial m_{j+}} + d_{j-}\frac{\partial q_i}{\partial m_{j-}} \qquad (203)$$

Equations for single ion activity coefficients can now be formulated as follows: Multiply Eq. (197a) by d_j; substitute for the Debye-Hückel term, $d_j \ln\gamma^{DH}_{j+}$, from Eq. (176); apply additivity to the hydration number, h_j, and partial molal volume parameter, q_j, in the second to seventh terms on the right hand side of the equation; substitute for the terms $d_j \ln[(q_i + h_j)/(q^o_j + h^o_j)]$, $\partial h_i/\partial m_j$ and $\partial q_i/\partial m_j$ from Eqs. (199, 202 and 203) respectively; i.e.

$$\begin{aligned} d_j \ln\gamma_{j\pm} = d_{j+}[\ &\ln\gamma^{DH}_{j+} + \frac{0{,}018\ q_{j+}A'}{B''} + (h_{j+} - 1)\ln B' - h_{j+}\ln C' \\ &+ (h^o_{j+} - h_{j+} - \sum_i m_i \frac{\partial h_i}{\partial m_{j+}})\bar{G}^{o\prime}_{fw} - (h_{j+} - h^o_{j+}) - (q_{j+} - q^o_{j+}) \\ &+ \ln\{(q_{j+} + h_{j+})/(q^o_{j+} + h^o_{j+})\} - \sum_i m_i \frac{\partial h_i}{\partial m_{j+}}\{X\} - \sum_i m_i \frac{\partial q_i}{\partial m_{j+}}\{Y\}] \end{aligned}$$

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$$+ d_{j-}[\ln\gamma_{j-}^{DH} + \frac{0{,}018\ q_{j-}A'}{B''} + (h_{j-} - 1)\ln B' - h_{j-}\ln C'$$

$$+ (h^{o}_{j-} - h_{j-} - \sum_{i} m_{i} \frac{\partial h_{i}}{\partial m_{j-}})\bar{G}^{o\prime}_{fw} - (h_{j-} - h^{o}_{j-}) - (q_{j-} - q^{o}_{j-})$$

$$+ \ln\{(q_{j-} + h_{j-})/(q^{o}_{j-} + h^{o}_{j-})\} - \sum_{i} m_{i} \frac{\partial h_{i}}{\partial m_{j-}}\{X\} - \sum_{i} m_{i} \frac{\partial q_{i}}{\partial m_{j-}}\{Y\}]$$

(204)

Comparing the right hand sides of Eqs. (197b and 204), the equations for single ion activity coefficients γ_{j+} and γ_{j-} for the component ions of salt 'j' in a *binary system* can be written,

$$\ln\gamma_{j\#} = \ln\gamma_{j\#}^{DH} + \frac{0{,}018\ q_{j\#}A'}{B''} + (h_{j\#} - 1)\ln B' - h_{j\#}\ln C'$$

$$+ (h^{o}_{j\#} - h_{j\#} - m_{j} \frac{\partial h_{j}}{\partial m_{j\#}})\bar{G}^{o\prime}_{fw} - (h_{j\#} - h^{o}_{j\#}) - (q_{j\#} - q^{o}_{j\#})$$

$$+ \ln\{(q_{j\#} + h_{j\#})/(q^{o}_{j\#} + h^{o}_{j\#})\} - m_{j} \frac{\partial h_{j}}{\partial m_{j\#}}\{X\} - m_{j} \frac{\partial q_{j}}{\partial m_{j\#}}\{Y\}$$

(205)

where

$$\ln\gamma_{j\#}^{DH} = \frac{-\ 2{,}303\ z_{\#}^{2}\ A\sqrt{\mu}}{1 + B\mathring{a}\sqrt{\mu}} \qquad (206)$$

and

j# = either j+ or j-

By means of Eq. (205) single ion activity coefficients in binary systems can be determined provided that values for the following parameters are known or can be calculated:

(i) the distance of closest approach parameter, å, and values for the parameters h_j, r_j and q_j;

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(ii) single ion partial molal volume parameters at infinite dilution, q^{o}_{j+} and q^{o}_{j-}, and finite dilution, q_{j+} and q_{j-};

(iii) the changes in the salt partial molal volume parameter q_i with ionic species concentration, i.e. $\partial q_i/\partial m_{j-}$ and $\partial q_i/\partial m_{j+}$;

(iv) single ion hydration numbers at infinite dilution, h^{o}_{j+} and h^{o}_{j-}, and finite dilution, h_{j+} and h_{j-};

(v) the change in the salt hydration number, h_j, with ionic species concentration, $\partial h_j/\partial m_{j+}$ and $\partial h_j/\partial m_{j-}$.

(i) *Parameters $\mathring{a}$, h_j, r_j and q_j*

The distance of closest approach parameter for salt 'j', $\mathring{a}$, is obtained from the fit of Eq. (189) for $\gamma_\pm$ of the salt to observed data, see Table 4; values of h_j, r_j and q_j of salt 'j' are determined from data listed in Table 4.

(ii) Single ion partial molal volumes at infinite and finite dilutions

Estimation of single ion partial molal volumes at infinite dilution was discussed in detail earlier in this chapter, Section 3.5.2, and values for ions of common interest are listed in Table 2(b). Estimation of values for single ion partial molal volumes at finite dilution are determined using Eqs. (74b and 75), i.e. putting q_j equal to $\bar{V}_j/\bar{V}^{o}_{w}$ in Eq. (74b)

$$q_{j-} = \frac{1}{18}\left(\bar{V}^{o}_{j-} + \frac{z_{j-}^{2}\,2^{1/2}\sqrt{\mu}}{1 + B\mathring{a}\sqrt{\mu}} + \frac{1}{2}\,z_{j-}^{2}\cdot 2{,}1\cdot C_j\right) \qquad (206)$$

and, for the cation species, putting $q_j = \bar{V}_j/\bar{V}^{o}_{w}$ in Eq. (75)

$$q_{j+} = (q_j - d_{j-}q_{j-})/d_{j+}.$$

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(iii) *Change in salt partial molal volume with ionic species molalities, i.e. $\partial q_j/\partial m_{j-}$ and $\partial q_j/\partial m_{j+}$*

In binary systems the changes in partial molal volume of salt 'j' with anion and cation molalities, i.e. $\partial q_j/\partial m_{j-}$ and $\partial q_j/\partial m_{j+}$ respectively, are determined by differentiating the relationship for q_j in terms of ionic strength, i.e. for $\partial q_j/\partial m_{j-}$

$$\frac{\partial q_j}{\partial m_{j-}} = \frac{\partial q_j}{\partial \mu} \cdot \frac{\partial \mu}{\partial c_{j-}} \cdot \frac{\partial c_{j-}}{\partial m_{j-}} \tag{207}$$

where c_j and m_j = molarity and molality of species j respectively. Assuming in Eq. (207) that $dc_{j-}/dm_{j-} = 1$ (see Eq. 191) and putting $\partial\mu/\partial c_{j-} = \frac{1}{2} z^2_{j-}$ gives

$$\frac{\partial q_j}{\partial m_{j-}} \simeq \frac{1}{2} z^2_{j-} \frac{\partial q_j}{\partial \mu} \tag{208}$$

An equation for q_j in terms of ionic strength is obtained from either the Redlich-Meyer equation, Eq. (43), or the Masson equation, Eq. (38), depending on the form in which experimental data for partial molal volume (or apparent partial molal volume) is listed. If formulated in terms of the Redlich-Meyer equation, then from Eq. (192)

$$q_j = \frac{1}{18} \{\bar{V}^{\circ}_j + (d_{j+} z^2_{j+} + d_{j-} z^2_{j-})\, 2^{1/2} \sqrt{\mu} + \frac{4b_j \mu}{(d_{j+} z^2_{j+} + d_{j-} z^2_{j-})}\} \tag{209a}$$

or, if formulated in terms of the Masson equation

$$q_j = \frac{1}{18} \{\bar{V}^{\circ}_j + \frac{1{,}5\, S^*_v \,.\, 2^{1/2}\sqrt{\mu}}{(d_{j+} z^2_{j+} + d_{j-} z^2_{j-})^{1/2}}\} \tag{209b}$$

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(iv) *Single ion hydration numbers at infinite and finite dilution*

From the extended approach, single ion hydration numbers at infinite dilution are determined using the plot of salt hydration versus cation Pauling radius for the alkali halide salts, Figure 5, and applying the same arguments as set out for the Glueckauf approach in Section 6.4.1, i.e. because for any particular cation the hydration numbers for Cl^-, Br^- and I^- salts are closely equal, and because the anions have very different Pauling radii, the only rational conclusion is that

$$h^o_{Cl^-} = h^o_{Br^-} = h^o_{I^-} = \text{zero.}$$

Accepting that the chloride ion has a hydration number equal to zero, one can calculate the cation hydration numbers at infinite dilution using the additivity principle; for example, the hydration number for the magnesium ion is given by

$$h^o_{MgCl_2} = h^o_{Mg^{++}} + 2h^o_{Cl^-}$$

$$= h^o_{Mg^{++}}(+ 0).$$

Single ion hydration numbers for the alkali and alkaline earth species and H^+ were determined using $h^o_{Cl^-} = 0$ as a basis and are listed in Table 7. Very similar results, differing at the most by 0,2, can be calculated using as a basis either $h^o_{Br^-} = 0$ or $h^o_{I^-} = 0$.

In the hydration numbers of single ion species at finite dilutions, one again commences with the chloride ion. At infinite dilution the hydration number of Cl^- is accepted as zero, hence at finite dilution, because the hydration number always decreases with concentration increase, the hydration number for the chloride ion must remain equal to zero. Consequently, with increase in salt

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Table 7.
Single ion hydration numbers at infinite dilution, determined from salt hydration numbers from the extended equation, Eq. (189), and assuming $h^{\circ}_{Cl^-} = 0$.

Ionic species	h°
H^+	4,09
Li^+	4,20
Na^+	2,40
K^+	1,01
Rb^+	0,60
Cs^+	0,2
Mg^{++}	8,12
Ca^{++}	7,05
Sr^{++}	6,43
Ba^{++}	5,00

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concentration the change in hydration number for the salt is due only to the change in the hydration number of the cation.Applying additivity to the hydration number for the salt species 'j'

$$h_j = d_+h_{j+} + d_-h_{j-}$$
$$= d_+h_{j+} \ (+\ 0) \tag{210}$$

Equating Eq. (210) and Eq. (194), and solving for h_{j+}

$$h_{j+} = (h^{\circ}_j - y_jm^{x_j})/d_{j+}$$
$$= h^{\circ}_{j+} - y_jm^{x_j}/d_{j+} \tag{211}$$

(v) Change in salt hydration number with ionic species molality $\partial h_j/\partial m_{j+}$ *and* $\partial h_j/\partial m_{j-}$

In order to formulate expressions for the parameters $\partial h_j/\partial m_{j+}$ and $\partial h_j/\partial m_{j-}$, Eq. (202) expresses the change in hydration number of salt 'j' in terms of the molality of salt 'j', hence

$$\frac{\partial h_j}{\partial m_j} = d_{j+} \cdot \frac{\partial h_j}{\partial m_{j+}} + d_{j-} \cdot \frac{\partial h_j}{\partial m_{j-}} \tag{212}$$

In Eq. (212), j- refers to Cl^- which is assumed to have zero primary hydration. Now, because we hypothesize that the change in hydration number with salt molality arises from a competition for free water molecules, the effect of an ionic species with zero primary hydration will not cause a change in the salt hydration number, i.e. $\partial h_j/\partial m_{j-} = 0$ and solving for $(\partial h_j/\partial m_{j+})$ in Eq. (212) and substituting for $(\partial h_j/\partial m_j)$ from Eq. (194)

$$\partial h_j/\partial m_{j+} = \frac{1}{d_{j+}} (h_j^{o} - y_j m^{x_j}) \tag{213}$$

Values for h_j^{o}, y_j and x_j for salt j are listed in Table 4.

Equation (205) and the assumption that Cl^- has zero primary hydration allows determination of the single ion activity coefficients for binary unassociated chloride solutions. These are listed in Table 8(a) and 8(b). For comparison, also listed in those tables are the single ion activity coefficients calculated by Bates *et al.* (1970) based on the Stokes-Robinson approach, see Section 6.3.2, and single ion activity coefficients determined by us using our decomposition of the Glueckauf equation, see Section 6.4.2.

Comparing single ion activity coefficients predicted from the extended approach, Eq. (205), with those from the decomposed Glueckauf equation, Eq. (179), and those predicted by Bates *et al.*: For

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1-1 salts, within the ionic strength region where all three approaches give a satisfactory fit of $\gamma_{\pm}$ against observed $\gamma_{\pm}$ data, all the approaches give closely the same result. However, for 1-2 salts, even in the range where $\gamma_{\pm}$ fits are close to observed data, the Bates - Stokes-Robinson values for the single ion activities differ significantly from those using the Glueckauf and extended approaches. The latter two again give results closely equal in the ionic strength region where the Glueckauf equation fits the observed $\gamma_{\pm}$ values.

It is difficult to assess *ab initio* which of the three approaches above give the best predictions of single ion activity coefficients. However, considering the basic inconsistency in the Stokes-Robinson approach for mean activity coefficients, i.e. $h_{XCl} < h_{XBr} < h_{XI}$, the single ion values given by the extended and Glueckauf approaches are probably more reliable.

A comment on the extended approach to single ion activities, this approach places the effects of change in hydration totally on the cation species (i.e. Cl^- is assumed to have zero primary hydration). Now as mentioned earlier, in Section 6.4.1, the change in hydration effect is modelled empirically - such that good fits are obtained between observed and calculated mean activity coefficients - but there is no surety that the change in hydration is the only effect to be considered. Consequently, by placing this effect (which causes an increase in the calculated value for activity coefficient) totally on the cation species, the values predicted for γ_+ will be maximum values.

Example:

Estimate the single ion activity coefficients γ_{Na^+} and γ_{Cl^-} in a 2 molal solution of NaCl at 25°C.

Assuming that Cl^- has zero primary hydration the equation for γ_{Cl^-} from Eq. (205) reduces to:

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$$\ln\gamma_{Cl^-} = \frac{-1,1706\, z_-^2\sqrt{\mu}}{1 + B\mathring{a}\sqrt{\mu}} + \frac{0,018\, q_-A'}{B''} - \ln B' - (q_- - q_-^o)$$

$$+ \ln(q_-/q_-^o) - m\,\frac{\partial q}{\partial m_-}\,\{Y\} \qquad (214)$$

where

$A' = m(q + h - d)$

$B'' = 1 + 0,018\ mq$

$B' = 1 + 0,018\ mr$

$Y = \{1 - (0,018A'/B'') - d/(q + h)\}$

Subscript '−' refers to Cl^-

No subscript refers to the salt value, i.e. m = molality of NaCl, etc.

In order to utilize Eq. (214), the following parameters (for NaCl and Cl^-) must be known or determined: $\mathring{a}$, q, r, h (for NaCl) and q_-^o, q_- (for Cl^-) and $\partial q/\partial m_-$. In Table 4, for NaCl $\mathring{a} = 4,95$. Quantitative values for the parameters q, r, h and μ for a 2 molal solution of NaCl already have been determined in the example set out in Section 6.5.1 as q = 1,146, r = 1,072, h = 2,3995 and μ = 1,926.

The parameters q_-^o and q_- are determined from Table 2(b) and Eq. (206) respectively, i.e. for q_-^o (equal to $\bar{V}_-^o/\bar{V}_w^o$) from Table 2(b)

$q_-^o = 25,2/18 = 1,40$

and for q_- from Eq. (206)

$$q_- = \frac{1}{18}\,(\bar{V}_-^o + \frac{z_-^2\ .\ 2^{1/2}\sqrt{\mu}}{1 + B\mathring{a}\sqrt{\mu}} + \frac{1}{2}\ .\ z_-^2\ .\ 2,1\ .\ C)$$

$$= 1,546.$$

The parameter $\partial q/\partial m_-$ is determined from Eqs. (208 and 209a) using values for the constant b in Eq. (209a) for NaCl from Table 4, i.e.

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$$\frac{\partial q}{\partial m_-} = \frac{z_-^2}{36} \cdot \frac{\partial}{\partial \mu} (\bar{V}^\circ + 2^{3/2}\sqrt{\mu} + 2b\mu)$$

$$= \frac{1}{36} (\frac{2^{1/2}}{\sqrt{\mu}} + 2b$$

$$= 0{,}031$$

Substituting for m, q, r, h, μ, q_-^o, q_- and q/ m_- as determined above in Eq. (214)

$$\gamma_{Cl^-} = 0{,}587$$

For γ_{Na^+},

$$\gamma_{Na^+} = \gamma^2_{NaCl\pm}/\gamma_{Cl^-}$$

$$= (0{,}669)^2/0{,}587$$

$$= 0{,}763.$$

7.1 Activity of the water component

The various factors giving rise to deviations from ideality of partial molal free energies of components in aqueous electrolyte solutions are listed in Section 6.1. All of these factors apply to both the solvent and solute components. Consequently, to formulate an equation for the activity of the solvent component an approach can be adopted which parallels that used for formulating equations for activity coefficients of solute species, see Section 6.1. Here again, because the input data to the system is in terms of the total moles of water to make up the solution, the parameter of interest to the user is the activity relative to the *total water component*, a_w, defined through Eq. (102) as

$$\bar{G}_w = \bar{G}_w^o + RT\ ln\ a_w \qquad (215)$$

where $\bar{G}_w$ = partial molal free energy (chemical potential) of the total water component,

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and, from Eq. (101) for a binary system containing n_i moles of salt species 'i'

$$\bar{G}_w = (\partial G/\partial n_w)_{n_i} \tag{216}$$

Consequently, if we can formulate an expression for G incorporating all the deviations from ideality, then on differentiating this expression in accordance with Eq. (216), the differential gives an equation for $\bar{G}_w$ that includes ideal and non ideal terms. Equating this differential with Eq. (215) gives the required expression for a_w.

In Section 6.1 a number of expressions for G were formulated using some or all of the factors listed that give rise to non-ideality of the solution. These equations for G each lead to a different equation for the mean ionic activity coefficient of the solute, $\gamma_\pm$, depending on which of the non ideal factors were considered, e.g. the low salinity equation Eq. (145), the Stokes-Robinson equation Eq. (158), the Glueckauf equation Eq. (171) or the extended equation Eq. (189). A similar approach can be adopted for the solvent component and leads to corresponding expressions for a_w, i.e. a low salinity equation, a Stokes-Robinson equation, a Glueckauf equation or an extended equation. However, because of the greater consistency attained with the extended approach than with the Stokes-Robinson and Glueckauf approaches for $\gamma_\pm$, only the extended approach is considered below in formulating an expression for a_w in non-associated binary electrolytes.

An equation for a_w is developed using the extended approach by differentiating first the expression for G, Eq. (180a), in accordance with Eq. (216) and then equating this differential to Eq. (215), i.e.

$$\left(\frac{\partial G}{\partial n_w}\right)_{n_i} = \bar{G}^o_{fw}\left(1 - n_i\frac{\partial h}{\partial n_w}\right) + RT\left[\frac{(n_i h\bar{V}_w + V - dn_i\bar{V}_w - n_w\bar{V}_w)}{V}\right.$$

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Table 8(a).

Single ion activity coefficients for 1-1 non associated chloride salts at 25°C, from Bates *et al.* designated (B-S-R); from the decomposed Glueckauf equation, Eq. (179), designated (Gl); from the extended approach, Eq. (206), designated (Ext).

(i) HCl

m	γ_{H^+}			γ_{Cl^-}		
	(B-S-R)	(Gl)	(Ext)	(B-S-R-)	(Gl)	(Ext)
0,1	0,807	0,810	0,807	0,785	0,782	0,785
0,5	0,812	0,829	0,823	0,706	0,691	0,696
1,0	0,940	0,977	0,974	0,697	0,670	0,672
2,0	1,421	1,511	1,522	0,717	0,674	0,669
3,0	2,357	2,481	2,528	0,735	0,698	0,685
4,0			4,373			0,710
5,0			7,66			0,74
6,0			13,29			0,78

(ii) LiCl

m	γ_{Li^+}			γ_{Cl^-}		
	(B-S-R)	(Gl)	(Ext)	(B-S-R)	(Gl)	(Ext)
0,1	0,799	0,801	0,797	0,781	0,779	0,783
0,5	0,786	0,801	0,787	0,695	0,682	0,694
1,0	0,882	0,910	0,895	0,680	0,658	0,669
2,0	1,233	1,293	1,276	0,688	0,656	0,665
3,0	1,893	1,986	1,962	0,706	0,673	0,681
4,0			3,248			0,702
5,0			5,54			0,737

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Table 8(a) (continued)

(iii) NaCl

m	γ_{Na^+}			γ_{Cl^-}		
	(B-S-R)	(Gl)	(Ext)	(B-S-R)	(Gl)	(Ext)
0,1	0,783	0,783	0,781	0,773	0,773	0,775
0,5	0,701	0,701	0,695	0,661	0,661	0,667
1,0	0,697	0,696	0,690	0,620	0,621	0,626
2,0	0,756	0,756	0,756	0,590	0,590	0,590
3,0	0,870	0,881	0,890	0,586	0,579	0,573
4,0	1,038	1,070	1,087	1,591	0,573	0,564
5,0	1,272		1,369	0,600		0,558
6,0	1,594		1,745	0,610		0,557

(iv) KCl

m	γ_{K^+}			γ_{Cl^-}		
	(B-S-R)	(Gl)	(Ext)	(B-S-R)	(Gl)	(Ext)
0,1	0,773	0,771	0,775	0,768	0,769	0,765
0,5	0,659	0,651	0,656	0,639	0,647	0,642
1,0	0,623	0,617	0,625	0,586	0,596	0,588
2,0	0,610	0,600	0,617	0,538	0,547	0,532
3,0	0,626	0,629	0,647	0,517	0,515	0,500
4,0	0,659	0,666	0,701	0,506	0,500	0,475
4,5			0,731			0,465

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Table 8(a) (continued)

(v) RbCl

m	γ_{Rb^+}			γ_{Cl^-}		
	(B-S-R)	(Gl)	(Ext)	(B-S-R)	(Gl)	(Ext)
0,1	0,766	0,766	0,768	0,762	0,762	0,760
0,5	0,640	0,636	0,641	0,628	0,632	0,627
1,0	0,594	0,591	0,596	0,572	0,575	0,570
2,0	0,568	0,573	0,590	0,525	0,520	0,505
3,0	0,569		0,614	0,505		0,468
4,0	0,584		0,658	0,496		0,440
5,0	0,606		0,713	0,492		0,418

$$+ \ln \frac{(n_w - n_i h)\bar{V}_w}{V} + \frac{\partial h}{\partial n_w} \{-n_i + \frac{dn_i \bar{V}_w}{\bar{V}_{hi}} - n_i \ln \frac{(n_w - n_i h)\bar{V}_w}{V}\}$$

$$+ \frac{\partial \bar{V}_i}{\partial n_w} \{\frac{dn_i}{\bar{V}_{hi}} - \frac{dn_i^2}{V} - \frac{n_i(n_w - n_i h)}{V}\}$$

$$+ \frac{\partial \bar{V}_w}{\partial n_w} \{\frac{dn_i h}{\bar{V}_{hi}} - \frac{dn_i n_w}{V} + \frac{(n_w - n_i h)n_w}{V}\} + (\frac{\partial G^{el}}{\partial n_w})_{n_i} \quad (217)$$

Converting to molality, i.e. putting $m = n_i/(0{,}018\ n_w)$,

$$(\partial h/\partial n_w)_{n_i} = \frac{h}{\partial m} \cdot \frac{\partial m}{\partial n_w} = -m\, \frac{\partial h}{\partial m}/n_w \quad (218a)$$

$$(\partial \bar{V}_i/\partial n_w)_{n_i} = -m\, \frac{\partial V_i}{\partial m}/n_w \quad (218b)$$

$$\frac{\bar{V}_w}{\partial n_w} = -m\, \frac{\partial \bar{V}_w}{\partial m}/n_w \quad (218c)$$

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Table 8(b)

Single ion activity coefficients for 1-2 non associated chloride salts at 25°C, from Bates *et al.* (1970) designated (B-S-R); from the decomposed Glueckauf equation, Eq. (179), designated (Gl); from the extended approach, Eq. (206), designated (Ext).

(i) $MgCl_2$

m	$\gamma_{Mg^{++}}$			γ_{Cl^-}		
	(B-S-R)	(Gl)	(Ext)	(B-S-R)	(Gl)	(Ext)
0,1	0,279	0,286	0,280	0,726	0,719	0,727
0,2	0,239	0,250	0,243	0,697	0,684	0,694
0,5	0,234	0,256	0,249	0,688	0,659	0,669
1,0	0,344	0,414	0,404	0,732	0,669	0,677
2,0	1,439	2,185	2,161	0,898	0,731	0,735

(ii) $CaCl_2$

m	$\gamma_{Ca^{++}}$			γ_{Cl^-}		
	(B-S-R)	(Gl)	(Ext)	(B-S-R)	(Gl)	(Ext)
0,1	0,269	0,272	0,266	0,719	0,715	0,723
0,2	0,224	0,229	0,222	0,685	0,678	0,689
0,5	0,204	0,216	0,208	0,665	0,645	0,658
1,0	0,263	0,300	0,290	0,690	0,646	0,657
2,0	0,768	1,043	1,029	0,804	0,690	0,695

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Table 8(b) (continued)

(iii) $SrCl_2$

m	$\gamma_{Sr^{++}}$			γ_{Cl^-}		
	(B-S-R)	(Gl)	(Ext)	(B-S-R)	(Gl)	(Ext)
0,1	0,266	0,263	0,258	0,717	0,712	0,719
0,2	0,218	0,218	0,211	0,681	0,673	0,683
0,5	0,190	0,196	0,189	0,653	0,636	0,649
1,0	0,226	0,247	0,237	0,667	0,630	0,643
2,0	0,542	0,693	0,670	0,753	0,659	0,670

(iv) $BaCl_2$

	$\gamma_{Ba^{++}}$			γ_{Cl^-}		
	(B-S-R)	(Gl)	(Ext)	(B-S-R)	(Gl)	(Ext)
0,1	0,259	0,252	0,247	0,712	0,704	0,711
0,2	0,204	0,199	0,194	0,668	0,662	0,671
0,5	0,165	0,164	0,158	0,630	0,618	0,629
1,0	0,167	0,171	0,165	0,602	0,601	0,611
1,8	0,229	0,247	0,243	0,642	0,606	0,610

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Substitute for $\partial h_i/\partial n_w$, $\partial \bar{V}_i/\partial n_w$ and $\partial \bar{V}_w/\partial n_w$ from Eqs. (218a to 218c) into Eq. (217), neglect the term involving $\partial \bar{V}_w/\partial m$ (see Section 6.5.1), put $q = \bar{V}_i/\bar{V}^o_w$ and $m = n_i/(0,018\ n_w)$ in Eq. (217) and simplify

$$\bar{G}_w = \bar{G}^o_{fw}(1 + 0,018\ m_i^2 \frac{\partial h}{\partial m_i}) + RT[\frac{0,018\ m_i(h + q - d)}{1 + 0,018\ mq}$$

$$+ \, ln \, (\frac{1 - 0{,}018 \, mh}{- + 0{,}018 \, mq}) - 0{,}018 \, m^2 \, \frac{\partial h}{\partial m} \, \{ \frac{d}{q+h} - 1 - ln \, (\frac{1 - 0{,}018 \, mh}{1 + 0{,}018 \, mq}) \}$$

$$- \, 0{,}018 \, m^2 \, \frac{\partial q}{\partial m} \, \{ \frac{d}{q+h} - \frac{1 + 0{,}018 \, m \, (d-h)}{1 + 0{,}018 \, mq} \} + (\frac{\partial G^{el}}{\partial n_w})_{n_i} \qquad (219)$$

An equation for a_w is now formulated by equating Eq. (219) to the equation defining a_w, Eq. (215), and rearranging terms, i.e.

$$RT \, ln a_w = \{ \bar{G}^{o}_{fw} - \bar{G}^{o}_{w} + 0{,}018 \, m^2 \, \frac{h}{m} \, . \, \bar{G}^{o}_{fw} \} + RT \, [\text{corresponding terms on the right hand side of Eq.(219)}] + (\frac{\partial G^{el}}{\partial n_w})_{n_i} \qquad (220)$$

The constants in the first term on the right hand side of Eq.(220) are determined by considering the system at infinite dilution, i.e. $m \rightarrow 0$.

For $m = 0$, $ln a_w = 0$ and $(\partial G^{el}/\partial n_w) = 0$, and Eq. (220) reduces to

$$\bar{G}^{o}_{fw} = \bar{G}^{o}_{w}$$

Making this substitution in Eq. (220) and rearranging terms, for finite dilution

$$ln a_w = \frac{1}{RT} \, (\frac{\partial G^{el}}{\partial n_w})_{n_i} + \frac{0{,}018 \, m \, (h + q - d)}{1 + 0{,}018 \, mq} + ln \, (\frac{1 - 0{,}018 \, mh}{1 + 0{,}018 \, mq})$$

$$+ \, 0{,}018 \, m^2 \, \frac{\partial h}{\partial m} \, \{ 1 + \bar{G}^{o\prime}_{fw} - \frac{d}{q+h} + ln \, (\frac{1 - 0{,}018 \, mh}{1 + 0{,}018 \, mq}) \}$$

$$+ \, 0{,}018 \, m^2 \, \frac{\partial q}{\partial m} \, \{ \frac{1 - 0{,}018 \, m \, (h - d)}{1 + 0{,}018 \, mq} - \frac{d}{q+h} \} \qquad (221)$$

Where $\bar{G}^{o\prime}_{fw} = \bar{G}^{o}_{fw}/RT = 30$ at 25°C (by convention, see Section 6.5.1).

The electrostatic term on the right hand side of Eq. (221) is reduced as follows:

From Glueckauf (1957), in the region $\mu < 6$ one can accept

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$$\frac{1}{RT}\left(\frac{\partial G^{el}}{\partial n_w}\right)_{n_i} \simeq \frac{1}{RT}\left(\frac{\partial G^{el}}{\partial n_{fw}}\right)_{n_i}$$

Utilizing this assumption and the explicit solution of Fowler and Guggenheim (1939) for $(\partial G^{el}/\partial n_{fw})_{n_i}$ then

$$\frac{1}{RT}\left(\frac{\partial G^{el}}{\partial n_w}\right)_{n_i} = 2{,}303\ A.\frac{2}{3000}\ \mu^{3/2}\ \bar{V}_w\ \sigma(x) \qquad (222)$$

where

$$\sigma(x) = \frac{3}{x^3}\{(1 + x) - (1 + x)^{-1} - 2ln\ (1 + x)\}$$

$$x = B\mathring{a}\mu^{1/2}$$

The activity of the water component in binary electrolyte systems can be determined directly from Eq. (221) using data listed in Table 4 for the values of $\mathring{a}$, h, q, $\partial q/\partial m$ and $\partial h/\partial m$ for the salt component in the system.

Example:

Determine the activity of water a_w using the extended equation for a 2 molal NaCl aqueous solution at 25°C.

To determine a_w using Eq. (221) first values must be known or determined for the parameters $\mathring{a}$, μ, q, $\partial q/\partial m$, h and $\partial h/\partial m$. From Table 4 for NaCl, $\mathring{a} = 4{,}95$; from the example set out in Section 6.5.1, $\mu = 1{,}926$, $q = 1{,}146$, $\partial q/\partial m = 0{,}0614$, $h = 2{,}3995$ and $\partial h/\partial m = -0{,}00048$. Substituting these values into Eq. (221) and putting $\bar{G}^o_{fw}/RT = 30$ (by convention)

$$\frac{1}{RT}\left(\frac{\partial G^{el}}{\partial n_w}\right)_{n_i} = 0{,}0058$$

$$\frac{0{,}018\ m(h+q-d)}{1 + 0{,}018\ mq} = 0{,}0536$$

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$$ln\ (\frac{1 - 0{,}018\ mh}{1 + 0{,}018\ mq}) = - 0{,}1309$$

$$0{,}018\ m^2\ \frac{\partial h}{\partial m}\ .\ \{X\} = - 0{,}0010$$

$$0{,}018\ m^2\ \frac{\partial q}{\partial m}\ .\ \{Y\} = 0{,}0017$$

i.e. $ln a_w = - 0{,}0708$

and $a_w = 0{,}9317$

This value is in agreement with the experimentally determined value for a_w in 2 molal NaCl solution reported by Robinson and Stokes (1955)* i.e. $a_w = 0{,}9317$.

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* Data reported by Robinson and Stokes for a_w for numerous binary electrolyte solutions is in terms of the osmotic coefficient Φ which is linked to a_w as follows:

$ln a_w = - 0{,}018\ dm\Phi$

where

d = moles of ions formed on dissociation of 1 mole of salt

m = molality of the salt

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Appendix 2A

Estimation of Minimum Radius of a Primary Hydrated Ion

A minimum value for the radius of primary hydrated ionic species is estimated using the theory of partial molal volumes, Section 3.4.1, and assuming all the primary hydrated water to be equally strongly bound about a central ion; the analysis is as follows:

The volume/mole of primary hydrated ionic species i, $\bar{V}^o_{PH_i}$, is the sum of the ionic crystal volume/mole, $\bar{V}^o_{X_i}$, and the volume/mole effect of primary hydrated water, $h_i\ \bar{V}^o_{hw_i}$, i.e.

$$\bar{V}^o_{PH_i} = \bar{V}^o_{x_i} + h_i\ \bar{V}^o_{hw_i} \tag{A}$$

In Eq. (A), $\bar{V}^o_{x_i}$ can be estimated from reported data for the Pauling crystal radius; the term $h_i\ \bar{V}^o_{hw_i}$ is estimated from the equation for partial molal volume of species i, Eq. (28), i.e.

$$h_i\ \bar{V}^o_{hw_i} = \bar{V}^o_i - \bar{V}_{INT_i} + h_i\ \bar{V}^o_w \tag{B}$$

and substituting for $h_i\ \bar{V}^o_{hw_i}$ from Eq. (B) into Eq. (A) gives

$$\bar{V}^o_{PH_i} = \bar{V}^o_{x_i} + \bar{V}^o_i - \bar{V}^o_{INT} + h_i\ \bar{V}^o_w \tag{C}$$

The intrinsic volume/mole, $\bar{V}_{INT_i}$, can be estimated from Eq. (58) i.e. $\bar{V}^o_{INT_i} = Ar^3_{x_i}$, and Eq. (C) becomes

$$\bar{V}^o_{PH_i} = \bar{V}^o_{x_i} + \bar{V}^o_i - Ar^3_{x_i} + h_i\ \bar{V}^o_w \tag{D}$$

The constant A in Eq. (D) is determined by assuming that Br^- and I^- have no primary hydration, see Section 3.5.2. Using this assumption:

$$\bar{V}^o_{I^-} = \bar{V}^o_{INT_{I^-}} = Ar^3_{I^-} = 43{,}4\ cm^3/mole$$

i.e.

$A = 4,33$

and, in general

$\bar{V}_{INT_i} = 4,33\ r_{x_i}^3$

where r_{x_i} = crystal radius in Ångstrom units.

The radius of the primary hydrated ion is then determined from Eq. (D) as:

$$4/_3\ \pi\ r_{h_i}^3 \ .\ 10^{24}\ .\ N = \bar{V}_i^o + h_i \bar{V}_w^o + (4/_3\ \pi\ r_{x_i}^3\ .\ 10^{24} N - 4,33\ r_{x_i}^3)$$

Putting $N = 0,607.10^{24}$ (i.e. Avogadro's number) and solving for r_{h_i}

$$r_{h_i} = \left\{\frac{\bar{V}_i^o + h_i \bar{V}_w^o + (2,52 - 4,33) r_{x_i}^3}{2,52}\right\}^{1/3} \qquad \text{(E)}$$

Appendix 2B

Ionic strength

Ionic strength, μ, is defined in terms of either the molality or molarity of ionic species in solution. In terms of molal units, for a solution containing i charged species (i.e. both free and ion paired charged species),

$$\mu = 0,5 \sum_i m_i\ z_i^2 \qquad \text{(F)}$$

where m_i = molality of the i^{th} charged species

z_i = charge on the i^{th} species.

In terms of molar units,

$$\mu = 0,5 \sum_i C_i\ z_i^2 \qquad \text{(G)}$$

where C_i = molarity of i^{th} charged species.

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Stoichiometric ionic strength, I, is defined in terms of either the *analytical* (i.e. stoichiometric) molality or molarity, m_{Ti} or C_{Ti} respectively. That is, in Eqs (F and G) m_i and C_i are replaced by m_{Ti} and C_{Ti} respectively.

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NON-ASSOCIATED MIXED SYSTEMS

1. INTRODUCTION

In this chapter the extended hydration theory for estimating mean and single ion activity coefficients for binary systems (Chapter 2) is extended further to provide estimates of these coefficients in non-associated mixed electrolytes, with one exception - ion pairing of the sulphate species in the electrolyte is included.

Historically the significant endeavours to determine *mean* activity coefficients, $\gamma_\pm$ in mixed systems are (i) the ionic strength principle of Lewis and Randall (1961), (ii) the specific interaction model of Brønsted (1922) and Guggenheim (1935), (iii) extension of the Stokes-Robinson hydration approach for binary systems to ternary systems.

The basic tenets of the approaches listed above will now be reviewed very briefly to indicate the difficulties associated with each and to bring to the fore the problems that have to be resolved in developing a general theory.

(i) Ionic strength principle approach

The ionic strength principle is based on the hypothesis that the mean activity coefficient of a salt in a mixed system has the same value as the mean activity coeffient of the pure salt in a binary system at the same ionic strength as the mixed system. This approach offers a very sinple means for estimating mean activity coefficients in mixed systems. It seems adequate for ionic strengths $\mu < 0{,}05$. For $\mu > 0{,}05$, comparisons of predicted and observed $\gamma_\pm$ values in ternary systems indicate that the approach becomes progressively more inaccurate as μ increases, Reilly, Wood and Robinson (1971).

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With regard to single ion activity coefficients, the ionic strength principle cannot be used directly to estimate these. Whenever single ion activities are to be determined some extra non thermodynamic assumption(s) needs to be made. In the ionic strength principle approach it has become customary to estimate single ion activities by using the MacInnes assumption that γ_{K^+} equals γ_{Cl^-}. By linking the MacInnes assumption to the ionic strength principle the further assumption is implied that γ_{Cl^-} has the same value in all solutions at the same ionic strength. In terms of the hydration theory both of these assumptions, i.e. that γ_{K^+} equals γ_{Cl^-} and, that γ_{Cl^-} has the same value in all solutions at the same ionic strength, appear to be tenuous.

(ii) <u>Brønsted-Guggenheim approach</u>

The specific interaction model of Brønsted and Guggenheim gives the log mean activity coefficient of a particular dissolved salt in a mixed electrolyte as the sum of two effects, (a) a general long range electrostatic effect expressed by the Debye-Hückel equation having a common $\mathring{a}$ value for all salts, and (b) a series of terms describing specific interaction effects between each of the ionic species of the dissolved salt in question with each of the ionic species of opposite charge in the total electrolyte (specific interactions between ions of like charge are not considered).

The equation of Brønsted and Guggenheim for the activity coefficient of salt MA in a mixed electrolyte system with k cation species and j anion species is

$$ln\gamma_{MA} = ln\gamma^{el} + \frac{\delta_A}{\delta_M+\delta_A}\sum_k \beta_{k,A}m_k + \frac{\delta_M}{\delta_M+\delta_A}\sum_j \beta_{M,j}m_j \qquad (1)$$

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where

δ_M, δ_A = moles of cation species M and anion species A formed on complete dissociation of one mole of salt MA and termed the stoichiometric number of cation M and anion A, respectively.

$\beta_{k,A}$ and $\beta_{M,j}$ = interaction constants between the anion of interest, species A, and each of the cation species k in solution, and, between the cation species of interest, species M, and each of the anion species j in solution.

Values for the interaction constants for each pair of anion and cation species of interest (i.e. $\beta_{k,A}$ and $\beta_{M,j}$ in Eq. 1) are determined using Eq. (2a) and the ionic strength principle. For example, for the interaction coefficient for the salt MC in a mixed system with stoichiometric ionic strength, I

$$\ln\gamma^{o}_{MC} = \ln\gamma^{el} + V_{MC}\beta_{MC}\; m'_{MC} \qquad (2a)$$

where

m'_{MC} = molality of salt species MC that gives stoichiometric ionic strength equal to that of the mixed electrolyte

γ^{o}_{MC} = mean activity coefficient of salt species MC in a binary system with a molality m'_{MC}

V_{MC} = harmonic mean of the stoichiometric numbers for cation and anion species of the salt MC, i.e. for a 1-1 salt $V_{MC} = 1$, for a 1-2 salt $V_{MC} = 4/3$ and for a 2-2 salt $V_{MC} = 2$.

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The value for γ^{o}_{MC} in Eq. (2a) is obtained from reported $\gamma_{\pm}$ data for a binary system of salt MC at a molality determined assuming the total ionic strength of the mixture, I, is made up only of salt MC. The value of the interaction constant $\beta_{M,C}$ is then determined by solving for this parameter in Eq. (2a), i.e.

$$\beta_{M,C} = ln(\gamma^{o}_{MC}/\gamma^{el})/(V_{MC}\cdot m'_{MC}) \qquad (2b)$$

The approach above has the merit of simplicity and only requires reported $\gamma_{\pm}$ data for binary systems to estimate $\gamma_{\pm}$ values for species in mixed systems. However, the theory cannot be used to model binary solution behaviour because the β value changes with salt molality and this change has to be determined from the binary salt data itself, i.e. β is an implicit function of the stoichiometric ionic strength. Comparison of observed $\gamma_{\pm}$ data in ternary systems, with $\gamma_{\pm}$ values predicted using the specific interaction theory, indicates that for most ternary systems the approach gives only an approximation to observed data, Robinson and Stokes (1955). In addition, if sulphate ions are present in high concentration a further difficulty arises: When $\gamma_{HCl}^{\pm}$ is to be determined and $SO_4^{=}$ comprises a significant part of the ionic matrix of the solution, the interaction effect between the H^{+} and $SO_4^{=}$ cannot be determined from $\gamma_{\pm}$ data for the H_2SO_4 binary system, as required by the theory. The reason for this is that in a binary aqueous solution of H_2SO_4 incomplete dissociation occurs and the system HSO_4^{-} - $SO_4^{=}$ forms a weak acid buffering system which is pH dependent - reported data for $\gamma_{H_2SO_4}^{\pm}$ are in fact pH dependent. Consequently, interaction effects between H^{+} and $SO_4^{=}$ for a mixed system at some pH (say pH = 7)

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cannot be estimated from reported data for H_2SO_4 in ternary systems, inevitably determined at some pH << 7.*

Considering estimation of single ion activity coefficients using the Brønsted-Guggenheim interaction model, the estimation forms an integral part of the theory, Whitfield (1973). However, when applied to aqueous binary systems comprised of symmetrical salts, the theory always gives $\gamma(\text{cation}) = \gamma(\text{anion})$ and this equality is not acceptable when judged in terms of the physical characteristics of the component ions for most salts. Inadequacy for binary symmetrical salt systems, the simplest of systems, implies inadequacy in the more complex mixed systems.

(iii) Extended interaction approach

Extensions to the Bronsted-Guggenheim approach for estimating mean activity coefficients in mixed systems have been proposed by numerous research workers. Probably the most widely accepted of these is that due to Pitzer (1973), Pitzer and Mayorga (1973, 1974) and Pitzer and Kim (1974). The basis of the approach is that deviations from ideality are assumed to arise due to (a) pairwise interactions between each of the cation and anion species in solution, (b) interactions between ionic species of like charges, (c) ternary interactions between three ions, and, (d) an electrostatic effect the value of which depends only on the

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* The problem of incorporating sulphate in conjunction with a trace concentration of H^+ into the activity coefficient theory is raised repeatedly in this chapter, its solution is crucial for estimation of $\gamma_{H^+}{}^{tr}$ in most high salinity waters and consequently a review of the theories requires *inter alia* an assessment of the capabilities of these theories to deal with this aspect.

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ionic strength and charges of the ions of the salt of interest (at some constant temperature and pressure). For binary solutions, only the effects of (a) and (d) need be considered; for mixed systems, all four effects should be considered although in the application of the approach to mixed systems where $\mu < 1,0$ many workers have neglected the effects of (b) and (c) above, Robinson and Bates (1979) and Whitfield (1975).

Application in mixed systems proceeds by first determining the interaction effects, (a) above, as follows: The mixed system is "broken down" into a set of binary salts from the combination of cations and anions in the mixed solution. For each of the binary salts, considered as a separate binary system, the Pitzer equation for $\gamma_{\pm}$ includes a term to account for interactions between the cation and anion of the salt under consideration. This interaction term is modelled as a semi-empirical function of ionic strength of the binary system, i.e. as an explicit function of ionic strength, and incorporates four constants. The values of the four constants are determined by fitting the equation for the binary salt against observed data. For most of the salts investigated by Pitzer and Mayorga their equation predicts $\gamma_{\pm}$ values accurately for binary systems up to a molality of at least 2,5 M. Two important exceptions are K_2SO_4 and $CaSO_4$ where the molality limits were 0,7 and 0,011 M respectively.

Pitzer and Mayorga (1973, 1974) list values for the constants for determining interactions between oppositely charged ions for numerous 1-1, 1-2, 2-1 and 2-2 salts, also the molal limits to the fits.

For mixed systems the constants developed above for binary systems are used in the Pitzer equation but at the stoichiometric ionic strength, I, of the mixed system. The Pitzer equation also includes terms to account for interactions between like ions and interactions between ternary ionic species (i.e. interactions between three ion species). The equation for $\gamma_{\pm}$ models the former effect using two constants for each interaction between a pair of like ions, and the latter effect using a single constant for each interaction between three ionic species. *Each of these constants is modelled as being independent of ionic strength and ionic matrix of the mixture.* Values for these constants can be determined only by fitting the Pitzer equation against observed $\gamma_{\pm}$ data for ternary systems.* Though the fitting procedure is rather complex, requiring a statistical fitting procedure, values for the various constants have to be determined only once. Consequently, a large bank of constants can be built up from observations on binary and ternary systems. This bank of information together with the Pitzer equation readily allows analyses of large matrices of salt mixtures, using a digital computer.

There is little information in the literature on application of the approach to quaternary and higher order aqueous-salt mixtures. Whitfield (1975) and Robinson and Bates (1979) have applied the approach to determination of mean activity coefficients of the principal ionic species in seawater, however in their

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* The inclusion of ternary data in the description of mixed systems constituted a major advance, as will become apparent later.

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analyses they neglect interactions between ions of like charge and treble ion interactions. Using this simplified approach the values determined for the mean activity coefficients differ insignificantly from the values determined using the Brønsted-Guggenheim approach.

For general application the Pitzer approach, although thermodynamically consistent, suffers from two major inadequacies: First, when estimating $\gamma_{HCl}^{\pm}$ in waters with high $SO_4^{=}$ content, the approach is subject to the same limitation as the original Brønsted-Guggenheim approach, as discussed previously. Second, with regard to single ion activity theory, the approach again gives rise to the unacceptable result that for a binary system of a symmetrical salt γ(cation) equals γ(anion).

(iv) Robinson and Stokes approach

Robinson and Stokes (1955),using the same approach as for binary systems, extended their theory to mixed systems. They expressed the total free energy of the systems in two ways, (a) in terms of hydrated species and free water and, (b) in terms of anhydrous species and total water, both on the mole fraction scale. They introduced the hydration number concept by expressing the moles of free water in (a) above as the total moles of water less the moles of water hydrated by each of the salt species. By equating these two expressions for the total free energy, they obtained equations for the mean activity coefficient of each of the salt species. Each of these equations contains a Debye-Hückel term, and a number of terms incorporating the hydration number and molality of each of the salt species. This

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approach is virtually identical to that in their treatment of binary systems. They tested the theory against observed data in ternary systems and concluded that usually the predictions are only approximate but generally, for a particular salt in a ternary system, the theory predicts the observed trend of the deviation of $\gamma_\pm$ from the $\gamma_\pm$ values determined using $\overset{o}{a}$ and h values for binary systems; the magnitude of the deviation however is not correctly given. For example, for the ternary system HCl-NaCl-H_2O, their theory predicts, as observed, that $\gamma_{HCl\pm}$ has a lower value in this system than in an aqueous binary system of HCl at an equivalent ionic strength, and the converse for $\gamma_{NaCl\pm}$. In this respect then the theory is superior to the ionic strength principle approach, but quantitatively it is still inadequate. The reason for the poor predictions arises from three sources: (a) use of mole fraction statistics in the formulation of the free energy of the system; this approach leads to inconsistencies in the hydration numbers, already discussed in Chapter 2, (b) assumption of a constant hydration number for a salt,also discussed in Chapter 2, and (c) acceptance that this hydration number remains the same within a mixed system. i.e. interaction effects are neglected. Indeed it was because of the inconsistencies within binary systems arising from (a) and (b) above that further attention had to be given to the binary theory, for example by Glueckauf (1955) (see Chapter 2).

The effects of (a) and (b) above were removed by redeveloping the Stokes-Robinson approach incorporating the modifications suggested by Glueckauf. However, this did not lead to any observable improvement in predictions of $\gamma_\pm$ for mixed systems so that it was concluded that the main cause for the inadequacy of the Stokes-Robinson approach is the neglect of interaction effects.

No extension of the Stokes-Robinson theory for the determination of single ion activity coefficients in mixed systems has been reported.

From the discussion above it would seem that the ionic strength principle and specific interaction approaches do not provide a basis for a satisfactory general method for estimating both mean and single ion activity coefficients. The hydration approach of Stokes-Robinson, with Glueckauf's modifications, is satisfactory for binary systems but not so for mixed systems principally because interaction effects are neglected.

In the hydration approach the interactive effects would be exhibited by changes in the hydration numbers and partial molal volumes of the salts. Experimental information on the magnitudes of such interactions cannot be obtained from binary systems so that *analyses of mixed systems must be based on data obtained from some form of mixed system; here the simplest is the ternary system.* A ternary system will supply essential information for the analysis of ternary systems, but again it cannot fully represent the interaction effects in say quaternary systems. The measure in which the ternary system fills the gap will, in the final assessment, depend on how closely the observed $\gamma_\pm$ values in higher systems are predicted utilizing the information found from ternary systems.

With regard to a framework in which the interaction effects can be incorporated in the hydration approach, in this monograph these effects will be analysed in terms of the extended hydration theory discussed in Chapter 2. In this theory both the hydration number and the partial molal volume of a salt are regarded as variables

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dependent on the concentration of the salt in solution. It is a relatively simple matter (in this approach) to reformulate the equation for the activity coefficient of a salt in a mixed system assuming the hydration numbers and partial molal volumes for each of the salts to be dependent not only on the concentration of the salt itself (as in binary systems) but also on the concentration of each of the other salts in the solution. Such an approach allows derivation of an equation for the mean activity of salt 'j', i.e. $\gamma_{j\pm}$ in a mixed system containing 'i' types of salts ($k = 1,2,....j, ...i$), see Eq. (16) of this chapter. This equation is similar in form to that for a binary system for salt 'j' but includes additional terms for describing the effects of (i) the hydration number and partial molal volume of each of the salts in the system on $\gamma_{j\pm}$, and (ii) the changes in the hydration numbers and partial molal volumes of each of the salts with addition of salt j, i.e. $m_k\, \partial h_k/\partial m_j$ and $m_k\, \partial \bar{V}_k/\partial m_j$ ($k = 1,2,3....j,....i$). The difficulty in this approach lies in estimating the magnitudes of these changes. Clearly estimates should be made from experimental data but the estimates will depend on how the effects are formulated. Two approaches to formulation were tested, i.e.

(i) The ionic strength principle applied to $\bar{V}_k$ and a ternary fit for h_j

(ii) Adjusted ionic strength principle applied to $\bar{V}_k$ and h_j.*

Each of these approaches will now be discussed briefly in order to assess their relative usefulness and to select the most appropriate one for application in Eq. (16).

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* Note that in the original application of the ionic strength principle, the principle is applied directly to $\gamma_{\pm}$. In the proposed approach for determining $\gamma_{\pm}$ the principle is applied to $\bar{V}$ and h.

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(i) The ionic strength principle applied to $\bar{V}_k$ and a ternary fit for h_j

To incorporate the volumetric effects of each of the salts in the mixed system into the equation for determining the mean activity coefficient of a particular salt (i.e. $\gamma_{j\pm}$) it is necessary to formulate: (a) an equation for the total volume of the system in terms of the partial molal volumes of each of the salts, and (b) an equation for the change in partial molal volume of the salt species in solution with addition of salt 'j', i.e. $\partial\bar{V}_k/\partial m_j$.

With regard to (a), Young's Rule gives an excellent approximation, Young and Smith (1954). Briefly, this rule is as follows:

The total volume of an aqueous system is estimated on the basis that the apparent partial molal volumes for each of the salts have values equal to those for pure binary systems at an ionic strength equal to that of the mixed system. Generally this rule gives a very good approximation to observed data, for example for mixtures of an aqueous ternary system of NaCl and $MgCl_2$ at a total ionic strength $\mu = 4$, predicted and observed volumes agreed to within 0,3 mℓ/kg water.

With regard to (b), the ionic strength principle applied to *partial molal volumes* is utilized. That is, it is assumed that the partial molal volume of a salt in a mixed system equals partial molal volume in a pure binary system of the salt at an ionic strength equivalent to that of the mixed system. For some systems (e.g. KCl, NaCl in water) the application of the ionic strength principle gives an excellent

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approximation while for others (e.g. NaCl, HCl in water) it gives only a first approximation, Wirth (1937, 1940). However, the values estimated for use in the extended hydration equation are not very sensitive to the values for $\bar{V}_k$ and $\partial\bar{V}_k/\partial m_j$. Consequently, use of the ionic strength principle for estimating deviations from ideality of partial molal volumes, though not exact, will have only a slight effect on the determination of $\gamma_{j\pm}$. Accepting these approximations the difference between the true deviations of partial molal volume and those estimated from the ionic strength principle are then incorporated in the adjustable parameters for the change in hydration number, $\partial n_k/\partial m_j$.

To incorporate the hydration effects of each of the salts in the mixed system into the equation for determining the mean activity coefficient of a particular salt (i.e. $\gamma_{j\pm}$), the hydration number of each of the salts in a mixed system are formulated using a method analogous to that in Chapter 2 for binary systems except that the hydration number of a salt now depends on the concentrations of each of the salts in solution. This dependence is formulated empirically for salt 'j' in a system made up of i salts, i.e. k = 1,2,....j,....i, as follows:

$$h_j = (h_j^o - k'_{1j} m_j^{\,k'_{2j}}) - \sum_k (k'_{3k} m_k - + k'_{4k} m_j^{\,k'_{5k}} . m_k)$$

where

k = 1,2,3 ....j-1, j+1, ...i

k'_{1j}, k'_{2j} are constants determined from binary systems of salt 'j'

k'_{3k}, k'_{4k}, k'_{5k} are constants determined from ternary systems of salt 'j' with salt 'k'.

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The first term is the same as that for a pure aqueous binary system of salt 'j' and the constants h_j^o, k'_{1j} and k'_{2j} are determined by fitting the theoretical equation for $\gamma_{j\pm}$ against observed data. In ternary systems, the constants k'_{3k}, k'_{4k} and k'_{5k} relate to the interactions of salt 'k' on salt 'j' and are determined by fitting the theoretical equation for $\gamma_{j\pm}$ to observed data for $\gamma_{j\pm}$ for the ternary system made up of salts 'j' and 'k' where k = 1,2, ...j ....i.

By using this approach the action of each of the salts on the salt in question can be determined readily from the observed data on the various ternary systems. In this way a bank of data can be accumulated of the specific effect of each of all the salts on any particular salt.

Application of the approach to ternary systems allows excellent agreement between observed and predicted values for $\gamma_{j\pm}$ up to an ionic strength of at least $\mu = 2$. For general validity comparison with quaternary systems needs to be made, but experimental information on these systems is too scarce to test the model adequately.

For single ion activities, the structure of the extended equation (for both binary and mixed systems) has the merit that it can be decomposed to give equations for single ion activity coefficients. This decomposition requires three non thermodynamic assumptions, (1) that the hydration number of the chloride ion is zero and therefore does not change with addition of salt species, (2) that $\overset{o}{a}$ for an ion now reflects the mean

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distance between that primary hydrated ion and all the primary hydrated ions of opposite charge weighted in proportion to their respective molalities, and (3) that the partial molal volume of the chloride ion at finite ionic strength can be estimated using the approach set out in Chapter 2, Eq. (74b). This approach for estimating mean and single ion activity coefficients in mixed systems has a number of deficiencies. Apart from the fact that it is time consuming to determine the constants in the equations for $m_k \partial h_k/\partial m_j$ by fitting calculated values for $\gamma_{j\pm}$ against observed data (using the appropriate ternary system), utilization of the ionic strength principle to determine $\bar{V}_i$ *constitutes only a first approximation and the error made here is lumped into the parameter* $\partial h_k/\partial m_j$. *Furthermore, in determining single ion activity coefficients the total effects of* $\partial h_k/\partial m_j$ *are placed on the cation species because* Cl^- *is assumed to have zero primary hydration;* for single ion activity coefficients this leads to an over-estimation of γ_{j+} and an underestimation of γ_{j-} to an indeterminate degree.

For these reasons the approach was abandoned even though it appears to be adequate at least up to $\mu = 2$. Evidently attention should be focussed on an approach that does not implicate the change in hydration as the sole specific interaction effect giving rise to the differences between observed and calculated values in ternary systems. An approach that avoids this problem is discussed in (ii) below.

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(ii) Adjusted ionic strength principle applied to $\bar{V}_k$ and h_k

If both $\bar{V}_k$ and h_k for salt k are determined from a binary system of this salt, and the ionic strength principle is applied to these two parameters when analysing mixed systems, $\gamma_{j\pm}$ can be calculated using the extended equation, Eq. (16). However, application to ternary systems indicates that the approach gives only an approximation to the observed $\gamma_{j\pm}$ data, although the predicted and observed values are quite close. This deviation arises because the values for $\bar{V}_k$ and h_k are obtained from binary systems - specific interaction effects affecting the values of $\bar{V}_k$ and h_k in the mixed systems in fact are neglected. However, two important general observations, when taken in conjunction, indicate an extension of the approach to incorporate interaction effects and thereby to accurately model observed $\gamma_\pm$ data in ternary systems. First, the method always gives the correct trends in the changes observed for $\gamma_{j\pm}$ for salt species 'j' between a binary solution containing salt species 'i' and 'j' and with the species 'j' at a trace concentration. Second, a plot of the logarithm of the calculated values for $\gamma_{j\pm}$ versus the molality of the second salt (or the ionic strength contribution of the second salt) is always closely linear for a solution with a fixed total ionic strength. Now this type of linear plot is noted also for the observed $\gamma_\pm$ data for ternary systems. Consequently, *the slight difference in slope between observed and calculated values can be ascribed to the specific interaction effects which are neglected in the calculated value for $\gamma_\pm$ if the ionic strength principle is used to determine $\bar{V}_k$ and h_k.* The approach adopted to solve this problem was to formulate an equation for $\gamma_{\pm}$ as the sum of two parts, (a) log $\gamma_{\pm}$ (calc), determined from binary data using the extended equation and the ionic strength principle for $\bar{V}_k$ and h_k, and (b) an interaction term, determined from the difference in slope between the plots of the calculated and observed values for log $\gamma_{\pm}$ versus the molality of the second salt, i.e.

$$\ln \gamma_{j\pm} = \ln \gamma_{j\pm}\ (\text{calc.}) + \beta_{ji} m_i$$

where

$\gamma_{j\pm}$ = the mean activity coefficient for salt 'j' in a mixture of salts 'i' and 'j'

$\gamma_{j\pm}$(calc) = calculated value for $\gamma_{j\pm}$ determined using the extended equation and the ionic strength principle for values for $\bar{V}_k$ and h_k

β_{ji} = a constant for some total ionic strength value of the solution.

The nature of this equation is such that extension to quaternary and higher systems can be readily accomplished provided one accepts that secondary interactions are negligible; in this event extension of the approach to multiple salt solutions should give a close description of the mean activity coefficients. This was indeed found to be the case for $\gamma_{HCl\pm}$ and $\gamma_{NaCl\pm}$ in the system H_2O-HCl-$NaCl$-$CaCl_2$-$MgCl_2$. Predicted and observed $\gamma_{\pm}$ values agree to within 0,002 activity coefficient units for the mixtures investigated. This approach showed so much promise that it was adopted as the basic one in the analyses and mixed systems and is discussed in detail later in this chapter.

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Effect of Ion Pairing

The discussion so far has been restricted to solutions in which ion pairing is assumed totally negligible. In natural highly saline waters the ionic matrices usually contain ionic species which form ion pairs in solution. Two categories of ion pairing (or ionic association)* are identified:

(a) Ionic association of species in *trace* concentrations: these are of vital importance in analyses of pH control and in the distribution of various trace elements in high salinity waters. However, their concentrations are so low that they have negligible effect on the matrix of the principal ionic species. The carbonate species which associate significantly with the cation species Mg^{2+}, Ca^{2+}, Na^{+} and K^{+}, is an example.

(b) Ionic association between *species constituting the principal ionic matrix;* ionic associations of this type effect implicitly the ionic concentrations of unassociated species, the ionic strength of the solution and the activities of all species. The ion implicated here is $SO_4^{=}$. Usually, highly saline waters contain sulphate ions at relatively high concentrations and this species associates significantly with the principal cationic species likely to be encountered in these waters, e.g. Na^{+}, K^{+}, Mg^{2+} and Ca^{2+}.

Ionic association of trace species, (a) above, will be considered in Chapter 4. However, ionic association occurring between species comprising a principal part of the ionic matrix, (b) above, in

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* The terms *ion pairing* and *ionic association* describe the same phenomenon. The term ionic association is preferable as the term ion pairing tends to be applied to 'ion pairs' *per se* whereas ionic association includes both 'ion pairs' and 'triple ions'.

particular association of the sulphate ion, needs to be considered in this chapter because of its effect on the matrix of principal species. It is possible to consider sulphate association prior to considering the association problem in its wider context because sulphate species are independent of pH for pH $\gtrsim 4$, the usual pH of terrestrial waters, whereas this is not so for the carbonate and bicarbonate ion pairs.

Occurrence of sulphate association is identified by fitting the theoretical equation for $\gamma_{\pm}$ (Eq.(18), Chapter 2) against observed $\gamma_{\pm}$ data for any of the sulphate salts; generally it is not possible to obtain a good fit for any of the sulphate salts except for Cs_2SO_4 for which an excellent fit is obtained up to the limit of reported data ($I^* = 5,4$). Lack of fit is ascribed to the effects of ionic association, consequently the excellent fit for Cs_2SO_4 is interpreted as indicating that no association occurs between Cs^+ and SO_4^{2-}. The conclusion that no association occurs in $CsSO_4$ solutions is important, for this affords a means by which it is possible to determine the hydration number and hydrated radius of SO_4^{2-}:

> By fitting Eq. (181) to the observed $\gamma_{\pm}$ data, the sum of the hydrated radii, $\mathring{a}$, and the hydration number, h, for Cs_2SO_4 are determined. Knowing the hydration number and hydrated radius of Cs^+, see Table 7, Chapter 2, and using the additivity principle the hydrated radius and hydration number for the free SO_4^{2-} species are obtained. Having this information on the free SO_4^{2-} species and knowing the hydration numbers and hydrated radii of the cation species Na^+, K^+, Mg^{2+} etc. (see Table 7 Chapter 2) using the additivity principle it

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* 'I' indicates the stoichiometric ionic strength which is based on the moles of salt/kg of water. See Appendix 2B to this Chapter for definitions.

is possible to determine directly h and $\overset{o}{a}$ for the *free* species of the salts Na_2SO_4, K_2SO_4, $MgSO_4$, etc.

Thus the fact that Cs_2SO_4 does not associate allows considerable information to be generated re the free ion species in solutions containing sulphates irrespective of whether association occurs between sulphate and cations other than Cs^+.

When ionic association is present in a binary system then, strictly speaking, the system is no longer a binary one and the binary approach is no longer valid. The magnitude of the concentration of associated species that form will be implicitly tied to the concentration of salt added to the solution but the formation of associated species makes it necessary to determine the free and associated species concentrations and their corresponding activity coefficients in the solution. One approach to resolving this problem is as follows:

- Accept that a 'binary system' containing associated species can be treated as if it is a mixed system made up of free and ion paired and treble ion species even though these concentrations are not explicitly known.

In this approach it is necessary to take account that sulphate ion pairs can be either charged or neutral depending on whether the salt added is *unsymmetrical* or *symmetrical* respectively; treble ion species invariably are neutral species. The analysis of these two systems needs to be treated separately for reasons that will become apparent below.

(1) Unsymmetrical sulphate salts: The analysis is based on the formation of both ion pair and treble ion species (e.g. for the 2-1 salt M_2SO_4, the charged ion pair MSO_4^- and the neutral treble ion $M_2SO_4^o$). For the purposes of analysis one requires (a) a means for determining the mean activity coefficients of the free ion

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species and the charged ion paired species respectively (i.e. $\gamma_{M_2SO_4}{}^{\pm}$ and $\gamma_{M^+,MSO_4^-}{}^{\pm}$), and (b) the equilibrium constants for both the ion paired and treble ion species.

(a) Mean activity coefficients: The basis for determination of the mean activity coefficients for free species in solution in which ion pairing is as follows: It will be shown, below, that Cs_2SO_4 does not form ion pairs, neither does CsCl (see Section 6, Chapter 2). Consequently, it is possible to form a first estimate theoretically of the $\gamma_{\pm}$ values for Cs_2SO_4 and CsCl (with Cs^+ at a trace concentration) in any solution by using the non associated theory, i.e. assuming no ion pairing. (In (b) below, we show how to determine the hydration numbers and equilibrium constants for the associated species). Using an iterative process the free and associated species concentrations and the exact theoretical values of $\gamma_{\pm}$ for Cs_2SO_4 and CsCl (with Cs^+ at a trace concentration) can be determined in an aqueous solution of M_2SO_4. Also, the γ_{Cl^-} value can be estimated using the procedures outlined in Section 6.5.2, Chapter 2, for unassociated solutions. This allows estimation of γ_{Cs^+} and $\gamma_{SO_4^=}$ for the *free* sulphate species. The activity coefficients for the non associated species NaCl, KCl, HCl, $MgCl_2$, $CaCl_2$ etc. also can be estimated as for the CsCl. Knowing γ_{Cl^-}, then γ_{Na^+}, γ_{K^+}, etc, can be estimated. Hence the mean activity coefficients for the *free* species $\gamma_{Na_2SO_4}{}^{\pm}$, $K_{K_2SO_4}{}^{\pm}$ can be determined. Knowing the free and associated species concentrations and the free ion activity coefficients, the total species activity coefficients (i.e. the stoichiometric mean activity coefficients which are the parameters observed

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in practice) can be determined for all of the salts.

In the procedure above for determining $\gamma_{CsCl\pm}$ and $\gamma_{Cs_2SO_4\pm}$ in an aqueous solution of M_2SO_4, it is required that the ionic association equilibrium constants and the hydration numbers for the associated species be known. The principles involved in the determination of these parameters are as follows:

(b) Ionic association equilibrium constants: For the determination of the equilibrium constants we consider a binary aqueous solution of the salt M_2SO_4. The approach is to determine the equilibrium constants by fitting the theoretically predicted stoichiometric mean activity coefficient, $\gamma_{T\pm}$, against observed values for a range of values of total salt molality, M_T. (The activity coefficient $\gamma_{T\pm}$, being determined as set out in (a) above). Now in the determination of $\gamma_{T\pm}$ it is required that the hydration numbers be known, *inter alia*, for the associated species MSO_4^- and $M_2SO_4^o$.

For 1-2 salts where both ion pair and treble ion species are formed it is necessary to make an assumption on the hydration loss in the formation of the associated species to obtain a solution. We assume a loss of one molecule of hydrated water in the formation of the ion pair MSO_4^- and a loss of two molecules of hydrated water in the formation of the treble ion species $M_2SO_4^o$. This assumed loss of one and two molecules of hydrated water is justified as follows: Formation of an ion pair invariably involves the loss of at least some of the hydrated water, Eigen and Tamm (1962), Fisher (1962) and

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Millero (1971). The loss can be expected to be greater for treble ions than for ion pairs. The hydration number of 1-2 sulphate salts is relatively small compared with 2-2 salts. The magnitude of the hydration loss in 1-2 salts has only a very minor effect on *the values determined for the ion pairing constants* in binary systems, and in mixed systems, only a very small effect on the value determined for the activity coefficients of the various species. For this reason the token loss as given above is more to satisfy the physical behaviour of the system than an attempt to obtain greater accuracy.

(2) Symmetrical sulphate salts: Symmetrical sulphate salts give rise to neutral ion paired species in solution. In contrast to 1-2 salts, for 2-2 sulphate salts both the equilibrium constant for ion pairing and the mean activity coefficients of species in mixed systems (with a high concentration of the 2-2 salt in question) are affected significantly by the value chosen for the hydration loss on ion pair formation. However, in this case an estimate of the loss is possible because one associated species only, the ion pair MSO_4^o, is formed and this allows solution for the hydration number of the ion pair. For the purposes of analyses one again requires (a) a means of determining the mean activity coefficient of free species and also that for the neutrally charged ion paired species, and (b) the ion pairing equilibrium constant.

(a) For the mean activity coefficient of the free species M^{2+} and SO_4^{2-}, $\gamma_{MSO_4\pm}$, the approach is similar to that for unsymmetrical salts discussed above. That is, $\gamma_{CsCl\pm}$, $\gamma_{CsSO_4\pm}$, $\gamma_{MCl_2\pm}$, γ_{Cl^-} and the free and ion paired species concentrations are determined from the equilibrium constant for ion pairing using the unassociated theory

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for binary systems in Chapter 2:

(i) The mean activity coefficient of say species 'j' is defined in terms of the partial molal free energy of species 'j' on the *anhydrous scale* using Eq. (123) Chapter 2,

$$\bar{G}_j = \bar{G}_j^\circ + dRT\,ln\,\gamma_{j\pm} m_{j\pm} \tag{3}$$

(ii) An equation for the total free energy of the system is formulated in terms of the free energy contributions of each of the *hydrated* salts and free water (using volume fraction statistics) plus a term G^{el} to account for the long range electrostatic contributions. For an aqueous solution made up of $n_1, n_2 \ldots n_i$ moles of salt species 1,2 ....i(i.e. k = 1,2,....i) in n_w moles of water, the free energy equation becomes

$$\begin{aligned} G &= n_1\bar{G}_1^h + n_2\bar{G}_2^h + \ldots\ n_i\bar{G}_i^h + n_{fw}\bar{G}_{fw} + G^{el} \\ &= \sum_k n_k\bar{G}_k^h + n_{fw}\bar{G}_{fw} + G^{el} \end{aligned} \tag{4}$$

where

n_k = moles of salt species k in solution

n_{fw} = moles of free water in solution

$\bar{G}_k^h$ = partial molal free energy of hydrated species k.

(ii) From Eq. (4), an expression for $\bar{G}_j$ (on the *anhydrous* scale) is obtained by differentiating this equation partially with respect to the moles of species 'j' keeping constant the other components, i.e. salt species 1, 2, ... j-1, j+1, -...i and the *total moles of water* in solution, n_w, i.e.

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$$\bar{G}_j = (\frac{\partial G}{\partial n_j})_{T,P,n_1,n_2,\dots .n_{j-1},\ n_{j+1},\dots .\ n_i,n_w} \qquad (5)$$

(iv) Equating Eq. (5) to Eq. (3) gives an expression for $\gamma_{j\pm}$ on the molal (anhydrous) scale.

In order to differentiate Eq. (3) in accordance with Eq. (5) it is necessary first to reformulate Eq. (4) so that (i) the moles of free water, n_{fw}, and (ii) each of the partial molal free energy terms for the salts is modelled in terms of basic parameters for the system. This is carried out as follows:

(i) Considering the moles of free water in the system, n_{fw}, this parameter can be linked to the total moles of water, n_w, through the hydration numbers, h_k, for each of the salts in solution, see Eq. (4) Chapter 2, i.e.

$$n_{fw} = n_w - \sum_k n_k h_k \qquad (6)$$

(ii) Considering the partial molal free energies of each of the hydrated salt species in the solution, these are modelled as the sum of the respective standard partial molal free energies plus an entropy term formulated in terms of volume fractions of hydrated species. For the partial molal free energy of hydrated salt species k

$$\bar{G}_k^h = \bar{G}_k^{oh} + d_{k^+} RT\,ln\,\frac{d_{k^+} n_{k^+} \bar{V}_{k^+}^h}{V} + d_{k^-} RT\,ln\,\frac{d_{k^-} n_k \bar{V}_{k^-}^h}{V} \qquad (7)$$

where

superscript 'h' = hydrated species

V = total volume of the solution

$= \Sigma n_i \bar{V}_i + n_w \bar{V}_w$

$= \Sigma n_i \phi_i + n_w \bar{V}_w^o$

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$\bar{V}_k^h$ = partial molal volume of hydrated species 'k'

$= \bar{V}_k + h_k\bar{V}_w$

Substituting for n_{fw} and G_k^h from Eqs. (5 and 7) respectively i to Eq. (4), we can express G as follows:

$$G = \sum_k n_k(\bar{G}_k^{oh} + d_{k+} \cdot RTln \frac{d_{k+}n_k\bar{V}_{k+}^h}{V} + d_{k-}RTln \frac{d_{k-}n_k\bar{V}_{k-}^h}{V})$$

$$+ (n_w - \sum_k n_kh_k)(\bar{G}_{fw}^o + RTln \frac{(n_w - \Sigma n_kh_k)\bar{V}_{fw})}{V} + G^{el} \qquad (8)$$

This equation is still set suitable for differentiation due to the presence of the terms $\bar{V}_{k+}^h$ and $\bar{V}_{k-}^h$. It was shown in Eq. (199) Chapter 2 that the geometric mean of the hydrated partial molal volumes of the component ions of a salt closely equals the arithmetic mean, i.e.

$$d_{k+}\, ln\bar{V}_{k+}^h + d_{k-}ln\bar{V}_{k-}^h = d ln(V_{k+}^{hd_+} . \bar{V}_{k-}^{hd_-})^{1/d}$$

$$= d ln \frac{(d_{k+}\bar{V}_{k+}^h + d_{k-}\bar{V}_{k-}^h)}{d}$$

$$= d ln\bar{V}_k^h - d ln d \qquad (9)$$

Inserting this approximation in Eq. (8), $\bar{G}$ is now expressed in terms of basic parameters.

Differentiating the modified Eq. (8) for G with respect of n_j in accordance with Eq. (5) and rearranging terms

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$$\bar{G}_j = (-h_j-\Sigma_k m_k \frac{\partial h_k}{\partial m_j}).\bar{G}^c_{fw}+\bar{G}^{oh}_j+RT[\mathcal{l}n d_{j+}^{d_{j+}} d_{j-}^{d_{j-}} - d_j \mathcal{l}n d_j + d_j \mathcal{l}n(\frac{0{,}018 m_j n_w}{V})$$

$$+ d_j \mathcal{l}n \bar{V}^h_j + \Sigma_k \frac{d_k m_k}{\bar{V}^h_k} \frac{\partial \bar{V}^h_k}{\partial m_j} - h_k \mathcal{l}n\{\bar{V}^o_w n_w (1 - 0{,}018 \Sigma_k m_k h_k)\}$$

$$+ \frac{(d_j-h_j)V - \{1 + 0{,}018(\Sigma m_k d_k - \Sigma m_k h_k)\}n_w \bar{V}_j}{V} + \frac{(n_w-\Sigma n_k h_k)}{\bar{V}_{fw}} \frac{\partial \bar{V}_{fw}}{\partial n_j}$$

$$- \Sigma m_k \frac{\partial h_k}{\partial m_j} \{1 + \mathcal{l}n \frac{(\bar{V}^o_w n_w (1 - 0{,}018\ \Sigma m_k h_k))}{V}\}] + (\frac{\partial G^{el}}{\partial n_j})_{n_w} \qquad (10)$$

Equation (10) now expresses Eq. (5) in functional form, and we can equate $\bar{G}_j$ in Eq. (5) to $\bar{G}_j$ in Eq. (3): For convenience define $r_k = \phi_k/\bar{V}^o_w \simeq \phi_k/\bar{V}_w$ and $q_k = \bar{V}_k/\bar{V}^o_w \simeq \bar{V}_k/\bar{V}_w$ (see Eq. (183), Chapter 2). Equating Eqs.(2 and 10) and simplifying:

$$dRT\mathcal{l}n\gamma_{j\pm} = \bar{G}^{oh}_j - \bar{G}^o_j + (-h_j-\Sigma_k m_k \frac{\partial h_k}{\partial m_j})\bar{G}^o_{fw} + RT[-d_j \mathcal{l}n d_j + d_j \mathcal{l}n(\frac{0{,}018}{1+0{,}018\Sigma m_k r_k})$$

$$+ d_j \mathcal{l}n(\bar{V}^h_k/\bar{V}^o_w) + \Sigma_k \frac{d_k m_k}{\bar{V}^h_k} (\frac{\partial \bar{V}^h_k}{\partial m_j}) - h_j \mathcal{l}n \frac{1-0{,}018\Sigma m_k h_k}{1+0{,}018\Sigma m_k r_k}$$

$$-\Sigma m_k \frac{\partial h_k}{\partial m_j} \{1+\mathcal{l}n(\frac{1-0{,}018\Sigma m_k h_k}{1+0{,}018\Sigma m_k r_k})\} + \frac{(n_w-\Sigma n_k h_k)}{\bar{V}_{fw}} . \frac{\partial \bar{V}_{fw}}{\partial n_j}] + (\frac{\partial G^{el}}{\partial n_j})_{n_w} \qquad (11)$$

In Eq. (11) two terms must still be simplified, these are:

(i) $\frac{(n_w-\Sigma n_k h_k)}{\bar{V}_{fw}} . \frac{\partial \bar{V}_{fw}}{\partial n_j}$ and (ii) $\Sigma_k \frac{d_k m_k}{\bar{V}^h_j} . \frac{\partial \bar{V}^h_k}{\partial m_j}$

(i) In the term $\frac{(n_w-\Sigma n_k h_k)}{\bar{V}_{fw}} . \frac{\partial \bar{V}_{fw}}{\partial n_j}$,

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to determine $\partial\bar{V}_{fw}/\partial n_j$, from Eq. (13) Chapter 2, the total volume V of the system can be formulated in terms of the partial molal volumes of *hydrated* species, $\bar{V}_k^h$, and the partial molal volume of *free* water, $\bar{V}_{fw}$,

$$V = \sum_k n_k \bar{V}_k^h + n_{fw}\bar{V}_{fw} \quad .$$

Differentiating this expression partially with respect to n_j keeping the total moles of water constant, gives an expression for $\bar{V}_j$ (by definition),

$$\bar{V}_j = (\bar{V}_j + h_j\bar{V}_w) + \sum_k n_k \frac{\partial\bar{V}_k^h}{\partial n_j} + (n_w - \sum_k n_k h_k)\,\frac{\partial\bar{V}_{fw}}{\partial n_j} - h_j\bar{V}_{fw}$$

$$- \sum_k n_k \bar{V}_{fw}\,\frac{\partial n_k}{\partial n_j}$$

and solving for $\dfrac{(n_w - \sum_k n_k h_k)}{\bar{V}_{fw}} \cdot \dfrac{\partial\bar{V}_{fw}}{\partial n_j}$ in the above expression

$$\frac{(n_w - \sum_k n_k h_k)}{\bar{V}_{fw}} \cdot \frac{\partial\bar{V}_{fw}}{\partial n_j} = \sum_k n_k \cdot \frac{\partial h_k}{\partial n_j} - \sum_k \frac{n_k}{\bar{V}_{fw}} \cdot \frac{\partial\bar{V}_k^h}{\partial n_j}$$

$$= \sum_k n_k \frac{\partial h_k}{\partial n_j} - \sum \frac{n_k}{\bar{V}_{fw}} \cdot \frac{\partial}{\partial n_j}(\bar{V}_k + h_k\bar{V}_w)$$

$$= \sum_k m_k \frac{\partial q_k}{\partial m_j}\,(1 - \sum_k 0{,}018\, m_k h_k) \qquad (12)$$

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(ii) In the term $\sum_k \frac{d_k n_k}{\bar{V}_k^h} \cdot \frac{\partial \bar{V}_k^h}{\partial n_j}$,

from Eq, (17), Chapter 2, $\bar{V}_k^h = \bar{V}_k + h_k \bar{V}_w$, i.e.

$$\sum_k \frac{d_k n_k}{\bar{V}_k^h} \cdot \frac{\partial \bar{V}_k^h}{\partial n_j} = \sum_k \frac{d_k n_k}{\bar{V}_k + h_k \bar{V}_w} \cdot \left(\frac{\partial \bar{V}_k}{\partial n_j} + \bar{V}_w \frac{\partial h_k}{\partial n_j} + h_k \frac{\partial \bar{V}_w}{\partial n_j}\right) \tag{13}$$

For the term $h_k \partial \bar{V}_w / \partial n_j$ in Eq. (13) the total volume of the system can be written in terms of the partial molal volume of the components,

$$V = n_1 \bar{V}_1 + n_2 \bar{V}_2 + \ldots . + n_w \bar{V}_w$$

and, differentiating this expression partially with respect to the moles of component 'j' gives $\bar{V}_j$ by definition,

$$\frac{\partial V}{\partial n_j} = \bar{V}_j = \Sigma n_k \frac{\partial \bar{V}_k}{\partial n_j} + \bar{V}_j + n_w \frac{\partial \bar{V}_w}{\partial n_j} \tag{14}$$

and solving for $h_k \partial \bar{V}_w / \partial n_j$ in Eq. (14)

$$h_k \partial \bar{V}_w / \partial n_j = \frac{-h_k}{n_w} \sum_k n_k \frac{\partial \bar{V}_k}{\partial n_j} \tag{15}$$

Substituting for $h_k \partial \bar{V}_w / \partial n_j$ from Eq.(15) into Eq. (13) and simplifying:

$$\sum_k \frac{d_k m_k}{\bar{V}_k^h} \cdot \frac{\partial \bar{V}_k^h}{\partial n_j} = \sum_k m_k \frac{\partial q_k}{\partial m_j} \left(\frac{d_k}{q_k + h_k} - 0{,}018 \sum_k \frac{d_k m_k h_k}{(q_k + h_k)}\right)$$

$$+ \sum_k \frac{d_k m_k}{(q_k + h_k)} \cdot \frac{\partial h_k}{\partial m_j} \tag{16}$$

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Having simplified the two terms in Eq. (11) we substitute their respective values from Eqs. (12 and 16) into Eq. (11).

We can now solve for the constant

$$\bar{G}_j^{oh} - \bar{G}_j^{o} - \bar{G}_{fw}^{o}\,(h_j - \Sigma m_k \frac{\partial h_k}{\partial m_j})$$

in Eq. (11) by imposing the condition $\underset{k}{\Sigma} m_k = 0$ (as in binary systems Chapter 2) to give

$$\bar{G}_j^{oh} - \bar{G}_j^{o} = h_j^o \bar{G}_{fw}^{o} + RT[d_j\, ln d_j - d_j\, ln\, 0{,}018 - d_j\, ln(q_j^o + h_j^o)$$

$$+ (q_j + h_j - d_j) - (q_j - q_j^o) - (h_j - h_j^o)] \qquad (17)$$

The constant $(\bar{G}_j^{oh} - \bar{G}_j^{o})$ from Eq. (17) is inserted in Eq. (11) and the term rearranged to give the required expression for $\gamma_{j\pm}$ in an aqueous solution containing k salt components, as:

$$ln\gamma_{j\pm} = ln\gamma_j^{DH} + \frac{0{,}018\, q_j(\Sigma m_k q_k + \Sigma m_k h_k - \Sigma m_k d_k)}{d_j(1 + 0{,}018\, \Sigma m_k q_k)}$$

$$+ \frac{h_j - d_j}{d_j}\, ln\,(1 + 0{,}018\, \Sigma m_k r_k) - \frac{h_j}{d_j}\, ln\,(1 - 0{,}018\, \Sigma m_k h_k)$$

$$- \frac{(q_j - q_j^o)}{d_j} - \frac{(h_j - h_j^o)}{d_j} + ln(\frac{q_j + h_j}{q_j^o + h_j^o}) + (h_j^o - h_j - \Sigma m_\kappa \frac{\partial h_k}{\partial m_j})\, \frac{\bar{G}_{fw}^{o}}{d_j RT}$$

$$- \frac{1}{d_j}\, \Sigma m_k \frac{\partial h_k}{\partial m_j}\, \{X\} - \frac{1}{d_j}\, \Sigma m_k \frac{\partial q_k}{\partial m_j}\, \{Y\} \qquad (18)$$

where

$$ln\gamma_j^{DH} \simeq - \frac{1{,}1706\, z_-^2\sqrt{\mu}}{1 + B\mathring{a}_-\ \sqrt{\mu}}\, (\frac{d_-}{d_j}) - \frac{1{,}1706\, z_+^2\sqrt{\mu}}{1 + B\mathring{a}_+\ \sqrt{\mu}}\, (\frac{d_+}{d_j})$$

$\bar{G}_{fw}^{o}/RT = 30$ (by convention, see Page 2.113, Chapter 2)

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$$\{X\} = \{\frac{q_k + h_k - d_k}{q_k + h_k} + \ln\left(\frac{1 - 0{,}018\ \Sigma m_k h_k}{1 + 0{,}018\ \Sigma m_k r_k}\right)\}$$

$$\{Y\} = \{\frac{q_k + h_k - d_k}{q_k + h_k} - \sum_k \left(0{,}018\ m_k h_k \frac{(q_k + h_k - d_k)}{q_k + h_k}\right)\}$$

In Eq. (18) the first four terms correspond to the Glueckauf equation for a mixed system with the values for q, r and h equal to the respective values at infinite dilution, Eq. (171), Chapter 2. The last six terms in Eq. (18) account for changes in the partial molal volumes and hydration numbers of each of the salt species in solution with changes in molality of the particular salt for which $\gamma_\pm$ is to be determined.

In order to use Eq. (18) to determine the activities coefficient of salt component, say 'j', in a mixed system with i salt components, values must be known for (i) the distance of closest approach parameter $\mathring{a}_j$ in the Debye Hückel term, (ii) the partial and apparent partial molal volumes and hydration numbers of each of the salt species, and (iii) the changes in the latter two parameters with addition of salt species 'j'.

(i) In the original derivation of the Debye-Hückel equation, $\mathring{a}$ was defined for both the cation and anion species in a binary solution. In the formulation for a binary system $\mathring{a}_+ = \mathring{a}_- = \mathring{a}$. This equivalence however arises because of the binary nature of the solution. In a mixed system the original Debye-Hückel interpretation is retained as follows: The Debye-Hückel term formulated as the sum of the contributions to the partial molal free energy due to the component ions of the salt of interest (see Eq. 18) with the $\mathring{a}_{j+}$ and $\mathring{a}_{j-}$ values determined as follows: For $\mathring{a}_{j+}$, the value for this parameter is taken as the sum of the hydrated radius for the cation of the

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salt species under consideration (i.e. species 'j') and the molar mean value of the hydrated radii of all the anion species in solution; similarly the value for $\mathring{a}_{j-}$ is taken as the sum of the hydrated radius of the anion of salt species 'j' and the molar mean value of the hydrated radii of all the cation species in solution. Values for the individual ion hydrated radii are determined from å values for salts listed in Table 4, Chapter 2, using the additivity principle and assuming that Cl^- has a hydration number equal to zero and hence $r^h_{Cl} = 1,81$ Angstrom units (see Table 1).

Table 1. Hydrated radii of single ions determined from å values listed in Table 4, Chapter 2 and assuming Cl^- has zero primary hydration

Ionic species	r^h
Cl^-	1,81
H^+	3,79
Li^+	3,53
Na^+	3,14
K^+	2,54
Rb^+	2,09
Cs^+	1,45
Ca^{++}	3,84
Mg^{++}	3,79
Ba^{++}	3,19

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(ii) and (iii)

> For the partial and apparent partial molal volumes and hydration numbers of each of the salt species in the mixed system there are neither rigorous theoretical means nor reported experimental data for predicting the values and the changes in these parameters with salt molality in a mixed electrolyte system.

From (ii) and (iii) no solution is possible by means of Eq. (18) unless some method of estimation is found for the partial molal volumes and hydration numbers for each of the salt species in solution and the changes in each of these parameters with the molality of the salt species for which the activity coefficient is to be determined, i.e. $\partial h_k/\partial m_j$ and $\partial \bar{V}_k/\partial m_j$ where k represents any one of the various salts in the solution and j the particular salt for which $\gamma_{j\pm}$ is to be determined. Recognising that the values for each of these parameters cannot be estimated accurately, an *approximate* solution can be obtained by accepting that the ionic strength principle applies to the changes in partial molal volume, q_k, and the hydration number h_k. Accepting this principle the $\gamma_\pm$ values can be determined completely from binary data. The error made by doing so can be checked by comparing the predicted $\gamma_\pm$ values with observed data on ternary systems. This approach is developed below.

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2.2 Utilization of the ionic strength principle for $\bar{V}_k$ and h_k to determine $\gamma_\pm$

Application of the ionic strength principle in obtaining an approximate solution is best illustrated by examples. We will consider two ternary systems, H_2O - NaCl - KCl and H_2O - NaCl - $MgCl_2$ in which the mean activity coefficients of each of the salts is to be estimated: (i) Determine $\gamma_{NaCl\pm}$ and $\gamma_{KCl\pm}$ in an aqueous ternary system (i.e. two 1-1 salts) with a total ionic strength

$\mu = 3$, and (ii) determine $\gamma_{NaCl\pm}$ and $\gamma_{MgCl_2\pm}$ in an aqueous ternary system of NaCl and $MgCl_2$ (i.e. a 1-1 salt and a 1-2 salt) with a total ionic strength $\mu = 3$.

(i) The ternary system H_2O - NaCl - KCl with $\mu = 3$

The partial molal volumes and hydration numbers for each of the salts are determined using the ionic strength principle and data listed in Table 4, Chapter 2 for binary systems, i.e.

$$q_{NaCl} = \frac{1}{18}(\bar{V}^{o}_{NaCl} + 1{,}5 \cdot 1{,}868\sqrt{\mu} + 2{,}0 \cdot 0{,}048\,\mu)$$
$$= 1{,}208 \qquad (19a)$$

$$r_{NaCl} = \frac{1}{18}(\bar{V}^{o}_{NaCl} + 1{,}868\sqrt{\mu} + 0{,}048\,\mu)$$
$$= 1{,}111 \qquad (19b)$$

$$h_{NaCl} = h^{o}_{NaCl} - 0{,}00014\,\mu^2$$
$$= 2{,}399 \qquad (19c)$$

$$q_{KCl} = \frac{1}{18}(\bar{V}^{o}_{KCl} + 0{,}66 - 1{,}868\sqrt{\mu} + 0{,}2\,\mu)$$
$$= 1{,}792 \qquad (19d)$$

$$r_{KCl} = \frac{1}{18}(\bar{V}^{o}_{KCl} + 1{,}868\sqrt{\mu} + 0{,}1\,\mu)$$
$$= 1{,}685 \qquad (19e)$$

$$h_{KCl} = h^{o}_{KCl} - 0{,}00017\,\mu^2$$
$$= 1{,}009 \qquad (19f)$$

For the determination of $\gamma_{NaCl\pm}$:

Assuming the ionic strength principle for q_K

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$$\frac{\partial q_{NaCl}}{\partial m_{NaCl}} \simeq \frac{dq_{NaCl}}{d\mu} \cdot \frac{\partial \mu}{\partial m_{NaCl}} = \frac{dq_{NaCl}}{d\mu}$$

$$= \frac{1}{18} (0{,}75 \cdot 1{,}868/\surd\mu + 0{,}096)$$

$$= 0{,}050 \qquad (19g)$$

$$\frac{\partial q_{KCl}}{\partial m_{NaCl}} \simeq \frac{dq_{KCl}}{d\mu}$$

$$= 0{,}056 \qquad (19h)$$

and assuming the ionic strength principle for h_k

$$\frac{\partial h_{NaCl}}{\partial m_{NaCl}} \simeq \frac{dh_{NaCl}}{d\mu} \cdot \frac{\partial \mu}{\partial m_{NaCl}}$$

$$= -\ 0{,}00028\ \mu$$

$$= -\ 0{,}00084 \qquad (19i)$$

$$\frac{\partial h_{KCl}}{\partial m_{NaCl}} \simeq \frac{dh_{KCl}}{d\mu} \cdot \frac{\partial \mu}{\partial m_{NaCl}} = \frac{dh_{KCl}}{d\mu}$$

$$= -\ 0{,}00034\ \mu$$

$$= -\ 0{,}00102 \qquad (19j)$$

For the determination of $\mathring{a}_{Na^+}$ and $\mathring{a}_{Cl^-}$:

From Table 1

$$\mathring{a}_{Na^+} = r^h_{Na} + r^h_{Cl} = 4{,}95 \qquad (19k)$$

$$\mathring{a}_{Cl} = r^h_{Cl} + \frac{m_{Na^+}}{m_{Na^+} + m_{K^+}} (r^h_{Na}) + \frac{m_{K^+}}{m_{Na^+} + m_{K^+}} (r^h_{K}) \qquad (19\ell)$$

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Substituting values for q_k, h_k, $\partial q_k/\partial m_j$ and $\partial h_k/\partial m_j$ from Eq. (19a to 19j) into Eq. (18) and for $\mathring{a}_{j+}$ and $\mathring{a}_{j-}$ from Eqs. (19k and 19ℓ) allows determination of $\gamma_{NaCl\pm}$ for a range of concentration of NaCl and KCl subject to the restriction that μ remains constant and equal to three.

For the determination of $\gamma_{KCl\pm}$:

Assuming the ionic strength principle for q_k

$$\frac{\partial q_{NaCl}}{\partial m_{KCl}} \simeq \frac{dq_{NaCl}}{d\mu} \cdot \frac{\partial \mu}{\partial m_{KCl}} = \frac{dq_{NaCl}}{d\mu}$$

$$= 0{,}050 \tag{20a}$$

$$\frac{\partial q_{KCl}}{\partial m_{KCl}} \simeq \frac{dq_{KCl}}{d\mu} \cdot \frac{\partial \mu}{\partial m_{KCl}} = \frac{dq_{KCl}}{d\mu}$$

$$= 0{,}056 \tag{20b}$$

and assuming the ionic strength principle for h_k

$$\frac{\partial h_{NaCl}}{\partial m_{KCl}} \simeq \frac{dh_{NaCl}}{d\mu} \cdot \frac{\partial \mu}{\partial m_{KCl}} = \frac{dh_{NaCl}}{d\mu}$$

$$= -\ 0{,}00084 \tag{20c}$$

$$\frac{\partial h_{KCl}}{\partial m_{KCl}} \simeq \frac{dh_{KCl}}{d\mu} \cdot \frac{\partial \mu}{\partial m_{KCl}} = \frac{dh_{KCl}}{d\mu}$$

$$= -\ 0{,}00102 \tag{20d}$$

For the determination of $\mathring{a}_{K+}$ and $\mathring{a}_{Cl-}$:

$$\mathring{a}_{K+} = r^{h}_{K} + r^{h}_{Cl} = 4{,}35 \tag{20e}$$

$\mathring{a}_{Cl-}$ is given by Eq. (19ℓ).

Substituting values for q_k, r_k and h_k from Eqs. (19a to 19f) and for $\partial q_k/\partial m_j$ and $\partial h_k/\partial m_k$ from Eqs. (20a to 20d) into Eq. (18) allows

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determination of $\gamma_{KCl\pm}$ for a range of concentrations of KCl and NaCl subject to μ remaining constant and equal to three.

In Fig. 1 are plotted the logarithms of the activity coefficients for NaCl and KCl respectively (when the molarity of NaCl varies from 0 to 3 m and KCl correspondingly varies from 3 to 0 m) with μ constant and equal to three. Also plotted in Fig. 1 are the observed $\gamma_\pm$ data from Robinson (1961).

In Fig. 1 comparing the observed $\gamma_\pm$ values with values calculated using Eq. (18) and ionic strength principle for q_k and h_k, two points are noted:

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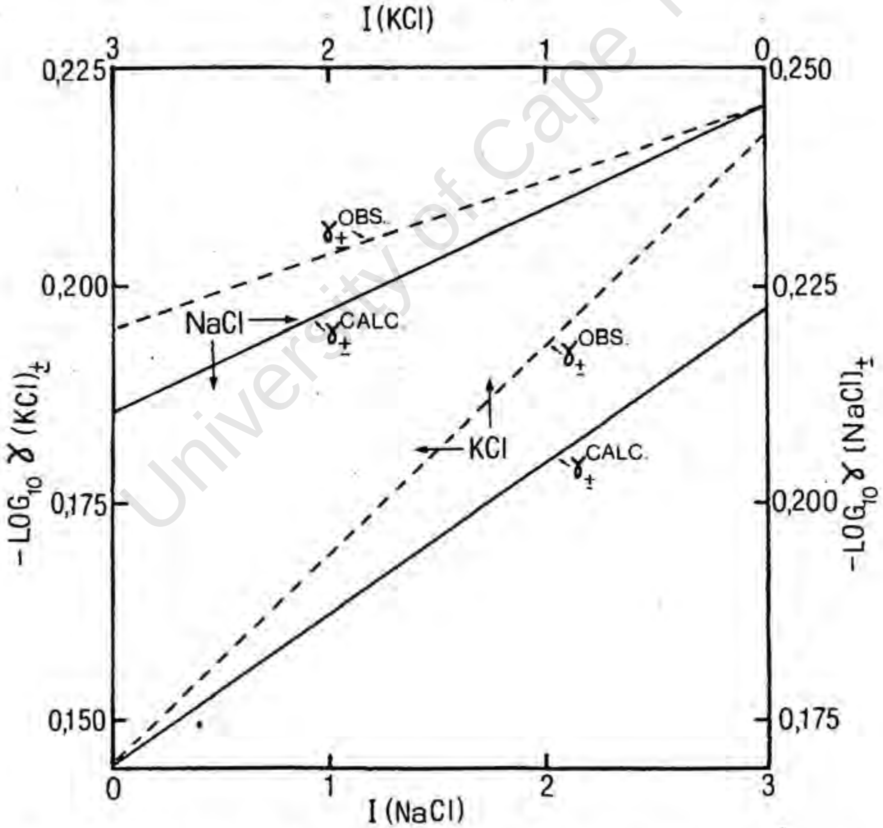

Figure 1. Comparison of calculated and observed mean activity coefficients for NaCl and KCl in a ternary system with a total ionic strength I = 3.

$$= - 0{,}0012\ \mu$$

$$= - 0{,}0036 \qquad (22f)$$

$$\frac{\partial h_{MgCl_2}}{\partial m_{NaCl}} \simeq \frac{dh_{MgCl_2}}{d\mu} \cdot \frac{\partial \mu}{\partial m_{NaCl}}$$

$$= - 0{,}004\ \mu$$

$$= - 0{,}0012 \qquad (22g)$$

For the determination of $\overset{o}{a}_{Mg}$, $\overset{o}{a}_{Na}$ and $\overset{o}{a}_{C-}$- :

From Table 1

$$\overset{o}{a}_{Mg} = r^h_{Mg} + r^n_{Cl} = 5{,}60$$

$$\overset{o}{a}_{Na} = r^h_{Na} + r^h_{Cl} = 4{,}95$$

$$\overset{o}{a}_{Cl} = r^h_{Cl} + \frac{m_{Mg}}{m_{Mg}+m_{Na}}\,(r^h_{Mg}) + \frac{m_{Na}}{m_{Mg}+m_{Na}}\,(r^h_{Na})$$

Substituting values for q_{NaCl}, r_{NaCl} and h_{NaCl} (from Eqs. 19a to 19c), and $\partial h_{NaCl}/\partial m_{NaCl}$, $\partial h_{NaCl}/\partial m_{MgCl_2}$ and $\partial q_{NaCl}/\partial m_{MgCl_2}$ (from Eqs. 19g, 21b and 21a), and q_{MgCl_2}, r_{MgCl_2}, $\partial q_{MgCl_2}/\partial m_{MgCl_2}$, $\partial q_{MgCl_2}/\partial m_{NaCl}$, h_{MgCl_2}, $\partial h_{MgCl_2}/\partial m_{MgCl_2}$ and $\partial h_{MgCl_2}/\partial m_{NaCl}$ (from Eqs. 22a to 22g) into Eq. (18) allows $\gamma_{NaCl\pm}$ and $\gamma_{MgCl_2\pm}$ to be determined in the solution at a total ionic strength $\mu = 3$ as the ionic strength contribution of NaCl varies from zero to three (and concurrently the ionic strength of $MgCl_2$ varies from three to zero).

In Figure 2 are plotted the logarithms of the activity coefficients for NaCl, $\gamma_{NaCl\pm}$, and $MgCl_2$, $\gamma_{MgCl_2\pm}$, for a total ionic strength $\mu = 3$) and I_{NaCl} (the ionic strength contribution of NaCl on the molal scale) varying from 0 to 3 and, I_{MgCl_2} varying from

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3 to 0. Also plotted in Figure 2 are the observed activity coefficients from Lanier (1965). Comparing observed $\gamma_{\pm}$ data with values determined from Eq. (18) using the ionic strength principle for q_k and h_k, again it is observed that (i) the predicted values for $\gamma_{\pm}$ follow the observed trend, and (ii) both observed and predicted data give a linear plot for the logarithm of $\gamma_{\pm}$ versus the ionic strength contribution (I) of the second salt.

The examples above are typical of the differences found between predicted and observed $\gamma_{\pm}$ values in ternary systems at $\mu = 3$ when using the ionic strength principle approximation for q and h.

Generally this approach gives a good approximation for mean activity coefficients in ternary systems up to an ionic strength $\mu = 1$, to within about 0,02 activity coefficient units. At higher ionic strengths divergence between observed data and calculated values becomes increasingly larger.

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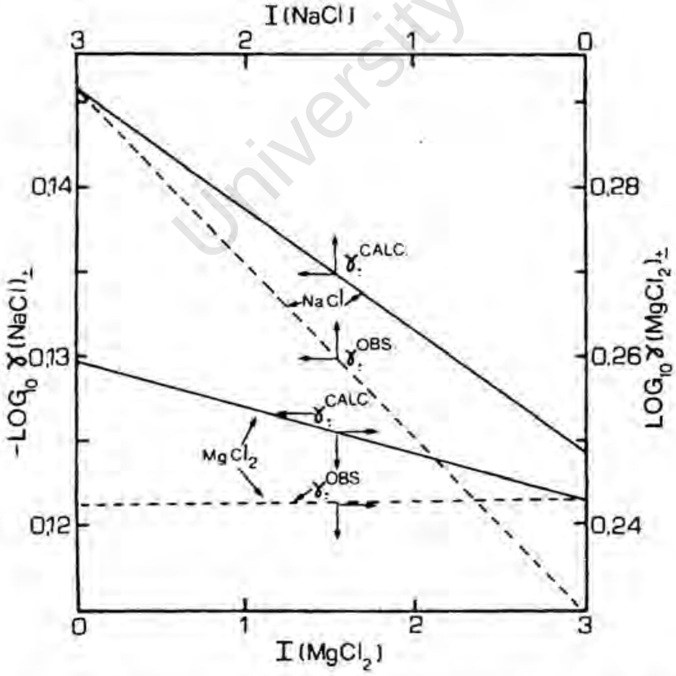

Figure 2. Comparison of calculated and observed mean activity coefficients for NaCl and $MgCl_2$ in a ternary system with a total ionic strength, I = 3.

The error in the theoretical determination of $\gamma_{\pm}$ resides in the six terms from $(q_j - q_j^{\circ})/d_j$ to $(\Sigma_k m_k \cdot \partial q_k/\partial m_j \cdot \{Y\})/d_j$ in Eq. (18). At an ionic strength of unity, utilization of the ionic strength principle to determine q_j, h_j, $\partial q_k/\partial m_j$ and $\partial h_k/\partial m_j$ can give rise to an error of about 0,02 activity coefficient units, but the contribution of each of the six terms is almost impossible to isolate. However, the following points should be noted: (i) *for all non associated ternary systems at some constant total ionic strength both observation and theory (utilizing the ionic strength principle for q and h) gives closely a linear plot for the logarithm of the activity coefficient of the one salt versus the ionic strength contribution of the second salt,* and (ii) *the calculated values generally give the correct trends for the change in $\gamma_{\pm}$ of a salt when the composition of the solution is altered from a pure solution of that salt to a ternary system containing only a trace concentration of that salt.*

The two observations outlined above, form a basis from which it is possible to formulate a correction term to be applied to Eq. (18) (incorporating the ionic strength principle) to give the observed activity coefficients in ternary systems. This of course would be of little general use as most solutions contain three or more salts. However, the nature of the correction term is such that extension to quaternary and higher systems can be readily accomplished. Then, if one accepts that the secondary effects on the interactions are negligible, the extension of the correction to multiple salt solutions should give a close description of the mean activity coefficient.

2.3 *The adjusted ionic strength principle approach*

2.3.1 *Ternary systems*

Accepting that the difference arising between observed and calculated values for $\gamma_{\pm}$ in ternary systems results from utilization of the ionic strength principle to determine partial molal volumes

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and hydration numbers, the values utilized in Eq. (18) for these parameters should be written as the sum of the ionic strength principle value and a delta term to account for the interaction effects of the second salt on each of these parameters. Such an approach leads to a very complex equation for $\gamma_{\pm}$ in which it is not practical to model the individual delta values (i.e. the individual interaction effects). A significant simplication is possible based on the observation that for ternary systems experimental data and theoretical values (determined using Eq. 18) for the logarithm of $\gamma_{\pm}$ both exhibit a linear variation with the ionic strength contribution of the second salt for some total ionic strength of solution. Consequently, all the interaction effects can be lumped into a single delta value to account for the difference in slopes of the plots of the observed and calculated $ln\gamma_{\pm}$ values versus the molality (or ionic strength contribution) of the second salt at some total constant ionic strength. That is, an equation for $ln\gamma_{j\pm}$ in a ternary system of salt species 'k' and 'i', (i.e. k = j,i), can be formulated as the sum of two parts (i) $ln\gamma_{j\pm}$ (calc.) determined from Eq. (18) using the ionic strength principle to determine q_k, h_k, $\partial q_k/\partial m_j$ and $\partial h_k/\partial m_j$ and, (ii) a correction term expressed as a constant times the molality of the second salt, i.e.

$$ln\gamma_{j\pm} = ln\gamma^{c}_{j\pm} + \beta_{ji}\, d_i m_i \tag{23}$$

where

$\gamma_{j\pm}$ = the mean activity coefficient for salt 'j' in a mixture of salts 'i' and 'j'

$\gamma^{c}_{j\pm}$ = calculated value for $\gamma_{j\pm}$ determined using Eq. (18) and the ionic strength principle for values for q_k, h_k, $\partial q_k/\partial m_j$ and $\partial h_k/\partial m_j$

β_{ji} = a constant for some total ionic strength value of the

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In Eq. (23) values for $ln\gamma^{c}_{j\pm}$ are determined from data for binary systems (see Table 4, Chapter 2) using Eq. (18) and the ionic strength principle for $\bar{V}_{K}$ and h_{k}. Values for the interaction term β_{ji} are determined from reported $\gamma_{\pm}$ data for ternary systems.

Determination of the interaction term γ_{ji} in Eq. (23) for a ternary system is carried out as follows:

(i) $ln\gamma^{c}_{j\pm}$ is determined at a trace concentration of salt 'j' in a ternary system of salts 'i' and 'j' having a total ionic strength say I_1 (i.e. salt species 'i' has an ionic strength contribution equal to I_1) using Eq. (18) and the ionic strength principle for $\bar{V}_{K}$ and h_{k}

(ii) β_{ji} is determined for a total ionic strength of solution equal to I_1 using Eq. (23) and the observed value for $\gamma_{j\pm}$ and the value for $\gamma^{c}_{j\pm}$ determined in (i) above, i.e.

$$\beta_{ji} = (ln\gamma_{j\pm} - ln\gamma^{c}_{j\pm})/d_{i}m_{i} \qquad (24)$$

(iii) For the selected value of I_1, in order to check that the value determined for β_{ji} represents all $\gamma_{j\pm}$ for mixtures of salt species 'i' and 'j' steps (i) and (ii) above are repeated for various ratios of the molalities of these two salt species.

(iv) Steps (i) to (ii) are then repeated for a series of values of I and β_{ji} values are determined.

2.3.2 *Mixed systems without sulphate species*

To extend Eq. (23) to an aqueous mixture comprising of more than two salts, first it is necessary to examine the implications of introducing the interaction term in this equation on the equation

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for the total free energy of the system, G in Eq. (8). Recognizing that the equation for $\gamma_{j\pm}$, Eq. (18). is developed by partial differentiation of the total free energy equation, Eq. (8), with respect to the moles of salt species 'j', then integration of the expression for $\gamma_{j\pm}$ must again give the expression for G. Now, the interaction term in Eq. (23) is introduced to compensate for utilization of the ionic strength principle in the determination of values for $\bar{V}_k$ and h_k. Consequently, in the equation for G if the values for $\bar{V}_k$ and h_k are those given by the ionic strength principle, this equation also should include an interaction term. Furthermore, the interaction term in the equation for G should be such that partial differentiation of this term leads to the term $\beta_{ji} d_i m_i$ *in the equation for* $ln\gamma_{j\pm}$ *in a ternary system,* Eq. (23), i.e.

$$G = G^c + d_j n_j . (\beta_{ji} d_i n_i / n_w) \qquad (25)$$

where

G^c = the equation for the total free energy of the mixture, i.e. Eq. (8), in which values for $\bar{V}_k$ and h_k are given by the ionic strength principle

β_{ji} = a constant.

For an aqueous solution made up of more than two salts, say 'i' salt species (with k = 1,2,....j....i), Eq. (25) can be extended to give a value for G provided secondary interactions are neglected,

$$G = G^c + \sum_{k=1}^{i-1} d_k n_k \Big(\sum_{k'=k+1}^{i} \beta'_{kk'} d_{k'} n_{k'} / n_w \Big) \qquad (26)$$

and the equation for $\gamma_{j\pm}$ corresponding to Eq. (26) for G becomes

$$ln\gamma_{j\pm} = ln\gamma^c_{j\pm} + \sum_k \beta_{jk} d_k m_k \qquad (27)$$

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Table 2. Interaction constants, β_{ji} in Eq. (23), for ternary systems of chloride salts in aqueous solutions, (i.e. k = j,i) $ln\gamma_{j\pm} = ln\gamma^{c}_{j\pm} + \beta_{ji} d_i m_i$

SALT 'j' 'i'	HCl	NaCl	KCl	$MgCl_2$	$CaCl_2$
HCl	0	0,020 *	0,030 − 0,007 m_i *		
NaCl	0,024 + 0,002 m_i *	0	−0,015 + 0,002 m_i **	0,0165 − 0,004 m_i ††	0,0085 ††
KCl	0,027	−0,004	0,0 #	0,0 #	0,0 #
$MgCl_2$	0,014 m_i †(1)	0,007 ††	−0,011 #	0,0	−
$CaCl_2$	0,031 − 0,020 m_i †(2)	0,0 ††	−0,015 #	−	0,0

* Harned and Owen (from)

** Harned and Robinson (from)

†(1) Khoo, K.H., Chee-Yan Chan, Lim, T.K., J. of Sol.Chem., 6. 855, 1977

†(2) Khoo, K.H., Chee-Yan Chan, Lim, T.K., J. of Sol.Chem., 6, 651, 1977

†† Lanier, R.D., J. of Phys.Chem., 69, 3992, 1965

Christenson, P.G. and Gieskes, J.M., J. of Chem. and Eng. Data, 16, 398, 1971

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where

β_{jk} = a constant the value of which is determined from ternary data

$= 0{,}018\ \beta'_{kk'}/RT$

As in ternary systems the term $ln\gamma^{c}_{j}$ in Eq. (27) is determined using Eq. (18) and data from binary systems listed in Table 4, Chapter 2 (i.e. the binary data is used together with the ionic strength principle to determine $\bar{V}_k$, h_k, $\partial V_k/\partial m_j$ and $\partial h_k/\partial m_j$ as outlined in the previous example). Values for each of the interaction constants, β_{jk}, are determined from *ternary* data listed in Table 2 for each of the systems H_2O-salt 'j'-salt 'k'.

A check on the approach is the determination of $\gamma_{j\pm}$ in systems with more than two salt species present in solution. One such check is given below as an example, the determination of $\gamma_{HCl\pm}$, at a trace concentration, in synthetic seawater. In Table 3 are compared values for $\gamma_{HCl\pm}$ observed (from Khoo, Ramette, Culberson and Bates, 1977) and calculated values (determined using Eq. 27) in synthetic seawater in which Na_2SO_4 was replaced by NaCl) with I (molal scale) = 0,673, diluted seawater I = 0,381 and concentrated seawater, I = 0,872. The agreement in all cases is excellent and lends support to the approach.

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Example

Determine $\gamma_{HCl\pm}$ using Eq. (22) in synthetic seawater with the following molal composition: NaCl = 0,4644, KCl = 0,0106, $CaCl_2$ = 0,0108, $MgCl_2$ = 0,0552, HCl = 0,01 and temperature is 25 deg.C.

The term $\gamma'_{j\pm}$ in Eq. (27) is determined using Eq. (18) and binary data listed in Table 4, Chapter 2; the values determined for d_k, r_k, h_k, $\partial q_k/\partial m_{HCl}$ and $\partial h_j/\partial m_{HCl}$ (as outlined in the previous example) are listed below in Table 4.

Substituting the values from Table 4 into Eq. (18) and putting $a_H = 5{,}60$ and $a_{Cl} = 4{,}98$, $h^{o}_{HCl} = 4{,}09$ and $q^{o} = 0{,}991$ from Table 4 Chapter 2, gives $ln\gamma^{c}_{HCl} = -\ 0{,}335$.

Table 3. Comparison of $\gamma_{HCl\pm}$ observed (Khoo, Ramette, Culberson and Bates, 1977) with $\gamma_{HCl\pm}$ calculated using Eqs. (18 and 27) for synthetic seawater having the following molalities, NaCl = 0,4644, KCl = 0,016, $CaCl_2$ = 0,0108, $MgCl_2$ = 0,0552 and HCl = 0,01 (for dilution and concentration I/m_{Cl} = 1,107).

	I = 0,381	I = 0,673	I = 0,872
$\gamma_{HCl\pm}$(observed)	0,730	0,729	0,738
$\gamma_{HCl\pm}$(calculated)	0,733	0,732	0,738

Table 4. Values determined for q_k, r_k, h_k, $\partial q_k/\partial m_{HCl}$ and $\partial h_k/\partial m_{HCl}$ using the ionic strength principle and binary data listed in Table 4, Chapter 2.

Salt species 'k'	q_k	r_k	h_k	$\partial q_k/\partial m_{HCl}$	$\partial h_k/\partial m_{HCl}$
HCl	1,069	1,033	4,0895	0,0484	- 0,0011
NaCl	1,052	1,047	2,40	0,1004	- 0,00020
$MgCl_2$	1,007	0,940	8,12	0,1514	- 0,00027
$CaCl_2$	1,250	1,171	7,05	0,1763	- 0,00024
KCl	1,625	1,583	1,01	0,1062	- 0,00024

The interaction constants β_{jk} in Eq. (27) are determined from the data listed for these parameters in Table 2, i.e.

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β_{jk} = (HCl, NaCl) = 0,024

β_{jk} = (HCl, $MgCl_2$) = 0,001

β_{jk} = (HCl, $CaCl_2$) = 0,047

β_{jk} = (HCl, KCl) = 0,027

i.e.

$$\Sigma\beta_{jk}d_k m_k = 2\beta(HCl,NaCl).m_{NaCl} + 3\beta(HCl,MgCl_2).m_{MgCl_2}$$

$$+ 3\beta(HCl,CaCl_2).m_{CaCl_2} + 2\beta(HCl,KCl).m_{KCl}$$

$$= 0{,}0230$$

Substituting for $ln\gamma^c_{HCl} = -\,0{,}3350$ and $\Sigma\beta_{jk}d_k m_k = 0{,}023$ into Eq. (27)

$$ln\gamma_{HCl} = -\,0{,}335 + 0{,}023$$

i.e.

$$\gamma_{HCl\pm} = 0{,}732$$

2.3.3 *Single ion activity coefficients*

In Section 6.5.2 Chapter 2 it was shown that the equation for $ln\gamma_{j\pm}$ in an aqueous binary system can be decomposed to give equations for the single ion activity coefficients $ln\gamma_j+$ and $ln\gamma_j-$. Using the same approach it is possible to decompose the equation for $ln\gamma_{j\pm}$ in a mixed system to give equations for the single ion activity coefficients.

For a mixed system made up of a number of chloride salts, Eqs. (18 and 27) supply the means of writing down equations for the mean activity coefficients for each of the salt species in the solution. Decomposition of any of these equations leads to an equation for $ln\gamma_{Cl^-}$. Now, for a consistent approach, irrespective of which mean activity coefficient equation is decomposed, in each case the decomposition must lead to exactly the same equation for $ln\gamma_{Cl^-}$. The approach we shall use will be developed initially for the ternary systems in order to bring out the salient points, thereafter extension to mixtures with a larger number of salts in solution will be readily appreciated.

Consider the aqueous ternary system prepared by mixing m_1 and m_2 moles of salt species M_1Cl and M_2Cl respectively in a kilogram of water. From Eq. (23) the mean activity coefficients of each of these species is

$$ln\gamma_{M_1Cl\pm} = ln\gamma^{calc}_{M_1Cl} + \beta_{12}d_2m_2 \tag{28a}$$

and

$$ln\gamma_{M_2Cl} = ln\gamma^{calc}_{M_2Cl} + \beta_{21}d_1m_1 \tag{28b}$$

Now, in Eqs. (28a and 28b) the terms $ln\gamma^{calc}_{M_1Cl}$ and $ln\gamma^{calc}_{M_2Cl}$ respectively, can be decomposed using exactly the same procedure as in the formulation of $ln\gamma_{Cl^-}$ in Eq. (205) Chapter 2. Decomposition of $ln\gamma^{calc}_{M_1Cl}$ and $ln\gamma^{calc}_{M_1Cl}$ *in both cases leads to an identical equation for* $ln\gamma^{calc}_{Cl^-}$ *irrespective of the concentrations* m_1 *and* m_2 i.e. from Eq. (205) and assuming that the hydration number for Cl^- is zero

$$ln\gamma^{calc}_{Cl^-} = ln\gamma^{DH}_{Cl^-} + \frac{0{,}018\; q_-A'}{B''} - lnB' - (q_- - q^{\circ}_-) + ln(q_-/q^{\circ}_-) - \sum_{j=1,2} m_j \frac{\partial q_j}{\partial m_{Cl^-}} \{Y\} \tag{29}$$

where

$$ln\gamma^{DH}_{Cl^-} = \frac{-\,2{,}303\; z_-^2\; .\; A\sqrt{\mu}}{1 + \beta \mathring{a}\; \sqrt{\mu}}$$

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$$\mathring{a} = r^{h}_{Cl^-} + \frac{[M_1^+]}{m_T} r^{h}_{M_1^+} + \frac{[M_2^+]}{m_T} r^{h}_{M_2^+}$$

$$A' = \sum_j mq + \sum_j mh - \sum_j md$$

$$B'' = (1 + 0{,}018 \sum_j mq)$$

$$B' = (1 + 0{,}018 \sum_j mr)$$

$$Y = \{\frac{q_j + h_j - d_j}{q_j + h_j} - \sum_j (0{,}018\ m_j h_j \frac{(q_j + h_j\ 1\ d_j)}{q_j + h_j})\}$$

In order to write down the complete equation for $ln\gamma_{Cl^-}$, consideration must be taken of the interaction terms $\beta_{12}d_2m_2$ and $\beta_{21}d_1m_1$ in Eqs. (28a and 28b) respectively. From the argument below, these two terms can be considered as cation-cation interaction terms the values of which have no influence.

> Consider the ternary system made up of the two chloride salts M_1Cl and M_2Cl where M_1Cl is at a trace concentration. For this condition, whereas the term $\beta_{21}d_1m_1$ in Eq. (28b) equals zero, the term $\beta_{12}d_2m_2$ in Eq. (28a) has some finite value. Consequently, if these interaction terms are considered to influence γ_{Cl^-}, an inconsistency arises because the value for $ln\gamma_{Cl^-}$ will now depend on which equation is decomposed to give the equation for $ln\gamma_{Cl^-}$. The only means of maintaining consistency is to assume that the interaction terms arise from cation-cation effects and have no influence on the value of γ_{Cl^-}, i.e.
>
> $$ln\gamma_{Cl^-} = ln\gamma^{calc}_{Cl^-}$$

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The reasoning above, i.e. to place the interaction effects $\beta_{12}d_2m_2$ and $\beta_{21}d_1m_1$ totally on the cation species, is to satisfy the necessity of obtaining a consistent equation for $ln\gamma_{Cl^-}$, that is, to obtain exactly the same equation for $ln\gamma_{Cl^-}$ irrespective of which equation for $ln\gamma_{MCl}$ is decomposed. However, there are further theoretical factors which tend to support the approach adopted, as follows:

> The interaction terms $\beta_{12}m_2$ and $\beta_{21}m_1$ arise in the mixed system analyses because of the necessity of utilizing the ionic strength principle to predict hydration numbers and partial molal volumes of the species and the changes in these parameters with chemical dosing (see Eq. 18). However, for Cl^- the hydration number is accepted as zero so that the error arising from the utilization of the ionic strength principle to predict hydration numbers is attributed totally to the cation species. Furthermore, for the partial molal volume of Cl^- in a mixed system, this parameter is estimated using the semi empirical expression, Eq. (74) Chapter 2, and not the ionic strength principle. The interaction terms therefore account for deviations in the cation species hydration numbers and partial molal volumes on mixing different salt types.

Once the chloride ion activity coefficient has been determined using Eq. (29) and the mean activity coefficient determined using Eq. (27), the various cation species activity coefficients are then determined, i.e. for the salt MCl_x,

$$\gamma_{M^{x+}} = (\gamma_{MCl_{x\pm}})^{x+1}/\gamma_{Cl^-}^{\ x}$$

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Example

Determine γ_{Cl^-} in synthetic seawater with the following molal composition: NaCl = 0,4644, KCl = 0,0106, $CaCl_2$ = 0,0108, $MgCl_2$ = 0,0552, HCl = 0,01 and temperature is 25°C.

To determine γ_{Cl^-} using Eq. (29), first values must be determined for the following parameters: q_j, r_j, h_j, $\overset{o}{a}_{Cl}$, q^o_{Cl}, q_{Cl} and $\partial q_j/\partial m_{Cl}$ where 'j' is the generic salt term and refers to either NaCl, KCl, $CaCl_2$, $MgCl_2$ or HCl.

Values for the parameters q_j, r_j and h_j were determined in the previous example and are listed in Table 4.

For $\overset{o}{a}_{Cl^-}$, from Eq. (19b) and Table 1:

$$\overset{o}{a}_{Cl^-} = r^h_{Cl^-} + \sum_j \frac{m_{j+}}{m_T} \cdot r^h_{j+}$$

$$= 1,81 + (0,4644.3,14\ 0,0106.2,54 + 0,0108.3,84 + 0,0552.3,79$$

$$+ 0,01.3,79)/0,551$$

$$= 5,03 \text{ Angstrom units} \qquad (30a)$$

For q^o_{Cl}, from Table 2b) Chapter 2:

$$q^o_{Cl} = \bar{V}^o_{Cl}/18,0 = 1,40 \qquad (30b)$$

For q_{Cl}, from Eq. (76) Chapter 2:

$$q_{Cl} = (\bar{V}^o_{Cl} + \frac{z_-^2\ 2^{\frac{1}{2}}\sqrt{\mu}}{1 + B\overset{o}{a}\sqrt{\mu}} + \frac{1}{2} z_-^2\ k\sum_i C_i)/18$$

$$= (25,2 + 1,07)/18 = 1,46\ ^* \qquad (30c)$$

---

* The change predicted here in $\bar{V}_{Cl}$ from its value at infinite dilution in pure water to its value in seawater, i.e. 1,07 mℓ/mole, is very close to that predicted by Millero (1969), i.e. 1,0 mℓ/mole, determined using the same empirical approach of Mukerjee (1961).

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For $m_j.\partial q_j/\partial m_{Cl}$, from the ionic strength principle

$$m_j = \frac{\partial q_j}{\partial m_{Cl}} = m_j \frac{\partial q_j}{\partial \mu} . \frac{\partial \mu}{dm_{Cl}}$$

$$= \frac{1}{2} m_j \frac{\partial q_j}{\partial \mu}$$

$$= [\tfrac{1}{4} m_j \; 1{,}5S_v^*/\{(\tfrac{1}{2}d_{j+}z_{j+}^2 + \tfrac{1}{2}d_{j-}z_{j-}^2)\mu\}^{1/2}]/18{,}0 \qquad (30d)$$

Substituting for å from Eq. (30a) into Eq. (29)

$$ln\gamma_{Cl}^{DH} = \frac{-1{,}1706\mu^{1/2}}{1 + 0{,}328.5{,}03\ \mu^{1/2}} = -\ 0{,}4089$$

Substituting for h_j, q_j and r_j from Table 4 and for q_- from Eq. (30c)

$$\frac{0{,}018\ q\text{-}A'}{B''} - lnB' = 0{,}0126$$

Substituting q- and q_-^o from Eqs. (30b and 30c) respectively into Eq. (29)

$$ln(q_-/q_-^o) - (q_- - q_-^o) = 0{,}0420 - 0{,}060 = -\ 0{,}018$$

For the term $\sum_j m_j \frac{\partial q_j}{\partial m_{Cl^-}} \{Y\}$ in Eq. (29): Substituting for q_j and h_j from Table 4 and for S_v^* from Table 4, Chapter 2 gives

$$\sum_j m_j \frac{\partial q_j}{\partial m_{Cl}} \{Y\} = -\ 0{,}022$$

i.e.

$$ln\gamma_{Cl^-} = -\ 0{,}4089 + 0{,}0126 - 0{,}018 - 0{,}022 = -\ 0{,}436$$

i.e.

$$\gamma_{Cl^-} = 0{,}646$$

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3. MEAN ACTIVITY COEFFICIENTS IN SOLUTIONS WHERE IONIC ASSOCIATION OCCURS

3.1 Mixed systems containing sulphate species

When ionic association occurs the ionic matrix differs from that indicated by a salt analysis. Ion association causes (i) a reduction in the concentrations of the various free ion species, (ii) a reduction in the ionic strength of the solution, and (iii) a change in the theoretical mean activity coefficients of all the free ions. Consequently, cognisance must be taken of ion association in the prediction of mean and single ion activity coefficients.

Ion association can be divided into two categories:

(a) Ion association of species in trace concentrations; these are of vital importance in analyses of pH control and in the distribution of various trace elements in high salinity waters. However, their concentrations are so low that they have insignificant effect on the matrix of the principal ionic species. The carbonate species which ion pair significantly with the principal cation species Ca^{2+}, Mg^{2+}, Na^{+} and K^{+} are examples. Their effects are considered in detail in Chapter 4.

(b) Ion association between species constituting the principal ionic matrix; These affect implicitly the ionic strength, the ionic concentrations of free species and the activities of all species, as listed in (i) to (iii) above. Sulphate ions are an important example of this category for natural high salinity waters. In these waters sulphate species often form a significant fraction of the principal ions in the solution. Sulphate

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ions readily associate with Mg^{2+}, Ca^{2+}, Na^{+} and K^{+} and may have a significant effect on the ionic matrix of the principal ions.

To incorporate ion association in the matrix analyses the following need to be accepted:

(i) The analytical mass of salt species is given by the sum of the free and ion associated species.

(ii) The formation of associated species results in the loss of hydrated water by the species forming the ion pair.

(iii) The activities of associated species and the constituent free ions exist in a state of equilibrium expressed by an equilibrium equation.

Incorporation of sulphate ion association is simplified considerably by accepting that ion pairing does not occur between the cesium and sulphate ions.

If sulphate does not ion pair with a particular cation, then a binary solution of that cation and sulphate should be amenable to fitting $\gamma_\pm$ in accordance with Eq. (189) Chapter 2 as for any non-associated electrolyte. This in fact appears to be the case for a binary sulphate solution with Cs^{+} as cation, but *not* for binary solutions with Mg^{2+}, Ca^{2+}, Na^{+} or K^{+} respectively as cations, indicating that in the latter group of solutions there are factor(s) present other than those due to non-association, for example, ion pairing.

The fit of $\gamma_\pm$ (Cs_2SO_4) using Eq. (189) Chapter 2 with observed values is shown in Table 5. The fit is remarkably good up to I = 5,4 (the upper limit of reported data) lending strong support to the hypothesis that Cs^{+} does not ion pair with $SO_4^{=}$. Note that the fit required $\mathring{a} = 3{,}45$ and $h = 0{,}4$.

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Table 5. Comparison of observed data for $\gamma_\pm$ (Cs_2SO_4)* with theoretical values determined from Eq. (189) Chapter 2 with $\mathring{a} = 3{,}45$ and h = 0,4**

m (molality)	I	$\gamma_\pm$(predicted)	$\gamma_\pm$(observed)
0,1	0,3	0,450	0,456
0,5	1,5	0,292	0,291
1,0	3,0	0,237	0,235
1,6	4,8	0,209	0,207
1,8	5,4	0,204	0,201

* Observed data taken from Robinson and Stokes (1955)

** In the determination of $\gamma_\pm$ from Eq. (189) Chapter 2, no data could be found in the literature for the apparent and partial molal volumes for Cs_2SO_4. Consequently, values for $\bar{V}^\circ$ and ϕ° were determined using the additivity principle and single ion $\bar{V}^\circ$ values listed in Table 2b, Chapter 2 and the deviations from ideality determined using the Redlich-Rosenfeld equation, i.e.

$$\bar{V}_i = \bar{V}_i^\circ + 1{,}5\, S_v\sqrt{C} = 42{,}7 + 1{,}5.14{,}944\, \sqrt{C}$$

$$\phi_i = \phi_i^\circ + S_v\sqrt{C} = 42{,}7 + 14{,}944\, \sqrt{C}$$

3.1.1 *Properties of the sulphate ion*

The importance of the conclusion that Cs^+ does not associate with $SO_4^=$ lies in the opportunity it affords to determine both the hydration number and the hydrated radius for $SO_4^=$. Once this information is available, by using the additivity principle it would be possible to assign values for $\mathring{a}$ and h for the *unassociated ionic species* of the salts $Mg\,SO_4$, $Ca\,SO_4$, Na_2SO_4 etc. in aqueous solutions.

The hydration number and hydrated radius for $SO_4^=$ are determined from the values determined for $\overset{o}{a}$ and h for binary systems of CsCl and Cs_2SO_4 using the additivity principle as follows:

> For Cs^+ it was shown in Section 6 Chapter 2 that the hydration number and hydrated radius have values of 0,2 and 1,45 Angstrom units respectively, for the salt Cs_2SO_4, from Table 5, the sum of the hydration number and the sum of the hydrated radii of Cs^+ and $SO_4^=$ (i.e. $\overset{o}{a}$) have values of 0,4 and 3,45 Angstrom units respectively. Hence, applying the additivity principle to determine the hydration number of $SO_4^=$,
> $h(SO_4^=) = h(Cs_2SO_4) - 2h(Cs^+) = 0{,}4 - 0{,}4 = 0{,}0$
> and for the hydrated radius of SO_4,
> $r^h_{SO_4} = \overset{o}{a}(Cs^+:SO_4^=) - r^h_{Cs} = 3{,}45 - 1{,}45 = 2{,}00$
> Angstrom units.

Having established values for the hydration number and hydrated radius for $SO_4^=$ from the Cs_2SO_4 system, and values for the various alkali and alkaline earth metals from the binary chloride systems discussed in Chapter 2, applying the additivity principle gives the hydration numbers and $\overset{o}{a}$ values for the unassociated salt species $MgSO_4$, $CaSO_4$, etc. For example, for the *unassociated* salt species Na_2SO_4 from Table 4 Chapter 2 the hydration number and hydrated radius for Na^+ are 2,40 and 3,14 Angstrom units respectively, applying the additivity principle.

$$\overset{o}{a}(Na^+:SO_4^{2-}) = r^h_{Na} + r^h_{SO_4} = 3{,}14 + 2{,}00 = 5{,}14 \text{ Angstrom units}$$

$$h(Na_2SO_4) = 2h_{Na} + h_{SO_4} = 4{,}80 + 0{,}0 = 4{,}8$$

In Table 6 are listed $\overset{o}{a}$ and hydration numbers for the unassociated species of various metal sulphate salts likely to constitute a principal part of the ionic matrix of naturally occurring highly saline waters.

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Having established $\mathring{a}$ and hydration numbers for the unassociated species of various metal sulphate solutions, it is now possible to analyse sulphate solutions in which ion pairing occurs.

Table 6. Distance of closest approach and hydration numbers for the *unassociated* species of various alkali and alkaline earth metal sulphate solutions

Species	r_+^h	r_-^h	h_+	h_-	$\mathring{a}$ (cation-anion)	h(salt)
$MgSO_4$	3,79	2,00	8,12	0,00	5,79	8,12
$CaSO_4$	3,84	2,00	7,05	0,00	5,84	7,05
Na_2SO_4	3,14	2,00	2,4	0,00	5,14	4,8
K_2SO_4	2,54	2,00	1,01	0,00	4,54	2,02
Cs_2SO_4	1,64	2,00	0,2	0,00	3,55	0,4

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3.1.2 *Binary sulphate systems including ionic association*

The mean activity of a binary salt, $a_\pm$, is amenable to experimental measurement. In general, $a_\pm$ can be expressed either in terms of stoichiometric concentrations and a stoichiometric mean activity coefficient, i.e.

$$a_\pm = \gamma_{T\pm} \cdot m_{T\pm} \tag{31a}$$

or in terms of free species concentrations and the mean activity coefficient of the free species, i.e.

$$a_\pm = \gamma_\pm \cdot m_\pm \tag{31b}$$

where

$m_{T\pm}$ = mean molality of the total ionic species concentrations, i.e. the mean molality of the analytical ionic species concentrations

$\gamma_{T\pm}$ = the stoichiometric mean activity coefficient

$m_{\pm}$ = mean molality of the free species concentrations

$\gamma_{\pm}$ = mean ionic activity coefficient of the free species.

The link between the stoichiometric scale and free species scale is obtained by equating Eqs. (31a and 31b), i.e.

$$\gamma_{T\pm} \cdot m_{T\pm} = \gamma_{\pm} \cdot m_{\pm} \qquad (31c)$$

Usually mean activity coefficient data are reported on the stoichiometric scale. This is because $a_{\pm}$ is measured and $m_{T\pm}$ is known from input data to the system. However, for the purposes of *predicting* mean activity coefficients, whereas the stoichiometric values can be predicted only by using an empirical approach, the free species values can be predicted from basic theory. From this standpoint, the free species scale is the more useful. Furthermore, if the complete ionic matrix is required then it is necessary to utilize the mean activity in terms of the mean ionic molality of the free (unassociated) species), $m_{\pm}$, and the corresponding mean activity coefficient, $\gamma_{\pm}$, i.e. from Eq. (31b)

$$m_{\pm} = a_{\pm}/\gamma_{\pm} \qquad (32)$$

If either $m_{\pm}$ or $\gamma_{\pm}$ can be evaluated (and $a_{\pm}$ is measured), then in fact an exact description of the ionic matrix and its properties is available because the ion associated species molality can then be determined from mass balance considerations. For example, if $\gamma_{\pm}$ can be determined and $a_{\pm}$ is measured, $m_{\pm}$ is found from Eq. (32). The ion associated species molality, $m_{\pm}$, then is determined from mass balance considerations as follows:

For a symmetrical sulphate salt forming the ion paired species MSO_4°

$$[MSO_4^{\circ}] = m_{T\pm} - m_{\pm} \qquad (33)$$

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For an unsymmetrical salt forming both ion paired and treble ion species MSO_4^- and $M_2SO_4^{\circ}$ respectively:

mass balance of the cation species M in solution gives

$$2m_T = [M^+] + [MSO_4^-] + 2[M_2SO_4^{\circ}] \tag{34a}$$

a mass balance of the anion sulphate species

$$m_T = [SO_4^{2-}] + [MSO_4^-] + [M_2SO_4^{\circ}] \tag{34b}$$

a charge balance of the system (ignoring the water terms H^+ and OH^- which have equal (and negligible) concentrations)

$$[M^+] = 2[SO_4^{2-}] + [MSO_4^-] \tag{34c}$$

By definition of the mean free ion molality, $m_{\pm}$,

$$m_{\pm} = \{[M^+]^{d_+}[SO_4^{2-}]^{d_-}\}^{1/d} \tag{34d}$$

Equations (34a to 34d) for a binary system containing an unsymmetrical salt constitute four equations with four unknown parameters, $[M^+]$, $[SO_4^{2-}]$, $[MSO_4^-]$ and $[M_2SO_4^{\circ}]$, so that (theoretically at least) it is possible to determine the ion associated species concentrations provided that the value for $\gamma_{\pm}$ in Eq. (31) is known.

In the description above it was assumed that values for $\gamma_{T\pm}$, $m_{T\pm}$ and $\gamma_{\pm}$ are known. However, in practice for binary systems this is not usually the case; usually data is reported for $\gamma_{T\pm}$ and $m_{T\pm}$ and it is required to determine $\gamma_{\pm}$ and the free and ion paired species concentrations. This introduces $\gamma_{\pm}$ as an extra unknown parameter in the system of equations and requires introducing an extra equation(s) and/or making some assumption in order to resolve the unknowns. An extra equation(s) is available from ion association equilibrium considerations:

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For a symmetrical sulphate salt, MSO_4, in an aqueous solution there is only one associated species, the neutral ion paired species MSO_4^o, and the equilibrium equation is

$$(\gamma_{2+}[M^{2+}]\ \gamma_{2-}[SO_4^{2-}])/(\gamma_N[MSO_4^o]) = K_{sy}$$

i.e.

$$(\gamma_{\pm}\ m_{\pm})^2/(\gamma_N[MSO_4^o]) = K_{sy} \qquad (35)$$

where

K_{sy} = equilibrium dissociation constant for the ion paired species MSO_4^o

subscript 'N' = neutral species.

For an unsymmetrical sulphate salt, M_2SO_4, in an aqueous solution there are two associated species, a charged ion paired species MSO_4^- and an uncharged treble ion species, $M_2SO_4^o$. For the dissociation of the charged ion paired species MSO_4^-:

$$\frac{\gamma_+[M^+]\gamma_{2-}[SO_4^{2-}]}{\gamma_{I-}\ [MSO_4^-]} = K_{u1}$$

i.e.

$$\frac{(\gamma_+[M^+])^2(\gamma_{2-}[SO_4^{2-}]}{\gamma_+[M^+]\ \gamma_{I-}[MSO_4^-]} = K_{u1}$$

i.e.

$$\frac{(\gamma_{\pm}m_{\pm})^d}{(\gamma_{I\pm}m_{I\pm})^{d_i}} = K_{u1} \qquad (36a)$$

where

$m_{I\pm}$ = mean ionic molality of cation species M^+ and the negatively charged ion pair species MSO_4^-

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d_i = moles of cation and ion paired species required to associate to form one mole of salt species M_2SO_4.

K_{u1} = equilibrium dissociation constant for ion pairing.

For the dissociation of the treble ion species $M_2SO_4^o$:

$$\frac{(\gamma_+[M^+])^2(\gamma_{2-}[SO_4^2])}{\gamma_N[M_2SO_4^o]} = K_{u2}$$

i.e.

$$\frac{(\gamma_\pm m_\pm)^d}{\gamma_N[M_2SO_4^o]} = K_{u2} \qquad (36b)$$

Acceptance of the equilibrium expression(s), Eqs. (35 or 36a and 36b), as an extra equation(s) in itself introduces an unknown parameter γ_N for symmetrical salts, and $\gamma_{I\pm}$ and γ_N for unsymmetrical salts. Furthermore, the equilibrium constants K_{sy} or K_{u1} and K_{u2} for symmetrical or unsymmetrical salts may be either known or unknown. That is, for symmetrical salts we now have three equations (Eqs. 31, 33 and 36) with four unknowns $\gamma_\pm$, γ_N, $m_\pm$ and m_I (and if the equilibrium constant is unknown, five unknowns). For unsymmetrical salts we have seven equations (Eqs. 31, 34a to 34d, 36a and 36b) with eight unknowns $\gamma_\pm$, $\gamma_{I\pm}$, γ_N, $[M^+]$, $[SO_4^{2-}]$, $[MSO_4^-]$, $[M_2SO_4^o]$ and $m_\pm$ (and if the equilibrium constants K_{u1} and K_{u2} are unknown, ten unknowns). Solution therefore can be carried out only if some assumption(s) are made (the number of assumptions to be made depending on whether the values of the equilibrium constants are known).

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With regard to the equilibrium constants, values reported in the literature for the various sulphate ion pairs show great dispersion depending on the method of estimation; for example, for $MgSO_4^o$ reported values for the equilibrium dissociation constant range from 0,0033 to 0,0075. It is not possible to select which of the reported values is the best. Therefore it would appear that the best approach is to determine the value of one of the other unknown parameters by some theoretical means, for example $\gamma_\pm$ for a symmetrical salt, and to redetermine a value for the equilibrium constant in terms of the method used for determining $\gamma_\pm$. This at least ensures consistency between the equilibrium constant, K, and the values determined for $\gamma_\pm$ and the free and ion paired species concentrations.

Now, from basic considerations, it is not possible using, for example, the approach set out in the formulation of Eq. (18) for $\gamma_\pm$ in a mixture of non-associated salts, to formulate an equation for $\gamma_\pm$ between a cation and anion species that ion pair with each other. However, an indirect solution procedure to the problem is possible if one considers an aqueous sulphate solution as a mixed system containing trace (or actual) concentrations of the ions Cs^+ and Cl^-.

Briefly, the indirect approach for determining $\gamma_\pm$ is as follows:

> The approach hinges around the two observations earlier that Cs^+ does not form ion pairs with SO_4^{2-} and that Cl^- does not form ion pairs with any of the cation species of interest here. Consequently it is possible to formulate equations for $\gamma_{CsCl\pm}$, $\gamma_{Cs_2SO_4\pm}$ and $\gamma_{MCl_2}{}^\pm$ (for an aqueous binary system containing the salt MSO_4) using the mixed electrolyte non associated theory, i.e. Eqs. (18 and 27)*. Furthermore, it is possible to formulate an equation for γ_{Cl^-} in the solution from Eq. (29). Now, for a symmetrical salt, each of these

equations will include the hydration number for the ion paired species, $h(MSO_4^o)$, which initially is unknown. If the value of $h(MSO_4^o)$ were known then it would be possible to determine each of the mean activity coefficients $\gamma_{CsCl\pm}$, $\gamma_{CsSO_4^\pm}$, $\gamma_{MCl_2^\pm}$ and also γ_{Cl^-}. Hence it would be possible to determine $\gamma_{MSO_4^\pm}$ and the free and ion paired species concentration for any input values of $\gamma_{T\pm}$ and $m_{T\pm}$. However, the approach does not give directly the value for the equilibrium constant, K_{sy}, but gives the product of γ_N and K_{sy} for each of the input data. Now, the neutral species form dipoles in solution, Kester (1969), and consequently there will be an electrostatic contribution to the activity coefficient of the neutral species, but this contribution is not known so that it is not possible to model it and therefore we cannot formulate a theoretical model for predicting γ_N. For this reason the procedure above was modified and *the assumption is made that the neutral ion paired species activity coefficient,* γ_N, *always equals unity.* Using this assumption the theoretical value determined for $\gamma_{T\pm}$ is fitted against the observed value for a

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* Extension of Eqs. (18 and 27) to $\gamma_\pm$ for chloride salts in systems containing $SO_4^=$ is based on the theory for single ion activity coefficients, Section 2.3.3. In that section it was shown that the effects of the interaction constants (i.e. β_{ji} in Eq. (27) had to be placed totally on the cation species - this was necessary so that the equation for the activity coefficient of Cl^- was consistent, i.e. that one obtained an identical expression for γ_{Cl^-} irrespective of which salt mean activity coefficient equation was decomposed. Based on this requirement, it was shown that m_i in Eq. (27) is the molality of cation species i and that β_{ji} is an interaction constant of cation species 'i' on cation species 'j' where $ln\gamma_{j\pm}$ is to be determined.

range of $m_{T\pm}$ values by adjusting the values of the equilibrium constant, K_{sy}, and the hydration number for MSO_4^o. The approach, therefore, is to lump the neutral species activity coefficient effects into the hydration number determined for the neutral species.

For unsymmetrical salts the approach is similar to that above for symmetrical salts. That is, the mean activity coefficient between M^+ and SO_4^{2-}, $\gamma_{M_2SO_4^{\pm}}$, in an aqueous binary system of M_2SO_4 is again determined by considering the solution to contain trace concentrations of Cs^+ and Cl^- and determining $\gamma_{CsCl\pm}$, $\gamma_{Cs_2SO_4^{\pm}}$, $\gamma_{MCl\pm}$ and γ_{Cl^-} using the unassociated theory. However, for unsymmetrical salts these equations for $\gamma_{\pm}$ and γ_{Cl^-} include the hydration numbers of both the ion pair species, MSO_4^-, and the treble ion species, $M_2SO_4^o$. Furthermore, the equilibrium dissociation equation for MSO_4^-, Eq. (36a), also includes a term for the mean activity coefficient for the species M^+ and MSO_4^-, i.e. $\gamma_{I\pm}$. In order to resolve systems involving unsymmetrical sulphate salts it becomes necessary to assume values for the hydration numbers of each of the species MSO_4^o and $M_2SO_4^o$ and also for the hydration radius of the species MSO_4.

The essence of the approaches to binary solutions of symmetrical and unsymmetrical sulphate salts is similar but there are broad differences in the assumptions necessary to resolve problems arising with each of these systems as outlined above. The assumptions and the repercussions in utilizing these are discussed in detail below

(a) Symmetrical 2-2 sulphate salts

For symmetrical sulphate salts two principal problems arise. First, to determine the ion pairing equilibrium constant from reported data for $\gamma_{T\pm}$ versus $m_{T\pm}$, and second, to determine $\gamma_{T\pm}$ in any electrolyte solution using the equilibrium constant determined earlier.

The solution techniques to both these problems are essentially identical. However, whereas for the first problem a value calculated for $\gamma_{T\pm}$ is fitted to the observed value by adjusting K_{sy} and the hydration number for MSO_4°, in the second case K_{sy} and $h(MSO_4^\circ)$ are known and $\gamma_{T\pm}$ is determined directly. The technique involved in determination of $\gamma_{T\pm}$, and $h(MSO_4^\circ)$ is set out below:

(1) Consider initially a 0,1 molal solution of the 2-2 salt MSO_4 in water.

(2) Assume initial values for (i) the equilibrium dissociation constant for ion pairing, K_{sy}, as equal to any of the values reported in the literature, and (ii) the hydration number of the ion paired species MSO_4° as equal to the sum of the hydration numbers for M^{2+} and SO_4^{2-}.

(3) Make an initial estimate of the mean activity coefficient for the *free species*, $\gamma_\pm$, using say the Davies equation and assuming the ionic strength of the solution is equal to the stoichiometric value based on m_T.

(4) Determine the free and ion paired species concentrations $[SO_4^{2-}]$, $[M^{2+}]$ and $[MSO_4^\circ]$ from the mass balance expressions below.

For $[SO_4^{2-}]$:

$$[SO_4]_T = [SO_4^{2-}](1 + \frac{\gamma_\pm^2[M]_T/K_{sy}}{(1 + [SO_4^{2-}]\gamma_\pm^2/K_{sy})})$$

For $[M^{2+}]$:

$$[M^{2+}] = [M]_T/(1 + [SO_4^{2-}]\gamma_\pm^2/K_{sy})$$

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and for $[MSO_4^o]$:

$$[MSO_4^o] = m_T - [M^+]$$

(5) Redetermine the ionic strength of the solution using the free and ion paired species concentrations from (4) above.

(6) Determine $\gamma_{CsCl\pm}$, $\gamma_{Cs_2SO_4^{\pm}}$ and $\gamma_{MCl_2^{\pm}}$ using the equation for the mean activity coefficient for species which do not form ion pairs in a mixed solution, Eqs. (18 and 27), and for γ_{Cl^-} from Eq. (29).

(7) Determine $\gamma_{\pm}$ for the free species M^{2+} and SO_4^{2-} from the values for $\gamma_{CsCl\pm}$, $\gamma_{Cs_2SO_4^{\pm}}$, γ_{MCl_2} and γ_{Cl^-} determined in (6) above

$$\gamma_{SO_4^{2-}} = \gamma^3_{Cs_2SO_4^{\pm}} \cdot \gamma_{Cl^-}/\gamma^2_{CsCl}$$

$$\gamma_{M^{2+}} = \gamma^3_{MCl_{2\pm}}/\gamma^2_{Cl^-}$$

$$\gamma_{MSO_4^{\pm}} = (\gamma_{M^{2+}} \cdot \gamma_{SO_4^{2-}})^{1/2}$$

$$= \gamma\pm$$

(8) Determine $\gamma_{T\pm}$ from Eq. (31c), i.e.

$$\gamma_{T\pm} = \gamma_{\pm} \cdot m_{\pm}/m_{T\pm}$$

(9) Repeat steps (4) to (8) until two successive values determined for $\gamma_{T\pm}$ do not differ by more than 10^{-4} activity coefficient units (usually only about three iterations are required).

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(10) Compare the value determined for $\gamma_{T\pm}$ with reported data for the particular salt molality under investigation. Two molalities are investigated initially, at (i) a low molality, and (ii) a high molality.

(i) Low molality: At a low molality, say $m_T = 0,1$ the value determined for $\gamma_{T\pm}$ is very sensitive to the value assumed for K_{sy}, but comparatively insensitive to the value assumed for $h(MSO_4^\circ)$. Consequently, where a low molality is investigated, if the value determined for $\gamma_{T\pm}$ differs from the observed value by more than 0,003 activity coefficient units then K_{sy} is adjusted and steps (4) to (10) repeated keeping constant the value for $h(MSO_4^\circ)$ determined in (ii) below;

(ii) High molality: At a relatively high molality, say $m_T = 1,0$, the value determined for $\gamma_{T\pm}$ is very sensitive to the values assumed for both K_{sy} and $h(MSO_4^\circ)$. Consequently, where a relatively high molality is investigated, if the value determined for $\gamma_{T\pm}$ differs from the observed value by more than 0,003 activity coefficient units then $h(MSO_4^\circ)$ is adjusted and steps (4) to (10) repeated keeping constant the value for K_{sy} determined in (i) above.

(11) Steps (10.i) and (10.ii) are repeated until a good fit is obtained between calculated and observed $\gamma_{T\pm}$ values in both the high and low molality regions.

In Table 7a are listed values determined for K_{sy} and $h(MgSO_4^\circ)$ for $MgSO_4^\circ$ using the technique set out above and experimental $\gamma_{T\pm}$ data for this salt reported by Glasstone (1966), Robinson and Stokes (1955).

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For $CaSO_4^o$ it was not possible to analyze the system as set out above. Calcium sulphate is an extremely insoluble salt so that it is not possible to obtain the activity coefficient data over the wide range of salt molality required in our approach, i.e. in the region $0{,}1 < m_T < 1{,}0$.

For $CaSO_4$ the approach is as follows: It is assumed that the ratio of $K(MgSO_4^o)$ to $K(CaSO_4^o)$ is a constant; the actual K values depending on the experimental method used. The value for this ratio can be determined by adjusting the apparent constants $K'(MgSO_4^o)$ and $K'(CaSO_4^o)$ reported by Kester and Pytkowicz (1968, 1969), i.e. 0,0980 and 0,0926 respectively, for activity coefficient effects. The values for the relevant activity coefficients for seawater determined in this monograph are listed in Table 15, Chapter 4, giving $K(MgSO_4^o)/K(CaSO_4^o) = 1{,}150$. Accepting this ratio and using our value for $K(MgSO_4^o) = 0{,}0040$ gives $K(CaSO_4^o) = 0{,}0036$. For the hydration number for $CaSO_4^o$. we assume an equal loss of primary hydrated water in the formation of both $MgSO_4^o$ and $CaSO_4^o$ from Mg^{2+} and SO_4^{2-}, and, from Ca^{2+} and SO_4^{2-} respectively, i.e. $h(CaSO_4^o)$ is estimated as

$$h(CaSO_4^o) = h(Ca^{2+}) + h(SO_4^{2-}) - \{h(Mg^{2+}) + h(SO_4^{2-}) - h(MgSO_4^o)\},$$

see Table 7b.

(b) Unsymmetrical 2-1 sulphate salts

For unsymmetrical sulphate salts (e.g. Na_2SO_4) in aqueous solution two ion associated species are assumed, a charged ion paired species MSO_4^- and a neutral treble ion species $M_2SO_4^o$. Consequently two equilibrium constants need to be determined. These constants can be determined using a similar approach to that set out above for symmetrical salts provided that (1) the hydration numbers are known for the associated species MSO_4^- and $M_2SO_4^o$, and (2) the mean activity coefficient for the species M^+ and MSO_4^-, $\gamma_{I\pm}$ in Eq (36a) and the neutral species activity coefficient, γ_N in Eq (36b) are known or can be determined.

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(1) Hydration numbers for MSO_4^- and $M_2SO_4^\circ$:

There is no independent means by which values for these parameters can be determined. Now in the analyses below it is found that the value determined for $\gamma_{T\pm}$ for unsymmetrical salts is very *insensitive* to the values assumed for the hydration numbers of the two associated species MSO_4^- and $M_2SO_4^\circ$. Knowing that associated species are formed with the loss of primary hydrated water from the free species forming the complex, and, noting that the analysis is insensitive to the mass of hydrated water lost, the assumptions made here are that in the formation of the ion pair, MSO_4^-, one molecule of hydrated water is lost, while in the formation of the neutral treble ion species, $M_2SO_4^\circ$, two molecules of hydrated water are lost,* i.e.

$$h(MSO_4^-) = h(M^+) + h(SO_4^{2-}) - 1{,}0 \ *$$

and

$$h(M_2SO_4^\circ) = 2.h(M^+) + h(SO_4^{2-}) - 2{,}0*$$

(2) For the mean activity coefficient $\gamma_{I\pm}$

An equation for $\gamma_{I\pm}$ can be written down using the non associated mixed electrolyte theory, i.e. Eq. (18) if it is assumed that a binary solution of a sulphate salt

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* The numerical assumption of hydrated water loss of one and two molecules for MSO_4^- and $M_2SO_4^\circ$ respectively is more to indicate that water is lost. The actual numerical values accepted are not crucial.

be considered a 'mixed' system made up of the species M^+, SO_4^{2-}, MSO_4^- and $M_2SO_4^o$. In order to utilize Eq. (18) the hydrated radius for MSO_4^- must be known (so that $\mathring{a}$ can be determined) as well as the hydration numbers and concentrations of the free and ion paired species. The values for the hydration numbers of species were dealt with in (1) above; the determination of free and ion paired species concentrations is dealt with below in a detailed analysis of 2-1 sulphate salts; the hydrated radius for the MSO_4^- species cannot be determined and some assumption must be used here. *We assume that the hydrated radius for* MSO_4^- *equals that for* SO_4^{2-} and accept that the error arising from this assumption is reflected in the values determined for the equilibrium constants K_{u1} and K_{u2} in Eqs. (36a and 36b) respectively; the neutral species activity coefficient γ_N in Eq. (36b) is assumed to be unity for the same reasons outlined above for symmetrical sulphate salts.

The solution technique involved in the determination of the free and ion paired species concentrations and the equilibrium constants K_{u1} and K_{u2} for unsymmetrical sulphate salts is set out below:

(1) Consider initially a 0,1 molal solution of the 2-1 salt M_2SO_4 in water.

(2) Assume initial values for (i) the equilibrium constant for ion pairing, K_{u1}, as equal to any of the values reported in the literature, (ii) the equilibrium dissociation constant for treble ion species, K_{u2}, as being negligible. (The hydration numbers for MSO_4^- and $M_2SO_4^o$ are set at the values discussed

previously, and the neutral species activity coefficient is assumed equal to unity).

(3) Make an initial estimate of the mean activity coefficient for the free species, $\gamma_{\pm}$, using say the Davies equation and assuming the ionic strength of the solution is equal to the stoichiometric value based on m_T.

(4) Determine the free and ion paired species concentrations from the mass balance equations.

For $[SO_4^{2-}]$

$$[SO_4]_T = [SO_4^{2-}] + \frac{[M^+][SO_4^{2-}]\gamma_{\pm}^3}{\gamma_{I\pm}^2 \cdot K_{u1}} + \frac{[M^+]^2[SO_4^{2-}]\gamma_{\pm}^3}{K_{u2}} \qquad (37a)$$

where

$$[M^+] = \{-B + (B^2 - 4[M]_T A)^{1/2}\}/2A \qquad (37b)$$

and $$B = 1 + \frac{[SO_4^{2-}]\gamma_{\pm}^3}{\gamma_{I\pm}^2 \cdot K_{u1}}$$

and $$A = [SO_4^{2-}]\gamma_{\pm}^3/K_{u2}$$

$[SO_4^{2-}]$ is determined from Eqs. (37a and 37b) using a method of successive approximation.

For $[M^+]$, substituting the value determined above for $[SO_4^{2-}]$ into Eq. (37b) gives $[M^+]$ directly.

For $[MSO_4^-]$, from Eq. (36a)

$$[MSO_4^-] = [M^+][SO_4^{2-}]\gamma_{\pm}^3/(\gamma_{I\pm}^2 \cdot K_{u1})$$

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and for $[M_2SO_4^o]$ from Eq. (36b)

$$[M_2SO_4^o] = \{[M^+]^2[SO_4^{2-}] \, . \, \gamma_\pm^3\}/K_{u2}$$

(5) Redetermine the ionic strength of the solution using the free and ion paired species concentrations determined in (4) above.

(6) Determine $\gamma_{CsCl\pm}$, $\gamma_{Cs_2SO_4^\pm}$ and $\gamma_{MCl_2^\pm}$ using the equation for the mean activity coefficient in a mixed system for species which do not form associated species, Eq. (18), and for γ_{Cl^-} from Eq. (29).

(7) Determine $\gamma_\pm$ for the free species M^+ and SO_4^{2-}, $\gamma_{M_2SO_4^\pm}$, from the values for $\gamma_{CsCl\pm}$, $\gamma_{Cs_2SO_4^\pm}$, $\gamma_{MCl\pm}$ and γ_{Cl^-} determined in (6) above

$$\gamma_{SO_4^2} = \gamma^3_{Cs_2SO_4^\pm} \, . \, \gamma_{Cl}/\gamma^2_{CsCl\pm}$$

$$\gamma_{M^+} = \gamma^2_{MCl\pm}/\gamma_{Cl^-}$$

$$\gamma_{M_2SO_4^\pm} = (\gamma^2_{M^+} \, . \, \gamma_{SO_4^{2-}})^{1/3}$$

$$= \gamma_\pm$$

(8) Determine the stoichiometric (total) mean activity coefficient for M_2SO_4, $\gamma_{T\pm}$, from Eq. (31c)

$$\gamma_{T\pm} = \gamma_\pm \, . \, m_\pm/m_{T\pm}$$

(9) Repeat steps (4) to (8) until two successive values determined for $\gamma_{T\pm}$ do not differ by more than 10^{-4} activity coefficient units

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(10) Compare the value determined for $\gamma_{T\pm}$ with reported data for the particular salt molality under investigation. For the purposes of determining the two association constants, K_{u1} and K_{u2}, initially two molalities are investigated, (i) a low molality, and (ii) a high molality.

(i) Low molality: At a low molality, say $m_T = 0{,}1$ the value determined for $\gamma_{T\pm}$ is very sensitive to the value assumed for the ion pairing equilibrium constant, K_{u1}, but comparatively insensitive to the value assumed for the treble ion equilibrium constant, K_{u2}. Consequently, where a low molality is investigated, if the value determined for $\gamma_{T\pm}$ differs from the observed value by more than 0,003 activity coefficient units then K_{u1} is adjusted and steps (4) to (10) repeated keeping constant the value of K_{u2} determined in (ii) below;

(ii) High molality: At a relatively high molality say $m_T = 3{,}0$, the value determined for $\gamma_{T\pm}$ is very sensitive to the values assumed for both K_{u1} and K_{u2}. Consequently, where a relatively high molality is investigated, if the value determined for $\gamma_{T\pm}$ differs from the observed value by more than 0,003 activity coefficient units then K_{u2} is adjusted and steps (4) to (10) repeated keeping constant the value for K_{u1} determined in (i) above.

(11) Steps (10.i) and (10.ii) are repeated until a good fit is obtained between calculated and observed $\gamma_{T\pm}$ values in both the high and low molality regions.

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The calculation procedures set out above for determining mean activity coefficients and/or ionic association equilibrium constants are complex and utilize iterative procedures. Consequently, in practice these calculations are practical only with the aid of a computer. In Supplement A to this monograph is listed a computer program print out for carrying out such computations. Values for the partial molal volumes, hydrated radii and hydration numbers of the various species utilized in the program for the determination of ionic association equilibrium constants are summarized in Tables 7a to 7d. Also listed are the values determined for the equilibrium constants from activity coefficient data on binary systems for $MgSO_4$ (from Glasstone, 1966) and K_2SO_4 and Na_2SO_4 (from Robinson and Stokes, 1968).

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4. VERIFICATION OF MIXED ELECTROLYTE THEORY

The severest test of the mixed electrolyte theory is the degree in which it can predict the behaviour of high salinity waters containing sulphate ions. In the previous section equilibrium constants are determined for ionic association between SO_4^{2-} and the principal cations likely to occur in natural waters, i.e. Mg^{2+}, Ca^{2+}, Na^+ and K^+. For the purposes of these determinations each of the binary aqueous sulphate systems were considered to be ternary systems with Cl^- at a trace concentration. Consequently, the analytical method and the computer program to carry out the analyses (listed in Supplement A), can be used directly for predicting activity coefficients in systems where Cl^- is present at significant concentrations. For these systems there is a wealth of experimental data reported in the literature so that it is possible to compare predicted with observed activity coefficient data and thereby assess the validity of the model.

For the purposes of assessing the model, observed and predicted activity coefficients are compared in the following systems:

(i) $\gamma^{T}_{NaCl\pm}$ in aqueous mixtures of NaCl and Na_2SO_4 at stoichiometric ionic strengths of 1,0 and 3,0 using reported data from Wu, Rush and Scatchard (1969) and Lanier (1965), see Fig. 3.

(ii) $\gamma^{T}_{Na_2SO_4\pm}$ in aqueous mixtures of NaCl and Na_2SO_4 at a stoichiometric ionic strength of unity using reported data from Synnot and Butler (1968), see Fig. 3.

(iii) $\gamma^{T}_{NaCl\pm}$ in aqueous mixtures of NaCl and $MgSO_4$ at stoichiometric ionic strengths of 1,0, 2,0 and 3,0 using data from Wu *et al* (1969), see Fig, 4.

(iv) $\gamma^{T}_{NaCl\pm}$ in aqueous mixtures of $MgCl_2$ and Na_2SO_4 at stoichiometric ionic strengths of 0,9, 1,5 and 3,0 using data from Wu, Rush and Scatchard (1969), see Fig. 5.

(v) $\gamma^{T}_{KCl\pm}$ in aqueous mixtures of KCl and $MgSO_4$ at a stoichiometric ionic strength of unity using data from Christenson and Gieskes (1971), see Fig. 6.

(vi) $\gamma^{T}_{KCl\pm}$ in aqueous mixtures of KCl and K_2SO_4 at a stoichiometric ionic strength of unity using data from Christenson and Gieskes (1971), see Fig. 7.

(vii) $\gamma^{T}_{NaCl\pm}$, $\gamma^{T}_{KCl\pm}$, $\gamma^{T}_{Na_2SO_4\pm}$, $\gamma^{T}_{K_2SO_4\pm}$, $\gamma_{HCl\pm}$ and $\gamma^{T}_{CaSO_4\pm}$ in seawater and synthetic seawater using data listed by Whitfield (1975), see Table 8.

For all the solutions investigated above, the predicted and observed activity coefficients agree to within 0,01 activity coefficient units. Further supporting evidence arises from predicted and observed activity coefficient data in those aqueous mixtures comprised of a chloride salt and a sulphate salt each with a different cation species, i.e. $\gamma^{T}_{NaCl\pm}$ in solutions of NaCl and $MgSO_4$

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Table 7a. Values for salt and single ion species parameters utilized in the determination of the ion pairing equilibrium constant for $MgSO_4^\circ$ at 25°C with Cs^+ and Cl^- at trace concentration

$$MgSO_4^\circ \rightleftarrows Mg^{2+} + SO_4^{2-};\ K = 0{,}0040;\ pK = 2{,}40$$

Species	$\bar{V}_i$ ** mℓ/mole	$h_i = h_i^\circ - \Delta h$ (see Table 4 Chapter 2)	Hydrated radius r^h	$\mathring{a}_+$ and $\mathring{a}_-$ in Eq.(18)	Cation interaction effect. θ_{ij} (See Table 2)
CsCl	$39{,}15 + 2{,}81\ \mu^{1/2}$	$0{,}2 - 1{,}2.10^{-4}.\mu^2$			0,0 (No data)
Cs_2SO_4	$56{,}7 + 14{,}55(\mu/3)^{1/2}$	$1{,}0^\dagger$			0,0 (No data)
$MgCl_2$	$14{,}5 + 7{,}73\ (\mu/3)^{1/2}$	$8{,}12^\dagger$			
Cs^+		$0{,}2^\dagger$	1,45	$1{,}45 + \sum_{i-} \frac{[A_i^-]}{m_{T-}} . r_{i-}^h$ #	
Cl^-	$25{,}2 + \Delta\bar{V}_{Cl}$	$0{,}0^\dagger$	1,81	$1{,}81 + \sum_{i+} \frac{[M_i^+]}{m_{T+}} . r_{i+}^h$ #	
SO_4^{2-}		$0{,}00^\dagger$	2,00	$2{,}00 + \sum_{i+} \frac{[M^+]}{m_{T+}} . r_{i+}^h$ #	
Mg^{2+}		$8{,}12^\dagger$	3,79	$3{,}79 + \sum_{i-} \frac{[A_i^-]}{m_{T-}} . r_{i-}^h$ #	
$MgSO_4^\circ$	- 7,20	$4{,}0^\dagger$			

† Δh values assumed equal to zero

** $\bar{V}_i = \bar{V}_i^\circ + 1{,}5.S_v^*\sqrt{m_i}$, where m_i is the equivalent molality of species i when ionic strength = μ

\# $[A_i^-]$ molality of anion species i; m_{T-} total molality of anions in solution; $[M_i^+]$ molality of cation species i; m_{T+} total molality of cations in solution

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Table 7b. Values for salt and single ion species parameters utilized in the determination of calcium sulphate activity coefficient $CaSO_4^o \rightleftarrows Ca^{2+} + SO_4^{2-}$; K = 0,0036; pK = 2,44

Species	$\bar{V}_i$ mℓ/mole	$h_i = h_i^o + \Delta h$ (see Table 4 Chapter 2)	hydrated radius r^h	$\mathring{a}_+$ and $\mathring{a}_-$ Eq.(18)	Cation interaction effect, b_{ij} (see Table 2)
CsCl	$39{,}15 + 2{,}81\ \mu^{1/2}$	$0{,}2 - 1{,}2.10^{-4}\ \mu^2$			0,0 (No data)
Cs_2SO_4	$56{,}7 + 14{,}55(\mu/3)^{1/2}$	1,0#			0,0 (No data)
$CaCl_2$	$17{,}78 + 9{,}0(\mu/3)^{1/2}$	$7{,}05 - 1{,}6.10^{-3}(\mu/3)^2$			
Cs^+		0,2	1,45	See Table 7a	
Cl^-	$25{,}2 + \Delta\bar{V}_{Cl}$*	0,0	1,81	"	
SO_4^{2-}		0,00	2,00	"	
Ca^{2+}		7,05	3,74	"	
$CaSO_4^o$	− 3,8**	3,00†			

* See Eq (74) Chapter 2 for $\Delta\bar{V}_{Cl}$

\# see Table 5

** Determined assuming $\bar{V}(CaSO_4^o) = \bar{V}(Ca^{2+}) + \bar{V}(SO_4^{2-})$; this assumption has negligible effect on the values determined for $\gamma_\pm$ (i.e. the assumption is that the loss of primary hydrated water has no effect on $\bar{V}$)

† Determined assuming that an equal loss of primary hydrated water occurs in the formation of both $MgSO_4^o$ and $CaSO_4^o$

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Table 7c. Values for salt and single ion species parameters utilized in the determination of ion association equilibrium constants for $NaSO_4^-$ and $Na_2SO_4^o$ at 25°C with Ca^+ and Cl^- at trace concentration

$NaSO_4^- \rightleftarrows Na^+ + SO_4^{2-}$ $(K = 0,27;\ pK = 0,57)$

$Na_2SO_4^o \rightleftarrows 2Na^+ + SO_4^{2-}$ $(K = 0,10;\ pK = 1,00)$

Species	$\bar{V}_i$ ml/mole	$h_i = h_i^o + \Delta h$ (see Table 4 Chapter 2)	hydrated radius r^h	$\mathring{a}_+$ and $\mathring{a}_-$ Eq.(18)	Cation interaction effect, υ_{ij} (see Table 2)
CsCl	see Table 7b				0,0
Cs_2SO_4	see Table 7b				0,0
NaCl	$16,61 + 2,81\ \mu^{1/2}$	$2,40 - 1,2.10^{-4}.\mu^2$			
Cs^+	$\bar{V}(CsCl)-\bar{V}(Cl)$	0,20	1,45	See Table 7a	
Cl^-	$25,2 + \Delta\bar{V}_{Cl}$**	0,0	1,81	"	
SO_4^{2-}	$\bar{V}(Cs_2SO_4)-2\bar{V}(Cs)$	0,00	2,00	"	
Na^+	$\bar{V}(NaCl)-\bar{V}(Cl)$	2,40	3,14	"	
$Na^+ : NaSO_4^-$	$12,0 + 2,81\ \mu^{1/2}$	$h(Na) + h(NaSO_4^-)$			
$NaSO_4^-$	20,16*	1,4†	2,00		
$Na_2SO_4^o$	12,0*	2,8†			

* Partial molal volume of associated species assumed equal to the sum of the constituent ions

** See Eq (74) Chapter 2

† Loss of one and two molecules of hydrated water is assumed for the formation of an ion pair and treble ion respectively

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Table 7d. Values for salt and single ion species parameters utilized in the determination of ion association equilibrium constants for KSO_4^- and $K_2SO_4^\circ$ at 25°C with Cs^+ and Cl^- at trace concentrations

$$KSO_4^- \rightleftarrows K^+ + KSO_4^- \; ; \qquad K_2SO_4^\circ \rightleftarrows 2K^+ + SO_4^{2-}$$

$$(K = 0{,}43; \;\; pK = 0{,}37) \qquad (K = 0{,}14; \;\; pK = 0{,}85)$$

Species	$\bar{V}$ mℓ/mole	$h_i = h_i^\circ + \Delta h$ (see Table 4 Chapter 2)	hydrated radius r^h	$\mathring{a}_+$ and $\mathring{a}_-$ Eq.(18)	Cation interaction effect, b_{ij} (see Table 2)
CsCl	see Table 7b				0,0
Cs_2SO_4	see Table 7b				0,0
KCl	$26{,}8 + 2{,}81\,\mu^{1/2}$	$1{,}01 - 1{,}2.10^{-4}\,\mu^2$			
Cs^+	$\bar{V}(CsCl) - \bar{V}(Cl)$	0,20	1,45	See Table 7a	
Cl^-	$25{,}2 + \Delta\bar{V}_{Cl}$ **	0,0	1,81	"	
SO_4^{2-}	$\bar{V}(Cs_2SO_4) - 2\bar{V}(Cs)$	0,00	2,00	"	
K^+	$\bar{V}(KCl) - \bar{V}(Cl)$	1,01	2,54	"	
K^+: KSO_4^-	$32{,}4 + 2{,}81\,\mu^{1/2}$	$h(K) + h(KSO_4^-)$			
KSO_4^-	30,6 *	0,01 †	2,00		
$K_2SO_4^\circ$	32,4 *	0,02 †			

* Partial molal volume of associated species assumed equal to the sum of the partial molal volumes of the constituent ions

** See Eq (74) Chapter 2

† A loss of one and two molecules of hydrated water is assumed for the formation of an ion pair and treble ion respectively

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at some constant stoichiometric ionic strength but varying ratio of NaCl to $MgSO_4$, see Fig. 4, and, $\gamma^T_{KCl\pm}$ in solutions of KCl and $MgSO_4$ at a constant stoichiometric ionic strength but varying ratio of KCl to $MgSO_4$, see Fig. 6. For both these solutions the plots of $ln\gamma_{\pm}^{T}$ versus ionic strength contribution of the sulphate salt exhibit similar trends:

> In the region where the ionic strength fraction of the sulphate salt is less than about 0,8, the plots are closely linear; at higher fractions non linearity arises with a sharply increasing value in the activity coefficient of the chloride salt reaching a maximum value where the chloride salt is at a trace concentration.

Many researchers have assumed that the observed non linearity in the region where the sulphate salt is greater than about 0,8, arises due to uncertainties in the activity coefficient measurement techniques. Consequently they assume linearity throughout. However, the theory presented here predicts the observed non linearity in the region where the fraction of sulphate salt is much greater than that of the chloride salt. Briefly, the non linearity in the stoichiometric activity coefficient arises due to competition between the cations of the chloride and sulphate species for ion pairing with SO_4^{2-}. This can be seen as follows: Consider a number of solutions of say NaCl and $MgSO_4$ each with the same stoichiometric ionic strength but varying fractions of the chloride and sulphate salts. With an increase in fraction of the sulphate salt an increased fraction of the SO_4^{2-} will be ion paired by the Mg^{2+} and a decreased fraction by the Na^+ (due to both the effects of Mg^{2+} on SO_4^{2-} and the decreased mass of Na^+ in solution). Consequently it is to be expected that a state will be reached where the effects of ion pairing on the activity coefficient of Na^+ decrease, i.e. the total (stoichiometric) activity coefficient for NaCl increases, and, in the limit where NaCl is at a trace concentration ion pairing has no effect on γ^T_{NaCl} and the free and stoichiometric activity coefficients are equal.

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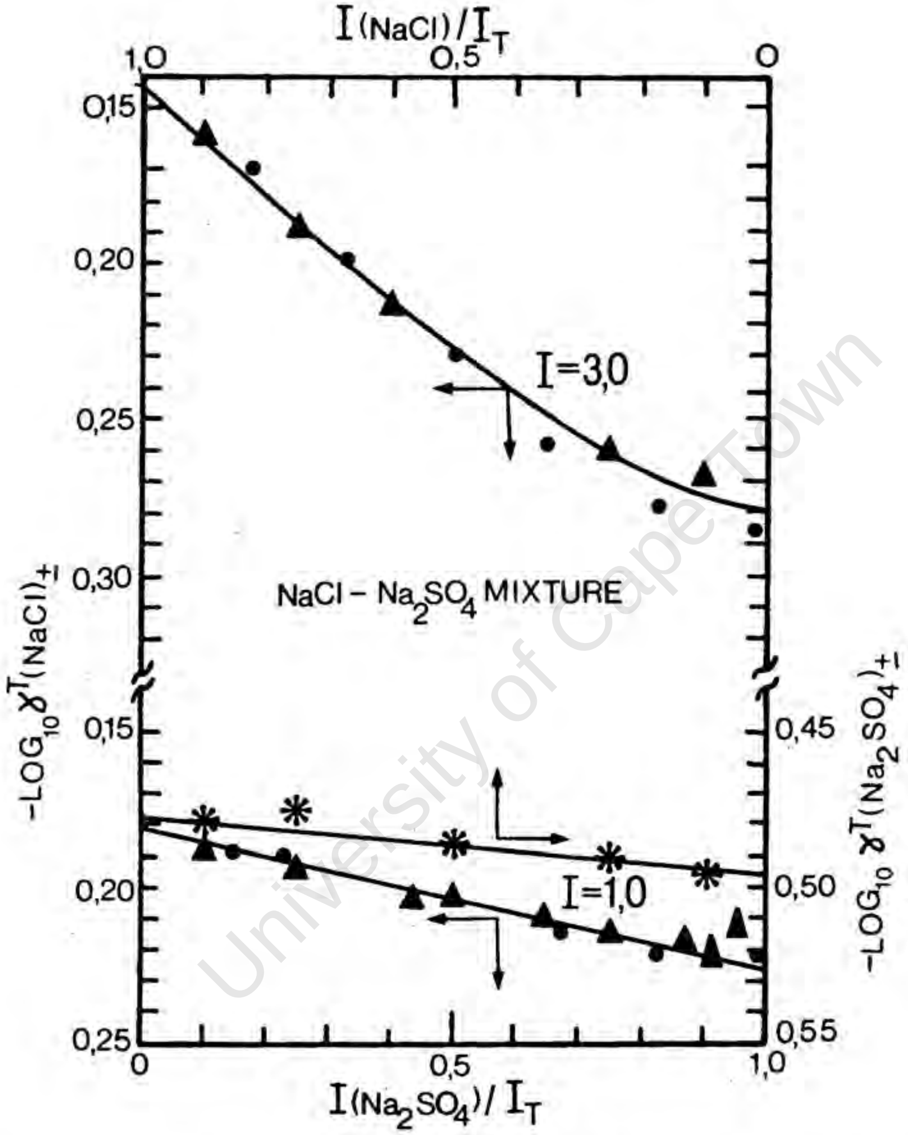

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Figure 3. Comparison of predicted (-) with observed data for the stoichiometric mean activity coefficients of NaCl, $\gamma_\pm{}^T(NaCl)$ ● *and* ▲, *and* Na_2SO_4, $\gamma_\pm{}^T(Na_2SO_4)$ ✱, *in ternary mixtures of salts* NaCl *and* Na_2SO_4

● *from Wu et al. (1969);* ▲ *from Lanier (1965);*
✱ *from Synnot and Butler (1968).*

$I(Na_2SO_4)$ = *stoichiometric ionic strength contribution of* Na_2SO_4.
I(NaCl) = *stoichiometric ionic strength contribution of* NaCl.
I_T = *total stoichiometric ionic strength.*

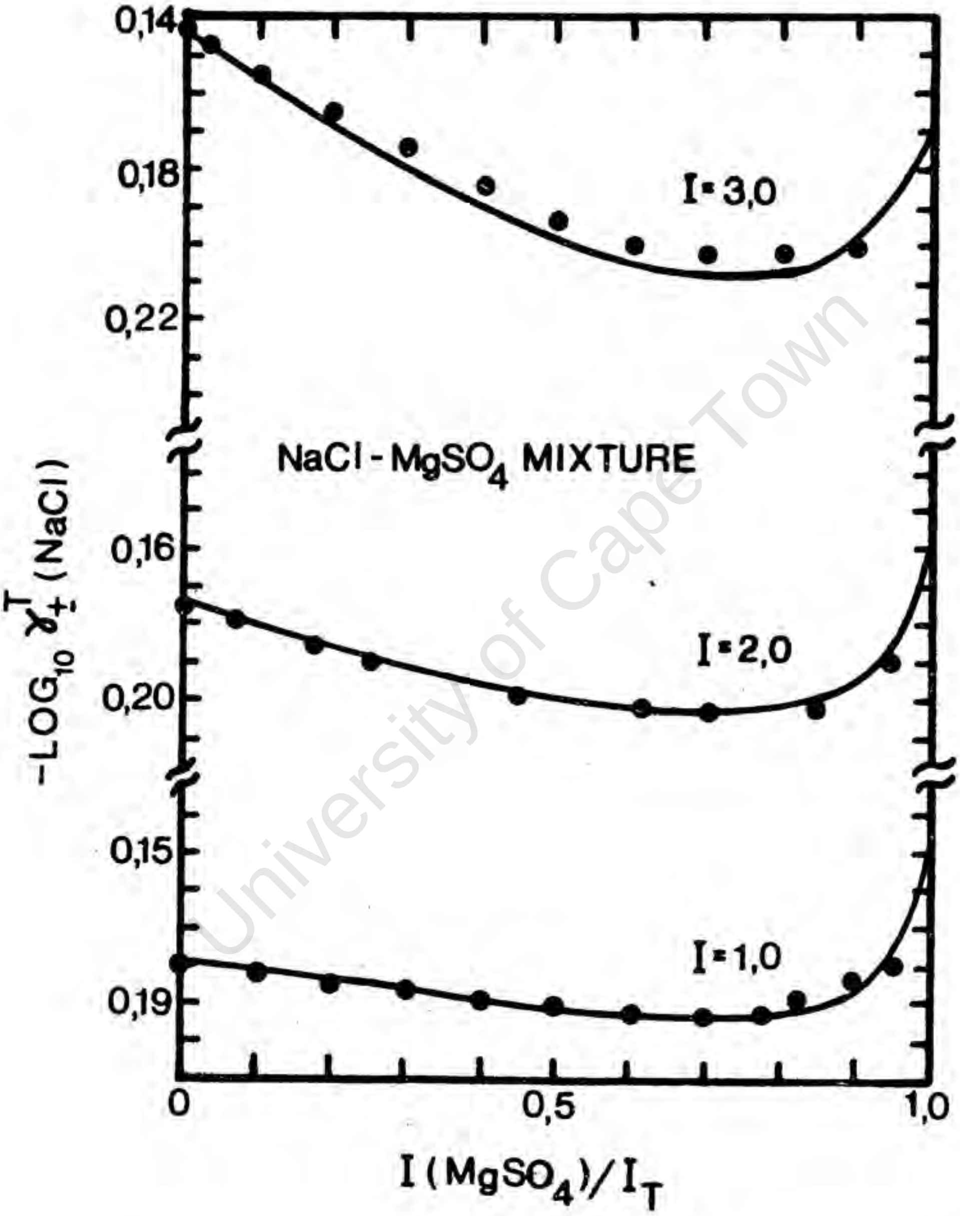

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Figure 4. Comparison of predicted (-) with observed data (●) for the mean stoichiometric activity coefficient of NaCl, $\gamma_{\pm}^{T}$(NaCl), *in solutions of* $MgSO_4$ *and* NaCl *salts.*

● *from Wu et al (1969)*

I($MgSO_4$) = *Stoichiometric ionic strength contribution of* $MgSO_4$.

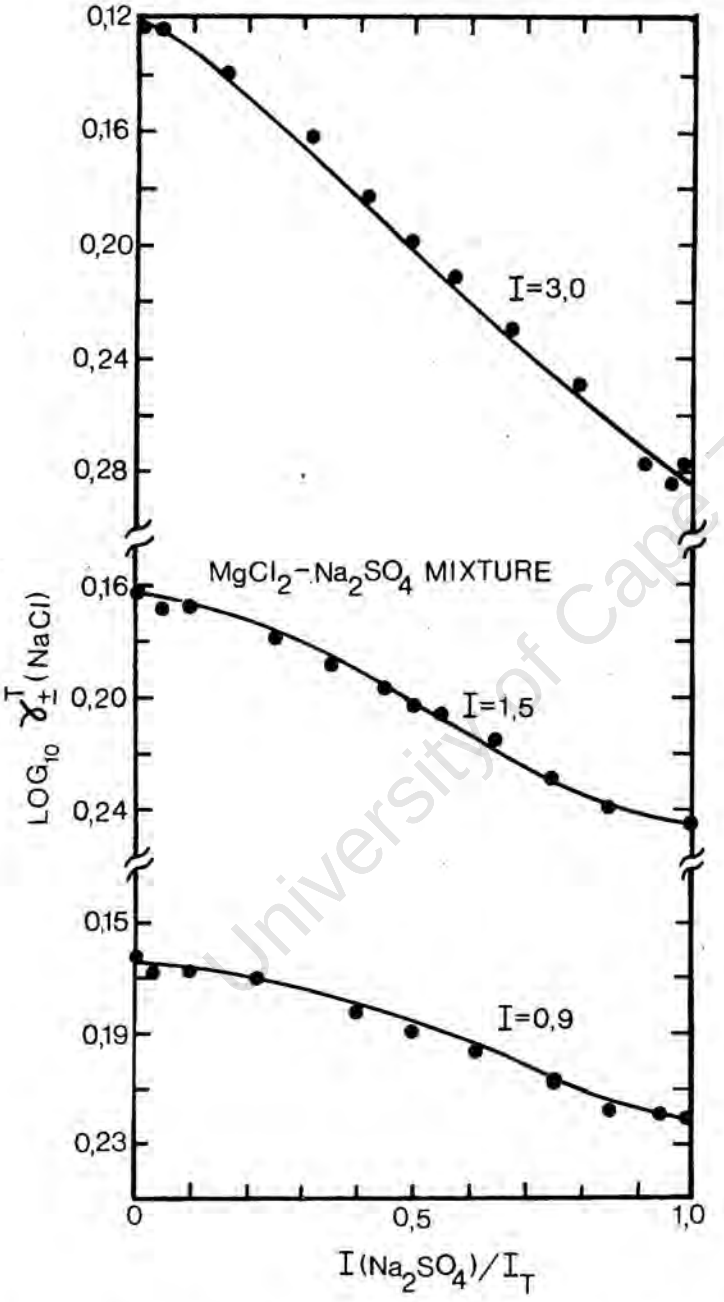

Figure 5. *Comparison of predicted (-) with observed data (●) for the mean stoichiometric activity coefficient for* NaCl, $\gamma^{T}_{NaCl\pm}$ *in solutions of* $MgCl_2$ *and* Na_2SO_4 *salts*

● *from Wu et al. 1969*

$I(Na_2SO_4)$ = *stoichiometric ionic strength contribution of* Na_2SO_4

I_T = *total stoichiometric ionic strength of the solution.*

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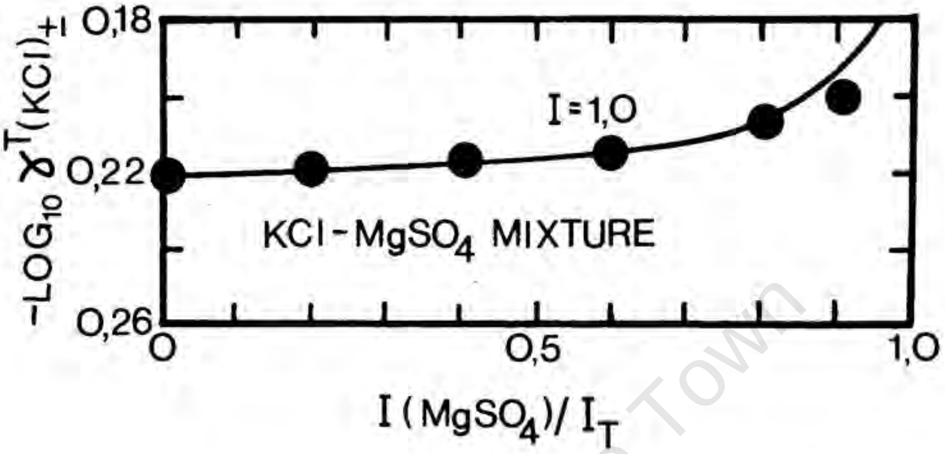

Figure 6. *Comparison of predicted (-) with observed data (●) for the stoichiometric mean activity coefficient of* KCl, $\gamma_\pm^T$(KCl), *in solutions of* KCl *and* $MgSO_4$ *salts (● interpolated from Christenson and Gieskes, 1971).*

I($MgSO_4$) = *stoichiometric ionic strength contribution of* $MgSO_4$

I_T = *total stoichiometric ionic strength of mixture.*

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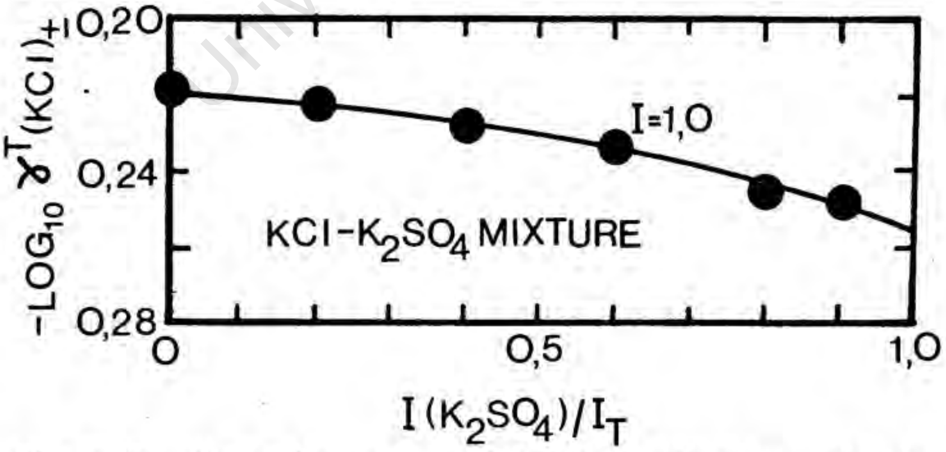

Figure 7. *Comparison of predicted (-) with observed data (●) for the stoichiometric mean activity coefficient of* KCl, $\gamma_\pm^T$(KCl),*in a mixed system of* KCl *and* K_2SO_4 *salts. (● interpolated from Christenson and Gieskes, 1971)*

I(K_2SO_4) = *stoichiometric ionic strength contribution of* K_2SO_4

I_T = *total stoichiometric ionic strength of mixture.*

Table 8. Comparison of predicted with observed stoichiometric (total) mean activity coefficients $\gamma_{\pm}^{T}$ for synthetic seawater (25°C, 1 atm. pressure, I = 0,7M)*

Salt	$\gamma_{\pm}^{T}$		
	Predicted	Observed	Reference (observed data)
NaCl	0,667	0,667 ± 0,002	Johnson and Pytkowicz (1981)
		0,668 ± 0,003	Gieskes (1966)
KCl	0,643	0,645 ± 0,008	Whitfield (1975)
Na_2SO_4	0,352	0,376 ± 0,017	Platford and Dafoe (1965)
K_2SO_4	0,343	0,352 ± 0,018	Whitfield (1975)
$CaSO_4$	0,146	0,136**	Culberson, Latham and Bates (1978)
HCl	0,729***	–	
	0,731†	0,729†	Khoo, Ramette, Culberson and Bates (1977)

* Constitution of syntnetic seawater given in Table 13, Chapter 4.

** Experimentally determined from $CaSO_4$ solubility in synthetic seawater where Mg^{2+} is replaced m/m by Ca^{2+} to keep the ionic strength μ the same.

*** $\gamma_{HCl\pm}^{tr}$

† Predicted and experimentally determined in sulphate free seawater where $SO_4^=$ is replaced by Cl to keep ionic strength μ the same.

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5. ACTIVITY OF THE WATER COMPONENT IN MIXED SYSTEMS

The approach to formulating an equation for the activity of water, a_w, in mixed systems is similar to that for binary systems in Chapter 2:

(i) The activity of the water species is defined in terms of the partial molal free energy of the *total* water, i.e. on the anhydrous scale, using Eq. (123), Chapter 2,

$$\bar{G}_w = \bar{G}^o_w + RT\,ln\,a_w \tag{38}$$

(ii) An equation for the total free energy of the system is formulated in terms of the free energy contributions of each of the *hydrated* salts and *free* water (using volume fraction statistics) plus a term G^{el} to account for the long range electrostatic contribution. For an aqueous solution made up of n_1, n_2 .... n_i moles of species 1, 2, ... i (i.e. k = 1, 2, ... i) in n_w moles of water, the free energy equation becomes (see Eq.2)

$$G = \Sigma n_k \bar{G}^h_k + n_{fw}\,\bar{G}_{fw} + G^{el} \tag{39}$$

(iii) From Eq. (39) an expression for $\bar{G}_w$ (on the anhydrous scale is obtained by differentiating this equation partially with respect to the *total* moles of water in solution, n_w, keeping constant the moles of each of the salt components, i.e.

$$\bar{G}_w = (\partial G/\partial n_w)_{T,P,n,\ldots\, n_i} \tag{40}$$

(iv) Equating Eqs. (38 and 40) gives an expression for the activity of the water species, a_w, on the molal (anhydrous) scale).

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In order to differentiate Eq. (39) in accordance with Eq. (40) it is necessary first to reformulate Eq. (39) so that (i) the moles of free water, n_{fw}, and (ii) each of the partial molal free energy terms, $\bar{G}_k^h$, for the salts is modelled in terms of basic parameters for the system. This is carried out by substituting for n_{fw} and $\bar{G}_k^h$ from Eqs. (6 and 7) respectively into Eq. (39) to give an expression for G as depicted in Eq. (8). Differentiating Eq. (8) in accordance with Eq. (40) and rearranging terms

$$\begin{aligned}\bar{G}_w = \bar{G}^o_{fw} - \bar{G}^o_{fw}\Sigma n_k \frac{\partial h_k}{\partial n_w} + RT[\Sigma\frac{d_k n_k}{\bar{V}_k^h}\frac{\partial \bar{V}_k^h}{\partial n_w} - \frac{\bar{V}_w}{V}\Sigma d_k n_k \\ + (1 - n_k \frac{\partial h_k}{\partial n_w})\, ln\{(n_w - \Sigma n_k h_k).\bar{V}_{fw}/V\} + (1 - \Sigma n_k \frac{\partial h_k}{\partial n_w}) \\ - (n_w - \Sigma n_k h_k)\bar{V}_w/V + (n_w - \Sigma n_k h_k)\frac{\partial \bar{V}_{fw}}{\partial n_w} / \bar{V}_{fw}] - (\frac{\partial G^{el}}{\partial n_w})_{n_k} \qquad (41)\end{aligned}$$

In order to simplify Eq. (41) further, the terms $\partial\bar{V}_w/\partial n_w$, $\partial h_k/\partial n_w$ and $\partial\bar{V}_k^h/\partial n_w$ must be simplified

For the term $\partial\bar{V}_w/\partial n_w$: By definition

$$V = \Sigma n_k \bar{V}_k + n_w \bar{V}_w$$

Differentiating this expression partially with respect to n_w and simplifying

$$n_w \frac{\partial \bar{V}_w}{\partial n_w} = - \Sigma n_k \frac{\partial \bar{V}_k}{\partial n_w} \qquad (42)$$

and, to write the right hand side of this expression in the molal form,

$$(\frac{\partial \bar{V}_k}{\partial n_w}) = \frac{\partial \bar{V}_k}{\partial m_k} \cdot \frac{\partial m_k}{\partial n_w} \qquad (43)$$

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where

$$m_k = n_k/(n_w \cdot 0{,}018) \tag{44}$$

and

$$\left(\frac{\partial m_k}{\partial n_w}\right) = - n_k/(n_w^2 \cdot 0{,}018) \tag{45}$$

Substituting for $(\partial \bar{V}_k/\partial n_w)$ and $(\partial m_k/\partial n_w)$ from Eqs. (43 and 45) respectively into Eq. (42) and simplifying

$$\left(\frac{\partial \bar{V}_w}{\partial n_w}\right)_{n_k} = \Sigma \frac{{n_k}^2}{0{,}018\ n_w^3} \cdot \frac{\partial \bar{V}_k}{\partial m_k} \tag{46}$$

For the term $\partial h_k/\partial n_w$:

$$\left(\frac{\partial h_k}{\partial n_w}\right)_{n_k} = \frac{\partial h_k}{\partial m_k} \cdot \frac{\partial m_k}{\partial n_w}$$

$$= \frac{- n_k}{0{,}018\ {n_w}^2} \cdot \frac{\partial h_k}{\partial m_k} \tag{47}$$

For the term $\partial \bar{V}_k^h/\partial n_w$: By definition

$$\bar{V}_k^h = \bar{V}_k + h_k \bar{V}_w$$

i.e.

$$\frac{\partial \bar{V}_k^h}{\partial n_w} = \frac{\partial \bar{V}_k}{\partial n_w} + h_k \frac{\partial \bar{V}_w}{\partial n_w} + \bar{V}_w \frac{\partial h_k}{\partial n_w} \tag{48}$$

Substituting for $(\partial \bar{V}_k^h/\partial n_w)$, $(\partial h_k/\partial n_w)$, $(\partial \bar{V}_w/\partial n_w)$ and for n_k from Eqs. (48, 47, 46, and 44) respectively into Eq. (41), equating Eqs. (41 and 38) and simplifying

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$$
\begin{aligned}
ln a_{w} = {} & \frac{1}{RT}\,[\bar{G}^{o}_{fw} - \bar{G}^{o}_{w} + 0{,}018\, G^{o}_{fw}\, \Sigma m_{k}{}^{2}\, \frac{\partial h_{k}}{\partial m_{k}}] \\
& + \frac{0{,}018(\Sigma m_{k}q_{k} + \Sigma m_{k}h_{k} - \Sigma m_{k}d_{k})}{(1 + 0{,}018\ \Sigma m_{k}q_{k})} + ln\frac{(1 - 0{,}018\ \Sigma m_{k}h_{k})}{(1 + 0{,}018\ \Sigma m_{k}q_{k})} \\
& + 0{,}018\ \Sigma m_{k}^{2}\, \frac{\partial h_{k}}{\partial m_{k}}\, (ln\{\frac{1 - 0{,}018\ \Sigma m_{k}h_{k}}{1 + 0{,}018\ \Sigma m_{k}q_{k}}\} + \frac{q_{k} + h_{k} - d_{k}}{q_{k} + h_{k}}) \\
& + 0{,}018\ \Sigma m_{k}^{2}\, \frac{\partial q_{k}}{\partial m_{k}} (\frac{q_{k} + h_{k} - d_{k}}{q_{k} + h_{k}} + 0{,}018\ \Sigma\, \frac{d_{k}m_{k}h_{k}}{q_{k} + h_{k}}) \\
& + \frac{1}{RT}\, (\frac{\partial G^{el}}{\partial\, n_{w}})_{n_{k}}
\end{aligned}
\qquad (49)
$$

The constants $\bar{G}^{o}_{w}$ and $\bar{G}^{o}_{fw}$ in Eq. (49) are determined by considering the condition where $\Sigma m_{k} \rightarrow 0$, i.e. $ln a_{w} \rightarrow 0$ giving $\bar{G}^{o}_{w} = \bar{G}^{o}_{fw}$. Making this substitution in Eq. (49) gives the desired expression for the activity of the water species, a_{w}

$$
\begin{aligned}
ln a_{w} = {} & 0{,}018\ (\frac{\Sigma mq + \Sigma mh - \Sigma md}{1 + 0{,}018\ \Sigma mq}) + ln\ (\frac{1 - 0{,}018\ \Sigma mh}{1 + 0{,}018\ \Sigma mq}) \\
& + 0{,}018\ \Sigma m_{k}^{2}\, \frac{\partial h_{k}}{\partial m_{k}}\, \{ln\ (\frac{1 - 0{,}018\ \Sigma mh}{1 + 0{,}018\ \Sigma mq}) + \frac{q + h - d}{q + h} + \frac{\bar{G}^{o}_{fw}}{RT}\} \\
& + 0{,}018\ \Sigma m_{k}^{2}\, \frac{\partial q_{k}}{\partial m_{k}}\, \{\frac{q_{k} + h_{k} - d_{k}}{q_{k} + h_{k}} + 0{,}018\Sigma\, \frac{d_{k}m_{k}h_{k}}{q_{k}+h_{k}}\} \\
& + \frac{1}{RT}\, (\frac{\partial G^{el}}{\partial n_{w}})_{n_{k}}
\end{aligned}
\qquad (50)
$$

where

$\bar{G}^{o\prime}_{fw} = \bar{G}^{o}_{fw}/RT = 30$ at 25°C (by convention, (50a)

see Section 6.5.1 Chapter 2)

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and

$$\frac{1}{RT}\left(\frac{\partial G^{el}}{\partial n_w}\right) = \frac{1}{RT}\left(\frac{\partial G^{el}}{\partial n_{fw}}\right)$$

$$= 2{,}303.A.\ \frac{2}{3\ 000}\ \mu^{3/2}\ \bar{V}_w\ \sigma(y)$$

$$\sigma(y) = \frac{3}{y^3}\{(1+y) - (1+y)^{-1} - 2ln(1+y)\}$$

$$y = B\mathring{a}\ \mu^{1/2} \tag{50b}$$

Utilization of Eq. (50) for determining a_w in a mixed system requires that values for each of the parameters $\bar{V}_k$(i.e. q_k) and h_k (and $\partial\bar{V}_k/\partial m_j$ and $\partial h_k/\partial m_j$) either be known or capable of determination. However, as set out in Section 2.2 (for the determination of the activity of a salt component in an aqueous mixed system) normally values cannot be determined for these components from independent theoretical considerations. For this reason, the ionic strength principle was used to estimate $\bar{V}_k$ and h_k in the equation for the total free energy of the system G, and interaction terms were introduced to account for this approximation (see Eq. 26), i.e. for an aqueous system containing 'i' salt species (with k = 1,2, ... i, and j = 1,2, ... i)

$$G = G^c + \sum_{k=1}^{i-1} d_k n_k \left(\sum_{k'=k+1}^{i} \beta'_{kk'}\ d_{k'} n_{k'}/n_w\right) \tag{51}$$

Consequently, the equation for a_w formulated above, Eq. (50), must include a series of interaction terms if the values for $\bar{V}_k$ and h_k in this equation are determined using the ionic strength principle. The interaction terms will be given by the partial differential with respect to n_w of the second term on the right hand side of Eq. (51),

$$\ln a_w = \ln a_w^c - \frac{0{,}018^2}{RT} \sum_{k=1}^{i-1} d_k m_k \Big(\sum_{k'=k+1}^{i} \beta'_{kk'} d_{k'} m_{k'} \Big) \tag{52}$$

where

$\ln a_w^c$ = Eq. (50) with the value of $\bar{V}$ and h determined from the ionic strength principle

$\beta'_{kk'}$ = a constant.

The value of the constant $\beta'_{kk'}$ is determined from observed data on ternary systems as follows: From Eq. (27)

$$\beta_{jk} = 0{,}018\ \beta'_{kk'}/RT \tag{53}$$

and, substituting for $\beta'_{kk'}$ from Eq. (43) into Eq. (52) gives the equation for $\ln a_w$ in terms of known parameters for β_{jk} (see Table 2), i.e.

$$\ln a_w = \ln a_w^c - 0{,}018 \sum_{j=1}^{i-1} d_j m_j \Big(\sum_{k=j+1} \beta_{jk} d_k m_k \Big) \tag{54}$$

where

$\ln a_w^c$ = $\ln a_w$ from Eq. (50) *if the partial molal volumes and hydration numbers of species are determined using the ionic strength principle*

β_{jk} = interaction constant between solute species j and k introduced to account for use of the ionic strength principle in the determination of partial molal volumes and hydration numbers; values for β_{jk} are listed in Table 2.

Equation (54) gives a practical approximate approach to determining the activity of the water in a mixed system. The same approximate approach was used to determine the mean activity

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coefficients of the ionic species in Eq. (22). In both equations the hydration numbers and partial molal volumes in the mixed solution are calculated using the ionic strength principle. In both this introduces an error which is partially corrected by including in Eq. (22 and 54) a series of interaction terms (where the respective constants in the interactive terms, β_{jk}, have been determined from ternary systems, see Table 2).

In the utilization of Eq. (54)(together with Eq. 50), to determine the activity of the water, a_w, the solution procedure is as follows:

(i) Calculate the free and ion paired species concentrations. This calculation involves implicitly the determination of the free and ion paired species activity coefficients, the partial molal volumes and hydration numbers of the solute species - values for the latter two parameters being determined using the ionic strength principle.The calculation procedure has already been set out in Section 3.1.2 and a computer program for this purpose is listed in Appendix A.

(ii) Calculate a_w^c. In Eq. (5)), a_w^c is determined by inserting the values determed in (i) above. The terms $\bar{G}^o_{fw}$ and $(\partial G^{el}/\partial n_w)/RT$ are determined from Eqs. (50a and 50b) respectively.

In Eq. (50b) a single value of å is required, whereas in Eq. (22) for determining the activity coefficient of any selected salt in a mixed system, two å values are required, one for each of the ionic species of the selected salt, where each å value represents the mean distance of closest approach of the ionic species of the salt with all the other species of opposite charge. In Eq. (50), one is not dealing with a selected particular salt and hence requires an å value

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that is representative of the mean distance of closest approach of the oppositely charged species in aggregation. The procedure for determining the $\overset{o}{a}$ value must be consistent in that if its value is inserted into Eq. (50) to determine a_w in a binary system (for which a large amount of experimental data are available), it will give the correct prediction. Consistency is achieved by defining the $\overset{o}{a}$ value sum of a mean cation hydrated radius, $\overset{o}{a}_+$, and a mean anion hydrated radius, $\overset{o}{a}_-$. The mean cation hydrated radius, $\overset{o}{a}_+$. is determined as the molar mean of all the cation species hydrated radii in the solution; similarly the anion hydrated radius, $\overset{o}{a}$, is determined as the molar mean of all the anion hydrated radii in the solution (see Section 2.3.2), i.e.

For the cation species, k_+, $k_+=1,2,\ ...\ i$

$$\overset{o}{a}_+ = \Sigma_{k+}(r^h_{k+}[m_{k+}]/\Sigma_{k+}[m_{k+}]) \qquad (55a)$$

and for the anion species, j_-, $j_-=1,2,$ ℓ

$$\overset{o}{a}_- = \Sigma_{j-}(r^h_{j-}[m_{j-}]/\Sigma_{j-}[m_{j-}]) \qquad (55b)$$

and

$$\overset{o}{a} = \overset{o}{a}_+ + \overset{o}{a}_- \ .$$

(iii) a_w is determined using Eq. (54) by inserting the value for a^c_w determined in (ii) above, and inserting the interaction constants for β_{jk} (listed in Table 2) in the interaction terms.

The solution procedure above is time consuming, and consequently determination of a_w is included in the computer program for solute species activity coefficient determination listed in Supplement A. To illustrate the calculation of a_w, the program was applied to sea

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water accepting the following stoichiometric chemical composition (expressed in molalities): $Na^+ = 0,4699$, $K^+ = 0,0101$, $Mg^2 = 0,0536$, $Ca^{2+} = 0,0104$, $Cl^- = 0,5518$ and $SO_4^{2-} = 0,0281$. The calculated free and ion paired species concentrations are listed in Table 9 (activity coefficients are already listed in Table 8); also the values inserted for the partial molal volumes and hydration numbers calculated using the ionic strength principle. The value of $\mathring{a}$ was determined from Eqs. (55a and 55b), using species concentrations in Table 9 and the species hydrated radii from Table 4, Chapter 2, i.e.

$$\mathring{a}_+ = 3,207$$

and

$$\mathring{a}_- + 1,826$$

i.e.

$$\mathring{a} = 3,207 + 1,826 = 5,033 \quad .$$

Substituting into Eq. (54) the values for species concentrations, partial molal volumes and hydration numbers from Table 9, the interaction coefficients β_{jk} from Table 2 and the $\mathring{a}$ value determined above gives a_w for seawater as

$$a_w = 0,9817 \quad .$$

This value for a_w is in excellent agreement with that determined experimentally by Robinson and Woods (1972), as $a_w = 0,9818$.

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Table 9. Free and ion paired species molalities, partial molal volumes and hydration numbers for seawater at 25°C and 1 Atm total pressure.

Species	Molality	Partial molal volume, $\bar{V}_i$ cc/mole	Hydration number, h
Na^+	0,4623	-7,46	2,4
$NaSO_4^-$	0,0027	21,72	1,4
$Na_2SO_4^o$	0,0049	12,0	2,8
K^+	0,0095	2,67	1,01
KSO_4^-	0,0002	31,80	0,01
$K_2SO_4^o$	0,0004	32,4	0,02
Mg^{2+}	0,04597	-34,68	8,12
$MgSO_4^o$	0,00763	-7,2	4,0
Ca^{2+}	0,0095	-30,81	7,05
$CaSO_4^o$	0,0009	-3,8	3,0
SO_4^{2-}	0,0143	33,13	0,0
Cl^-	0,5518	26,39*	0,0
μ	0,653		

* The *deviation* from ideality for $\bar{V}_{Cl^-}$ is determined here as 1,19 cc/mole which agrees closely with the value estimated by Millero (1971) for this entity in seawater as $\Delta\bar{V}_{Cl^-}$ = 1,0 cc/mole.

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pH AND WEAK ACID-BASE SYSTEMS

1. INTRODUCTION

In this chapter the principal concern is with the behaviour of weak acid-base systems in highly saline waters. In this regard a weak acid-base system of major importance is the carbonate system as it is intimately involved in the control of pH, exchange of CO_2 between air and water bodies and precipitation phenomena in terrestial waters and the seas.

A distinguishing feature of weak acid-base systems is the dependance of the species concentration on pH - a factor that did not arise in the analyses of solutions containing strong salts, with the exception of sulphate (see Chapter 3).

In low salinity waters analysis of weak acid systems is relatively simple because (i) the activity coefficients of species are dependant almost entirely on electrostatic effects which can be readily determined from the ionic concentrations, through the ionic strength, using say the Davies equation, (ii) the hydrogen ion activity is found directly from conventional pH measurements, and (iii) ion pairing of weak acid and cationic species is negligible. In contrast, in high salinity waters (i) estimation of activity coefficients of species is dependent not only on electrostatic effects but also on hydration of *all* the species in solution i.e. the estimation requires application of the hydration theory, discussed in Chapter 3, (ii) the hydrogen ion activity no longer can be established from conventional pH measurements due to residual liquid junction potential effects, and (iii) ion-pairing between weak acid and cation species can be significant, and this effect is interactive, ion pairing of the weak acid-base species affects the pH established in the solution and the pH in turn

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affects the distribution of free and ion paired weak acid species. These factors make that a weak acid-base system in highly saline waters is exceedingly complex to analyse.

We have stated above that weak acid species concentrations are pH dependant so that in high salinity waters determination of the pH of a solution and interpretation of this determination are central to analysing weak acid systems. The first requisite, therefore, in dealing with these systems in highly saline waters, is to establish clearly the relationship between the theoretical pH (i.e. the true pH) and its experimental counterpart, (pH_o), using a specific ion electrode, i.e. a pH meter.

In conventional pH measurement in aqueous solutions the measurement is made relative to low salinity pH standards. This measurement is termed the *operational pH*, designated here by the symbol 'pH_o', and always gives a reproducible value for a particular solution. The true pH, designated by the symbol 'pH' is defined as the negative logarithm of the hydrogen ion activity. In low salinity waters where the ionic strength and matrix of ions matches those for the standard solution, the operational and true pH values will be closely equal, i.e. $pH_o = pH$. In highly saline waters, however, pH_o and pH may differ significantly - principally, as we have said, due to a residual liquid junction potential arising from the reference electrode.

For a *general* approach to the solution of weak acid systems in highly saline waters a prime requirement is to determine the residual liquid junction potential in order to determine pH from pH_o. Later we will show in detail how an estimate of this potential can be obtained experimentally; in outline the procedure is as follows: (i) Using a Gran titration an *operational activity coefficient*, ($\gamma_{H^+(o)}$), for the hydrogen ion is obtained, (ii) utilizing the hydration theory in Chapter 3 the activity

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coefficient (γ_{H^+}) of the hydrogen ion is determined. Then it will be shown that the ratio of $\gamma_{H^+}/\gamma_{H^+(o)}$ serves as a parameter in terms of which the residual liquid junction potential effect of the reference electrode in that solution can be determined.

Once the true hydrogen ion activity is available, it is possible to determine the ion-pairing equilibrium constants for complexing between the various cation species and each of the weak acid species. Briefly, this is done as follows: (i) Using pH_o measurements an *operational apparent equilibrium constant* for the weak acid species can be determined. (ii) Knowing the residual liquid junction potential effect, the true pH can be determined, and using this true hydrogen ion activity the operational apparent equilibrium constant can be modified to give an *apparent weak acid equilibrium constant*, K_a'. This K_a' value is apparent because it still lumps together the activity coefficient and ion pairing effects of the weak acid-base species. (iii) By using the hydration theory one can now determine the activity coefficients for the free weak acid-base species and thereby isolate the ion pairing effects to give the *ion pairing equilibrium constants*.

In the past, due to the difficulty of establishing quantitatively the residual liquid junction effect in a particular solution, one approach in dealing with weak acid systems in highly saline waters, was to accept the pH_o value and to define the equilibrium constants of weak acid-base systems in terms of this measurement. This approach, which is quite acceptable, is subject to the restriction that the concentration of strong salts in the medium needs to remain the same. For this reason it has found its principal field of application in the analyses of seawater as this medium can usually be considered as invariant with regard to the principal ionic matrix. Due to the restriction on the principal ionic matrix, the approach is not appropriate for formulating a general model for analyses of high salinity waters having different ionic strengths and constitutions. Nevertheless, in a particular solution once the residual liquid junction potential is known, then theoretically one can determine the operation pH_o and operational equilibrium constants, and, the analyses can proceed in terms of these operational values; using the operational values reduces the analysis of high salinity systems to the same simplicity as that present in low salinity waters; this applies particularly in the application of graphical procedures which is convenient from a practical point of view. The link between the basic and operational approaches is, therefore, also of significant practical importance.

2. REVIEW OF LOW SALINITY WATERS

2.1 Interdependence of parameters

Most terrestial waters can be classified as low salinity waters (i.e. TDS less than about 1000 ppm). In these waters the effects of hydration and of ion pairing between cations and weak acid-base species usually can be neglected. In natural waters with low ionic strength (less than about 0,01), pH_o = pH and pH is controlled principally by equilibrium reactions between dissolved carbonate species (CO_2, H_2CO_3, HCO_3^- and $CO_3^=$) and water species (H^+ and OH^-). These relationships can be expressed either in terms of activities or concentrations. Due to the fact that pH in low salinity waters reflects the activity of H^+, and measurement of the carbonate species, say by Alkalinity measurement, is in terms of concentrations, it is often convenient to express the equilibria equations with H^+ in terms of activity and weak acid-base species in terms of concentrations. The equilibrium equations governing the system are then depicted as follows:

For the first dissociation reaction

$$(H^+)(HCO_3^-)/(H_2CO_3^*) = K_1 \qquad (a1)$$

$$(H^+)[HCO_3^-]/[H_2CO_3^*] = \gamma_{H_2CO_3^*} \cdot K_{.}/\gamma_{HCO_3^-} = K_1' \qquad (a2)$$

For the second dissociation reaction,

$$(H^+)(CO_3^{2-})/(HCO_3^-) = K_2 \qquad (b1)$$

or

$$(H^+)[CO_3^{2-}]/[HCO_3^-] = \gamma_{HCO_3^-} \cdot K_2/\gamma_{CO_3^-} = K_2' \qquad (b2)$$

For the dissociation of water,

$$(H^+)(OH^-) = K_w \qquad (c1)$$

or

$$(H^+)[OH^-] = K_w/\gamma_{OH^-} = K_w' \qquad (c2)$$

Where K_x = the equilibrium constant which varies with temperature

() = activity

[] = concentration, either molarity or molality.

Values for the equilibrium constants K_1, K_2 and K_w have been established in the temperature range 0 to 100°C, Helgeson (1969). Furthermore, the activity coefficients $\gamma_{HCO_3^-}$, $\gamma_{CO_3^{2-}}$ and γ_{OH^-} can be determined using the Debye-Hückel equation or some variation of it, e.g. the Davies equation. Neutral species activity coefficients can be assumed equal to unity.

In the equilibrium equation, Eq (a1), the term $H_2CO_3^*$ refers to the sum of the activities of molecularly dissolved CO_2, $(CO_2)_{aq}$, and the carbonic acid, (H_2CO_3). This form, termed the composite

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form, is convenient because of the analytical difficulties of separating out $(CO_2)_{aq}$ from H_2CO_3. The composite form shown in Eq (a1) is derived from the equilibrium relationships for $(CO_2)_{aq}$ and H_2CO_3 as follows:

For equilibrium between H_2CO_3, HCO_3^- and H^+

$$(H^+)(HCO_3^-)/H_2CO_3) = K_T \qquad (a3)$$

Where $K_T \cong 10^{-3,8}$ at 25°C.

For equilibrium between CO_{2aq} and H_2CO_3

$$(CO_2)_{aq}/(H_2CO_3) = K_c \qquad (a4)$$

Where $K_c \cong 10^{2,53}$ at 25°C.

To obtain the composite form, i.e. Eq (a1), first rearrange Eq (a4) as follows

$$(CO_2)_{aq} + (H_2CO_3) = (H_2CO_3)+(H_2CO_3).K_c$$

$$\text{i.e. } (H_2CO_3) = \{(CO_2)_{aq}+(H_2CO_3)\}/\{1+K_c\} \qquad (a5)$$

Substituting for H_2CO_3 from Eq (a5) into (a3) and rearranging

$$\frac{(H+)(HCO_3^-)}{\{(Co_2)_{aq}+(H_2CO_3)\}} = K_T/\{1+K_c\} = K_1 \qquad (a6)$$

Where $K_1 \cong 10^{-6,33}$ at 25°C.

The fraction of $H_2CO_3^*$ existing as H_2CO_3 is virtually constant and

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independent of pH, ionic strength and temperature. This fraction is given by the ratio of Eqs (a6 and a3), i.e.

$$(H_2CO_3)/(H_2CO_3^*) = K_1/K_T = 0{,}0026$$

that is, only 0,26 per cent of $H_2CO_3^*$ exists as H_2CO_3 and 99,74 per cent as molecularly dissolved CO_2.

The three equations, Eqs (a2, b2 and c2) incorporate five unknowns ($H_2CO_3^*$, HCO_3^-, CO^{2-}_3, OH^- and H^+), consequently, to solve these equations two independent unknowns need to be measured (independence is important; for example, in the unknowns above measurement of H^+ implies measurement of OH^-, i.e. these two unknowns are dependent. Two independent unknowns which can be measured directly are pH and $H_2CO_3^*$.

(1) pH: In low salinity waters residual liquid junction potential effects are negligible so that the observed pH directly gives an estimate of (H^+):

$$pH = -\log_{10}(H^+) \qquad (d)$$

pH (i.e. pH_o) can be readily measured with great reliability and will, virtually always, be included as one of the required independent unknowns. Although theoretically pH_o measurement is not imperative, its omission is likely to complicate the analysis and very likely reduce the accuracy of parameters determined from the analysis.

(2) $H_2CO_3^*$: The partial pressure of CO_2 in equilibrium with the water can be measured if the appropriate apparatus is available and directly gives an estimate of $H_2CO_3^*$ if the

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solubility constant for CO_2 and $H_2CO_3^*$ is known, i.e.

$$[H_2CO_3^*] = K_H \cdot p_{CO_2} \tag{e}$$

Where $[H_2CO_3^*]$ = the sum of molecularly dissolved CO_2 and H_2CO_3.

The unknowns HCO_3^- and $CO_3^=$ cannot be measured directly but can be established in terms of the sum of the weak acid-base species using one or more of seven mass parameters for the system:

(a) Total carbonate species concentration, C_T,

$$C_T = [H_2CO_3^*] + [HCO_3^-] + [CO_3^=] \tag{f}$$

(b) Alkalinity and acidity to the $H_2CO_3^*$ equivalence point, termed Total Alkalinity (or $H_2CO_3^*$ Alkalinity) and Mineral Acidity (or $H_2CO_3^*$ Acidity) respectively,

$$\text{Total Alkalinity} = 2[CO_3^=] + [HCO_3^-] + [OH^-] - [H^+] \tag{g}$$

$$\text{Mineral Acidity} = [H^+] - 2[CO_3^=] - [HCO_3^-] - [OH^-] \tag{h}$$

(c) Alkalinity and acidity to the HCO_3^- equivalence point, termed Phenolphthalein Alkalinity (or HCO_3^- Alkalinity) and CO_2 Acidity) respectively,

$$\text{Phenolpthalein Alk.} = [CO_3^=] + [OH^-] - [H^+] - [H_2CO_3^*] \tag{i}$$

$$CO_2 \text{ Acidity} = [H^+] + [H_2CO_3^*] - [OH^-] - [CO_3^=] \tag{j}$$

(d) Alkalinity and acidity to the $CO_3^=$ equivalence point, termed

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Caustic Alkalinity (or $CO_3^=$ Alkalinity) and Total Acidity (or $CO_3^=$ Acidity) respectively,

$$\text{Caustic Alkalinity} = [OH^-] - [H^+] - [HCO_3^-] - 2[H_2CO_3^*] \qquad (k)$$

$$\text{Total Acidity} = 2[H_2CO_3^*] + [HCO_3^-] + [H^+] - [OH^-] \qquad (l)$$

Each mass parameter adds a new variable to the system so that irrespective of the number of additional equations, the number of independent unknowns to be measured remains equal to two.

The facility for measurement of the various mass parameters and the accuracy with which a parameter can be measured will determine the choice of parameters, additional to pH, in any particular situation. If a total carbon analyser is available, C_T can be measured and Eq (f) can be utilized. If a p_{CO_2} meter is available, then $[H_2CO_3^*]$ can be determined from p_{CO_2} using Eq (e). However, neither of these instruments are commonly available; in this situation the most reliable parameter to measure is either Total Alkalinity (abbreviated to simply Alkalinity), see Eq (g), by titration to the $H_2CO_3^*$ equivalence point, or Phenolpthalein Alkalinity (i.e. HCO_3^- Alkalinity), see Eq (i), by titration to the HCO_3 equivalence point. However, the alkalinity (or acidity) to the HCO_3^- equivalence point is inadequate as an independent parameter when a zero titration is obtained (i.e. a water with an initial pH of about 8,3) - a zero value does not give any information regarding the total carbonate species concentration, C_T, as this *equivalence point* is independent of C_T, whereas the $H_2CO_3^*$ Alkalinity is not. (see Loewenthal and Marais, 1976). Direct measurement Total Acidity (abbreviated to simply Acidity), see Eq (l), by titration to the $CO_3^=$ equivalence point generally is not a reliable titration as the endpoint cannot be readily

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identified because it occurs in a region of high buffer capacity, i.e. pH > 11.

Summarizing, the most useful measurements will be pH and one of the following parameters - C_T, Alkalinity, Phenolpthalein Alkalinity and p_{CO_2}.

The seven mass parameters (i.e. C_T and the various forms of alkalinity and acidity) are not independent, for example from Eqs (f, g and h)

$$\text{Alkalinity} + \text{Acidity} = 2C_T \qquad \text{(m1)}$$

or, written more precisely

$$H_2CO_3^* \text{ Alkalinity} + CO_3^= \text{ Acidity} = 2C_T$$

and, from Eqs (g, i and l)

$$\text{Alkalinity} - \text{Acidity} = 2 \text{ Phenolpthalein Alkalinity} \qquad \text{(m2)}$$

i.e.

$$H_2CO_3^* \text{ Alkalinity} - CO_3^= \text{ Acidity} = 2HCO_3^- \text{ Alkalinity}$$

and, from Eqs (m1 and m2)

$$\text{Alkalinity} - \text{Phenolpthalein Alkalinity} = C_T \qquad \text{(m3)}$$

i.e.

$$H_2CO_3^* \text{ Alkalinity} - HCO_3^- \text{ Alkalinity} = C_T$$

Note that in general for any particular equivalence point the

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associated alkalinity equals the negative of the associated acidity, for example $H_2CO_3^*$ Alk. = $-H_2CO_3^*$ Acidity, see Eqs (g and h).

The interdependence between these mass parameters is best illustrated graphically in a diagram with Total Alkalinity and Total Acidity as co-ordinate parameters, see Figure 1. This diagram illustrates that measurement of any pair of alkalinity values (or any pair of acidity values) completely defines the remaining five mass parameters.

Lines representing pH can also be incorporated into Figure 1 by establishing a relationship between pH, Total Alkalinity and Total Acidity using Eqs (f, g and l) and equilibria equations Eqs (a to c), see Figure 2. Note that the lines representing the various

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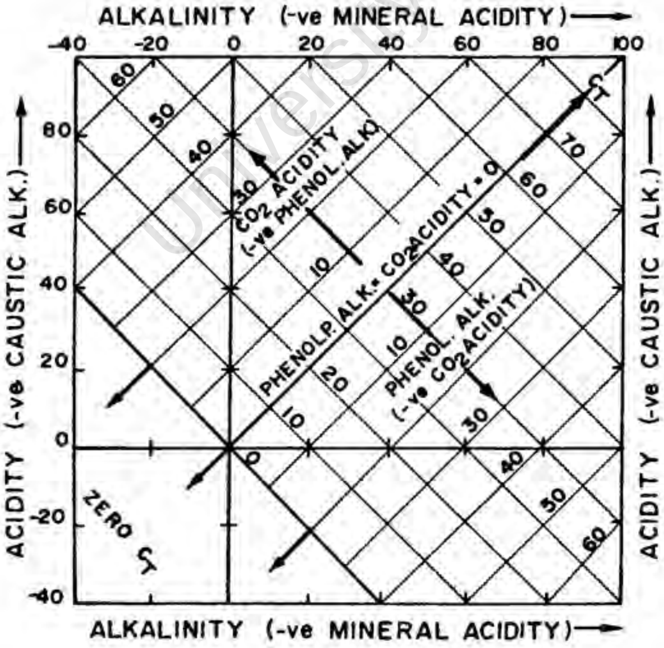

Figure 1. Inter-relation between C_T and the various forms of alkalinity and acidity.

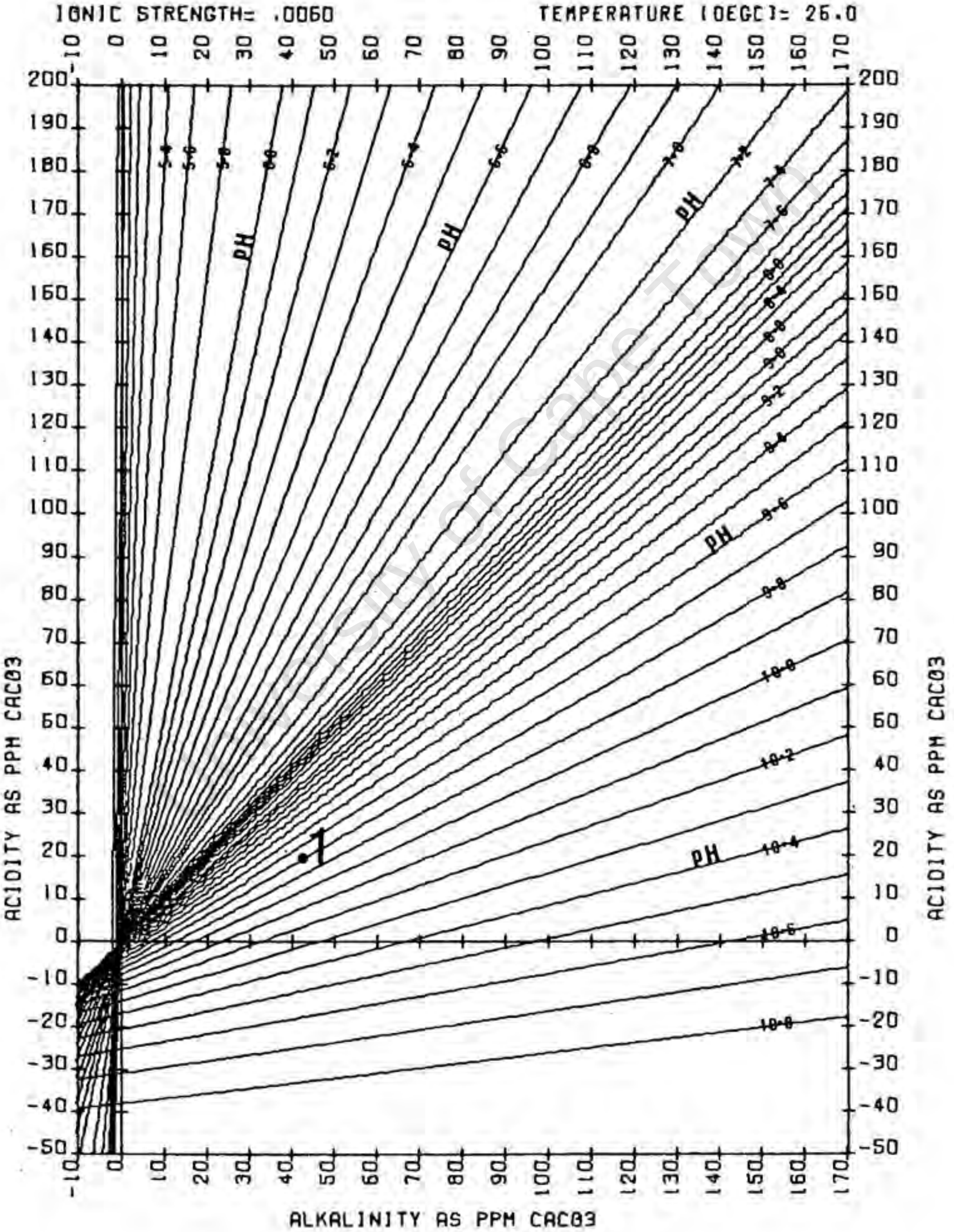

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Figure 2. Distribution of lines representing pH with co-ordinate parameters Alkalinity and Acidity.

forms of alkalinity and acidity (see Figure 1) are plotted using mass balance relationships and thus are independent of ionic strength and temperature. The distribution of pH lines however, requires using equilibria equations and thus each family of pH lines is specifically for a particular water with some ionic strength and temperature. Figures 1 and 2 can be superimposed thereby expressing graphically the interrelationships between pH and all the mass parameters for the carbonate system. The superimposed diagram is not shown here because the multiplicity of lines confuses more than it clarifies.

In Figures 1 and 2, lines representing measured values for any two independent parameters (i.e. Alkalinity and pH) intersect at a point. This point defines the remaining six parameters which can be estimated by interpolating their ordinate values on the appropriate co-ordinate axes.

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2.2 Species concentrations, titration curves and buffer capacity

The dependency of all the weak acid-base species concentrations on pH makes this parameter a convenient one for depicting graphically the distribution of these species in a solution. From Eqs (a to c, and f) it is possible to formulate relationships linking each of the weak acid-base species to C_T and H^+. Taking the logarithm of each of these relationships, and keeping C_T constant, gives the equations for plotting the log species - pH diagram, see Figure 3a. This plot is extremely useful, *inter alia* because it can be constructed very readily, without the direct use of the equations, by utilizing the behavioural characteristics of the species lines in the log species-pH diagrams, (Loewenthal and Marais, 1976).

The log species-pH diagram is basic in that from it it is possible to derive both the distribution of buffer capacity with pH and the strong acid (or base)-pH titration curves.

Buffer capacity, β, is defined as the mass of strong base required to cause a unit positive change in pH, i.e.

$$\beta = (\partial C_B/\partial pH)_{C_T} \qquad (n)$$

Where C_B = the molar mass of strong base added

= mass of strong base required to effect a unit positive change in pH.

Harremoes, Henze Christenson, Jorgensen and Dahi (1977) have shown that the logarithm of β (divided by 2,303) is given graphically by the dotted line shown in Fig 3(a). Alternatively the buffer capacity equation can be derived and the distribution of β with pH plotted using this equation, see Figure 3(c).

The titration curve for the weak acid is derived from the cumulative area under the buffer capacity curve between two pH values. The area under the β curve representing the mass of strong base (or acid) added to effect the change in pH. Thus, commencing at pH_3, addition of strong base to various pH values will be represented by the area under the β curve from pH_3 to the observed pH and gives rise to the titration curve shown in Fig 3(b). Conversely, the slope of the titration curve at a pH value gives β at that pH value.

In Figure 3 are compared the distribution of species, titration curve and buffer capacity with pH for a water with $C_T = 10^{-3}$ moles/ℓ. From this diagram the following relevant points are

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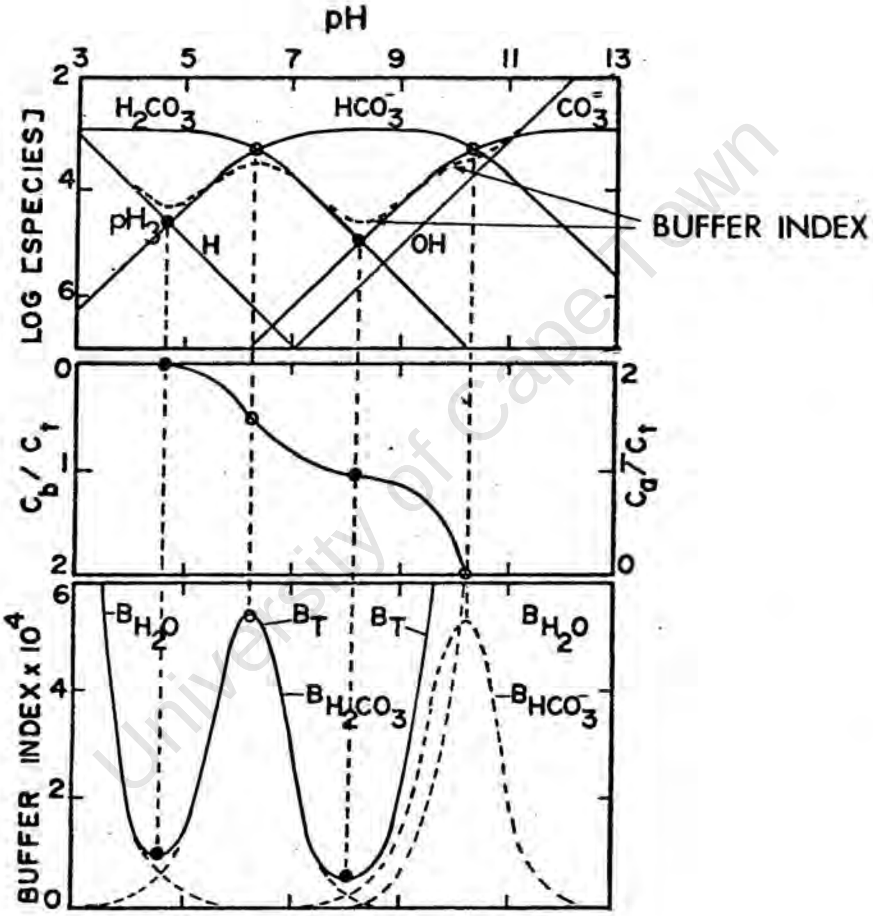

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Figure 3. Distribution of carbonic species, titration curve and buffer capacity versus pH for water with C_T = 10^{-3} moles/ℓ.

noted:

(1) Points 1 and 3 in the log species-pH diagram correspond to the $H_2CO_3^*$ and HCO_3^- equivalence points respectively. The pH values of these points are identified by clear inflection points in the titration curve and are points of minimum buffer capacity.

(2) Points 2 and 4 in the log species-pH diagram correspond to pH = pK_1' and pH = pK_2' respectively. These points are identified by clear inflection points in the titration curve and are points of maximum buffer capacity.

(3) Point 5 in the log species-pH diagram corresponds to the $CO_3^=$ equivalence point. No inflection point occurs at this pH in the titration curve thus making impractical the measurement of either Total Acidity or Caustic Alkalinity by titration.

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2.3 Measurement of Alkalinity and Acidity

Alkalinity or acidity values can be simply measured by acid or base titrations to the relevant equivalence points. However, a major practical problem is the identification of the particular equivalence point giving the endpoint to a titration measurement. From the Section 2.2 above, only the $H_2CO_3^*$ and HCO_3^- equivalence points can be identified from inflection points in the titration curve. Thus, the only alkalinity or acidity values which can be measured reliably by titration are those to these two inflection points. Furthermore, because these correspond to points of minimum buffer capacity, titration errors to these two points are minimized.

Numerous other problems associated with alkalinity and acidity measurement by titration, including the effects of ionic strength temperature, carbonate precipitation and CO_2 exchange with the atmosphere, are discussed by Loewenthal and Marais, 1976.

2.4 Determination of Species Concentrations

Each of the carbonate species concentrations can be estimated graphically in a log species-pH plot using the known values for C_T and pH (which were either initially measured or estimated from measured values of say, Total Alkalinity and Phenolphthalein Alkalinity). For example, suppose analysis of a water gives Total Alkalinity = 0,80 mM/ℓ and Ph. Alkalinity = 0,20 mM/ℓ, determine each of the carbonate species concentrations.

From Eq (m2)

Total Acidity = 0,8 - 2.0,2 = 0,4 mM/ℓ

and from Eq (m3)

C_T = 0,8 - 0,2 = 0,6 mM/ℓ

For the pH of the water: In Figure 2 lines representing Total Alkalinity 0,8 mM/ℓ (i.e. 40 ppm as $CaCO_3$) and Total Acidity 0,4 mM/ℓ (i.e. 20 ppm as $CaCO_3$) intersect at Point 1; the value of the pH line through Point 1 gives pH = 9,8. A log species-pH plot is now sketched for water with C_T = 0,6 mM/ℓ (see Figure 4). For pH 9,8 each of the species concentrations is given by the ordinate values of the log species lines at pH 9,8, in Figure 4, $[H_2CO_3^*]$ = 0,0003, $[HCO_3^-]$ = 0,46 and $[CO_3^=]$ = 0,14 mM/ℓ.

2.5 Chemical Dosing

Addition or removal of any chemical common to this system (e.g. H^+, OH^-, CO_2, HCO_3^- or $CO_3^=$) alters the equilibrium state of the water. The new equilibrium condition established will be

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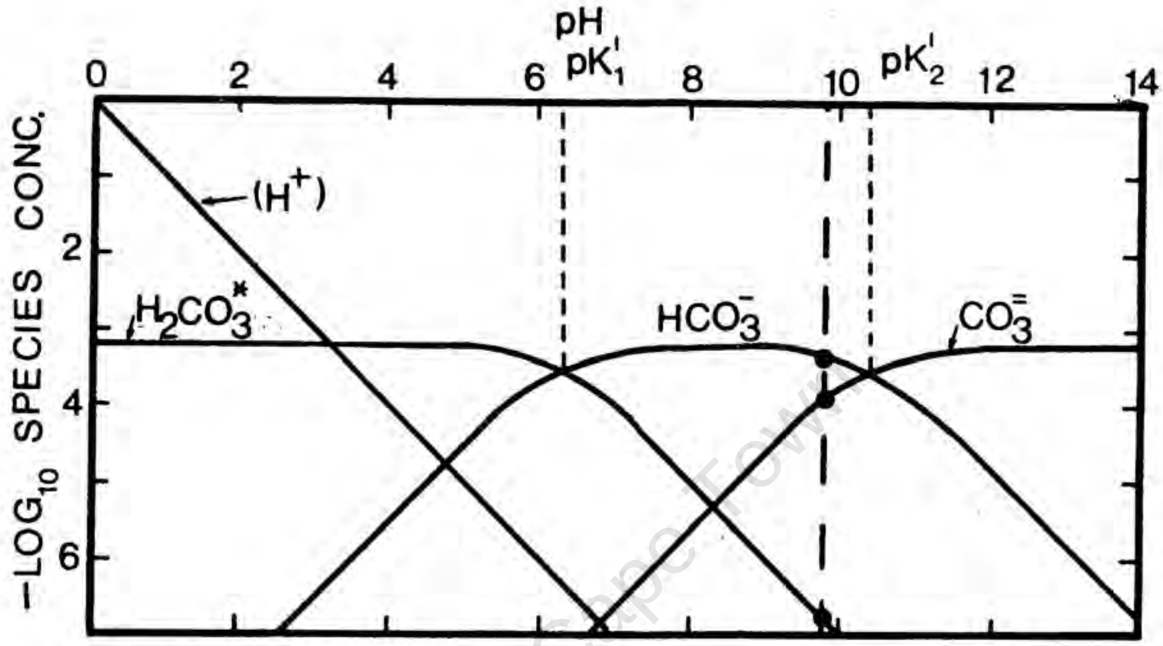

Figure 4. Estimation of individual species concentrations for water with C_T *= 0,6 mM/ℓ and pH = 9,8.*

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defined by a new pH and new values for the mass parameters.

In water treatment practice it is often desirable to be able to predict changes in the state of a water resulting from a particular chemical dosing process. Whereas the mass parameters change in a stoichiometric fashion with chemical dosing, the changes in pH (which are governed by equilibria reactions) are more complex.

Equations describing the stoichiometric changes in the values of the mass parameters with chemical dosing are set out below:

Alkalinity change $= 2\Delta[CO_3^=] + \Delta[HCO_3^-] + \Delta[OH^-] - \Delta[H^+]$ (o)

$=$ -ve Mineral Acidity change (p)

Phenolpthalein Alkalinity change $= \Delta[CO_3^=] + \Delta[OH^-] - \Delta[H_2CO_3^*]\ ]\ \Delta[H^+]$ (q)

$=$ -ve CO_2 Acidity change (r)

Caustic Alkalinity change $= \Delta[OH^-] - \Delta[H^+] - \Delta[HCO_3^-] - 2\Delta[H_2CO_3^*]$ (s)

$= -$ve Acidity change or

Acidity change $= 2\Delta[H_2CO_3^*] + \Delta[HCO_3^-] + \Delta[H^+] - \Delta[OH^-]$ (t)

C_T change $= \Delta[H_2CO_3^*] + \Delta[HCO_3^-] + \Delta[CO_3^=]$ (u)

where

= molar mass of chemical added.

Example:

0,01 moles of Na_2CO_3 are added to a litre of water, determine the changes in Alkalinity, Phenolphthalein Alkalinity and Acidity.

From Eq (o) :

Alkalinity change = 0,02 moles/ℓ

From Eq (q) :

Phenolphthalein Alkalinity change = 0,01 moles/ℓ

From Eq (t) :

Acidity change = 0.

The rather complex change in pH with chemical dosing is most simply estimated using the mass expressions, Eqs (o to u) and applying graphical techniques in the equilibrium diagram Figure 2 as follows:

(1). pH and Alkalinity of a water are measured (these are the two independent parameters most easily measured in practice). Intersection point of the lines representing the measured Alkalinity and pH in the water gives the initial Acidity.

(2) Acidity and Alkalinity values after chemical dosing are calculated from the equations relating to the *change* in each of these parameters with dosing, Eqs (o and t)

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respectively, giving

New Alkalinity = Original Alk. + Δ Alk.

New Acidity = Original Acidity + Δ Acidity

(3) The value of the pH line through the intersection point of the lines representing the new Alkalinity and Acidity values in the diagram defines the new pH.

3. ESTABLISHMENT AND MEASUREMENT OF pH

The analyses of the carbonate system as set out in Section 2 above essentially requires knowledge of the activity of the hydrogen ion, (H^+). Hence, from a practical point of view it is necessary to measure this activity.

Thermodynamically there is no theoretical basis on which the hydrogen ion activity (or any other single ion activity) can be determined because it is not possible to add a single ionic species to a solution. To resolve single ion activities theoretically, it is necessary to make some non-thermodynamic assumption, or alternatively, assumptions which depend on the factors affecting the activity. In Section 2 Chapter 3 it was shown that the activity of an ion depends on a number of factors arising from electrostatic and hydration effects. In low salinity waters the electrostatic effects are dominant, the hydration effects negligible and activity can be determined using the electrostatic approach of Debye-Hückel, the non-thermodynamic assumption arising in the distance of closest approach parameter. In high salinity waters both electrostatic and hydration effects are significant. Hence, a further non-thermodynamic assumption, additional to that for the electrostatic effect, needs to be made to accommodate the hydration effect, and should be based on the physico-chemical characteristics of the ionic species - in Section 6.5.2, Chapter 2, the assumption was made that Cl^- has zero primary hydration.

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These two assumptions are basic to the development of a theory to determine all the single ion activities in a solution from the mean activity values of the salts and acids.

In low salinity waters because hydration effects are negligible and the electrostatic effects can be modelled, apparently, very accurately, calculation of H^+ activity can be accepted to be accurate. However, as the ionic strength increases so modelling of the electrostatic effect becomes less reliable. Furthermore, modelling of the hydration effect is based on simplifying assumptions and thereby introduces a measure of unreliability into the calculation of the hydration effects. As a consequence estimations of single ion activities in high salinity waters generally cannot be expected to be as reliable as those in low salinity waters. These aspects are recognised in setting up standards for pH by establishing these standards in a relatively low ionic strength region ($\mu \not> 0,01$).

3.1 Establishment of pH standards

We have noted that the determination of single ion activity requires measurement of the mean activity of a salt or acid. Consequently, determination of H^+ requires that the mean activity of the acid HCl, $(HCl)_\pm$, first must be measured. Measurement of $(HCl)_\pm$ usually is done using electrochemical cells. The method by which $(HCl)_\pm$ is measured and the procedure by which a pH value is ascribed to a solution is best explained by considering the example of pH measurement of a solution using a cell involving a hydrogen, silver-silver chloride electrode system. This cell can be depicted as: Hydrogen electrode/solution, Cl^-/silver-silver chloride electrode, where (/) denotes a boundary across which there is a potential difference. The electrode reactions that occur for this cell are

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$$\tfrac{1}{2}\, H_{2(g)} = H^{+} + e^{-} \tag{2a}$$

and

$$Ag_{(s)} + Cl^{-} = AgCl_{(s)} + e^{-} \tag{2b}$$

where subscripts (g) and (s) refer to the gas and solid phases respectively.

The potential of the $H_{2(g)}$ electrode, E_H for reaction (2a), is established in part by the activity of H^+ in the solution under investigation. An equation for this potential can be written down using the Nernst expression, i.e.

$$E_H = E^o_H + \frac{RT}{F}\, ln\, \{(H^+)\ (e^-)/\rho_{H_2}^{\frac{1}{2}}\} \tag{3}$$

ρ_{H_2} = partial pressure of H_2 at the hydrogen electrode, equal to unity

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and, for the potential for the silver-silver chloride half cell, E_s, from reaction (2b)

$$E_s = E^o_s - \frac{RT}{F}\, ln\, \{(Cl^-)/(e^-)\} \tag{4}$$

where

E_H = potential of the hydrogen electrode at the reference pressure of 760 mm dry hydrogen.

E^o_H = standard potential of the hydrogen electrode which by convention equals zero at all temperatures.

E_s = potential of the silver-silver chloride reference electrode.

E^o_s = standard potential of the reference half cell, the value of which is known with temperature.

R = gas constant = 8,3143 joules/deg/mole

T = absolute temperature = t°C + 273,15

F = the Faraday constant = 96 500 coulombs/equiv.

The e.m.f. of cell (3) is given by the difference between the half cell potentials

$$E_{cell} = E_s - E_H$$

$$= E_s^o - \frac{RT\mathit{ln}10}{F} \log (H^+)(Cl^-) \qquad (5)$$

The pH of a particular solution can now be expressed by rearranging Eq (5) and solving for $-\log(H^+)$,

$$pH = \frac{(E_{cell} - E_s^o)F}{RT\mathit{ln}10} + \log (Cl^-) \qquad (6)$$

In order to determine pH of a solution using Eq (6) and an E_{cell} measurement of the solution, consider the right hand side of this equation: Values for the constants E_s^o, F and R are known with temperature, T; the only remaining unknown is the activity of chloride in the solution. Consequently, pH can be determined only if *both* the *concentration* and *activity coefficient of* Cl^- are known. Generally this is not the case for most solutions so that the method is not practical for routine pH measurements. However, the method is suitable to establish the pH of standard (reference) solutions wherein the concentration of Cl^- can be specified, and the activity coefficient of Cl^- can be closely estimated - for low ionic strength solutions γ_{Cl^-} can be estimated using the Debye-Hückel theory, Bates (1964). This approach has formed the basis for establishing the NBS Standards for pH.

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3.2 pH Measurements relative to a standard

In order to by-pass the problem of having to estimate the Cl^- activity in routine measurements of pH, the silver-silver chloride reference electrode of the electrode system in Eq (1) is replaced by a reference electrode immersed in a solution with a constant activity for Cl^- (such as a saturated KCl solution), termed a bridge solution. With the bridge solution, the potential of the reference cell has a value independent of the Cl^- activity in the test solution. However, it is dependent on the Cl^- activity of the bridge solution, i.e. dependent on the Cl^- activity in the saturated KCl solution, and this activity is not known accurately. Consequently, the pH cannot be established accurately, but, the activity of Cl^- in the bridge solution remains constant and this confers a distinct advantage: In the equations defining the system, see Eqs (11, 12 and 13), the constant Cl^- activity arising from the cell reactions in the standard and test solutions cancel out. Consequently, if the cell is calibrated against a known H^+ activity in a standard solution then the H^+ activity in the test solution can be measured without the need for Cl^- determination. This measurement of pH is called a relative pH observation because it is relative to a standard.

The system of relative pH measurement is not without inherent difficulties - strictly, the relative pH will give the true H^+ activity in a test solution only if the principal ionic constitutions of the test and standard solutions are identical. The reason for this is as follows: due to the difference in ionic constitution between the test and the KCl (or bridge) solutions a liquid junction potential arises across the liquid (or salt) bridge connecting the two solutions. This potential will vary with the ionic constitutions of the test and standard solutions. When the system is calibrated against the *standard* pH solution

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the effect of the liquid junction is calibrated out, but if the *test* solution has an ionic constitution different from that of the standard a *residual* liquid junction potential will arise and accordingly cause the observed pH to differ from the true value.

The effects, described above, are analysed as follows: Consider the cell reactions involved in a relative pH observation. The cell is depicted as,

Hydrogen (or glass) electrode/test solution//KCl (sat'd)/
silver-silver chloride electrode (7)

where // depicts a liquid junction between the test solution and the saturated KCl salt bridge solution surrounding the reference electrode.

Irrespective of whether the standard or test solution is in the cell, the cell potential, E_{cell}, is comprised of the sum of three individual potentials; E_H for the hydrogen (or glass) electrode, E_j for the potential across the liquid junction boundary between the solution and the saturated KCl solution and E_R for the potential of the reference electrode, i.e. in general

$$E_{cell} = E_R^o - E_H^o + E_j - \frac{RT}{F} ln(H+)(Cl^-)_B \qquad (8)$$

where (H^+) = hydrogen ion activity
$(Cl^-)_B$ = Cl^- activity of the bridge solution.

Consequently, when the *standard solution* is in the cell, the cell potential, $E_{cell(s)}$, is given as follows:

$$E_{cell(s)} = E_R^o - E_H^o + E_{j(s)} - \frac{RT}{F} ln(H^+)_s(Cl^-)_B \qquad (9)$$

and, when the *test solution* is in the cell, the cell potential,

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$E_{cell(x)}$, is

$$E_{cell(x)} = E^o_R - E^o_H + E_{j(x)} - \frac{RT}{F}ln(H^+)_x(Cl^-)_B \tag{10}$$

where subscripts 's' and 'x' denote the standard and test solution values respectively.

Rearranging each of Eqs (9 and 10) gives the pH of each of these cells in terms of the cell potentials. For the cell with the pH standard solution

$$pH_{(s)} = (E_{cell(s)} - E^o_R - E_{j(s)} + E^o_H)\frac{F}{RTln10} + \log(Cl^-)_B \tag{11}$$

and, for the pH of the test solution, $pH_{(x)}$

$$pH_{(x)} = (E_{cell(x)} - E^o_R - E_{j(x)} + E^o_H)\frac{F}{RTln10} + \log(Cl^-)_B \tag{12}$$

The effects of the Cl^- activity of the saturated KCl in the salt bridge, $(Cl^-)_B$, is common to both the standard and test solutions. Subtracting Eq (11) from Eq (12) gives the relationship linking the pH of the test solution to the cell potentials and liquid junction potentials in the standard and test solutions, i.e.

$$pH_{(x)} = pH_{(s)} + \frac{(E_{cell(x)} - E_{cell(s)})F}{RTln10} - \frac{(E_{j(x)} - E_{j(s)})F}{RTln10} \tag{13}$$

That is, the pH of the test solution is independent of the activity of the Cl^- surrounding the reference probe, i.e. independent of (Cl^-) in the saturated KCl solution. Consequently, by introducing the saturated KCl to surround the reference electrode (and thereby to separate this KCl solution from the cell solution by a liquid junction) the Cl^- activity in the cell solution (i.e. standard or test solution) has no effect on the H^+ determination.

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However, the necessity for a salt bridge (i.e. a liquid junction) now introduces a residual liquid junction potential error between observations in standard and test solutions, reflected by the term $F(E_{j(x)}-E_{j(s)})/RT\mathit{ln}10$ in Eq (13) above. Occurrence of this residual potential requires that relative pH observations either be adjusted to compensate for this error (to give the true pH), or, the residual liquid junction effect is accepted in the observation, i.e. the relative pH measurement including the residual error is accepted as the observed pH. This pH observation is called the *operational pH* and constitutes the usual pH measurement in low salinity waters.

For low ionic strength solutions, $\mu \lesssim 0{,}05$, the residual liquid junction effect is small and can usually be neglected except in very accurate work. In high salinity waters however, the operational pH can differ significantly from the true pH, for example for seawater, with $\mu \cong 0{,}66$, by approximately 0,08 pH units. Under these conditions the operational pH cannot serve as a substitute for true pH in analyses of weak acid base systems incorporating true pH in the equilibrium expressions. There are then two options open, either (i) evaluate the residual liquid junction potential and estimate the true pH from the operational pH, or (ii) re-evaluate all the equilibrium constants for a particular solution in terms of operational values. The second option is practical only if a large number of analyses are to be made on a water with some ionic constitution, for example, seawater. The first option allows the analyses to be general for all waters. To exercise the second option introduces the problem of estimating the residual liquid junction potential, i.e. the relationship between operational and true pH.

3.3 Operational pH, pH_O

In Eq (13), $pH_{(x)}$ is presumed to represent the true pH in a test

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solution relative to the pH in the standard buffer solution $pH_{(s)}$, and the terms $(E_{cell(s)}-E_{cell(x)})$, $E_{j(x)}$ and $E_{j(s)}$. Now $pH_{(s)}$ is specified and $(E_{cell(s)}-E_{cell(x)}$ is measured, but neither the liquid junction potential associated with the test solution, $E_{j(x)}$, nor that associated with the standard solution, $E_{j(s)}$, are known. Consequently, the pH observed will differ from the true pH in the measure that $E_{j(x)}$ differs from $E_{j(s)}$, i.e. $(E_{j(x)}-E_{j(s)})$, and this difference is not known. Although unknown, if this difference is added to $pH_{(x)}$ in Eq (13), one obtains the definition of the operational pH, pH_o, i.e.

$$pH_o = pH_{(x)} + (E_{j(x)} - E_{j(s)})F/RTln10 \qquad (14a)$$

pH_o is now directly linked to the e.m.f measurement, Bates (1964) as

$$pH_o = pH_s + (E_{cell(x)} - E_{cell(s)})F/(RTln10) \qquad (14b)$$

and can be read directly from the display of a pH meter. Though pH_o reflects a highly reproducible number, this reading does not usually reflect the true pH of a test solution, the difference between true pH, pH and pH_o being given by

$$pH - pH_o = -(E_{j(x)} - E_{j(s)})/(RTln10) \qquad (15)$$

where the right hand side defines the residual liquid junction potential.

3.4 Determination of residual liquid junction potential

Theoretical methods for estimating the ideal contribution to liquid junction potentials have been proposed by Planck (1890) and Henderson (1903). A clear exposition on the utilization of these methods is given by MacInnes (1961). However, the accuracy of these theoretical estimates is unknown because both approaches neglect the non ideal effects on activity and mobilities of ions,

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i.e. activities and mobilities of ions are assumed to have their values at infinite dilution.

Recognizing that the theoretical approaches above probably give only a very rough estimate of the residual liquid junction potential, one seeks some alternative approach that is more reliable. Such an approach is possible through activity coefficient theory for H^+. In essence this approach to estimating residual liquid junction potentials is as follows: Consider the operational hydrogen ion activity $(H^+)_o$ as the product of an *operational H^+ activity coefficient*, $\gamma_{H(o)}$, and the molality of H^+, $[H^+]$, i.e.

$$pH_o = -\log_{10}\{\gamma_{H(o)}[H^+]\}, \text{ or, } (H^+)_o = \gamma_{H(o)}\cdot[H^+] \qquad (18)$$

Now, $\gamma_{H(o)}$ is linked to the true H^+ activity coefficient, γ_{H+}, and the residual liquid junction potential through Eq (17) as follows:

$$pH_o = pH + pk_{1j} \qquad (19)$$

i.e.

$$\gamma_{H(o)}/\gamma_{H+} = k_{1j} \qquad (20)$$

where

pk_{1j} = residual liquid junction potential effect on pH, i.e.

$$-\log k_{1j} = \frac{(E_{j(x)} - E_{j(s)}).F}{RT\ln 10} \qquad (21)$$

Thus, from Eq (20), for a particular solution, if both $\gamma_{H(o)}$ and γ_H either can be measured, or determined from theory, then it is possible to determine the residual liquid junction potential.

Determination of the true activity coefficient, γ_{H+}, has been dealt with already in Section (2.3.3) Chapter 3. It was shown in that section that γ_{H+} is determined from the mean activity

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$$\hat{=} \gamma_{H(o)} \, \bar{C}_a . (v_x - V_{CO_2})/(1 + \frac{\gamma_H . \gamma_{SO_4} . [SO_4^=]}{K_a \gamma^T_{HSO_4}}) \qquad (25b)$$

$$= \gamma_{H(o)} \, \bar{C}_a . (v_x - V_{CO_2})/(1 + k_G) \qquad (25c)$$

where γ^T = total (stoichiometric) species activity coefficient.

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The first Gran titration for water with sulphate species is obtained in exactly the same way as for waters without sulphate species, and the measured slope of the plot of $F_{1(x)}$ versus v_x is labelled $\bar{S}$. This measured slope is linked to $\gamma_{H(o)}$ through the theoretical slope obtained by differentiating Eq (25c) with respect to v_x. In Eq (25c) the term k_G is closely a constant in the region pH>3 (i.e. in this region $[SO_4] >> [HSO_4^-]$[*], consequently the theoretical slope, $\partial F_{1(x)}/\partial v_x$ is

$$\partial F_{1(x)}/\partial v_x = \gamma_{H(o)} \, \bar{C}_a/(1 + k_G)$$

$$= \bar{S}$$

and, solving for $\gamma_{H(o)}$

$$\gamma_{H(o)} = \bar{S}.(1 + k_G)/\bar{C}_a \qquad (26)$$

where $k_G = \gamma_H . \gamma_{SO_4} \, [SO_4^=]/(K_{HSO_4} . \gamma^T_{HSO_4})$

---

[*] A condition for constancy of the residual liquid junction potential is that the principal ionic matrix of the test solution should not vary in the pH range of interest. This condition is satisfied if the weak acid-base species in the solution do not make up a principal part of the ionic matrix. Generally this requirement is satisfied in natural highly saline waters.

K_{HSO_4} = 0,0102 at 25°C, MacInnes (1962).

To determine $\gamma_{H(o)}$ using Eq (26), $\bar{S}$ and $\bar{C}$ are known from experiment and the terms γ_{H+}, $\gamma^T_{SO_4}$ and $[SO_4]_T$ are determined from the hydration theory for activity coefficients using the iterative method outlined in Section 3.1.2, Chapter 3 (incorporated in the computer program listed in Supplement A). The remaining problem is estimation of the stoichiometric activity coefficient for HSO_4^-, $\gamma^T_{HSO_4}$.

Determination of $\gamma^T_{HSO_4}$ requires that values be known for the free species activity coefficient, $\gamma_{HSO_4^-}$, and the equilibrium constants for ion pairing between HSO_4^- and the various principal cation species comprising the ionic matrix. However, there are no reported data which can be used to determine values for these parameters, and consequently these are assumed to have the same values as those for HCO_3^-. This assumption is based on the finding (see Section 5 of this Chapter) that in seawater the total activity coefficient for HSO_4^-, $\gamma^T_{HSO_4}$, determined from data reported by Khoo, Ramette, Culberson and Bates (1977) closely equals that for HCO_3^-, $\gamma^T_{HCO_3}$.

Having obtained the operation H+ activity coefficient, $\gamma_{H(o)}$, either from Eq (26) or Eq (24) depending on whether sulphates are present or not, and having the true activity coefficient, γ_{H+}, from Eq (22), the residual liquid junction constant, k_{1j}, is calculated using Eq (20). The residual liquid junction potential, ΔE_j, expressed in volts is then determined using Eq (21), i.e.

$$\Delta E_j = -\frac{RT}{F}\, ln\ 10.\log k_{1j} \qquad (27)$$

$$= -0,0591 \log k_{1j} \text{ at } 25^\circ C$$

where the values for R and F are those listed in Eq (4).

The approach above was used to determine the residual liquid junction potential in (a) synthetic seawater with no sulphate species, and (b) synthetic seawater with sulphate species.

(a) Residual liquid junction potential in synthetic seawater without sulphate species.

Synthetic seawater with the following composition was prepared in the laboratory: $[Na^+] = 0{,}4953$, $[Mg^{2+}] = 0{,}054$, $[Ca^{2+}] = 0{,}0108$, $[Cl^-] = 0{,}623$ and $\mu = 0{,}70$ all expressed in molalities, and temperature 25°C.

(i) Determine the true hydrogen ion activity coefficient γ_{H+}: $\gamma_{HCl\pm}$ and γ_{Cl-} were computed using Eqs (22 and 29) Chapter 3 respectively with the computer program listed in Appendix A as

$$\gamma_{HCl\pm} = 0{,}732$$

$$\gamma_{Cl-} = 0{,}657$$

and, from Eq (22)

$$\gamma_{H+} = (0{,}732)^2/0{,}657 = 0{,}816$$

(ii) Determine operational activity coefficient, $\gamma_{H(o)}$: Titration of the test solution with standard strong acid ($\bar{C}_a = 0{,}09583$) gives a series of observed values for pH_o versus the volume of strong acid added, v_x. Values for the Gran junction $F_{1(x)}$ are determined by substituting corresponding values for $pH_{o(x)}$ and v_x in the region $3<pH_o<4$ into Eq (23a). The measured slope of this plot gives the value for $\bar{S}$ to be used in Eq (24), in this case

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$\bar{S} = 0{,}0946$

Thus, from Eq (24)

$$\gamma_{H(o)} = \bar{S}/\bar{C}_a = 0{,}0946/0{,}09583$$

$$= 0{,}987$$

(iii) Determine residual liquid junction potential: The residual liquid junction potential constant, k_{lj}, is determined by substituting the values for γ_{H+} and $\gamma_{H(o)}$ from (i) and (ii) above, into Eq (20),

$$k_{lj} = \gamma_{H(o)}/\gamma_{H+} = 0{,}987/0{,}816$$

$$= 1{,}211$$

The residual liquid junction potential, ΔE_j, is determined by substituting the value for k_{lj} above into Eq (27),

$$\Delta E_j = -59{,}1 \log k_{lj} = -59{,}1 \log (1{,}211)$$

$$= -4{,}9 \text{ mV}.$$

(b) Residual liquid junction potential in synthetic seawater containing sulphate species.

Synthetic seawater with the following *stoichiometric* composition was prepared in the laboratory:

$[Na^+]_T = 0{,}467$, $[Mg^{2+}]_T = 0{,}054$, $[Ca^{2+}]_T = 0{,}0108$, $[Cl^-] = 0{,}539$, $[SO_4^{2-}]_T = 0{,}0282$ all expressed in molalities, and temperature 25°C.

(i) Determine free species concentrations and activity coefficients:

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When sulphate species are present in the test solution, ion pairing causes that free species concentrations in the solution initially are unknown so that activity coefficients cannot be determined directly from Eq (22) Chapter 3 as was done in the previous example, (a) above. In this case free species concentrations and activity coefficients are determined following the iterative procedure described in Chapter 3 and incorporated in the computer program listed in Supplement A. Using this procedure gives values for $[SO_4^=]$, $\gamma_{SO_4^=}$, $\gamma_{HCl\pm}$, γ_{Cl^-} and $\gamma^T_{HSO_4}$ listed below:

$[SO_4^{2-}] = 0,0145$

$\gamma_{SO_4} = 0,177$

$\gamma_{HCl\pm} = 0,729$

$\gamma_{Cl-} = 0,649$

$\gamma^T_{HSO_4} = 0,592$

(ii) Determine the true activity coefficient for H^+, γ_{H+}: Substituting the values determined for $\gamma_{HCl\pm}$ and γ_{Cl^-} determined in (i) above into Eq (22)

$\gamma_{H+} = (0,729)^2/0,649 = 0,819$

(iii) Determine the operational activity coefficient, $\gamma_{H(o)}$: Titration of the test solution with standard strong acid ($\bar{C}_a = 0,1010$) gives a series of observed values for pH_o versus the volume of strong acid added, v_x. Values for the Gran junction, $F_{1(x)}$, are found by substituting the

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corresponding values for $pH_{o(x)}$ and v_x, in the region $3<pH_o<4$, into Eq (23a). The measured value for the slope of this plot gives the value of $\bar{S}$ to be used in Eq (26), as $\bar{S} = 0{,}0720$.

Substituting the values for γ_{SO_4}, $[SO_4^{2-}]$ and $\gamma^T_{HSO_4}$ found in (i) above, γ_{H+} from (ii) above and the value for $\bar{S}$ into Eq (26),

$$\gamma_{H(o)} = \bar{S}\ \{1+\gamma_H \cdot \gamma_{SO_4}[SO_4^{2-}]/(K_{HSO_4} \cdot \gamma^T_{HSO_4})\}/\bar{C}_a$$

$$= 0{,}0720\ \{1+0{,}819 . 0{,}177 . 0{,}0145/(0{,}0102 . 0{,}592)\}/0{,}0101$$

$$= 0{,}970$$

(iv) Determine the residual liquid junction potential: Substituting the values for γ_{H+} and $\gamma_{H(o)}$ from (ii) and (iii) above respectively into Eq (27),

$$\Delta E_j = -59{,}1 \log (0{,}970/0{,}819)$$

$$= -4{,}4 \text{ mV}$$

Assessment of the Gran titration method for estimating residual liquid junction potentials is possible by comparing predictions using this method with those using some other independent method, both on the same solution. In this respect observations on synthetic seawater reported by Bates and Macaskill (1975) form a useful basis for comparison.

Bates and Macaskill report potential measurements using cells with and without liquid junctions on synthetic seawater (with sulphates) buffered by a 0,02 M tris weak acid-base system at 25°C. From these measurements and using an estimate for γ_{Cl^-} it is possible to determine the residual liquid junction potentials in the

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synthetic seawater as follows:

From Eq (15) the residual liquid junction potential, ΔE_j, in terms of pH and operational pH, pH_o, is

$$\Delta E_j = (pH_o - pH).\frac{RT\ln 10}{F} \tag{28}$$

Determination of ΔE_j therefore requires knowing values for pH_o and pH of a particular solution, in this case tris buffered synthetic seawater.

(i) Determination of pH_o:

Bates and Macaskill report operational pH values observed in tris buffered synthetic seawater (with sulphates) as

$$pH_o = 8,208$$

(ii) Determination of pH:

For a cell without a liquid junction pH was determined from Eq (6) using the measured cell potential and estimating the Cl^- activity

$$pH = (E_{cell} - E^o_s)\frac{F}{RT\ln 10} + \log[Cl^-] + \log\gamma_{Cl} \tag{29}$$

Bates and Macaskill report $E_{cell} = 0,73900$ volts, $E^o_s = 0,2224$ volts, and $[Cl^-] = 0,5577$, and, using the value for $\gamma_{Cl^-} = 0,649$ determined in (b) above for synthetic seawater with sulphates, gives

$$pH = \frac{(0,73900-0,2224)}{0,0591} + \log(0,5577) + \log(0,649)$$

$$= 8,286$$

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(iii) Determine residual liquid junction potential, ΔE_j:

Into Eq (28) substitute the values for pH_o and pH from (i) and (ii) above respectively,

$$\Delta E_j = (8,208-8,286).59,1$$

$$= -4,6 \text{ mV}$$

This value agrees closely with that determined using the Gran titration approach i.e. $\Delta E_j = -4,4$ mV, and lends support to the approach proposed here for general estimation of residual liquid junction potentials.

Having developed a semi experimental procedure for estimating residual liquid junction potentials, an investigation was made to compare the estimated values with those predicted by the Henderson equation. Using a glass electrode coupled with a saturated calomel electrode system which were standardized in NBS pH buffer standards, residual liquid junction potentials were determined in a number of aqueous binary systems (i.e. NaCl, KCl, $MgCl_2$ and $CaCl_2$) for I up to about I = 3. Detailed observations and calculations can be found in Cavalcanti and Loewenthal (1981), the relevant parameters obtained in the investigation are summarized in Table 1. Also listed in Table 1 are the residual liquid junction potentials determined for each solution using the Henderson Equation as set out by MacInnes (1961).

Comparing the residual liquid junction potentials obtained by using the Gran titration method with the theoretical values determined using the Henderson equation, it is apparent that the experimental values are approximately twice as large as the theoretical values, except for KCl solutions where both the experimental and theoretical values are small and closely equal.

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Table 1. Comparison of residual liquid junction potentials in aqueous binary systems estimated using the Gran titration method and the Henderson equation.

Salt	Molarity	γ^{tr}_{HCl} *	γ_{Cl} **	γ_H	$\gamma_{H(o)}$ †	R.L.J.P. (mv)	
						from Gran titration	from Henderson
NaCl	0,1	0,788	0,773	0,803	0,840	- 1,2	-1,2
	0,5	0,728	0,661	0,802	0,919	- 3,5	-2,7
	1,0	0,754	0,619	0,918	1,122	- 5,2	-3,9
	2,0	0,886	0,588	1,335	1,758	- 7,1	-5,2
	3,0	1,105	0,577	2,116	2,955	- 8,6	-6,0
KCl	0,1	0,782	0,769	0,795	0,805	- 0,3	-0,8
	0,5	0,704	0,646	0,767	0,777	- 0,3	-1,8
	1,0	0,713	0,594	0,883	0,856	- 0,8	-2,0
	2,0	0,789	0,543	1,167	1,146	- 0,5	-2,3
	3,0	0,888	0,514	1,538	1,534	- 0,1	-2,6
$MgCl_2$	0,05	0,771	0,763	0,779	0,836	- 1,8	-1,2
	0,1	0,737	0,723	0,751	0,867	- 3,7	-1,8
	0,2	0,719	0,688	0,751	0,909	- 4,9	-2,4
	0,5	0,770	0,662	0,896	1,271	- 8,9	-3,5
	1,0	0,971	0,670	1,408	2,241	-11,9	-4,4
$CaCl_2$	0,05	0,766	0,758	0,773	0,819	- 1,5	-1,1
	0,1	0,730	0,715	0,747	0,866	- 3,8	-1,6
	0,2	0,707	0,677	0,739	0,879	- 4,5	-2,1
	0,5	0,747	0,645	0,865	1,209	- 8,6	-3,0
	1,0	0,915	0,644	1,300	2,040	-11,6	-3,8

* For NaCl and KCl, data from Harned and Owen (1958).
For $MgCl_2$ and $CaCl_2$, data Khoo, Chan and Lim (1977a) and Khoo, Chan and Lim (1977b) respectively.

** Determined from Eq (29) Chapter 3.

† Mean slope of at least two Gran titrations.

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Comparing the experimental and theoretical approaches, both utilize non-thermodynamic assumptions to estimate the residual liquid junction potential. However, the experimental approach depends only on the non-thermodynamic estimation of the chloride ion activity coefficient (which was shown in Chapter 2 to be consistent with physico-chemical observations) whereas the theoretical approach utilizes the assumption of ideality for both activities and mobilities of ions (which are inconsistent with physico-chemical observations). In this respect therefore the experimental approach can be expected to be superior to the theoretical approach.

4. EQUILIBRIA IN HIGH SALINITY WATERS*

4.1 Weak acid-base equilibria equations

For the carbonate system in the aqueous phase the following equilibrium weak acid reactions are pertinent:

For equilibrium between molecularly dissolved carbon dioxide, CO_{2aq}, and carbonic acid the equilibrium reaction and equation are

$$CO_{2(aq)} + H_2O = H_2CO_3$$

$$(H_2CO_3)/\{a_w.(CO_2)_{aq}\} = K_r \qquad (30)$$

where ( ) = activity

a_w = activity of the water species

K_r = an equilibrium constant the value of which is temperature dependent.

For the dissociation of carbonic acid,

$$H_2CO_3 = H^+ + HCO_3^-$$

---

*All units on molal scale.

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and the corresponding equilibrium equation is

$$(H^+)(HCO_3^-)/(H_2CO_3) = K_s \qquad (31)$$

An equation for what is conventionallytermed 'the first dissociation equation' for the carbonate system is formulated by solving for (H_2CO_3) in Eq (30), substituting into Eq (31) and rearranging terms to give

$$(H^+)(HCO_3^-)/\{a_w(CO_2)_{aq}\} = K_r.K_s = K_1 \qquad (32a)$$

For the second dissociation reaction and equation

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$$

i.e.

$$(H^+)(CO_3^{2-})/(HCO_3^-) = K_2 \qquad (32b)$$

and for the water species

$$H_2O \rightleftharpoons H^+ + OH^-$$

i.e.

$$(H^+)(OH^-)/a_w = K_w \qquad (32c)$$

Although the effects of temperature on the equilibrium constants K_1, K_2 and K_w have been firmly established, the expressions with species written in terms of activities, are not useful in analyses of the carbonate system where invariably one needs to link these equilibria expressions to operational pH measurements and to mass balance expressions in which species are expressed in terms of concentration, stoichiometric or free. For this reason it is customary to rewrite and utilize the equilibrium expressions

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in one of a number of apparent forms. The various useful apparent forms are set out in detail in Section 4.2.4. For the present it is sufficient to note that the equilibrium equations, Eqs (32a to 32c), can be transformed so that weak acid-base species are in terms of free species concentrations and the equilibrium constants become apparent constants as follows:

For the first weak acid dissociation reaction, Eq (32a),

$$(H^+)[HCO_3^-]/[CO_2] = K_1 \, a_w \, \gamma_{CO_2}/\gamma_{HCO_3}$$

$$= K_1' \qquad (33a)$$

For the second dissociation reaction, Eq (32b),

$$(H+)[CO_3^=]/[HCO_3^-] = K_2 \, \gamma_{HCO_3}/\gamma_{CO_3}$$

$$= K_2' \qquad (33b)$$

and, for the water species, Eq (32c)

$$(H^+)[OH^-] = K_w \, a_w/\gamma_{OH}$$

$$= K_w' \qquad (33c)$$

4.2 Ion pairing of weak acid-base species

In high salinity waters the relative concentrations of free weak acid-base species are affected not only by the weak acid-base equilibrium equations set out above, but also by significant ion pairing of these species with the principal cations in the solution.

The concept of ion pairing has been introduced in Chapter 3. In

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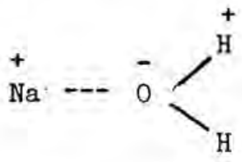
this Chapter it is the intention to integrate ion pairing into the equilibrium chemistry of the carbonate system.

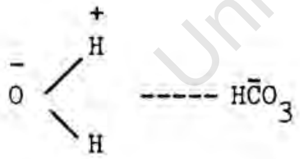
4.2.1 Mechanism of ion pairing of weak acid-base species

Robinson and Harned (1941) have hypothesized that the mechanism of ion pairing *of weak acid-base species* is one of 'localized hydrolysis'. That is, a fraction of the primary hydrated water surrounding cation is shared (temporarily) with a weak acid-base species giving rise to an ion paired molecule. The nature of this 'bond' can be visualized as follows: Consider an aqueous solution containing Na^+ and HCO_3^- species. A free sodium ion in the solution is surrounded by polarized primary hydrated water molecules and can be depicted as

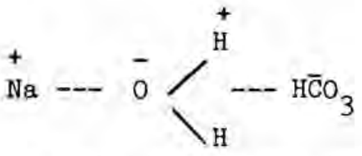


← polarized primary hydrated water

and, a hydrated free bicarbonate ion as



The formation of the ion pair $NaHCO_3^o$ arises when an HCO_3^- ion substitutes one of its molecules of hydrated water with a primary hydrated molecule of the sodium ion, i.e.



Consequently, in the formation of an ion pair where the anion is a weak acid-base species, this species releases part (or all) of its

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primary hydrated water, and, a prerequisite for such a bond is that both the free cation species and anion species each possess primary hydrated water molecules. In this regard, for the monovalent cations Li^+, Na^+, K^+, Rb^+ and Cs^+ one would expect the more heavily hydrated cations Li^+ and Na^+ to form ion pairs with weak acid-base species more readily than the sparsely hydrated K^+ and Rb^+ ions; Cs^+, with a hydration number very close to zero, should not form any ion paired molecules with these species. This latter observation is in agreement with the hydration theory proposed here, where, in terms of our theory, a good fit is obtained between calculated and observed mean activity coefficients for Cs_2SO_4 and CsOH without invoking ion pairing, see section 4.5.

4.2.2 *Equilibrium equations for ion paired species*

Bjerrum (1926) postulated that ion pairs in solution can be regarded as being in a state of dynamic equilibrium with the associating free ions. Thus, if a fraction of the ions A^+ and B^- in solution associate to form the ion pair AB°, at equilibrium applying the law of mass action gives the following equilibrium dissociation equation,

$$(A^+)(B^-)/(AB^\circ) = K, \text{ or}$$

$$[A^+][B^-]/[AB^\circ] = K_{AB}\ \gamma_{AB}/(\gamma_A \cdot \gamma_B)$$

$$= K'_{AB}$$

where

K_{AB} = the ion pair dissociation constant for ion-pair AB° and is temperature dependent

K'_{AB} = the apparent dissociation constant for ion-pair AB° and includes the adjustment for the long range ionic strength effects.

In most high salinity waters, for example seawater, the *principal* ionic species are the cations Na^+, K^+, Ca^{2+} and Mg^{2+} and the anions Cl^- and SO_4^{2-}. In contrast to these principal species, the weak acid-base systems governing pH in the region 4 pH 10 invariably contribute minimally to the ionic strength of such solutions (see Table 2). Considering the distribution of species in such highly saline aqueous solutions, generally it is accepted that an appreciable fraction of the weak acid species SO_4^{2-}, CO_3^{2-}, HCO_3^- and OH^- form ion pairs (and, in the case of $SO_4^=$, triple ions) with the cations Mg^{2+}, Ca^{2+}, Na^+, and, for SO_4^{2-} with K^+. No evidence of significant ion pairing between these cations and Cl^- has been observed.

Thus, for a water containing the principal ionic species of seawater, the following equilibrium equations must also be simultaneously satisfied together with the weak acid-base equations, Eqs (33a to 33c): For ion pairing of the sulphate species by Mg^{2+} and Ca^{2+},

Table 2 Molalities of principal stoichiometric species concentration in seawater.

Species	Molality.10^3
$[Mg]_T$	54,7
$[Ca]_T$	10,8
$[Na]_T$	470
$[K]_T$	10,4
$[SO_4]_T$	28,7
C_T	2,26

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$$[M_i^{2+}][SO_4^{2-}]/[M_iSO_4^{\circ}] = K_{M_iSO_4}\cdot\gamma_{M_iSO_4}/(\gamma_{M_i}\cdot\gamma_{SO_4})$$

$$= K'_{M_iSO_4} \qquad (34)$$

where M_i^{2+} = either Mg^{2+} or Ca^{2+}.

For ion pairing of the sulphate species by Na^+ and K^+,

$$[M_i^+][SO_4^{2-}]/[M_iSO_4^-] = K_{M_iSO_4}\ \gamma_{M_iSO_4}/(\gamma_{M_i}\cdot\gamma_{SO_4})$$

$$= K'_{M_iSO_4} \qquad (35)$$

and for triple ion association of the sulphate species with Na^+ and K^+ (see Chapter 3),

$$[M_i^+]^2[SO_4^{2-}]/[M_{i2}SO_4^{\circ}] = K_{M_{i2}SO_4}\cdot\gamma_{M_{i2}SO_4}/(\gamma_{M_i}^2\cdot\gamma_{SO_4})$$

$$= K'_{M_{i2}SO_4} \qquad (36)$$

where M_i^+ = either Na^+ or K^+

For ion pairing of CO_3^{2-} species by Mg^{2+} and Ca^{2+},

$$[M_i^{2+}][CO_3^{2-}]/[M_iCO_3^{\circ}] = K_{M_iCO_3}\cdot\gamma_{M_iCO_3}/(\gamma_{M_i}\cdot\gamma_{CO_3})$$

$$= K'_{M_iCO_3} \qquad (37)$$

where M_i = either Mg^{2+} or Ca^{2+}.

For ion pairing of CO_3^{2-} species by Na^+ (no significant ion pairing of $CO_3^=$ or HCO_3^- was found to occur with K^+, see Section 6),

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$$[Na^+][CO^{2-}_3]/[NaCO_3^-] = K_{NaCO_3}\cdot\gamma_{NaCO_3}/(\gamma_{Na}\cdot\gamma_{CO_3})$$

$$= K'_{NaCO_3} \tag{38}$$

For ion pairing of HCO_3^- species by Mg^{2+} and Ca^{2+},

$$[M_i^{2+}][HCO_3^-]/[M_iHCO_3^+] = K_{M_iHCO_3}\ \gamma_{M_iHCO_3}/(\gamma_{M_i}\cdot\gamma_{HCO_3}{}^0$$

$$= K'_{M_iHCO_3} \tag{39}$$

where M_i^{2+}= either Mg^{2+} or Ca^{2+}.

For ion pairing of HCO_3^- species by Na^+,

$$[Na^+][HCO_3^-]/[NaHCO_3^o] = K_{NaHCO_3}\ \gamma_{NaHCO_3}/(\gamma_{Na}\cdot\gamma_{HCO_3})$$

$$= K'_{NaHCO_3} \tag{40}$$

For ion pairing of OH^- by Mg^{2+} and Ca^{2+},

$$[M_i^{2+}][OH^-]/[M_iOH^+] = K_{M_iOH}\ \gamma_{M_iOH}/(\gamma_{M_i}\cdot\gamma_{OH})$$

$$= K'_{M_iOH} \tag{41}$$

where M_i^{2+} = either Mg^{2+} or Ca^{2+}

and, for ion pairing of OH^- by Na^+ and K^+

$$[M_i^+][OH^-]/[M_iOH^o] = K_{M_iOH}\ \gamma_{M_iOH}/(\gamma_{M_i}\ \gamma_{OH})$$

$$= K'_{M_iOH} \tag{42}$$

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where M_i^+ = either Na^+ or K^+.

Equilibrium constants have been determined for the above equilibrium equations at 25°C by a number of researchers. Values for these constants are listed in Table 3, including the values determined in this monograph. Referring to the data listed in Table 3, the values determined for the constants for any particular ion pair species show a wide dispersion, in some cases a difference of an order of magnitude. The principal cause for the wide spread of data are twofold. First, many researchers report ion pairing equilibrium constants determined from operational pH observations in high ionic strength solutions without taking account of residual liquid junction potential effects. Second, determination of ion pairing equilibrium constants from experimental observations invariably requires knowing the values for single ion activity coefficients. These values, however, cannot be determined absolutely, and can only be estimated from theory - the values estimated being dependent on non-thermodynamic assumptions used within the theoretical estimation. Consequently, the value determined for an ion pairing equilibrium constant is intimately bound to the theory and assumptions utilized in the estimation of single ion activity coefficients. This factor can have a profound effect on the value determined for an equilibrium constant even at relatively low ionic strengths. For example, Nakayama (1971) determined $pK(MgHCO_3) = 1,40$ by estimating $\gamma_{Mg} = 0,54$ using the Debye-Hückel theory with an $\mathring{a}$ value equal to 8,0 from Kielland (1937); alternatively, if one utilizes the Davies equation (an approach independent of $\mathring{a}$) one obtains $\gamma_{Mg} = 0,47$ and $pK(MgHCO_3) \cong 0,5$.

From the discussion above it is clear that *for an analysis of any particular test solution using the ion pairing theory and reported data or ion pairing equilibrium constants, where possible, activity*

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Table 3. Experimentally determined thermodynamic values for pK (dissociation) for ion-pairs reported in the Ca^{++} - Mg^{++} - Na^{+} - $H_2CO_3^*$ - HCO_3^- - $CO_3^=$ - H_2O system at 25°C and 1 atmosphere total pressure

Ion pair	pK value of ion pair						
$NaCO_3^-$	1,27(4)	0,65(11)					
$CaCO_3^{\circ}$	3,00(1)	3,94(1a)	3,20(5)	4,48(7)	3,10(8)	3,22(10)	3,16(11)
$MgCO_3^{\circ}$	2,37(1)	3,28(1a)	3,4(4)	3,24(9)	2,90(10)	2,95(11)	
$MgHCO_3^+$	0,77(1)	1,26(1a)	0,95(6)	1,23(9)	0,51(11)		
$NaHCO_3^{\circ}$	-0,25(5)	-0,55(11)					
$CaHCO_3^+$	0,80(1)	1,21(1a)	1,25(7)	0,59(11)			
$MgOH^+$	2,58(2)	2,08(10)	2,21(12)				
$NaOH^{\circ}$	-0,77(3)	-0,57(3)					
$CaOH^+$	1,37(3)	1,38(10)	1,15(13)				

(1)	Greenwald (1941)
(1a)	Greenwald (1941) corrected for ionic strength
(2)	Stock and Davies (1948)
(3)	Gimblett and Monk (1954)
(4)	Garrels, Thompson and Siever (1961)
(5)	Garrels and Thompson (1962)
(6)	Hostetler (1963)
(7)	Nakayama (1968)
(8)	Lafon (1970)
(9)	Nakayama (1971)
(10)	Larson, Sollo and McGurk (1973)
(11)	From this work
(12)	McGee and Hostetler (1975)
(13)	Baes and Mesmer (1976)

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coefficients must be determined using the same approach as in the determination of the ion pairing equilibrium constants.

In this monograph mean and single ion activity coefficients are determined using the hydration theory and volume fraction statistics. Consequently, to maintain consistency, the values determined here for ion pairing constants, and listed in Table 3, are determined in terms of this activity coefficient theory (for sulphate ion pairing determination see Chapter 3; for carbonate species ion pairing determination see Section 4.4).

4.2.3 *Mass balance equations and stoichiometric equilibrium constants*

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For systems in which ion pairing occurs, a fraction of each of the species entering into ion pairing reactions exists as free species and a fraction as ion paired species. Consequently, in addition to the equilibrium expressions set out above, a mass balance expression can be written down for each of the species which form ion pairs:

For the total (stoichiometric) magnesium species concentration, $[Mg]_T$,

$$[Mg]_T = [Mg^{2+}] + [MgSO_4^o] + [MgCO_3^o] + [MgHCO_3^+] + [MgOH^+] \qquad (43)$$

Rearranging Eqs (34, 37, 39 and 41) and substituting into Eq (43)

$$[Mg]_T = [Mg^{2+}]\{1 + [SO_4^{2-}]/K'_{MgSO_4} + [CO_3^{2-}]/K'_{MgHCO_3} + [OH^-]/K'_{MgOH}\} \qquad (44)$$

Similarly, for the total (stoichiometric) sodium species concentration, $[Na]_T$,

$$[Na]_T = [Na+]\{1+[SO_4^{2-}]/K'_{NaSO_4} + 2[Na^+][SO_4^{2-}]/K'_{Na_2SO_4} + [CO_3^{2-}]/K'_{NaCO_3} + [HCO_3^-]/K'_{NaHCO_3} + [OH^-]/K'_{NaOH}\} \tag{45}$$

For the total (stoichiometric) calcium species concentration, $[Ca]_T$,

$$[Ca]_T = [Ca^{2+}]\{1+[SO_4^{2-}]/K'_{CaSO_4} + [CO_3^{2-}]/K'_{CaCO_3} + [HCO_3^-]/K'_{CaHCO_3} + [OH^-]/K'_{CaOH}\} \tag{46}$$

For the total potassium species concentration, $[K]_T$,

$$[K]_T = [K^+]\{1+[SO_4^{2-}]/K'_{KSO_4} + 2[K^+][SO_4^{2-}]/K'_{K_2SO_4}\} \tag{47}$$

For the total sulphate species concentration, $[SO_4]_T$,

$$[SO_4]_T = [SO_4^{2-}]\{1+[Mg^{2+}]/K'_{MgSO_4} + [Ca^{2+}]/K'_{CaSO_4} + [Na^+]/K'_{NaSO_4} + [Na^+]^2/K'_{Na_2SO_4} + [K^+]/K'_{KSO_4} + [K^+]^2/K'_{K_2SO_4}\} \tag{48}$$

For the total hydroxide species concentration, $[OH]_T$,

$$[OH]_T = [OH^-]\{1+[Mg^{2+}]/K'_{MgOH} + [Ca^{2+}]/K'_{CaOH} + [Na^+]/K'_{NaOH}\} \tag{49}$$

For the total carbonate species concentration, $[CO_3]_T$,

$$[CO_3]_T = [CO_3^{=}]\{1+[Mg^{2+}]/K'_{MgCO_3} + [Ca^{2+}]/K'_{CaCO_3} + [Na^+]/K'_{NaCO_3}\} \tag{50}$$

For the total bicarbonate species concentration, $[HCO_3]_T$,

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$$[HCO_3]_T = [HCO_3^-]\{1+[Mg^{2+}]/K'_{MgHCO_3} + [Ca^{2+}]/K'_{CaHCO_3} + [Na^+]/K'_{NaHCO_3}\} \quad (51)$$

and, for the total carbonate weak acid base species concentration, C_T,

$$C_T = [H_2CO_3^*] + [HCO_3]_T + [CO_3]_T \quad (52)$$

The mass balance expressions linking the free and stoichiometric carbonate, bicarbonate and hydroxide species concentrations, Eqs (50, 51 and 49) respectively, are important as they form the basis to reformulating the apparent weak acid-base equilibrium expressions, Eqs (33a to 33c), in a very useful form with species concentrations in terms of stoichiometric concentrations, the great utility of this form being that the analyses of weak acid systems in highly saline waters reduces to that of low salinity waters.

The formulation of the stoichiometric equilibrium expressions is as follows:

For most highly saline waters both the carbonate and hydroxide weak acid-base species contribute minimally to the ionic strength of the solution. Consequently, whereas the effect of *carbonate and hydroxide* ion pairing on the relative concentrations of free and ion paired weak acid-base *is significant*, the effect on the concentrations of free cation species in solution usually is insignificant. Thus, for a particular water, the concentrations of free principal cation species often can be considered constant and independent of pH in the region $3 \leq pH \leq 10$, and each of the terms in curly brackets (i.e. {}) in Eqs (49 to 51) is a constant. The stoichiometric weak acid-base equilibrium equation for

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dissociation of H_2CO_3 is formulated by solving for $[HCO_3^-]$ from Eq (51) and substituting into Eq (33a) and simplifying to give

$$(H^+)[HCO_3]_T/[CO_2]_{aq} = K_1'\{1+[Mg^{2+}]/K'_{MgHCO_3} + [Ca^{2+}]/K'_{CaHCO_3}$$

$$+ [Na^+]/K'_{NaHCO_3}\} = K'_{T1} \tag{53}$$

and, for dissociation of HCO_3^-, solving for $[HCO_3^-]$ and $[CO_3^=]$ from Eqs (51 and 50) respectively and substituting into Eq (33b)

$$(H^+)[CO_3]_T/[HCO_3]_T = \frac{K_2'\{1+[Mg^{2+}]/K'_{MgCO_3}+[Ca^{2+}]/K'_{CaCO_3}+[Na^+]/K'_{NaCO_3}\}}{\{1+[Mg^{2+}]/K'_{MgHCO_3}+[Ca^{2+}]/K'_{CaHCO_3}+[Na^+]/K'_{NaHCO_3}\}}$$

$$= K'_{T2} \tag{54}$$

and, for the dissociation of water, from Eqs (49 and 33c)

$$(H^+)[OH]_T = K_w'\{1+[Mg^{2+}]/K'_{MgOH}+[Ca^{2+}]/K'_{CaOH}+[Na^+]/K'_{NaOH}\}$$

$$= K'_{Tw} \tag{55}$$

4.2.4 *Apparent weak acid equilibrium equations*

The form of the weak acid equilibrium equations, Eqs (a2,b2 and c2) is unambiguous for low salinity waters where (a) operational pH, (pH_o), can be assumed equal to the actual pH, (pH), in the water, (b) no significant ion association occurs between the carbonate species and the various cation species in solution, and (c) water and neutral species activity coefficients can be assumed equal to unity. In high salinity waters none of these assumptions are valid. Consequently there are a multiplicity of forms of expressing the apparent weak acid equilibrium equations depending on whether (1) the hydrogen ion activity and the corresponding weak acid equilibrium constant are on the operational or true activity scale, (2) the equilibrium constant value has been adjusted to include species activity coefficients so that species enter the equilibrium equation in the concentration form as opposed to the activity form, and (3) concentrations are expressed either as stoichiometric (i.e. total) or free ion.

To avoid confusion, the various forms of expressing the apparent weak acid equilibria equations and the nomenclature used in this text are summarized below. In the nomenclature:

(a) Subscript 'o' designates the operational value for either pH, hydrogen ion activity, hydrogen ion activity coefficient or the weak acid equilibrium constant corresponding to the use of the operational hydrogen ion activity in the equilibrium equation, i.e. pH_o, $(H^+)_o$, $\gamma_{H(o)}$ and ${}_oK$ respectively.

(b) The equilibrium constant is superscripted with a single prime when the equilibrium equation is formulated with the weak acid-base species in the free concentration form and the hydrogen ion species in the activity form, i.e. for a weak acid-base system in water,

$$(H^+)(A^-)/(HA) = K_a$$

i.e. $(H^+)\gamma_A[A^-]/(\gamma_{HA}[HA]) = K_a$

i.e. $(H^+)[A^-]/[HA] = K_a\gamma_{HA}/\gamma_A = K'_a$

(c) The equilibrium constant is superscripted with a double prime when the equilibrium equation is formulated with the weak acid-base *and* the hydrogen ion species in the concentration form, i.e.

$[H^+][A^-]/[HA] = K_a\gamma_{HA}/(\gamma_H\cdot\gamma_A) = K''_a$

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(d) Subscript 'T' is used to designate stochiometric (i.e. total) species concentrations, i.e. $[\,]_T$. When species concentrations are expressed on the stoichiometric scale in the equilibrium equations, the equilibrium constant is subscripted T to indicate that the ideal thermodynamic K value has been adjusted by stoichiometric activity coefficients, i.e. K'_{T1}, K'_{T2} and K'_{Tw}; when species concentrations are expressed in terms of free ion species in the equilibria expressions, the equilibrium constants have no extra subscript, i.e. K'_1, K'_2 and K'_w.

To illustrate the various forms of expressing the apparent equilibrium constants, the corresponding apparent equilibrium equations are set out below.

(a) Species are in terms of activities and the hydrogen ion activity is on the operational scale,

$$(H^+)_o(HCO_3^-)/\{a_w(CO_2)_{aq}\} = {}_oK_1 \qquad (56a)$$

$$(H^+)_o(CO_3^{2-})/(HCO_3^-) = {}_oK_2 \qquad (56b)$$

$$(H^+)_o(OH^-)/a_w = {}_oK_w \qquad (56c)$$

The link between the operational equilibrium constants, ${}_oK_x$, in Eqs (56a to 56c) and the thermodynamic values, K_x, in Eqs (32a to 32c) is established through the residual liquid junction potential effect on single ion activity measurement, k_{1j}, see Section 3.4, i.e. from Eq (20)

$$(H^+)_o = k_{1j}(H^+)$$

i.e.

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$$K_x = {}_oK_x \cdot k_{1j}$$

(b) Species are in terms of molalities on the *stochiometric* (i.e. total species) scale, that is, the equilibrium constant has been adjusted to include the weak acid stoichiometric activity coefficients and

(i) (H^+) is linked to the true hydrogen ion activity in the solution, i.e.

$$(H^+)[HCO_3^-]_T/[CO_2]_{aq}=K_1 \cdot a_w\gamma_{CO_2}/\gamma_{THCO_3}=K'_{T1} \qquad (57a)$$

$$(H^+)[CO_3^{2-}]_T/[HCO_3^-]_T=K_2 \cdot \gamma_{THCO_3}/\gamma_{TCO_3}=K'_{T2} \qquad (57b)$$

$$(H^+)[OH]_T=K_w a_w/\gamma_{TOH}=K'_{Tw} \qquad (57c)$$

(ii) H^+ is linked to the operational hydrogen ion activity in the the solution, $(H^+)_o$, i.e.

$$(H^+)_o[HCO_3^-]_T/[CO_2]_{aq}=K_1 \cdot k_{1j} \cdot a_w\gamma_{CO_2}/\gamma_{THCO_3}={}_oK'_{T1} \qquad (58a)$$

$$(H^+)_o[CO_3^{2-}]_T/[HCO_3^-]_T=K_2 \cdot k_{1j}\gamma_{THCO_3}/\gamma_{TCO_3}={}_oK'_{T2} \qquad (58b)$$

$$(H^+)_o[OH^-]_T=K_w \cdot k_{1j}a_w/\gamma_{TOH}={}_oK'_{Tw} \qquad (58c)$$

(iii) H^+ is linked to the hydrogen ion molality in the solution, $[H^+]$, i.e.

$$[H^+][HCO_3^-]_T/[CO_2]_{aq}=K_1 \cdot a_w \cdot \gamma_{CO_2}/\{\gamma_H \cdot \gamma_{THCO_3}\}=K''_{T1} \qquad (59a)$$

$$[H^+][CO_3^{2-}]_T=K_2 \cdot \gamma_{THCO_3}/\{\gamma_H \cdot \gamma_{TCO_3}\}=K''_{T2} \qquad (59b)$$

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$$[H^+][OH^-]_T=K_w.a_w/\{\gamma_H.\gamma_{TOH}\}=K''_{Tw} \qquad (59c)$$

(c) Species are in terms of molalities of the free ions, that is, the equilibrium constants have been adjusted to include the activity coefficients of the free weak acid species, and

(i) H^+ is linked to the true hydrogen ion activity in the solution, (H^+), i.e.

$$(H^+)[HCO_3^-]/[CO_2]_{aq}=K_1.a_w\gamma_{CO_2}/\gamma_{HCO_3}=K'_1 \qquad (60a)$$

$$(H^+)[CO_3^-]/[HCO_3^-]=K_2\gamma_{HCO_3}/\gamma_{CO_3}=K'_2 \qquad (60b)$$

$$(H^+)[OH^-]=K_w.a_w/\gamma_{OH}=K'_w \qquad (60c)$$

(ii) H^+ is linked to the operational hydrogen ion activity in the solution, $(H^+)_o$, i.e.

$$(H^+)_o[HCO_3^-]/[CO_2]_{aq}=K_1.k_{1j}.a_w\gamma_{CO_2}/\gamma_{HCO_3}={}_oK'_1 \qquad (61a)$$

$$(H^+)_o[CO_3^{2-}]/[HCO_3^-]=K_2.k_{1j}\gamma_{HCO_3}/\gamma_{CO_3}={}_oK'_2 \qquad (61b)$$

$$(H^+)_o[OH^-]=K_w.k_{1j}a_w/\gamma_{OH}={}_oK'_w \qquad (61c)$$

(iii) H^+ is linked to the molality of the hydrogen ion in the solution, $[H^+]$, i.e.

$$[H^+][HCO_3^-]/[CO_2]_{aq}=K_1.a_w\gamma_{CO_2}/\{\gamma_H.\gamma_{HCO_3}\}=K''_1 \qquad (62a)$$

$$[H^+][CO_3^{2-}]/[HCO_3^-]=K_2.\gamma_{HCO_3}/\{\gamma_H.\gamma_{CO_3}\}=K''_2 \qquad (62b)$$

$$[H+][OH^-]=K_w.a_w/\{\gamma_H.\gamma_{OH}\}=K''_w \qquad (62c)$$

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Equations (56 to 62) not only set out the various forms commonly used to express equilibrium in terms of apparent constants, but also give the means of linking these apparent constants. For example, the link between the two apparent equilibrium constants ${}_oK_1'$ and ${}_oK_{T1}'$ is obtained by solving for the thermodynamic equilibrium constant, K_1, in Eqs (61a and 58a) respectively, in terms of the apparent constants and activity coefficients:

For K_1 in terms of ${}_oK_1'$, from Eq (61a)

$$K_1 = {}_oK_1' \cdot \gamma_{HCO_3}/(k_{1j} \cdot a_w \gamma_{CO_2}) \tag{63}$$

and for K_1 in terms of ${}_oK_{T1}'$, from Eq (58a)

$$K_1 = {}_oK_{T1}' \cdot \gamma_{THCO_3}/(k_{1j} \cdot a_w \cdot \gamma_{CO_2}) \tag{64}$$

Equating Eqs (63 and 64) and solving for ${}_oK_1'$ gives

$${}_oK_1' = {}_oK_{T1}' \cdot \gamma_{THCO_3}/\gamma_{HCO_3} \tag{65}$$

The approach above is general so that it is possible to formulate equations linking any pair of apparent equilibrium constants (for a particular equilibrium equation) in terms of the relevant activity coefficients (and residual liquid junction potential effect, k_{1j}).

4.3 Determination of activity coefficients and ion pair constants for the carbonate weak acid-base system

Analysis of the carbonate system in highly saline waters requires utilizing one of the sets of apparent (or stoichiometric) equilibrium expressions set out in the previous section. This in turn requires that the values be known for the corresponding set of

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apparent constants for the equations utilized. In this regard, one of two approaches can be adopted. First, operational stoichiometric equilibrium constants are determined by experiment, termed the experimental approach. Second, the apparent equilibrium constants (operational, stoichiometric or otherwise) are determined from theory, termed the theoretical approach.

General application of the experimental approach is not practical as the approach requires redetermining the stoichiometric equilibrium constants by experiment for each water investigated. This means that an inordinately large volume of experimental research must be carried out on a particular water before any analyses can be effected. However, if a large amount of research is to be carried out on a particular water body, for example seawater, this experimental approach certainly may be feasible.

In the theoretical approach the analyses can be carried out either by using the set of apparent weak acid-base equilibrium equations and the corresponding ion pairing and mass balance equations; or, by using the set of stoichiometric equilibrium equations. If the set of apparent equilibrium equations are used in the analyses, then the corresponding set of apparent equilibrium constants are determined by adjusting the thermodynamic constants to take account of activity coefficient effects; the activity coefficients are determined from theoretical considerations, for example using the hydration theory (see Section 4.3.1). Alternatively, if the stoichiometric equilibrium equations are used, the corresponding set of stoichiometric equilibrium constants are determined by adjusting the thermodynamic constants to take account of both activity coefficient and ion pairing effects; this adjustment is carried out by substituting estimated activity coefficients and reported thermodynamic ion pairing equilibrium constants into Eqs (53 to 55).

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Irrespective of the set of equilibrium equations utilized in an analysis of a particular water using the theoretical approach, it is important that the thermodynamic ion pair equilibrium constants utilized be consistent with the activity coefficient estimation, that is, the same method be maintained in the estimation of activity coefficients in a solution under investigation as that used in the determination of the 'reported' thermodynamic ion pairing equilibrium constants.

From the discussion above, it is clear that the theoretical approach is more practical in its general application than the experimental approach. In the theoretical approach the values for the ion pairing constants only have to be measured once, thereafter, for each water investigated only the activity coefficients need to be determined. In the experimental approach extensive experimentation needs to be carried out on each water investigated.

Before dealing with an analysis of the carbonate system, first it is necessary to show how activity coefficients for this system are determined using the hydration theory, and second, to determine equilibrium constants for ion pairing between the carbonate weak acid-base species and the cations Mg^{2+}, Ca^{2+} and Na^{+}.

4.3.1 *Activity coefficients for carbonate weak acid-base species*

In essence the approach used here for estimating activity coefficients for carbonate species is similar to that for the sulphate species set out in Section 3.1 Chapter 3. That is, the assumption is used that Cs^{+} does not ion pair with weak acid-base species.*

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*With regard to ion pairing of Cs^{+} by weak acid-base species; It was shown in Chapter 2 that Cs^{+} has close to zero primary hydration. Consequently, in terms of the mechanism of 'localized hydrolysis' set out in Section 4.2.1 it is to be expected that Cs^{+} will not form ion pairs with HCO_3^{-} or $CO_3^{=}$ (or any other weak acid-base species). This expectation is borne out for Cs_2SO_4 in Chapter 3 where the excellent fit obtained between theoretical and observed values for $\gamma_{Cs_2SO_4}$ is assumed to indicate no ion pairing between Cs^{+} and SO_4^{2-}.

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Consequently, mean activity coefficients for $CsHCO_3$, Cs_2CO_3 and CsCl in a mixed system can be determined from the hydration theory using Eq (27) Chapter 3. The activity coefficient for Cl^- in a mixed system is determined using Eq (29) Chapter 3. The free carbonate species single ion activity coefficients are then determined as follows:

For $\gamma_{HCO_3^-}$:

$$\gamma_{CsCl\pm} = (\gamma_{Cs} \cdot \gamma_{Cl})^{\frac{1}{2}} \qquad (66a)$$

$$\gamma_{CsHCO_3^\pm} = (\gamma_{Cs} \cdot \gamma_{HCO_3})^{\frac{1}{2}} \qquad (66b)$$

Solving for γ_{Cs} from Eq (66a) substituting into Eq (66b) and solving for γ_{HCO_3} gives

$$\gamma_{HCO_3} = (\gamma_{CsHCO_3^\pm} / \gamma_{CsCl\pm})^2 \cdot \gamma_{Cl} \qquad (67)$$

For $\gamma_{CO_3^=}$:

$$\gamma_{Cs_2CO_3\pm} = (\gamma_{Cs}^2 \cdot \gamma_{CO_3})^{1/3} \qquad (68)$$

Solving for γ_{Cs} from Eq (66a), substituting into Eq (68) and solving for γ_{CO_3} gives

$$\gamma_{CO_3} = (\gamma_{Cs_2CO_3\pm}^3 / \gamma_{CsCl\pm}^4) \cdot \gamma_{Cl}^2 \qquad (69)$$

Fundamental to the determination of γ_{CO_3} and γ_{HCO_3} in any particular solution using the approach above is that values be known for the mean activity coefficients of Cs_2CO_3, $CsHCO_3$ and CsCl, and for the single ion activity coefficient for Cl^-. Theoretical estimation of $\gamma_{CsCl\pm}$ and γ_{Cl} in mixed systems has been considered in detail in

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Chapter 3; the remaining problem is estimation of $\gamma_{Cs_2CO_3\pm}$ and $\gamma CsHCO_3\pm$.

The mean activity coefficients for Cs_2CO_3 and $CsHCO_3$ in mixed systems can be estimated using Eq (27) Chapter 3 (with the *proviso* that no ion pairing occurs between Cs^+ and either CO_3^{2-} or HCO_3^-) provided that the chemical characteristics (i.e. hydration numbers and hydrated radii) for CO_3^{2-} and HCO_3^- are known. Generally, in this monograph the method used to determine these characteristics for a salt species is to fit the theoretical values for $\gamma_\pm$ in a binary system (determined from Eq (181) Chapter 2) against observed $\gamma_\pm$ data to obtain å and h values for the salt investigated; the single ion hydrated radii and hydration numbers then are determined using additivity. This approach, however, cannot be used for $CO_3^=$ and HCO_3^- because there is no reported data for $\gamma_\pm$ for the salts Cs_2CO_3 and $CsHCO_3$ in binary aqueous systems.

In the absence of reported data from which the chemical characteristics of $CO_3^=$ and HCO_3^- can be estimated, the only approach is to assume 'reasonable' values for the hydration numbers for these ions and to determine the corresponding hydrated radii from Eq (E) in Appendix to Chapter 2 using reported values from Millero (1969) for the bare ion radii of these species. For the hydration numbers of these species, it is to be expected that both CO_3^{2-} and HCO_3^- have relatively small hydration numbers because both these polyatomic ionic species are relatively large ions. Now, for species with low hydration numbers ($h \leq 1$) the value for $\gamma_\pm$ determined using Eq (181) Chapter 2 is insensitive to the value of h inserted into this equation. Consequently, for species with low hydration numbers any reasonable value for h (i.e. $h \leq 1$) will still give a close estimate of the activity coefficient. From the above, and noting that the bare ion radius of $CO_3^=$ is slightly less than that for SO_4^{2-} (i.e. 1,73 compared with 2,05 for SO_4^{2-}, Millero, 1969), a hydration number equal to 0,40 is assigned arbitrarily to CO_3^{2-}, see Table 4 below. A hydration number equal to 0,2 is assigned to HCO_3^- on the basis that this species should possess some primary hydrated water (which it loses to form ion pairs), and that the hydration number be close to zero as the bare ion radius for HCO_3^- is close to that for Cl^- (i.e. 1,92 compared with 1,81 for Cl^- which is assumed to have h = 0). For the charged ion paired species $NaCO_3^-$, $MgHCO_3^+$ it is not possible to formulate an equation for the (mean) activity coefficients for these species from theoretical considerations because it is not possible to add to a solution a 'salt' comprised of a cation (anion) and any one of these charged ion pairs keeping all other salt species concentrations constant. In the absence of a theoretical approach for estimating activity coefficients for these charged ion paired species, the approach here is to adopt a convention for estimating values for these activity coefficients and to determine ion pairing constants for these species in terms of this convention. The convention adopted here is to assume that the activity coefficients for singly charged ion pairs equals the activity coefficient for Na^+, γ_{Na^+}.

The remaining carbonate species for which activity coefficients need to be determined are the neutral ion paired species, $NaHCO_3^o$, $MgCO_3^o$ and $CaCO_3^o$, and the molecularly dissolved carbon dioxide, CO_2aq. For the neutral ion paired species it is thought that the principal factor affecting non-ideality of these species in aqueous solutions is a dipole effect (Kester, 1969; Reardon and Langmuir, 1976; Dickson and Whitfield, 1981); in terms of the hydration model proposed here, the high hydration numbers of these neutral ion paired species (see Table 4) also implicates hydration as a further factor affecting non-ideality of these species. At present it is not possible either to measure these species activities or to formulate a quantitative theoretical description of them.

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Table 4. Chemical properties of free and ion paired carbonate species.

Ionic species	bare ion radius	hydration number	hydrated radius**
CO_3^{2-}	1,73*	0,4†	1,85**
HCO_3^-	1,92*	0,2†	2,08**
$NaCO_3^-$		2,4†	
$MgHCO_3^+$		8,12†	
$CaHCO_3^+$		7,05†	
$MgCO_3^o$		8,12†	
$CaCO_3^o$		7,05†	

* From Millero (1969)

† Assumed equal to the characteristics for the cation

** Determined from Eq (E) in Appendix to Chapter 2

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Consequently, the convention accepted here is to assume that the activity coefficients of neutral ion paired species equals unity.

For the activity coefficient of molecularly dissolved CO_2, γ_{CO_2aq}, this parameter is defined as the ratio of the solubilities of CO_2 in pure water, $S^o_{CO_2}$, to that in a test solution, $S^t_{CO_2}$, both measured at a CO_2 fugacity equal to unity and at the same temperature,

$$\gamma_{CO_2(aq)} = (S^o_{CO_2})/(S^t_{CO_2}) \qquad (70)$$

Because the solubility of CO_2 can be measured in aqueous solutions, it is possible to determine γ_{CO_2} using Eq (70) in any test solution. Generally it has been found from experiment that for solutions containing only one salt species, γ_{CO_2aq} varies with ionic strength, μ, according to the empirical relationship

$$ln\gamma_{CO_2} = b.\mu \tag{71}$$

where b = a constant determined from experiment and varies with temperature.

In order to obtain a general method for predicting γ_{CO_2} in mixed electrolytes using an equation of the type shown in Eq (71), the constant b should be modelled in terms of physico-chemical properties of the solution. In this regard, using the hydration -volume fraction statistics approach adopted in this text, an equation for γ_{CO_2} is obtained from Eq (18) Chapter 3 by disregarding the Debye-Hückel electrostatic term and assuming that the neutral CO_2 molecule has zero primary hydration,

$$ln\gamma_{CO_2} = 0{,}018\ q_{CO_2}\ \frac{(\sum_i m_ih_i + \sum_i m_iq_i - \sum_i m_id_i)}{1 + 0{,}018\ \sum_i m_iq_i} - ln(1+0{,}018.\sum_i m_iq_i) \tag{72}$$

where all the terms have been defined previously.

Comparing γ_{CO_2} predicted using Eq (72) with observed data for electrolytes with only one salt species in solution, generally the predicted values are too low, although the approach predicts correctly the observed trends. For example, for a 1,0M NaCl solution, γ_{CO_2} (observed) = 1,246, and from Eq (72) γ_{CO_2} (predicted) = 1,081. From the above, it appears that either CO_2aq has some significant primary hydration (which is unlikely in view of it being a neutral molecule), or some other factor(s) (for example

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non-ideality of heats of mixing) should also be included in the theoretical description above.

In the absence of a theoretical approach for predicting γ_{CO_2} accurately, it is necessary to adopt an empirical approach. In this regard it is assumed that b in Eq (71) is independent of the salt species in the solution, and equals 0,22 at 25°C (Dickson and Whitfield, 1981), i.e.

$$ln\gamma_{CO_2} = 0,22\ \mu \qquad (73)$$

The assumption above that the constant b is independent of salt species in aqueous solutions, is justified partially from observations reported by Li and Tsui (1970). They found that, at any particular temperature, γ_{CO_2} has closely the same value in both seawater and an aqueous solution of NaCl at an equivalent ionic strength to seawater.

4.4 Determination of ion pairing constants for carbonate species

Earlier in this Chapter it was stressed that to maintain a consistent approach to the analysis of the carbonate system it is necessary that the same convention be used for determining activity coefficients in an analysis of a test solution as that used in the determination of ion pairing constants. The convention used here for determining carbonate species activity coefficients is set out in the previous section, it is now the intention to use this activity coefficient convention to determine ion pairing constants for the carbonate system.

The nub of the determination of carbonate species ion pairing constants centres around three distinct operations:

(i) Utilization of Gran functions (or some other means) to determine by experiment the operation stoichiometric equilibrium constants ${}_{o}K'_{T1}$ and ${}_{o}K'_{T2}$, and the operational activity coefficient for H^+, $\gamma_{H(o)}$, in solutions containing carbonate species and only one other chloride salt species.

(ii) Estimation of carbonate species activity coefficients using the convention outlined in Section (4.3) for each solution investigated.

(iii) Determination of ion pairing constants by substituting the values determined in (i) and (ii) above into the theoretical equation for ${}_{o}K'_{T1}$, Eq (53), for HCO_3^- ion pair constants, and into the equation for ${}_{o}K'_{T2}$, Eq (54), for the CO_3^{2-} ion pair constants.

Determination of the HCO_3^- and CO_3^{2-} ion pairing constants are dealt with separately below. This separation is convenient principally for two reasons. First, different Gran functions are used in the measurement of ${}_{o}K'_{T1}$ (for determining HCO_3^- ion pairing constants) and ${}_{o}K'_{T2}$ (for determining CO_3^{2-} ion pairing constants). Second, a much greater degree of ion pairing occurs between cations and CO_3^{2-} species than between cations and HCO_3^- species, i.e. $K_{MHCO_3} \gg K_{MCO_3}$; consequently, whereas CO_3^{2-} ion pairing constants can be determined from pH observations in relatively low ionic strength media, $\mu < 0{,}04$, the HCO_3^- constants have to be determined from pH observations on relatively highly saline media, $\mu > 0{,}5$, where cognisance must now be taken of residual liquid junction potential effects on pH.

4.4.1 *Bicarbonate ion pairing constants*

The underlying theory used in the determination of equilibrium constants for ion pairing between HCO_3^- and the cations Ca^{2+}, Mg^{2+} and Na^+ is as follows: Consider an aqueous solution at pH < 6,5 containing dissolved carbonate weak acid-base species (at a relatively low concentration) and one of the chloride salts NaCl or $MgCl_2$ or $CaCl_2$ (at a relatively high concentration). An equation for the equilibrium constant of the ion paired species $MHCO_3$ (where M represents either Na^+ or Mg^{2+} or Ca^{2+}) in terms of parameters whose values can be either measured or estimated is obtained by solving for K_{MHCO_3} in Eqs (53 and 56a) i.e.

$$K_{MHCO_3} = \frac{\gamma_{H(o)} \cdot K_1 \cdot a_w\, \gamma_{CO_2} \cdot \gamma_M\, [M] \;/\; \gamma_{MHCO_3}}{\{{}_oK'_{T1} \cdot \gamma_H - (K_1 \cdot a_w\, \gamma_{CO_2} \cdot \gamma_{H(o)})/\gamma_{HCO_3}\}} \tag{74}$$

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Determination of K_{MHCO_3} using Eq (74) requires

(i) measurement of both the operational stoichiometric equilibrium constant, ${}_oK'_{T1}$, and operational activity coefficient for H^+, $\gamma_{H(o)}$, and

(ii) determination of the various single ion activity coefficients.

(i) Measurement of ${}_oK'_{T1}$ and $\gamma_{H(o)}$:

Measurement of $\gamma_{H(o)}$ is effected by carrying out a Gran titration on the solution of interest in the pH region $3<pH<4$ as set out in Section 3.4. Measurement of ${}_oK'_{T1}$ is effected by carrying out a Gran titration in the region pH 6. From Section 5, in this pH region the second Gran function, F_2, is

$$F_{2(x)} = 10^{-pH_{o(x)}} (V_{CO_2} - v_x) \tag{75}$$

$$= (v_x - V_{HCO_3}) \cdot {}_oK'_{T1} \tag{76}$$

where

$pH_{o(x)}$ = operational pH after adding v_x mℓ of standard strong acid

V_{CO_2} = volume of standard strong acid required to titrate the test solution to the $H_2CO_3^*$ equivalence point

V_{HCO_3} = volume of standard strong acid to titrate the test solution to the HCO_3^- equivalence point

$F_{2(x)}$ = value of Gran function F_2 after adding v_x mℓ of standard strong acid.

In Eq (75), V_{CO_2} is known either (or both) from input experimental data or from the first Gran titration (see Section 5); v_x and $pH_{o(x)}$ are known from experimental observations; consequently, $F_{2(x)}$ can be determined for each set of $pH_{o(x)}$ and v_x values. A plot of values for $F_{2(x)}$ versus v_x constitutes the second Gran titration. The measured slope of this plot equals $\partial F_{2(x)}/\partial v_x$, which from Eq (76) equals ${}_oK'_{T1}$.

(ii) Determination of activity coefficients:

The conventions for estimating activity coefficients for the carbonate species are set out in Section 4.3, and, for other species (i.e. a_w, γ_M, γ_{Cl}) in Chapter 3. These are summarized in Table 5.

In Tables 6 and 7 are listed relevant experimental data and values for activity coefficients for the determination of ion pairing equilibrium constants using Eq (74) for $NaHCO_3^o$, $MgHCO_3^+$ and $CaHCO_3^+$. Details of experimental procedures and data are set out by Liesching and Loewenthal (1980).

4.4.2 *CO_3^{2-} ion pairing constants*

The underlying theory used in the determination of equilibrium constants for ion pairing between CO_3^{2-} and the cations Ca^{2+}, Mg^{2+} and Na^+ is as follows: Consider an aqueous solution containing carbonate species at a relatively low concentration, and one of the salts $CaCl_2$ or $MgCl_2$ or NaCl at a relatively high concentration ($\mu \cong 0{,}03$ for the Mg^{2+} and Ca^{2+} solutions; $\mu \cong 0{,}1$ for the Na^+

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Table 5. Summary of conventions used in the determination of activity coefficients for estimating HCO_3^- ion pairing constants.

Species activity coeff.	Convention	Reference
a_w		Eq (54) Chapter 3 and Supplement A
$\gamma_{MCl\pm}$		Eq (27) Chapter 3 and Supplement A
$\gamma_{CsCl\pm}$		-ditto-
$\gamma_{CsHCO_3\pm}$	Table 4	-ditto-
γ_{Cl}	h(Cl) = 0	Eq (29) Chapter 3 and Supplement A
γ_{Cs}	$\gamma^2_{CsCl\pm}/\gamma_{Cl}$	
γ_{HCO_3}	$\gamma^2_{CsHCO_3\pm}/\gamma_{Cs}$	
γ_M	$\gamma^2_{MCl\pm}/\gamma_{Cl}$	
γ_{CO_2}	$ln\gamma_{CO_2}=0,22\mu$	Eq (72)
$\gamma(NaHCO_3^o)$	$\gamma_N = 1,0$	Assumed (see text)
$\gamma(MgHCO_3^+)$	$\gamma = \gamma_{Na}$	Assumed (see text)
$\gamma(CaHCO_3^+)$	$\gamma = \gamma_{Na}$	Assumed (see text)

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Table 6. Values inserted into Eq (74) to determine pK($MgHCO_3^+$) and pK($CaHCO_3^+$) at 21°C giving pK($MgHCO_3^+$) = 0,51 ± 0,06
pK($CaHCO_3^+$) = 0,59 ± 0,03

[MCl_2]	M = Mg^{2+} 0,10	M = Ca^{2+} 0,05
a_w	0,995	0,997
γ_{Mg} or γ_{Ca}	0,288	0,338
γ_{HCO_3}	0,729	0,767
γ_H	0,761	0,783
$\gamma^*_{H(o)}$	0,945*	0,948*
γ_{CO_2}	1,068	1,034
γ_{MgHCO_3} or γ_{CaHCO_3}	0,720	0,753
pK_1**	6,375	6,375
$p_oK'_{T1}$	6,078*	6,147*

* Mean value for two experiments

** Harned and Davies (1943)

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Table 7. Values inserted into Eq (74) to determine $pK(NaHCO_3^o)$ at 21°C giving $pK(NaHCO_3) = -0{,}55 \pm 0{,}02$.

[NaCl]	1,002	0,500
a_w	0,967	0,984
γ_{Na}	0,698	0,697
γ_{HCO_3}	0,635	0,677
γ_H	0,923	0,807
$\gamma_{H(o)}$ *	1,148*	0,991*
γ_{CO_2}	1,247	1,116
γ_{NaHCO_3}	1,00	1,00
pK_1 **	6,375**	6,375**
$p_oK'_{T1}$ *	5,950*	6,049*

* Mean value of two experiments

** Harned and Davies (1943)

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solutions). An equation for the equilibrium constant for the ion paired species MCO_3 (where M represents either Ca^{2+} or Mg^{2+} or Na^+) is obtained by solving for K_{MCO_3} in Eq (54), i.e.

$$\frac{\gamma_{H(o)}}{\gamma_H} \cdot {}_oK'_{T2} = \frac{K'_2 \{1 + [M]/K'_{MCO_3}\}}{\{1 + [M]/K'_{MHCO_3}\}}$$

Solving for K_{MCO_3} and simplifying

$$K_{MCO_3} = \frac{K_2\ \gamma_{HCO_3}\ \gamma_M\ [M]}{\{k.{}_oK'_{T2}(1+[M]/K'_{MHCO_3})-K'_2\}} \qquad (77)$$

where

${}_oK'_{T2}$ = second stoichiometric equilibrium constant for the carbonate system

K'_2 = second apparent equilibrium constant for the carbonate system

K'_{MHCO_3} = apparent bicarbonate ion pairing (dissociation) equilibrium constant

$= K_{MHCO_3}\ \gamma_{MHCO_3}/(\gamma_M \cdot\ \gamma_{HCO_3})$

k = $\gamma_H/\gamma_{H(o)}$

Determination of K_{MCO_3} using Eq (77) requires that the stoichiometric constant ${}_oK'_{T2}$ be measured for a particular solution, and that the activity coefficients and free species concentrations be determined for the solution from theoretical considerations.

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Measurement of the stoichiometric constant for Mg^{2+} and Ca^{2+} solutions is effected by carrying out a Gran titration in the region 9<pH<9,5 as follows:

From Section 5, the Gran function, F_4, in the pH region 9<pH<9,5 is

$$F_{4(x)} = 10^{-pH_{o(x)}} (V_{HCO_3} - v_x) \tag{78}$$

$$= {}_oK'_{T2} (V_{CO_2} - 2V_{HCO_3} + v_x) \tag{79}$$

where

$pH_{o(x)}$ = pH after adding v_x mℓ of standard strong acid

V_{CO_2} = volume of standard strong acid to titrate the solution to the $H_2CO_3^*$ equivalence point

V_{HCO_3} = volume of standard strong acid to titrate the solution to the HCO_3^- equivalence point. The value for this parameter is known from the input data in an experiment.

A series of values for $F_{4(x)}$ are determined by substituting the corresponding experimental values for $pH_{o(x)}$ and v_x into Eq (78). A plot of $F_{4(x)}$ versus v_x constitutes the fourth Gran titration. The measured slope of this plot equals $\partial F_{4(x)}/\partial v_x$ and equals ${}_oK'_{T2}$ from Eq (79).

For the activity coefficients of single ion species in Mg^{2+} and Ca^{2+} solutions, these are determined from the Davies equation because the solutions investigated are all low ionic strength waters, i.e. $\mu \cong 0,03$.

For NaCl solutions, the stoichiometric constant, ${}_oK'_{T2}$ is determined somewhat differently to that above because experiments are carried out in the pH region pH>9,7 where the hydroxide contribution to alkalinity and acidity cannot be neglected, and Eqs (78 and 79) are not valid. The approach adopted to determine ${}_oK'_{T2}$ is to measure pH_o in solutions with known Alkalinity, Acidity and $\gamma_{H(o)}$ values. The determination of ${}_oK'_{T2}$ at a particular pH is then as follows:

(i) Determine single ion activity coefficients using the hydration theory and the computer program listed in Supplement A.

(ii) Determine $[OH^-]$ from observed pH_o and measured $\gamma_{H(o)}$ as

$$[OH^-] = (a_w.K_w\ \gamma_{H(o)})/(10^{-pH_o}.\gamma_H.\ \gamma_{OH})$$

(iii) Determine $[CO_3]_T$ and $[HCO_3]_T$ from known values for Alkalinity, Acidity and [OH] as

$$[HCO_3]_T = \text{Acidity} + [OH^-],\ \text{see Section 5}$$

and

$$[CO_3]_T = \{\text{Alkalinity} - [HCO_3]_T - [OH]\}/2,\ \text{see Section 5.}$$

(iv) Determine ${}_oK'_{T1}$ from observed pH_o and values for $[CO_3]_T$ and $[HCO_3]_T$ from (iii) above as

$${}_oK'_{T1} = 10^{-pH_o}\ [CO_3]_T/[HCO_3]_T$$

Once ${}_oK'_{T2}$ has been determined for a particular solution as outlined above, the ion pairing constant K_{MCO_3} can be determined by successive approximation using Eq (77) as follows:

(i) Assume $[M] = [M_T]$ and determine an initial value for μ.

(ii) Determine the activity coefficients from the estimated value of μ using the Davies equation for the Mg^{2+} and Ca^{2+}

solutions, and using Appendix A for the Na^+ solutions.

(iii) Determine an initial value for K_{MCO_3} by substituting into Eq (77) the measured value of K'_{T2}, activity coefficients determined in (ii) for the first iteration or from (iv) in subsequent iterations.

(iv) Determine a new value for [M] from a mass balance expression for the cation species, i.e.

$$[M_T]=[M] + \frac{[M].C_T}{(K'_{MCO_3}+[M])/(1+10^{pK'_{T2}-pH})} + \frac{[M]\ C_T}{(K'_{MHCO_3}+[M])(1+10^{pH-pK'_{T2}})} \tag{80}$$

where $[M_T]$, C_T and pH are known from experimental data.

(v) Redetermine μ from the free species concentrations determined in (iv).

(vi) Repeat steps (ii) to (v) until successive values for K_{MCO_3} vary only in the fourth significant figure.

In Tables 8 to 10 are listed relevant experimental data and activity coefficients used in the determination of the ion pairing constants (dissociation) for $NaCO_3^-$, $CaCO_3^o$ and $MgCO_3^o$ respectively. Details of the experiments and data are set out by Mclean and Loewenthal (1977).

4.5 Assessment of ion pairing constants in seawater

In the previous section ion pairing constants were determined for the carbonate system in waters containing either $MgCl_2$ or $CaCl_2$ or NaCl, using single ion activity coefficients determined from the hydration theory. An assessment of the values for these constants (and the approach in general) is possible by comparing measured

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Table 8. Determination of pK($NaCO_3^-$) dissociation at 25°C.

pK($NaCO_3^-$) = 0,85 ± 0,12

$\bar{C}_a$ = 0,05650(HCL) NaCl = 0,1002 moles/kg water

$\gamma_{H(o)}$ = 0,840, from first Gran titration

$\gamma_{HCl\pm}$ = 0,790 γ_{Cl} = 0,775 γ_H = 0,805

γ_{CO_3} = 0,384 γ_{HCO_3} = 0,780 γ_{NaHCO_3} = 1,0 γ_{OH} = 0,795

pH_o	Alk. mM	Acid mM	$[OH^-]$ mM	$[HCO_3]_T$ mM	$[CO_3]_T$ mM	$p_oK'_{T2}$
10,399	3,981	0,185	0,325	0,510	1,573	9,923
10,296	3,803	0,363	0,256	0,619	1,464	9,921
10,191	3,627	0,539	0,202	0,741	1,342	9,933
10,083	3,451	0,715	0,157	0,872	1,211	9,940
9,972	3,277	0,889	0,122	1,011	1,072	9,947
9,857	3,103	1,063	0,093	1,156	0,927	9,952

Mean 9,932 ± 0,015

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Table 9. Determination of $pK(CaCO_3^o)$ dissociation at 25°C.
$pK(CaCO_3^o) = 3{,}16$

$pK_2 = 10{,}329^*$ $\qquad p_oK'_{T2} = 9{,}612^{**}$ $\qquad pK(CaHCO_3) = 0{,}59^\dagger$

$C_T = 1{,}480$ mM/kg water $\qquad \mu = 0{,}019$

$CaCl_2 = 0{,}005464M$

$\gamma_{mono} = 0{,}872$ $\qquad \gamma_{Di} = 0{,}578$

pH_o	Alkalinity mM	$[Ca^{2+}]$ mM	$pK(CaCO_3^o)$ dissociation
9,030	1,81	5,16	3,16
9,186	1,91	6,09	3,16
9,318	2,01	5,02	3,16
9,440	2,11	4,95	3,16
9,550	2,21	4,89	3,16

* Harned and Scholes (1941)

** From the 4th Gran titration

† Table 6

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Table 10. Determination of $pK(MgCO_3^o)$ at 25°C.

$pK(MgCO_3^o) = 2,92$

$pK_2 = 10,329^*$; $p_oK'_{T2} = 9,792^{**}$ $pK(MgHCO_3) = 0,53^{\dagger}$

$C_T = 1,485$ mM/kg water $\mu = 0,018$

$MgCl_2 = 0,00501$ molal; $\bar{C}_b = 0,10420M(NaOH)$; $V_I = 0,508\ell$

Alkalinity mM	pH_o	$[Mg^{2+}]$ mM	$pK(MgCO_3^o)$ dissociation
1,71	9,015	4,82	2,93
1,81	9,214	4,76	2,92
1,91	9,370	4,71	2,91
2,01	9,503	4,66	2,92

* Harned and Scholes (1941)

** From the slope of the fourth Gran titration

† See Table 6

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values for ${}_oK'_{T1}$ and ${}_oK'_{T2}$ in mixed systems (seawater) with theoretical values determined from ion pairing constants and activity coefficients. In this regard, agreement between theoretical and observed values for the stoichiometric equilibrium constants implies agreement between the corresponding theoretical and observed titration curves (see Section 6).

(a) For ${}_oK'_{T1}$: The theoretical value for ${}_oK'_{T1}$ at 25°C is determined from Eqs (53, 58(a), 19 and 20)

$${}_oK'_{T1} = \frac{K_1 \cdot \gamma_{CO_2} \cdot a_w}{\gamma_{HCO_3}} \cdot \frac{\gamma_{H(o)}}{\gamma_H} \{1+\sum_i [M_i]/K'_{M_iHCO_3}\} \qquad (81)$$

Substituting values determined from theory for each of the parameters on the right hand side of Eq (81) gives the theoretical value for ${}_oK'_{T1}$.

For seawater, it is assumed that the free cation molalities are affected only by sulphate ion pairing (i.e. $C_T << M_i$). In Section 6.2 Chapter 3, the *free* species molalities, and single ion activity coefficients, for Mg^{2+}, Ca^{2+} and Na^+ in seawater were determined as $[Mg^{2+}] = 0,0457$ and $\gamma_{Mg} = 0,267$; $[Na^+] = 0,463$ and $\gamma_{Na} = 0,693$; $[Ca^{2+}] = 0,0099$ and $\gamma_{Ca} = 0,248$.

In Section 3.4, the ratio $\gamma_{H(o)}/\gamma_H$ for seawater was determined as $\gamma_{H(o)}/\gamma_H = 1,200$.

γ_{CO_2} and a_w are determined from Eq (73) and Eq (54) Chapter 3 respectively using the computer program listed in Supplement A as 1,164 and 0,9816 respectively. γ_{HCO_3} is determined from $\gamma_{HCO_3} = (\gamma_{CsHCO_3\pm}/\gamma_{CsCl\pm})^2 \cdot \gamma_{Cl}$; the mean activity coefficients $\gamma_{CsHCO_3\pm}$ and $\gamma_{CsCl\pm}$ are determined from Eq (27) Chapter 3 and

γ_{Cl} from Eq (29) Chapter 3 giving $\gamma_{HCO_3} = 0{,}669$.
For K_1, from Harned and Davies (1943), $pK_1 = 6{,}352$ at 25°C.
Substituting the values above into Eq (81) gives $p_oK'_{T1}$ (theoretical) = 5,997 at 25°C. This value agrees closely with the experimental values of 6,00 (Lyman, from Riley and Skirrow, 1975); 5,999 (Bates and Culberson, 1977) and 6,001 (Leishing and Loewenthal, 1978).

(b) For ${}_oK'_{T2}$: The theoretical value for ${}_oK'_{T2}$ is determined from Eqs (54, 58b, 19 and 20)

$$ {}_oK'_{T2} = \frac{K_2\cdot\gamma_{HCO_3}}{\gamma_{CO_3}}\cdot\frac{\gamma_{H(o)}}{\gamma_H}\left\{\frac{1+[Mg^{2+}]/K'_{MgCO_3}+[Ca^{2+}]/K'_{CaCO_3}+[Na+]/K'_{NaCO_3}}{1+[Mg^{2+}]/K'_{MgHCO_3}+[Ca^{2+}]/K'_{CaHCO_3}+[Na^+]/K'_{NaHCO_3}}\right\} \qquad (82)$$

Substituting values determined from theory for each of the parameters on the right hand side of Eq (82) gives the theoretical value for ${}_oK'_{T2}$. Values are listed in (a) above for the activity coefficients γ_{Mg}, γ_{Ca}, γ_{Na}, γ_H, $\gamma_{H(o)}$, γ_{HCO_3} and γ_{NIP} (neutral ion pairs) and also for the molalities of the free species Mg^{2+}, Ca^{2+} and Na^+.

The activity coefficient for CO_3^{2-}, γ_{CO_3}, is determined as

$\gamma_{CO_3} = (\gamma^3_{Cs_2CO_3\pm}\cdot\gamma^2_{Cl})/(\gamma^4_{CsCl\pm})$; the mean activity coefficients $\gamma_{Cs_2CO_3\pm}$ and $\gamma_{CsCl\pm}$ are determined from Eq (27) Chapter 3 and γ_{Cl} from Eq (29) Chapter 3 giving $\gamma_{CO_3} = 0{,}203$. For K_2, from

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Harned and Scholes (1941), $pK_2 = 10{,}329$ at 25°C.

Substituting the values above into Eq (82) gives $p_oK'_{T2}$ (theoretical) = 9,129 at 25°C.

This value agrees closely with that reported by Bates and Culberson (1977) of 9,127 at 25°C.

The excellent agreement between theoretical and experimental values for the operational stoichiometric activity coefficient for seawater indicates that the values determined here for ion pairing constants and the free species activity coefficients are consistent when applied to mixed systems, in particular, seawater.

4.6 Activity coefficients for hydroxide species

Generally it is accepted that in high ionic strength solutions OH^- forms a significant degree of ion pairing with Mg^{2+} and Ca^{2+}, and a lesser degree with Na^+ and K^+. Consequently, Eq (29) Chapter 3 cannot be used generally to determine activity coefficients for hydroxide species. This observation is reinforced by considering binary solutions of hydroxide salts where it is found not possible to fit theoretical values for $\gamma_\pm$ determined using Eq (181) Chapter 3 against measured values for $\gamma_\pm$, with the exception of CsOH. The lack of fit is assumed to indicate the occurrence of ion pairing.

For an aqueous binary system of CsOH an excellent fit is obtained between $\gamma_\pm$ determined from Eq (181) and observed data from Robinson and Stokes (1955) up to the maximum ionic strength of the reported data, $\mu = 1{,}0$ (see Table 11). This good fit is interpreted as indicating that Cs^+ does not ion pair with OH^-, and from this fit it is possible to determine the chemical characteristics (i.e. primary hydrated radius and hydration number) for OH^-. This is important, for once these characteristics have been established, it is possible then to determine the activity coefficient for OH^-

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in mixed systems (in which ion pairing may or may not occur).

The chemical characteristics of OH^- are calculated by applying additivity to the $\overset{o}{a}$ and h values for CsOH (determined from the fit of Eq 181 against observed data) as follows:

For the primary hydrated radius of OH^-,

$$\overset{o}{a}(CsOH) = 6,15 = r^h_{Cs} + r^h_{OH}$$

$$\text{i.e. } r^h_{OH} = 6,15 - r^h_{Cs} = 6,15 - 1,45$$

$$= 4,70 \text{ Angstrom units}$$

For the hydration number of OH^-,

$$h(CsOH) = h(Cs^+) + h(OH^-)$$

$$\text{i.e. } h(OH^-) = h(CsOH) - h(Cs^+)$$

$$= 3,92 - 0,20$$

$$= 3,72$$

Having established the chemical characteristics of OH^-, it is possible now to determine $\gamma^{trace}_{CsOH\pm}$ in a mixed system directly using Eq (27) Chapter 3 together with the computer printout listed in Supplement A. Thereafter, the single ion activity coefficient, γ_{OH}, is determined from the calculated values for γ^{trace}_{CsCl} (from Eq 27 Chapter 3) and γ_{Cl} (from Eq 29 Chapter 3), i.e.

$$\gamma_{OH} = (\gamma_{CsOH}/\gamma_{CsCl})^2 \cdot \gamma_{Cl}$$

With regard to ion pairing between OH^- and the principal cationic

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Table 11. Fit of $\gamma_{CsOH\pm}$ determined from Eq (181) Chapter 2 against observed data from Robinson and Stokes (1955) gives $\overset{o}{a}_{CsOH} = 6{,}15$ and h(CsOH) = 3,65

molality	$\gamma_\pm$ calculated*	$\gamma_\pm$ observed
0,1	0,793	0,795
0,3	0,743	0,744
0,5	0,739	0,739
0,8	0,754	0,754
1,0	0,771	0,771

* $\bar{V}$(CsOH) determined from $\bar{V}(CsOH) = \bar{V}^o + 1{,}5.1{,}868\sqrt{\mu}$

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species of the ionic matrix (i.e. Mg^{2+}, Ca^{2+}, Na^+ and K^+), in this monograph the principal concern of OH^- ion pairing is with the effects of this phenomena on the solubilities of Mg^{2+} and Ca^{2+} in solution. To estimate these effects requires that the respective ion pairing constants between both Mg^{2+} and Ca^{2+} and OH^- be known.

It is not possible to estimate these constants using the method adopted for the sulphate system and set out in Chapter 3 because of a lack of reported data for mean activity coefficients for $Mg(OH)_2$ and $Ca(OH)_2$. Consequently, our approach here is to accept reported values for these constants from the literature, and accept that the solubilities determined for Ca^{2+} and Mg^{2+} will be incorrect to the extent of the inconsistency between the activity coefficients determined for Mg^{2+}, Ca^{2+} and OH^- using the hydration theory and the activity coefficient values used for these ions in the determination of the ion pairing constants. Probably, the error involved is small. This can be appreciated by noting that the ion pairing constants determined here using the hydration theory for the carbonate species $NaCO_3^-$, $NaHCO_3^o$, $MgHCO_3^+$ and $CaHCO_3$ closely equal currently accepted values determined by other researchers (see Table 3).

In Table 12 are listed the values assumed for the constants (dissociation) for ion pairing between OH^- and each of the cation species Mg^{2+}, Ca^{2+} and Na^+.

Table 12. Ion pairing constants (dissociation) for hydroxide species at 25°C used in this text.

Species	pK
$MgOH^+$	2,08*
$CaOH^+$	1,38†
$NaOH^o$	-0,20††

* From Larson, Sollo and McGurk (1973)

† From Larson, Sollo and McGurk (1973)

†† Baes and Mesmer (1976)

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5. ANALYSES OF THE CARBONATE SYSTEM

Once the ion pairing constants and the free species activity coefficients have been determined, it is possible to formulate all the equilibrium equations in an apparent form as shown in Sections 4.2.3 and 4.2.4. In terms of this reformulation, the equations Eqs (34 to 42, 44 to 48, 52, 60a to 60c) constitute a set of twenty-five independent equations containing thirty-two unknown parameters, i.e. seven parameters must be measured in order to solve for the set. Five parameters can be determined using standard chemical analyses, these are $[SO_4]_T$, $[Ca]_T$, $[Mg]_T$, $[Na]_T$ and $[K]_T$. The activity of H^+ (operational or true) can be determined from pH measurement. This leaves one more parameter to be measured. If a p_{CO_2} meter is available, $[H_2CO_3^*]$ can be measured indirectly in accordance with Eq (e); if a total inorganic carbon analyzer is available, C_T can be determined experimentally. If neither of these instruments is available, the equation for C_T can be replaced by one in terms of some other measureable parameter. The most likely alternative being one of the various forms of alkalinity and acidity.

The equations for the various forms of alkalinity and acidity in low salinity waters, Eqs (g to l), are not valid when a significant degree of ion pairing occurs and they must be modified to incorporate their effect. Before modifying these equations it is necessary to investigate the effects of ion pairing on equivalent weak acid-base solutions and the distribution of free and ion paired species with pH. This investigation is most easily effected using a log species-pH diagram.

5.1 Distribution of free and ion paired species with pH

The occurrence of ion-pairing between carbonate species and the various cations in solution has a marked effect on the pH established in the solution. This effect is explained as follows: The pH established in water is fixed by equilibrium relationships between $H_2CO_3^*$, free HCO_3^-, free $CO_3^=$ and H^+. Because ion-pairing reduces the concentrations of free carbonate species in a solution with some fixed C_T, the equilibrium activity of H^+ is affected and hence pH is also affected.

In low salinity water the distribution of species with pH is quickly and simply presented by sketching a log species-pH diagram for a constant C_T value. However, when ion-pairing is also considered, the interdependence between pH and the free and ion paired weak acid-base species is more complex and there is no simple method for depicting these relationships graphically. A log (free and ion paired) species-pH plot can be obtained only by solving for each of the free and ion paired species concentrations in terms of the activity of H^+ (either the operational or true value) using Eqs (34 to 42, 44 to 48, 52, and 60a to 60c) for known values of C_T, $[SO_4]_T$, $[Mg]_T$, $[Ca]_T$, $[Na]_T$ and $[K]_T$. Computations are most effectively carried out by iteration techniques using a computer to solve for each of the species concentrations for a series of pH (or pH_o) values, see Supplement A. This calculation was applied to a water containing all the major constituents of seawater as reported by Whitfield (1974) and considering only the carbonate weak acid-base system, see Table 13. The ion pairing equilibrium constants used are those determined in this text, see Table 14; the activity coefficients are those determined from the hydration theory for synthetic seawater using the computer program listed in Supplement A, see Table 15. A plot of the results is shown in a log species-pH_o diagram, see Figure 5.

The plot shown in Figure 5 graphically illustrates the distribution of free and ion paired species with pH_o. Note that the two operational apparent equilibrium constants for the carbonate system p_oK_1' and p_oK_2' (i.e. incorporating both activity coefficient and

Table 13. Synthetic seawater used in the analyses of the carbonate system.

Species	Concentration m.molality (stoichiometric)
Na^+	475,2
K^+	10,0
Mg^{2+}	54,0
Ca^{2+}	10,4
Cl^-	554,3
SO_4^{2-}	28,4
C_T	2,676

Table 14. pK values for ion pairing (and triple ion) constants (dissociation) used in the analyses of the carbonate system at 25°C and 1 Atm.total pressure.

	SO_4^{2-}	CO_3^{2-}	HCO_3^-	OH^-
Mg^{2+}	2,40	2,92	0,51	2,08
Ca^{2+}	2,36	3,16	0,59	1,38
Na^+	0,57	0,85	-0,55	-0,20
Na_2^{2+}	1,00*			
K^+	0,37			
K_2^{2+}	0,85*			

* Triple ion species $Na_2SO_4^o$ and $K_2SO_4^o$

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Table 15. Single ion activity coefficients (for free species) used in the analyses of the carbonate system in seawater.

Species	γ	Species	γ
Na^+	0,693	SO_4^{2-}	0,205
K^+	0,632	CO_3^{2-}	0,203
Mg^{2+}	0,267	HCO_3^-	0,669
Ca^{2+}	0,248	Cl^-	0,649
H_2O	0,9817	Neutral ion pairs	1,00
CO_2	1,161		
γ_{H+}	0,817	2-1 ion pairs	γ_{Na}
$\gamma_{H(o)}$	0,980	OH^-	0,803

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and residual liquid junction potential effects) occur at pH_o values where $[H_2CO_3^*] = [HCO_3^-]$ and $[HCO_3^-] = [CO_3^{2-}]$ in accordance with Eqs (61a and 61b) respectively, i.e. $p_oK_1' = 6{,}038$ and $p_oK_2' = 9{,}736$.

The distributions of the total species concentrations $[HCO_3]_T$ and $[CO_3]_T$ are shown in broken lines. Note that the two operational stoichiometric equilibrium constants for the carbonate system p_oK_{T1}' and p_oK_{T2}' (i.e. incorporating activity coefficient, residual liquid junction potential and ion pairing effects) occur at pH_o values where $[H_2CO_3^*] = [HCO_3^-]_T$ and $[HCO_3^-]_T = [CO_3]_T$ in accordance with Eqs (58a and 58b) respectively, i.e. $p_oK_{T1}' = 5{,}995$ and $p_oK_{T2}' = 9{,}134$.

From Figure 5 it is evident that the solubility of carbonate

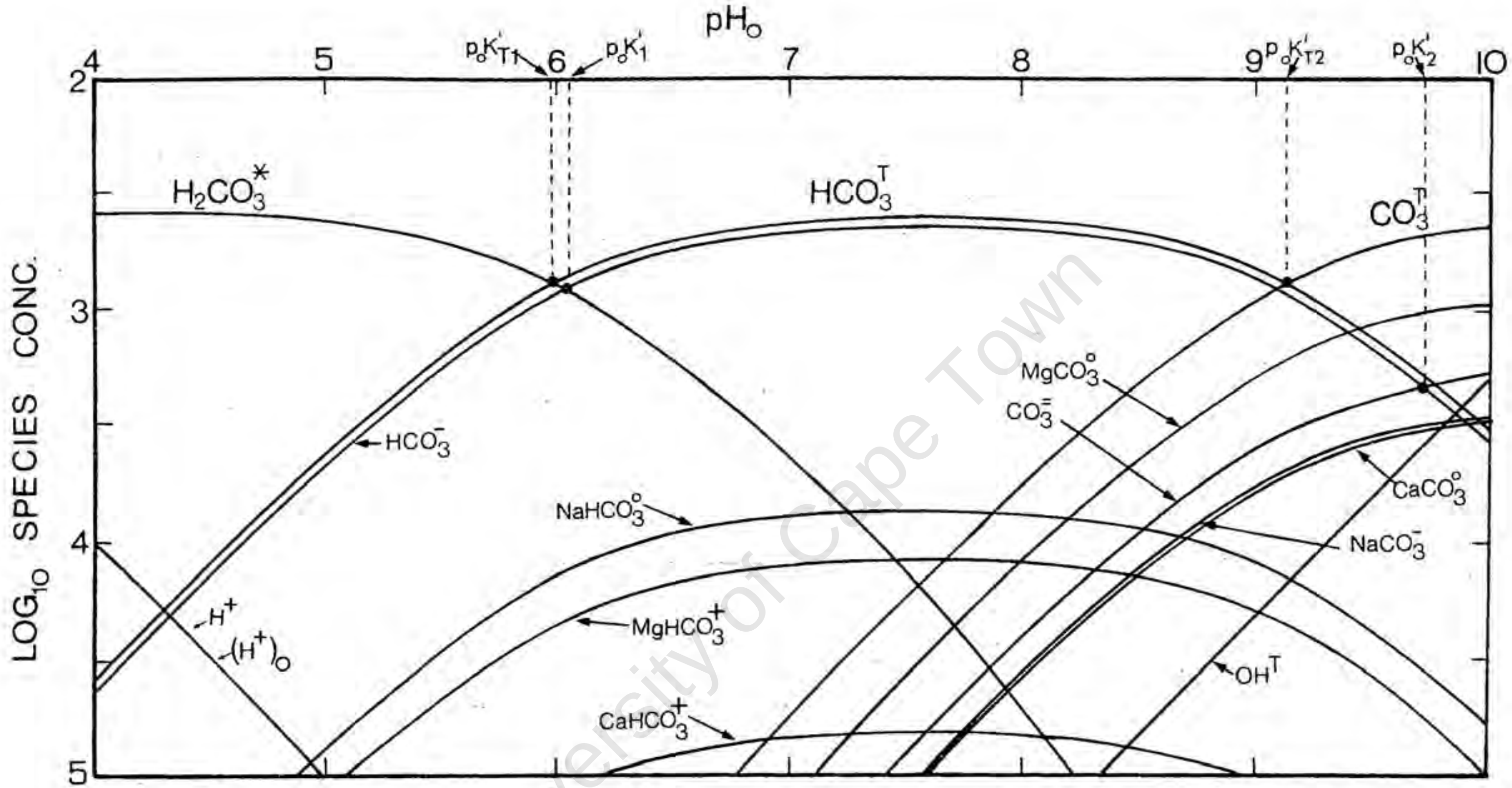

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Figure 5. Distribution of free and ion-paired carbonate species with pH for a synthetic seawater with a composition as set out in Table 13.

species in seawater is increased profoundly by ion pairing of CO_3^{2-} by the various cation species. This is illustrated by noting that the ratio log $([CO_3]_T/[CO_3^{2-}])$ is constant and equals approximately 0,52 over the range of pH values shown. Consequently, the solubility of carbonate minerals will be increased by a factor of three due to the effects of CO_3^{2-} ion pairing alone. Many other researchers theorize that the factor of three is in fact an underestimate of the effects of CO_3^{2-} ion pairing on carbonate solubility.

Whitfield (1974) lists percentages of free and ion paired species determined from theory and reported by a number of researchers for the system $Ca^{2+} - Mg^{2+} - Na^{+} - K^{+} - SO_4^{2-} - CO_3^{2-} - HCO_3^{-} - Cl^{-}$ in seawater at 25 deg C and 1 Atm. total pressure, see columns A to F in Table 16. It is of interest to compare the percentage values calculated from species concentrations in Figure 5 at $pH_o = 8,1$ with those values reported in Table 16. This can be done as follows: The concentrations of total, free and ion paired species are read off the plot at $pH_o = 8,1$ and the percentage of each species with respect to the total is calculated. These values are listed in column G of Table 16.

Referring to Table 16 for the free and ion paired species for the carbonate system, from the data reported by Whitfield (i.e. columns A to F) all the researchers determine that between 88 and 92 percent of CO_3^{2-} is ion paired, and that between 25 and 30 percent of HCO_3^{-} is ion paired (i.e. only about 10 percent and 70 percent of CO_3^{2-} and HCO_3^{-} respectively exist as free species). From the approach put forward in this text, the values determined for these percentages are, 77 percent of CO_3^{2-} is ion paired and 10 percent of HCO_3^{-} is ion paired. These values are significantly different from those reported by Whitfield and it is necessary to enquire into the significance of these differences. This is carried out as follows:

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Table 16. Distribution of free and ion paired species concentrations in synthetic seawater, Table 13, at $pH_o = 8,0$, 25 deg C and 1 Atm. total pressure.

Anion	Ion pair	% anion as ion pair						
		A	B	C	D	E	F	G
SO_4^{2-}	$NaSO_4^-$ *	18,3	21,9	37,6	24,7	21,9	37,2	19,3
	KSO_4^- *	0,6	0,7	0,4	0,8	0,7	0,4	0,5
	$MgSO_4^o$	22,7	23,5	19,6	24,2	23,5	19,4	31,3
	$CaSO_4^o$	3,2	3,7	2,7	3,9	3,7	4,0	3,9
	Free	55,2	50,2	39,5	46,4	50,2	39,0	45,0
CO_3^{2-}	$NaCO_3^-$	17,5	19,1	17,8	21,4	19,1	17,3	15,3
	$MgCO_3^o$	67,0	63,3	63,0	59,0	63,4	67,3	47,2
	$CaCO_3^o$	6,6	7,1	8,8	7,3	7,1	6,4	14,8
	Free	8,9	10,5	10,4	12,3	10,5	9,0	22,7
HCO_3^-	$NaHCO_3^o$	8,6	8,3	8,0	8,2	8,3	8,6	5,5
	$MgHCO_3^+$	17,1	14,5	9,5	12,4	14,5	17,8	3,4
	$CaHCO_3^+$	3,4	3,2	3,4	2,8	3,2	3,3	0,6
	Free	70,9	74,0	79,1	76,6	74,0	70,3	90,5

* These percentages include both ion pairs and triple ions

A Garrels and Thompson (1962), from Whitfield (1974)

B Berner (1971), from Whitfield (1974)

C Lafon (1969), from Whitfield (1974)

D Whitfield (1974)

E Whitfield (1974)

F Kester and Pytkowicz (1969), from Whitfield (1974)

G Values determined in this text using the hydration theory

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The first requisite for consistency of a model for the carbonate system in aqueous solution (in this case seawater) is that there be agreement between the theoretical and experimental titration curves. In this regard, the shape of the titration curve for a solution with a fixed value for C_T depends only on the values of the operational stoichiometric constants ${}_oK'_{T1}$ and ${}_oK'_{T2}$, see Section 5.5.2. Consequently, agreement between theoretical and experimental values for ${}_oK'_{T1}$ and ${}_oK'_{T2}$ means agreement between theoretical and experimental titration curves. Experimental values for ${}_oK'_{T1}$ and ${}_oK'_{T2}$ in seawater at 25 deg C have been well established, Bates and Culberson (1977), see Table 17. Theoretical values for ${}_oK'_{T1}$ and ${}_oK'_{T2}$ can be determined from the reported percentages of free and ion paired carbonate species concentrations and the single ion activity coefficients used in the determination of these percentages as follows:

For ${}_oK'_{T1}$, from Eq (58a)

$$ {}_oK'_{T1} = \frac{\gamma_{H(o)}}{\gamma_H} . \frac{K_1 \; a_w \; \gamma_{CO_2}}{\gamma_{HCO_3}} (1-X)/(XY) \qquad (83)$$

where $\gamma_{H(o)}/\gamma_H$ = residual liquid junction potential effect

= 1,199 (for r.l.j.p = 4,5 mv, Bates private communication, and Section 3)

pK_1 = 6,352, Harned and Davies, 1943.

a_w = 0,9817 (from Whitfield, 1973)

γ_{CO_2} = 1,161 (generally accepted value in seawater)

γ_{HCO_3} = 0,68 (Whitfield); 0,665 (value from this text)

X = fraction of $[HCO_3]_T$ as free $[HCO_3^-]$

Y = fraction of $[HCO_3]_T$ as ion paired species.

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Substituting values listed above for $\gamma_{H(o)}/\gamma_H$, pK_1, a_w, γ_{HCO_3} and γ_{CO_2} into Eq (83), and also for X and Y from Table 16 gives theoretical values for ${}_oK'_{T1}$, see Table 17.

For ${}_oK'_{T2}$, from Eq (58b)

$$ {}_oK'_{T2} = (\gamma_{H(o)}/\gamma_H) \frac{K_2\ \gamma_{HCO_3}}{\gamma_{CO_3}} \frac{\{(1-Q)/(QR)\}}{\{(1-X)/(XY)\}} \tag{84} $$

where pK_2 = 10,329, Harned and Scholes (1941)

γ_{CO_3} = 0,20 (Whitfield); 0,203 (from this text)

Q = fraction of $[CO_3]_T$ as free $[CO_3^{2-}]$

R = fraction of $[CO_3]_T$ as ion paired species.

Substituting the values above for K_2, $\gamma_{H(o)}/\gamma_H$, γ_{HCO_3}, and γ_{CO_3} into Eq (84) and also for X, Y, Q and R from Table 16 gives theoretical values for ${}_oK'_{T2}$, see Table 17.

Referring to Table 17, whereas the operational stoichiometric constants predicted from the approach presented in this text are virtually identical with observed data, the approach of Whitfield gives rise to a significant difference between observed and

Table 17. Comparison of experimental values for ${}_oK'_{T1}$ and ${}_oK'_{T2}$ (from Bates and Culberson, 1977) with theoretical values determined from data of (i) Whitfield (1974) and (ii) this work.

	Theoretical		Experimental
	Whitfield (1975)	This work	
p ${}_oK'_{T1}$	5,913	5,995	5,999
p ${}_oK'_{T2}$	9,196	9,134	9,127

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predicted data, i.e. from Whitfield's approach ${}_oK'_{T1}$ differs from the observed value by approximately 25 percent, and ${}_oK'_{T2}$ by approximately 15 percent. Consequently, whereas our predicted titration curve agrees with the experimental curve, the predicted curve from Whitfield's data is in error.

The good fit obtained between our predicted and the observed operational stoichiometric equilibrium constants indicates that our approach to the carbonate system in seawater is consistent in that the approach correctly predicts the *activities* of $H_2CO_3^*$, HCO_3^- and CO_3^{2-} in this medium. That is, the free species activity coefficients and the ion pairing equilibrium constants determined here from the hydration theory give rise to a distribution of free and ion paired species concentrations, and these three factors in conjunction give rise to correct values for the activities of the carbonate species at any pH.

The distribution of free and ion paired species concentrations shown in the log species-pH plot in Figure 5 not only gives a visual interpretation to the rather complex system of equations governing the equilibrium behaviour of the carbonate system, but also serves as an invaluable unifying agent in elucidating the concepts of equivalent solutions, alkalinity and acidity and buffer capacity in high salinity waters.

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5.2 Equivalent Solutions and Equivalence Points

When CO_2, HCO_3^- or $CO_3^=$ is dissolved into pure water the resulting solution is called an equivalent solution of $H_2CO_3^*$, HCO_3^- or $CO_3^=$ respectively. The pH value attained for each of these solutions is referred to as the equivalence point for the particular solution.

Loewenthal and Marais (1976) have shown that in low salinity waters the equivalence points are influenced only by C_T, ionic strength and temperature. The analyses are not repeated here and the reader is referred to their publication for further information.

In high salinity waters the definitions of equivalent solutions and equivalence points remain the same as for low salinity waters. However, in high salinity water the equivalence points depend not only on C_T, ionic strength and temperature, but also on the degree of ion pairing in solution. That is, the equivalence points are also dependent on the concentrations of the matrix of ions which form ion pairs (e.g. Ca^{++}, Mg^{++}, Na^{+}, $SO_4^{=}$, HCO_3^{-}, $CO_3^{=}$ and OH^{-}).

The behaviour of the equivalence points can be analysed most expeditiously by establishing the appropriate proton balance equation and graphically solving this equation on a log [species]-pH plot. This approach is applied to each of the equivalence points of the carbonate system.

In the development set out below equivalent solutions of CO_2, HCO_3^{-} and $CO_3^{=}$ are considered in a water with an ionic matrix of Cl^{-}, $SO_4^{=}$, Mg^{++}, Ca^{++} and Na^{+} equal to that of synthetic seawater as listed in Table 13. Carbonate species are introduced by adding either CO_2 or HCO_3^{-} or $CO_3^{=}$ to give a total carbonic species concentration equal to that for seawater, i.e. $10^{-2.57}$ moles/ℓ.

Each of the equivalence points is then analysed by developing a proton balance equation for the equivalent solution and then solving this equation in the log [species]-pH diagram for seawater, see Figure 5. From the proton balance equation it will become apparent that in each case the graphical solutions involve only total species concentrations depicted as heavy lines in Figure 5. These total species lines are shown in Figure 6 and constitute the log [total species]-pH diagram.

(i) $H_2CO_3^*$ Equivalence Point

A proton balance equation for addition of CO_2 to this synthetic

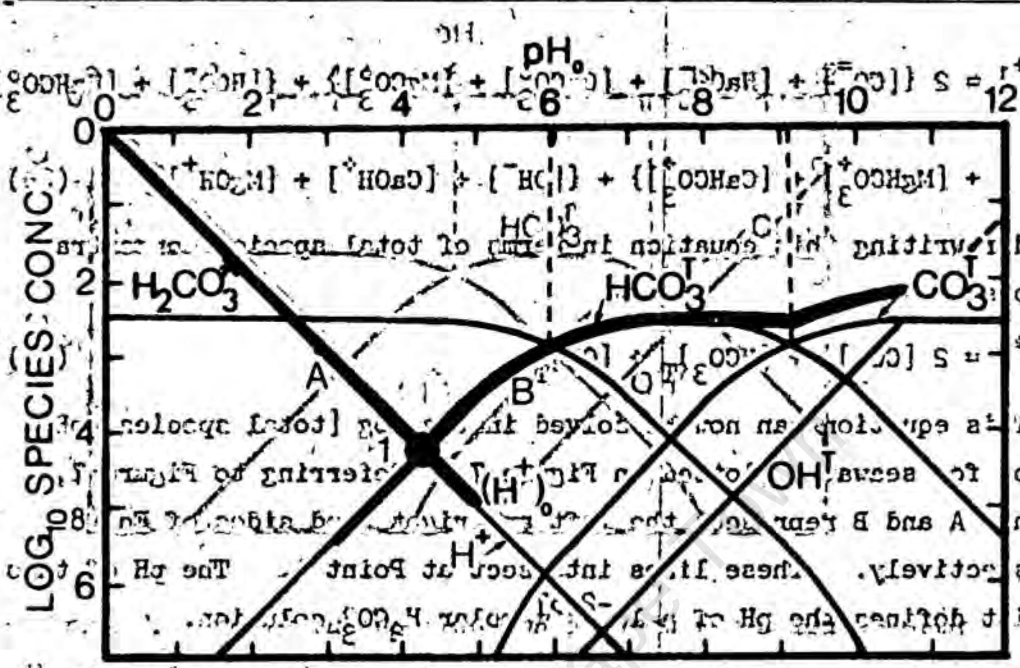

Figure 7. Point 1 with pH$_o$ = 4,27 is the $H_2CO_3^*$ equivalence point in seawater.

(ii) $CO_3^=$ Equivalence Point

Applying the concepts of proton levels for the addition of $CO_3^=$ to the synthetic seawater the following proton balance equation is established:

$$[OH^-] + [MgOH^+] + [CaOH^+] = [H^+] + \{[HCO_3^-] + [NaHCO_3^o] + [CaHCO_3^+] + [MgHCO_3^+]\} + 2[H_2CO_3^*] \qquad (87)$$

and rewriting this equation in terms of total species concentrations

$$[OH]_T = [H^+] + [HCO_3]_T + 2[H_2CO_3^*] \qquad (88)$$

Solving Eq (88) graphically in the log [total species]-pH plot, Figure 8. Lines A and B represent the left and right hand sides of Eq (88) respectively; these lines intersect at Point 2 in the diagram and the pH of this point, i.e. pH$_o$ = 9,93, gives the $CO_3^=$ equivalence point.

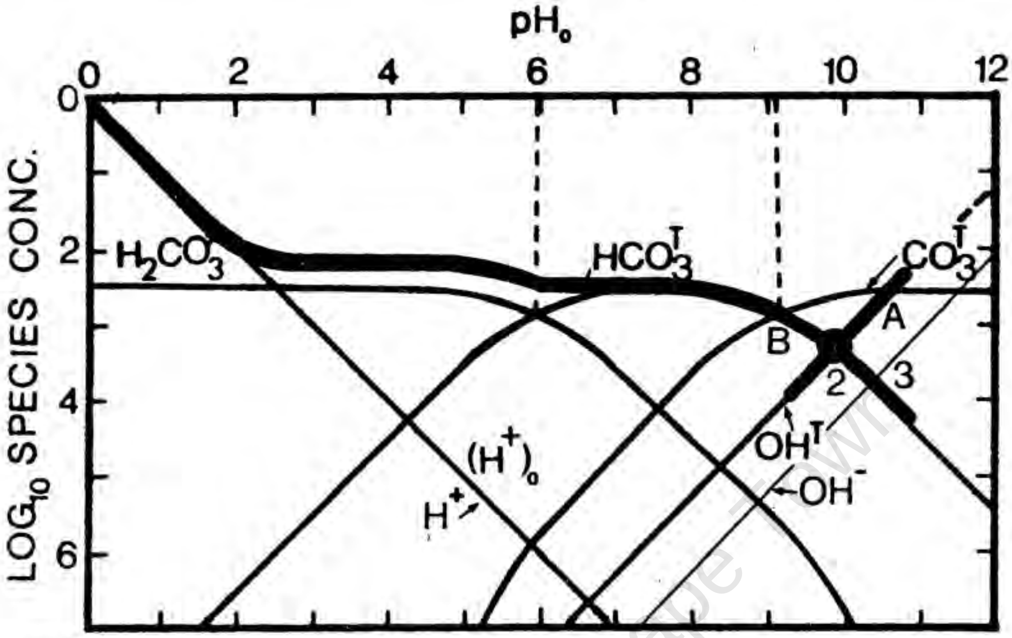

Figure 8. $CO_3^=$ *equivalence point for synthetic seawater occurs at Point 2 with* $pH_o = 9,93$.

Whereas the shift in the $H_2CO_3^*$ equivalence point is due to the bicarbonate ion pairs alone, the shift in the $CO_3^=$ *equivalence point* is due to the ion pairing of a number of species, HCO_3^-, $CO_3^=$ and OH^- species.

The shift in the *dissociation constant*, from a pH equal to p_oK_2' to p_oK_{T2}', arises principally from ion pairing of only the HCO_3^- and $CO_3^=$ species (i.e. ion pairing of HCO_3^- and $CO_3^=$ with Ca^{++}, Mg^{++} and Na^+) and is the cause for the apparent dissociation constant p_oK_{T2}' to occur at a lower pH value than the true dissociation constant p_oK_2', see Figure 8.

As the shift of the p_oK_{T2}' value is due to ion pairing of HCO_3^- and $CO_3^=$ species, the shift in the pH of the $CO_3^=$ *equivalence point* may be looked upon as due to the shift in p_oK_2' to p_oK_{T2}' and ion pairing of the OH^- species. This is illustrated in Figure 8 as follows: If no OH^- ion pairing takes place the $CO_3^=$ equivalence point will occur at the pH of Point 3 - the intersection of the

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line representing free OH^- and the line B. Thus the difference in pH between Point 2 (the true $CO_3^=$ equivalence point) and Point 3 equals the additional depression of this equivalence point due to OH^- ion pairing.

(iii) HCO_3^- Equivalence Point

A proton balance equation for addition of HCO_3^- to the synthetic seawater is derived from the proton levels giving:

$$[H^+] + [H_2CO_3^*] = \{[CO_3^=] + [NaCO_3^-] + [CaCO_3^o] + [MgCO_3^o]\}$$
$$+ \{[OH^-] + [CaOH^+] + [MgOH^+]\} \qquad (89)$$

Rewriting this equation in terms of total species concentrations:

$$[H^+] + [H_2CO_3^*] = [CO_3]_T + [OH]_T \qquad (90)$$

Solving Eq (90) in the log [total species]-pH diagram, see Figure 9, the HCO_3^- equivalence point is given by the pH of Point 4, $pH_o = 7,56$.

The effect of ion pairing on this equivalence point is as follows: If there is no ion pairing the equivalence point occurs midway between p_oK_1' and p_oK_2', i.e. at pH = 7,85 in Figure 9. If there is a significant degree of ion pairing the respective pK values are depressed to p_oK_{T1}' and p_oK_{T2}' as outlined in (i) and (ii) above; the HCO_3^- equivalence point now occurs midway between p_oK_{T1}' and p_oK_{T2}' as shown in Figure 9, i.e. pH = 7,56. The depression of this equivalence point thus results from (a) the shift in p_oK_{T1}' due to HCO_3^- ion pairing and (b) the shift in p_oK_{T2}', due to both HCO_3^- and $CO_3^=$ ion pairing.

6. ALKALINITY AND ACIDITY

The concepts of equivalent solutions and equivalence points have now been established in a quantitative manner for solutions in which there is a significant degree of ion pairing. The value of

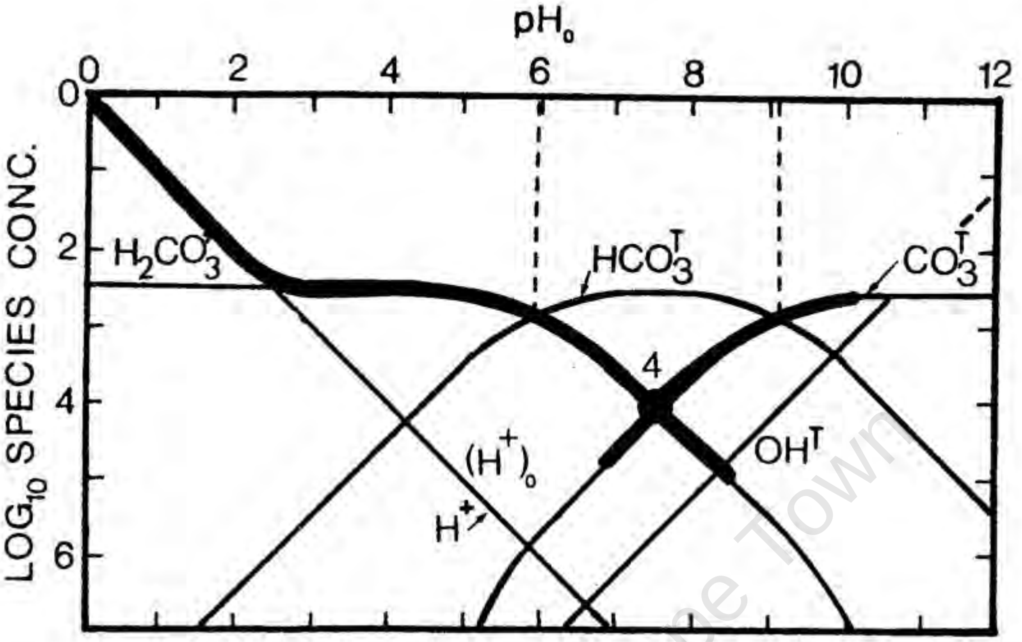

Figure 9. HCO_3^- equivalence point for synthetic seawater occurs at pH_o = 7,56.

these concepts becomes evident particularly when considering mixtures of either $H_2CO_3^*$, HCO_3^- or $CO_3^=$ with strong acids and bases.

6.1 Mixtures of Weak and Strong Acids and Bases

Using the concept of equivalent solutions one can separate out the weak acid and the strong acid (or base) species into an equivalent solution of either $H_2CO_3^*$ or HCO_3^- or $CO_3^=$ plus a mass of strong acid or base. The mass of strong acid or base associated with this equivalent solution is termed its alkalinity or acidity respectively. For example, considering the $H_2CO_3^*$ equivalence point there is associated with it $H_2CO_3^*$ Acidity and $H_2CO_3^*$ Alkalinity, (Loewenthal and Marais, 1976).

Now consider the following examples in which equivalent solutions of either CO_2 or HCO_3^- or $CO_3^=$ are mixed with a strong acid or base. In each case the total carbonate species added to the solution is $10^{-2,57}$ moles (as either CO_2 or HCO_3^- or $CO_3^=$). Prior to

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addition of the carbonate species, the ionic matrix is made up of Cl^-, $SO_4^=$, Ca^{++}, Mg^{++} and Na^+ with concentrations equal to those for seawater, as set out in Table 13.

A. Equivalent $H_2CO_3^*$ Solution

(i) CO_2 plus a strong base:

10^{-3} m/kg H_2O of strong base NaOH is added to an equivalent CO_2 solution with $C_T = 10^{-2,57}$ molal. A proton balance equation for this mixture is developed from the proton levels. This can be written as follows:

species formed by *gain* of 1 H^+	Na_b^+		H^+
initial proton condition	NaOH	$H_2CO_3^*$	H_2O
species formed by *loss* of 1 H^+		HCO_{3T}	OH_T
species formed by *loss* of 2 H^+		CO_{3T}	

where

subscript 'b' refers to the molal mass of strong base added

subscript 'T' refers to the total species, i.e. free plus ion paired species.

Comparing this table showing changes in the proton condition of the various species with that set out for Eq (85), the simplification is made of using total species concentrations to replace the sum of the free and ion paired species.

The proton balance equation can now be written

$$[Na^+]_b + [H^+] = 2[CO_3]_T + [HCO_3]_T + [OH]_T \tag{91}$$

The pH_o of the solution is determined by solving Eq (91) in the log [species]-pH_o diagram (Figure 10) giving pH_o = 5,80.

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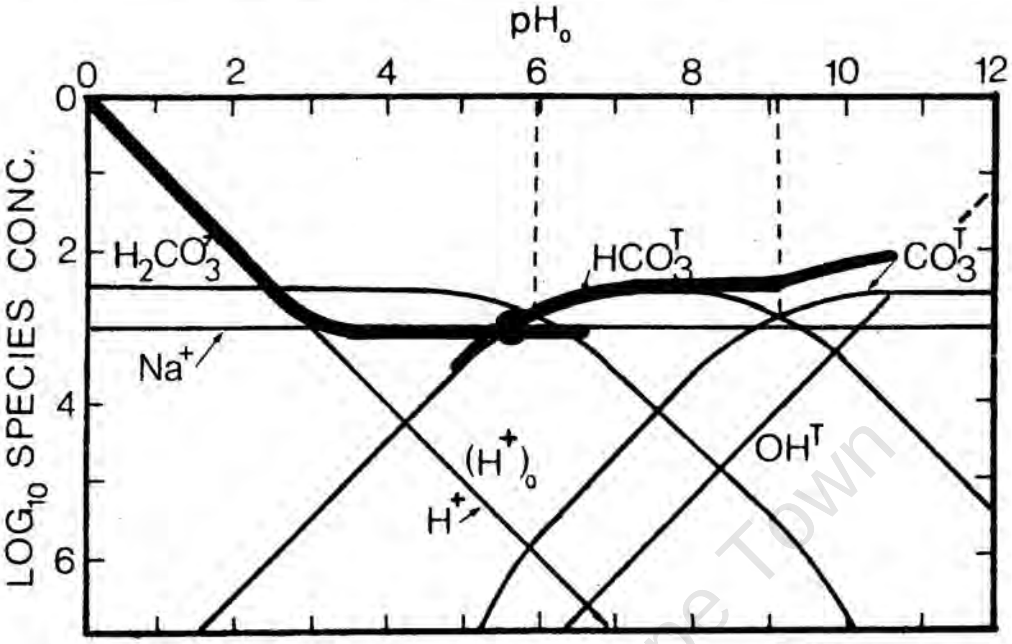

Figure 10. Addition to high saline water of $10^{-2,57}$ *molal* CO_2 *and* 10^{-3} *molal of strong base NaOH gives* $pH_o = 5,80$.

Presentation in terms of total species concentrations points to the influence of total species on the determination of pH once the $p_oK'_{T1}$ and $p_oK'_{T2}$ values have been determined.

The net strong base, $[Na^+]_b$, associated with the equivalent $H_2CO_3^*$ solution giving the observed pH is termed the $H_2CO_3^*$ Alkalinity or Total Alkalinity or, simply Alkalinity. Rearranging Eq (91) gives the equation for $H_2CO_3^*$ Alkalinity:

$$H_2CO_3^* \text{ Alk.} = [Na^+]_b = 2[CO_3]_T + [HCO_3]_T + [OH]_T - [H^+] \qquad (92)$$

(ii) CO_2 plus a strong acid:

10^{-4} m/kg H_2O of strong acid, HCl, is added to an equivalent CO_2 solution with $C_T = 10^{-2,57}$molal. The proton balance equation for this mixture is

$$[H^+] = 2[CO_3]_T + [HCO_3]_T + [OH]_T + [Cl^-]_a \qquad (93)$$

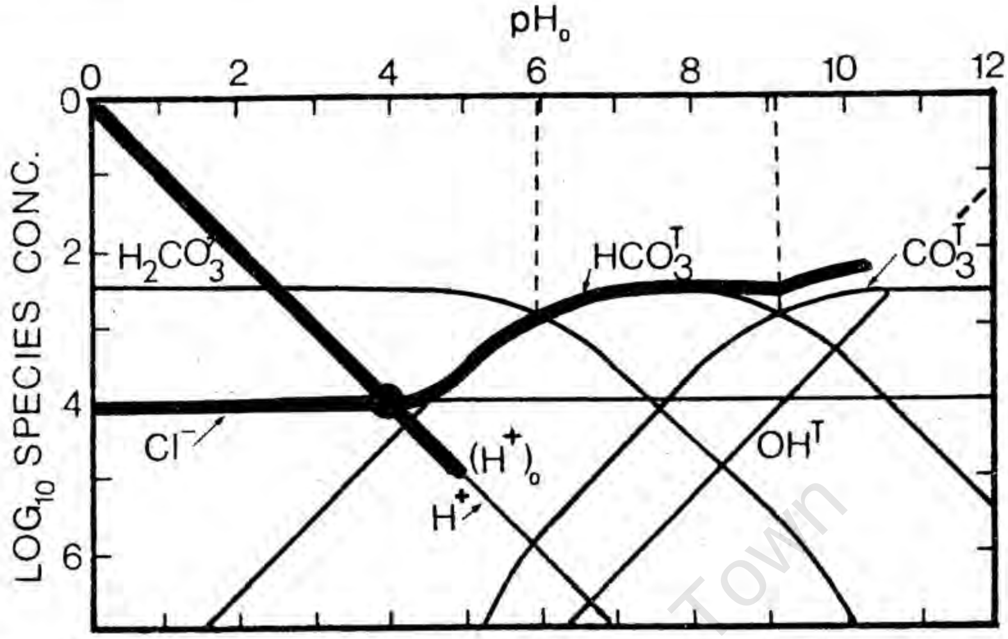

Figure 11. Addition to high saline water of $10^{-2,57}$ *molal* CO_2 *and* 10^{-4} *molal of strong acid HCl gives pH = 3,90.*

where

subscript 'a' refers to the molality of strong acid added to the solution.

The pH of the solution is determined by solving Eq (93) in the log [total species]-pH_o diagram (Figure 11), giving pH_o = 3,90.

The net strong acid, $[Cl^-]_a$, which together with the equivalent $H_2CO_3^*$ solution gives the observed pH is termed $H_2CO_3^*$ Acidity. Other terms also used to describe this parameter are Mineral Acidity or Negative Alkalinity (-ve Alk.). Rearranging Eq (93)

$$H_2CO_3^* \text{ Acidity (-ve Alk.)} = [Cl^-]_a = [H^+] - 2[CO_3]_T - [HCO_3]_T - [OH]_T \quad (94)$$

To show that $H_2CO_3^*$ Acidity is equal to negative Alkalinity (-ve $H_2CO_3^*$ Alkalinity) compare Eqs (94 and 92)

$$H_2CO_3^* \text{ Acidity} = \text{-ve } H_2CO_3^* \text{ Alkalinity} = \text{-ve Alkalinity} \quad (95)$$

Exactly the same procedures can be carried out for mixtures of

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equivalent solutions of HCO_3^- or $CO_3^=$ and strong acids or bases.

Introducing an alkalinity and acidity for each of these two equivalence points:

B. HCO_3^- Equivalent Solution

If a solution is prepared by mixing an equivalent solution of HCO_3^- and a *strong base*, the molar mass of strong base in the solution is termed HCO_3^- Alkalinity
where

$$HCO_3^- \text{ Alkalinity} = [CO_3]_T + [OH]_T - [H^+] - [H_2CO_3^*] \qquad (96)$$

and for addition of a *strong acid* to an equivalent HCO_3^- solution the molar mass of strong acid is termed HCO_3^- Acidity (or CO_2 Acidity), where

$$HCO_3^- \text{ Acidity} = [H^+] + [H_2CO_3^*] - [CO_3]_T - [OH]_T \qquad (97)$$

Comparing Eqs (96 and 97)

$$HCO_3^- \text{ Alkalinity} = -\text{ve } HCO_3^- \text{ Acidity } (-\text{ve } CO_2 \text{ Acidity}) \qquad (98)$$

C. $CO_3^=$ Equivalent Solution

If a solution is prepared by mixing an equivalent solution of $CO_3^=$ and a *strong base*, the molar mass of strong base is termed $CO_3^=$ Alkalinity (or Caustic Alkalinity), where

$$CO_3^= \text{ Alkalinity} = [OH]_T - 2[H_2CO_3^*] - [HCO_3]_T - [H^+] \qquad (99)$$

Similarly for the addition of a *strong acid* to an equivalent $CO_3^=$ solution, the molar mass of strong acid is termed $CO_3^=$ Acidity (or simply Acidity) where

$$\begin{matrix} CO_3^= \text{ Acidity} \\ \text{(i.e. Acidity)} \end{matrix} = 2[H_2CO_3^*] + [HCO_3]_T + [H^+] - [OH]_T \qquad (100)$$

and comparing Eqs (99 and 100)

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$CO_3^=$ Alkalinity = -ve CO_3 Acidity (i.e. -ve Acidity) (101)

The seven mass balance equations (six equations for the three forms of each of alkalinity and acidity, Eqs (92, 94, 96, 97, 99 and 100), and the equation for the total carbonate species concentration, C_T, Eq (52) do not constitute a system in seven independent parameters. The interdependence between these mass parameters is as follows:

From Eqs (95, 98 and 101):

X Alkalinity = -ve X Acidity (102)

where

'X' refers to the associated equivalent solution of either $H_2CO_3^*$ or HCO_3^- or $CO_3^=$

and from Eqs (92 to 100):

$CO_3^=$ Acidity + $H_2CO_3^*$ Alkalinity = $2C_T$ (103)

$CO_3^=$ Acidity + HCO_3^- Alkalinity = C_T (104)

$H_2CO_3^*$ Alkalinity + HCO_3^- Acidity = C_T (105)

$CO_3^=$ Acidity - $H_2CO_3^*$ Acidity = $2C_T$ (106)

$H_2CO_3^*$ Alkalinity - $CO_3^=$ Alkalinity = $2C_T$ (107)

Interdependence of C_T and the various forms of alkalinity and acidity are shown to advantage by a graphical presentation similar to that for low salinity water, Figure 1. Choosing $CO_3^=$ Acidity as abscissa and $H_2CO_3^*$ Alkalinity as ordinate, plots of the relationships in Eqs (102 to 107) are shown in Figure 12.

From this diagram the following observations are valid:

(i) If C_T and any one form of alkalinity or acidity are known,

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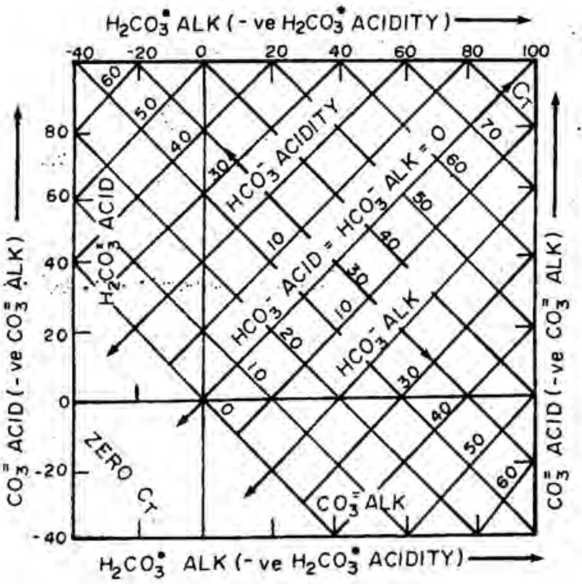

Figure 12. Interrelationships between alkalinity, acidity and C_T in high salinity water.

all the remaining mass parameters can be calculated (or simply read off the graphical plot).

(ii) If any two alkalinity or two acidity values or one alkalinity and one acidity value are known, the remaining mass parameters can be calculated. This, of course, excludes a set of alkalinity and acidity values associated with the same equivalent solution for then the alkalinity is simply negative acidity.

The mass parameters are independent of ion pairing. This can be shown to be so by noting, for example, that in the equations for the mass parameters alkalinity and acidity, Eqs. (103 to 107), the sum of the free and ion pair species concentrations always equals the total concentrations and hence the equations can always be written in terms of the total species concentrations irrespective of the degree of ion pairing.

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Earlier in this chapter it was shown that if C_T is known and a complete analysis is available of the concentrations of ions which form ion pairs in the solution, then a log [species]-pH diagram can be plotted for the system (see Figure 5). If pH (or pH_o) is also known then a unique solution is available, i.e. all species concentrations and alkalinities, acidities and C_T can be calculated. This leads to an alternative approach to the problem as follows: Measurement of any two independent parameters of the carbonate weak acid-base system can replace C_T and pH (for example, Alkalinity and Acidity) in the calculations above to give the complete solution to the system. Obviously it is most convenient to develop solution procedures around pairs of parameters which can be measured relatively simply in practice.

6.2 Measurement of Alkalinity and Acidity

In the previous section it was shown that the theoretical alkalinity or acidity associated with a particular equivalence point is that mass of strong base or acid respectively which gives the observed pH. Thus to measure either alkalinity or acidity, a strong acid or base is added to the solution to adjust the pH to a particular equivalence point.

A general practical problem arising in this type of measurement is to estimate the pH of the various equivalence points. In low salinity waters it was shown that the equivalence points could be identified by the pH values of the particular inflection points in the alkalimetric or acidimetric titration curve. The question now arises as to whether for high salinity waters the pH (or pH_o) of the inflection points corresponds to that of the equivalence points. This can only be answered by considering the effects of ion-pairing on buffering of pH in high salinity waters.

6.2.1 *Buffer index of low salinity waters*

Van Slyke (1922) defined pH-buffer index, β, as the molar mass of

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strong base, C_B, required to cause a unit positive change in pH, i.e.

$$\beta = (\partial C_B/\partial pH)_{A_T} \tag{108a}$$

can also be written in terms of strong acid added, C_A, as

$$\beta = -(\partial C_A/\partial pH)_{A_T} \tag{108b}$$

where A_T = mass concentration of total weak acid-base species. Hence, β always has a positive value.

Butler (1964) developed equations for β in low salinity waters for mono- and multiprotic weak acid-base systems. For an aqueous system containing a monoprotic weak acid-base system,

$$\beta = 2{,}303\{[H^+]+[OH^-]\}+\{\frac{2{,}303\ A_T\ K_a[H^+]}{(K_a+[H^+])^2}\} \tag{109a}$$

$$= \beta_{H_2O} + \beta_{HA} \tag{109b}$$

where A_T = molality of total weak acid-base species

β_{H_2O} = buffer capacity contribution by the water component

β_{HA} = buffer capacity contribution by the weak acid-base component.

For an aqueous system containing a diprotic weak acid-base system, H_2A-HA^--A^{2-},

$$\beta = \beta_{H_2O}+2{,}303\ A_T\ K_{a1}[H^+]\{\frac{[H^+]^2+4K_{a2}[H^+]+K_{a1}K_{a2}}{([H^+]^2+K_{a1}[H^+]+K_{a1}K_{a2})^2} \tag{110}$$

$$\cong \beta_{H_2O} + \frac{2{,}303\ A_T\ K_{a1}[H^+]}{(K_{a1}+[H^+])^2} + \frac{2{,}303\ A_T\ K_{a2}[H^+]}{(K_{a2}+[H^+])^2} \tag{111a}$$

$$= \beta_{H_2O} + \beta_{H_2A} + \beta_{HA^-} \tag{111b}$$

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Combining Eqs (122 and 123) and simplifying gives

$$\beta = \{2{,}303([H^+] + [OH^-])\}+\{2{,}303A_T\, K''_{Ta}[H^+]/([H^+]+K''_{Ta})^2\} \qquad (124)$$

$$= \beta_{H_2O} + \beta_{HA_T}$$

Equation (124) indicates that the buffer capacity is made up of two fractions, that due to the dissociation of water, β_{H_2O}, and that due to the stoichiometric dissociation of HA to $[A^-]_T$, β_{HA_T}.

Comparing Eqs (109a and 124), shows that the buffer capacity equation will have the same form irrespective of whether ion pairing occurs or not. Where ion pairing of weak acid-base species occurs, the curve representing $_{HA_T}$ will still be typically bell-shaped as shown in Figure 3c, but the curve will be centered about pK'_{TA} instead of pK'_a.

The buffering effects on pH due to the ion paired and free weak acid-base species can be isolated using the link between the stoichiometric dissociation constant in and the apparent dissociation constant in Eq (53), i.e.

$$K''_{Ta} = K''_a\ (1 + [M^+]/K'_c) \qquad (125)$$

Substituting for K''_{Ta} from Eq (125) into Eq (124) and simplifying gives

$$\beta = \{2{,}303([H^+]+[OH^-]) + \{\frac{A_T\ K''_a\ [H^+]}{([H^+]+K''_a+[M^+]K''_r)^2}\}+\{\frac{A_T[H^+][M^+]K''_r}{([H^+]+K''_a+[M^+]K''_r)^2}\} \qquad (126a)$$

where $K''_r = K''_a/K'_c$ (126b)

Equation (126) indicates that the buffer capacity is now made up of three fractions: that due to the dissociation of water, β_{H_2O} (the first term in Eq 126a); that due to the dissociation of the weak acid, β_{HA} (the second term in Eq 126a); that due to ion pairing, β_{MA^o} (the third term in Eq 126a). Thus Eq (126) can be

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rewritten as

$$\beta = \beta_{H_2O} + \beta_{HA} + \beta_{MA^\circ} \tag{126c}$$

Equations (124 and 126) can also be formulated in terms of weak acid-base species concentrations (either stoichiometric or free) as follows:

For the buffer equation in terms of stoichiometric concentrations, substitute for K''_{Ta}, K''_r and A_T from Eqs (117a, 126b and 114) respectively into Eq (124). Rearranging this equation and simplifying gives

$$\beta = 2{,}303([H^+]+[OH^-]) + 2{,}303\,\frac{[HA][A^-]_T}{([HA]+[A^-]_T)} \tag{127a}$$

$$= 2{,}303([H^+]+[OH^-]) + 2{,}303\,\frac{[HA][A^-]_T}{A_T} \tag{127b}$$

For the buffer equation in terms of free and ion paired species concentrations, substitute for $[A^-]_T$ from Eq (116) into Eq (127b) gives

$$\beta = 2{,}303([H^+]+[OH^-]) + 2{,}303\,\frac{[HA][A^-]}{A_T} + 2{,}303\,\frac{[HA][MA^\circ]}{A_T} \tag{128}$$

The form of Eqs (127a and 127b) is particularly useful in that it can be used to give equations for estimating titration errors associated with each of the equivalence points.

The analysis above can be generalized to a number of cationic species in solution each forming ion pairs with the weak acid anion, A^-, as follows:

From Eq (53), the link between the stoichiometric dissociation constant, K''_{Ta} and the apparent dissociation constant, K''_a, is

$$K''_{Ta} = K''_a\,(1 + \sum_i [M^+]_i/K'_{ci}) \tag{129}$$

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where K'_{ci} = apparent dissociation constant for ion pairing between cation species M_i^+ and A^-.

Substituting for K''_{Ta} from Eq (129) into Eq (124) and simplifying gives β as the sum of the buffer capacities of a water component, a free weak acid-base species component and a component for each of the ion pairs,

$$\beta = 2{,}303\ ([H^+]+[OH^-]) + 2{,}303\,\frac{A_T K''_a [H^+]}{(K''_a+[H^+]+\Sigma[M^+]_i K''_{ri})^2} + \sum_i 2{,}303\,\frac{A_T[H^+][M^+]_i K''_{ri}}{(K''_a+[H^+]+\sum_i[M^+]_i/K''_{ri})^2} \qquad (130)$$

where $K''_{ri} = K''_a/K'_{ci}$.

In terms of free and ion paired species concentration, Eq (130) becomes

$$\beta = 2{,}303([H^+]+[OH^-])+2{,}303\frac{[HA][A^-]}{A_T} + 2{,}303\sum_i\frac{[HA][M_iA]}{A_T} \qquad (131)$$

where M_iA = ion paired species formed by ion pairing between cation M_i and the weak acid-base species A^-.

(b) Diprotic systems:

The buffer capacity equation for a diprotic weak acid-base system is obtained by considering this acid as a mixture of two monoprotic weak acids with stoichiometric dissociation constants K''_{T1} and K''_{T2}. From Eqs (111a and 111b) the buffer equation is simply the buffer equation for the water component, β_{H_2O}, plus the buffer components of each of the monoprotic systems (in their stoichiometric form), β_{TH_2A} and β_{THA^-}, i.e.

$$\beta = \beta_{H_2O} + \beta_{TH_2A} + \beta_{THA^-} \qquad (132)$$

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Each of the terms on the right hand side of Eq (132) will now be considered.

β_{H_2O} is the buffering due to the dissociation of water, i.e. $\beta_{H_2O} = 2{,}303\ ([H^+] + [OH^-])$.

β_{TH_2A} is the buffer capacity resulting from interaction between undissociated acid, H_2A (which does not form ion pairs) and the stoichiometric dissociated species HA_T^- (which includes both free and ion paired HA species). From Eq (124)

$$\beta_{TH_2A} = \frac{2{,}303\ A_T\ [H^+]\ K''_{T1}}{([H^+] + K''_{T1})^2} \tag{133}$$

and, in terms of stoichiometric species concentrations, from Eq (127b)

$$\beta_{TH_2A} = 2{,}303\ \frac{[H_2A][HA^-]_T}{A_T} \tag{134}$$

and, in terms of free and ion paired components to the buffer capacity, from Eq (131)

$$\beta_{TH_2A} = 2{,}303\ \frac{[H_2A][HA^-]}{A_T} + 2{,}303\ \sum_i \frac{[H_2A][M_iHA]}{A_T} \tag{135}$$

where M_iHA = ion paired species due to ion pairing between cation M_i and weak acid-base species HA^-.

The first term on the right hand side of Eq (135) is the buffer capacity component due to the free weak acid-base species dissociation, and the second term is for the components arising from ion pairing.

β_{THA^-} is the buffer capacity resulting from interaction between the stoichiometric species HA_T^- and A_T^{2-} (where both HA^- and A^{2-} form ion pairs with the various cation species in the solution). From Eq (124)

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$$\beta_{THA^-} = \frac{2,303\ A_T[H^+]K''_{T2}}{([H^+] + K''_{T2})^2} \qquad (136)$$

and, in terms of stoichiometric species concentrations, from Eq (127b)

$$\beta_{THA^-} = 2,303\ \frac{[HA^-]_T[A^{2-}]_T}{A_T} \qquad (137)$$

and, in terms of free and A^{2-} ion paired components to the buffer capacity, from Eq (131)

$$\beta_{THA^-} = 2,303\ \frac{[HA^-]_T[A^{2-}]}{A_T} + 2,303 \sum_i \frac{[HA^-]_T[M_iA]}{A_T} \qquad (138)$$

(c) Hydroxide system:
In water with a high pH substantial fractions of calcium and magnesium cations ion-pair with OH^- to form $MgOH^+$ and $CaOH^+$ (Larson *et al*, 1973). Dissociation constants for these ion-pairs are given in Table 3.

The effects of the ion-pairs $MgOH^+$ and $CaOH^+$ on buffer capacity are developed from the fundamentals in a similar fashion to that for monoprotic acids and expressed in Eq (124) as follows.

Consider CO_2 free water containing only $CaCl_2$. C_B moles/ℓ of strong base NaOH are added to the water. Proton balance equation for this solution is

$$[Na^+] + [H^+] = [OH^-] + [CaOH^+]$$

Noting that $C_B = [Na^+]$ and simplifying

$$C_B = [OH^-] + [CaOH^+] - [H^+] \qquad (139)$$

Differentiating this equation with respect to pH gives the buffer equation for the system:

$$\frac{dC_B}{dpH} = 2,303\ \{[H^+] + [OH^-] + [CaOH^+]\}$$

or

$$\beta = 2{,}303\ \{[H^+] + [OH]_T\} \qquad (140)$$

Combining this equation with Eq (132) gives the general buffer capacity equation for a diprotic weak acid in water containing cations which ion-pair with both the weak acid species and OH^-:

$$\beta = 2{,}303\{[H^+]+[OH^-]_T\} + \frac{2{,}303A_T K''_{T2}[H^+]}{([H^+]+K''_{T2})^2} \qquad (141)$$

The equations for buffer capacity of a diprotic weak acid-base system in terms of stoichiometric species and free ion paired species, Eqs (133 to 138, 140 and 141), are now applied to the carbonate system in a highly saline water as follows: Consider a water with $C_T = 10^{-2.57}$ moles/ℓ and major ionic species molalities equal to those for seawater listed in Table 13. In Figure 13 are shown plots of the distribution of the total buffer capacity and the individual contributions to buffer capacity of the various ion pairs and free weak acid-base species versus pH_o.

Referring to Figure 13, the curves representing the buffer capacity for weak acid species (both free and ion paired) and ion paired species all plot as bell shaped curves centered about the operational stoichiometric constants $p_oK'_{T1}$ and $p_oK'_{T2}$.

Having established the buffer capacity relationships it is now possible to develop a theoretical titration curve and to link the buffer and titration curves to the log [species] diagram.

6.2.3 *Buffer Capacity and Equivalence Points*

The alkalimetric or acidimetric titration curve relationships are developed from the buffer capacity equations as follows:
From Eq (108a)

$$\partial C_B = \beta \partial pH_o$$

and integrating this equation

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$$\int_{\ell}^{m} dC_B = \int_{\ell}^{m} \beta dpH_{(o)} \qquad (142)$$

and, substituting for β from Eqs (133, 136 and 140)

$$\int_{\ell}^{m} dC_B = \int_{\ell}^{m} 2{,}303 \; \{(H^+)_o/\gamma_{H(o)} + {}_oK'_{Tw}/(H^+)_o\} \; dpH_o$$

$$+ \int_{\ell}^{m} 2{,}303 \; \{\frac{C_T \; {}_oK'_{T1} \; (H^+)_o}{[(H^+)_o + {}_oK'_{T1}]^2}\} dpH_{(o)}$$

$$+ \int_{\ell}^{m} 2{,}303 \; \{\frac{C_T \; {}_oK'_{T2} \; (H^+)_o}{[(H^+)_o + {}_oK'_{T2}]^2}\} dpH_{(o)} \qquad (143)$$

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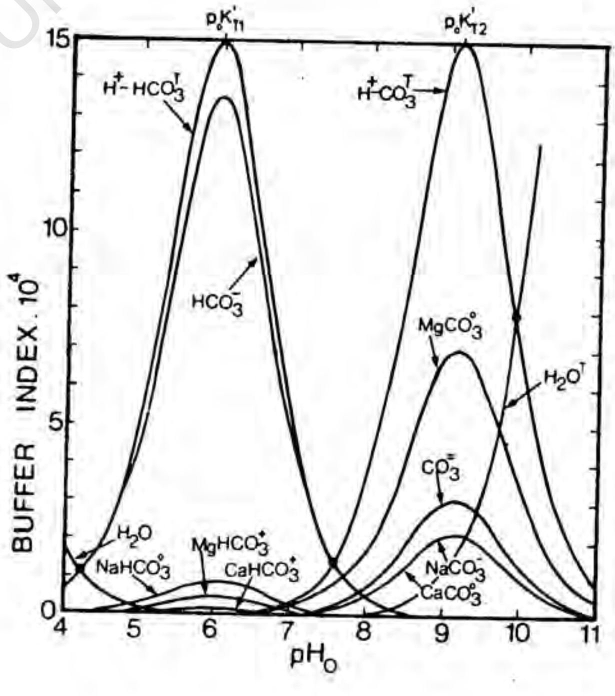
Figure 13. Distribution of the buffering effect of free species, ion pairs and total species for the carbonate system in seawater.



where the limits to the integration, ℓ and m, refer to the pH_o values at the start and end of the titration.

Equation (143) shows that the titration curve between $pH_{(o)\ell}$ and $pH_{(o)m}$ is given by the cumulative area under the buffer capacity curves between these two $pH_{(o)}$ values.

The buffer capacity diagram, titration curve and log [species] plot for the carbonate system in seawater is shown in Figure 14. Referring to this diagram the following observations are pertinent.

(a) The pH value for the point of minimum buffer capacity, Point A, corresponds to an inflection point in the titration curve and closely corresponds to the carbonic acid equivalence point, pH_a.

(b) The pH values for $p_oK'_{T1}$ and $p_oK'_{T2}$ correspond to inflection points in the titration curve and points of maximum buffer capacity.

(c) The pH value for the point of minimum buffer capacity, Point B, corresponds to an inflection point in the titration curve and closely corresponds to the bicarbonate equivalence point, pH_b.

(d) An *inflection point* (sometimes a minimum) occurs at Point C in the buffer capacity diagram. This point appears to correspond to the carbonate equivalence point pH_c. However, no corresponding clear inflection point is exhibited in the titration curve in this pH region. Hence the pH of this point is not clearly identified in the titration curve. This observation, coupled to the fact that the total buffer capacity in this pH region is high, indicates that large errors will result in alkalinity or acidity measurements to this equivalence point. Utilization of the carbonate equivalence point as an endpoint in titrations is therefore of little practical value and will

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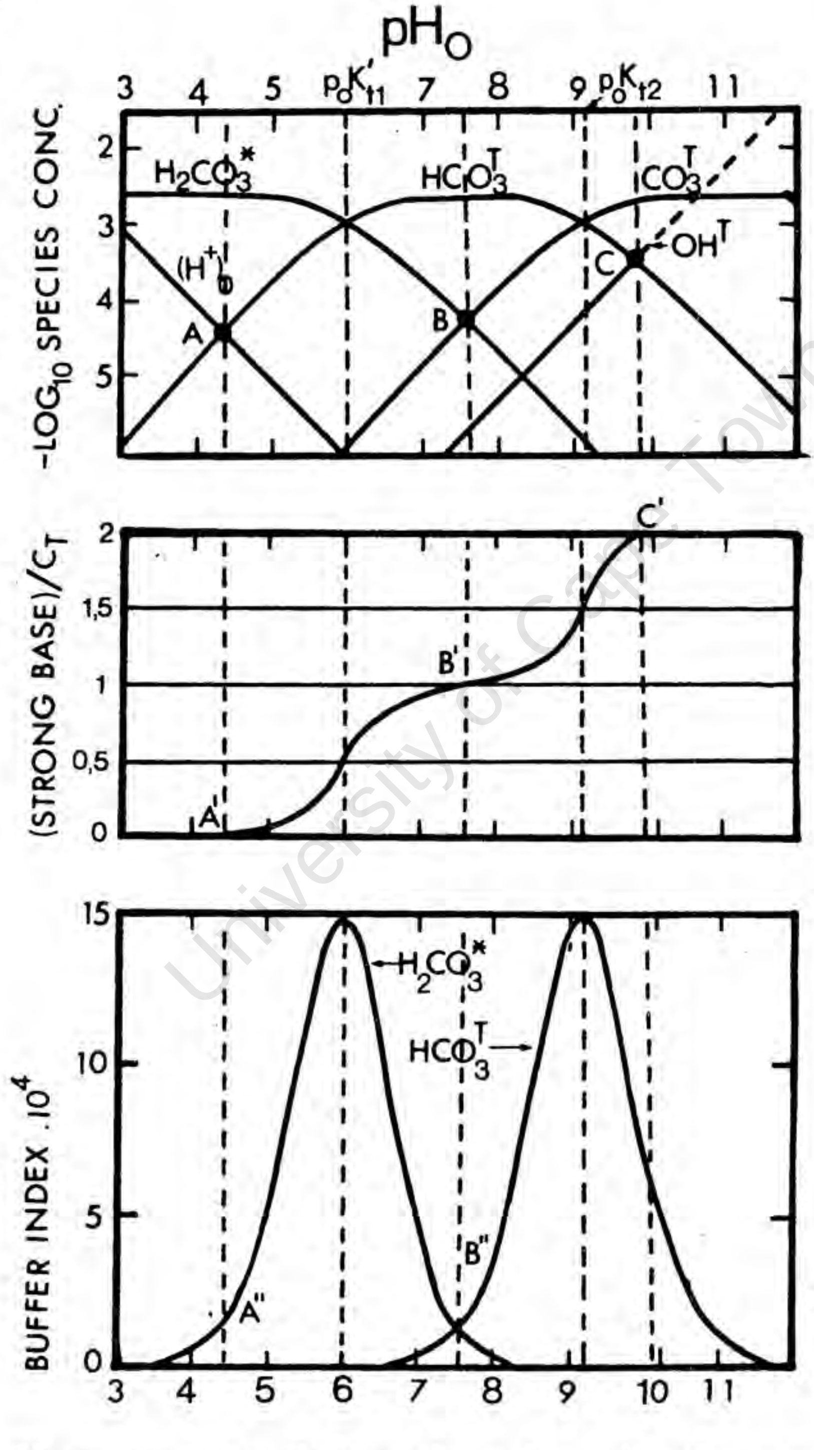

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Figure 14. Distribution of species, titration curve and buffer capacity for the carbonate system in seawater (assuming no precipitation or CO_2 loss).

not be discussed further. This same situation applies in low salinity waters (Loewenthal and Marais, 1976).

6.2.4 *Buffer Capacity and Equivalence Points*

It will now be shown theoretically that the $H_2CO_3^*$ and HCO_3^- equivalence points correspond closely to points of minimum buffer capacity and to points of inflection in the titration curve.

(i) *$H_2CO_3^*$ Equivalence Point:*

Differentiating the buffer equation, Eq (141), with respect to pH, setting this equation equal to zero and solving gives the pH of points of maximum and minimum buffer capacity. In the pH region of the $H_2CO_3^*$ equivalence point the buffering effect due to the dissociation of $[HCO_3]_T$ to $[CO_3]_T$ is negligible. Differentiating the first two terms of Eq (141) with respect to pH (keeping C_T constant),

$$\left(\frac{\partial\beta}{\partial pH}\right)_{C_T} = 2{,}303^2\left\{[OH]_T-[H^+]-\frac{C_T\,K''_{T1}[H^+]}{(K''_{T1}+[H^+])^2}+\frac{2C_T\,K''_{T1}[H^+]^2}{(K''_{T1}+[H^+])^3}\right\} \qquad (144)$$

From Eqs (133 and 134)

$$\frac{C_T\,K''_{T1}[H^+]}{(K''_{T1}+[H^+])^2} = \frac{[H_2CO_3^*][HCO_3]_T}{C_T} \qquad (145)$$

Substituting for $C_T\,K''_{T1}[H^+]/(K''_{T1}+[H^+])^2$ from Eq (145) into Eq (144) and simplifying

$$\left(\frac{\partial\beta}{\partial pH}\right)_{C_T} = 2{,}303^2\left\{[OH]_T-[H^+]-\frac{[H_2CO_3^*][HCO_3]_T}{A_T}+\frac{2[H_2CO_3^*]^2[HCO_3]_T}{A_T^{\,2}}\right\} \qquad (146)$$

For the condition of minimum β, equate Eq (146) to zero. Noting that in the region of the $H_2CO_3^*$ equivalence point (i.e. the pH region under consideration) $[OH]_T$ is negligible and $[H_2CO_3^*] \gg [HCO_3]_T \gg [CO_3]_T$, Eq (146) simplifies to $[H^+] \cong [HCO_3]_T$ (147)

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Equation (147) is the solution to the proton balance equation, Eq (86) for the equivalent $H_2CO_3^*$ solution. Thus, the $H_2CO_3^*$ equivalence point corresponds to a point of minimum β and an inflection point in the titration curve.

(ii) *HCO_3^- Equivalence Point:*

In the region of the HCO_3^- equivalence point: $K''_{T1} >> [H^+] >> K''_{T2}$ and $[H^+]$ and $[OH]_T$ are negligible, thus Eq (141) approximates to

$$\beta \cong \frac{C_T[H^+]}{K''_{T1}} + \frac{C_T K''_{T2}}{[H^+]} \qquad (148)$$

and for a minimum in β, $(\partial\beta/\partial pH)_{C_T}$ equals zero, i.e.

$$\left(\frac{\partial\beta}{\partial pH}\right)_{C_T} \cong \frac{C_T}{K''_{T1}} - \frac{C_T\ K''_{T2}}{[H+]^2} = 0$$

Solving for $[H^+]$

$$[H^+] = (K''_{T1} \cdot K''_{T2})^{\frac{1}{2}}$$

Substituting for K''_{T1} and K''_{T2} in the above equation

$$[H^+]^2 = \frac{[H^+][HCO_3]_T}{[H_2CO_3^*]} \cdot \frac{[H^+][CO_3]_T}{[HCO_3]_T}$$

and simplifying

$$[H_2CO_3^*] = [CO_3]_T \qquad (149)$$

Equation (149) is the solution to the proton balance euqation for the equivalent HCO_3^- solution, see Eq (90). Thus, the HCO_3 equivalence point corresponds to a point of minimum β and an inflection point in the titration curve.

6.2.5 *Alkalinity and Acidity Titration Errors*

The various sources of error leading to incorrect measurement of alkalinity and acidity by titration were discussed in detail by Loewenthal and Marais (1976). In high salinity waters one further

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point needs to be enlarged upon. As each of the equivalence points is affected by ion-pairing of the weak acid species, utilization of colour indicators (methyl red and phenolpthalein) to indicate the $H_2CO^*_3$ and HCO_3^- equivalence points respectively becomes completely unreliable. The HCO_3^- equivalence point is particularly affected by ion-pair formation in high salinity waters. This is illustrated by comparing the HCO_3^- equivalence point for low salinity water, which remains virtually constant at pH 8,35, with this equivalence point in seawater, which occurs at a pH of about 7,5 (see Figure 14). Consequently if phenolpthalein is used to indicate this endpoint an error of almost one pH unit can result.

Equations for the error in alkalinity or acidity measurement resulting from a titration to an incorrect endpoint pH are developed from the buffer capacity equation, Eq (141), as follows:

(a) $H_2CO_3^*$ Equivalence Point Error

In the pH region of the $H_2CO_3^*$ equivalence point the buffer capacity equation, Eq (141), approximates to

$$\beta \cong 2,303 \left([H^+] + \frac{C_T K''_{T1}}{[H^+]}\right) \qquad (150)$$

At the $H_2CO_3^*$ equivalence point the magnitudes of the two terms on the right in Eq (150) are equal, see Figure 7, thus at the equivalence point Eq (150) can be written in either of the two forms below:

$$\beta_e = 4,606[H^+]_e \qquad (151a)$$

or

$$\beta_e = 4,606\ C_T K''_{T1}/[H^+]_e \qquad (151b)$$

where subscript 'e' denotes the value at the equivalence point in question.

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Equation (151b) can be rewritten in terms of only C_T and K''_{T1} as follows. At the equivalence point $\partial\beta/\partial[H^+] = 0$, differentiating Eq (151b) with respect to $[H^+]$ and solving gives:

$$[H^+]_e = (C_T K''_{T1})^{\frac{1}{2}} \tag{152}$$

Substituting for $[H^+]$ from Eq (152) into Eq (151b)

$$\beta_e = 4{,}606(C_T K''_{T1})^{\frac{1}{2}} \tag{153}$$

The error associated with an alkalimetric or acidimetric titration to an equivalence point is determined by rewriting the buffer equation, Eq (108a), in the difference form and rearranging,

$$\Delta C_B = \beta_e \Delta pH \tag{154}$$

where

ΔC_B = the alkalinity or acidity error associated with the titration

β_e = the buffer capacity at the equivalence point

ΔpH = the error in pH units of the endpoint to the titration.

Thus, the error in the $H_2CO_3^*$ Alkalinity resulting from a titration endpoint error of ΔpH is determined by substituting for β_e from either Eq (151a) or Eq (151b) into Eq (154)

$$H_2CO_3^* \text{ Alk. error} = 4{,}606(C_T K''_{T1}).\Delta pH \tag{155a}$$

or

$$H_2CO_3^* \text{ Alk. error} = 4{,}606[H^+]_e.\Delta pH \tag{155b}$$

(b) HCO_3^- Equivalence Point Error

In the pH region of the HCO_3^- equivalence point the buffer equation, Eq (141), approximates to

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$$\beta = 2,303\ (\frac{C_T[H^+]}{K''_{T1}} + \frac{C_T K''_{T2}}{[H^+]}) \qquad (156)$$

At the HCO_3^- equivalence point $\delta\beta/\delta[H^+] = 0$. Differentiating Eq (156) with respect to $[H^+]$ and solving for $[H^+]_e$ gives

$$[H^+]_e = (K''_{T1} \cdot K''_{T2})^{\frac{1}{2}} \qquad (157)$$

Substituting for $[H^+]$ from Eq (157) into Eq (156) gives the buffer equation at the HCO_3^- equivalence point

$$\beta_e = 4,606\ C_T(K''_{T2}/K''_{T1})^{\frac{1}{2}} \qquad (158)$$

An equation for the HCO_3^- Alkalinity or Acidity error resulting from an endpoint titration error of ΔpH, is obtained by substituting for β_e from Eq (158) into Eq (159):

$$HCO_3^-\ \text{Alk. error} = 4,606\ C_T(K''_{T2}/K''_{T1})\ \Delta pH \qquad (159)$$

To calculate the titration error using Eqs (155a and 159) requires that both C_T and the apparent dissociation constants, K''_{T1} and K''_{T2}, are known initially. In practice an estimate of C_T can be made if two mass parameters are measured. For example, if both $H_2CO_3^*$ and HCO_3^- Alkalinity are measured, C_T can be calculated, i.e. C_T = $H_2CO_3^*$ Alkalinity - HCO_3^- Alkalinity. However, this estimate tends to be inaccurate because it is based on the difference between values for two experimentally measured parameters each with an associated end point error. A superior method of alkalinity and acidity measurement, without recourse to methods involving estimation of titration endpoints is by way of the Gran titration.

6.2.6 *Measurement of alkalinity and acidity using Gran Functions*

In order to bypass the problem of identifying a titration endpoint as outlined in the previous section, Gran (1952) developed titration functions such that a plot of the values for a particular

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function (i.e. for a particular titration) versus strong acid or base added, is linear; extrapolation of the linear plot to a function value equal to zero gives the net strong base (or acid) initially in the sample, i.e. the initial alkalinity (or acidity) present.

The titration functions developed by Gran are based on the finding that in the pH regions, above and below each equivalence point there exists a linear relationship between the increments of strong acid added and the corresponding increase in the hydrogen ion concentration. Consequently, for each equivalent point, two Gran functions can be formulated, one each for the titration above and below the particular equivalence point.

For the carbonate system six functions can be developed for the three equivalence points. However, those associated with the CO_3^{2-} equivalence point are of little value principally for the following three reasons. First, the titration is carried out in the high pH region where significant ion pairing occurs between OH^- and the cations Ca^{2+} and Mg^{2+}; if a significant degree of such ion pairing occurs, it is no longer possible to develop a simple Gran function linking $[H^+]$ to the incremental addition of strong acid (or base). Second, the possibility of hydroxide mineral precipitation is ever present; should such precipitation occur it will affect the accuracy of the titration. Finally, at the high pH values necessarily encountered in such titrations, carbon dioxide absorption from the air will introduce serious errors. For these reasons we will only consider those Gran functions associated with the $H_2CO_3^*$ and HCO_3^- equivalence points.

The Gran functions for alkalimetric and acidimetric titrations of a highly saline aqueous solution containing only the carbonate weak acid-base system are developed as follows: Let

V_I = initial volume of sample, mℓ

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v_x	= volume of standard strong acid added, mℓ
V_{CO_2}, V_{HCO_3}	= volume of standard strong acid required to titrate the sample to the $H_2CO_3^*$ or HCO_3^- equivalence points respectively
$\bar{C}_a$	= normality of standard strong acid in an aqueous solution with a background principal ionic matrix similar to that of the sample
Subscript 'x'	= value of a particular parameter *after* adding v_x mℓ of standard strong acid
Subscript 'i'	= value of a particular parameter initially, i.e. just before the titration is initiated.

(a) Gran functions for determining $H_2CO_3^*$ alkalinity

(i) Function for the titration in the pH region below the $H_2CO_3^*$ equivalence point: After adding v_x mℓ standard strong acid, in the region $3<pH_{ox}<4$ two expressions can be written down for the $H_2CO_3^*$ Alk_x. First, in terms of the volume of standard strong acid added,

$$H_2CO_3^*Alk_x = \frac{(V_{CO_2} - v_x)\,\bar{C}_a}{V_I + v_x} \tag{160}$$

Second, in terms of species concentrations; in the pH region under consideration $[H^+]_x >> [HCO_3]_{Tx} >> [CO_3]_{Tx}$ and $[OH]_{Tx}$ is negligible, so that Eq (92) approximates to

$$H_2CO_3^*Alk_x = -[H^+]_x \tag{161}$$

(Equation (161) is valid provided sulphates do not constitute a principal part of the ionic matrix; if sulphates are at a high concentration then the buffering effects of $HSO_4^- - SO_4^{2-}$ must also be considered, see later).

Equating Eqs (160 and 161) and rearranging terms

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$$[H^+]_x\ (V_I+v_x) = (v_x-V_{CO_2})\bar{C}_a \qquad (162)$$

and multiplying both sides of this equation by the operational activity coefficient for H^+, $\gamma_{H(o)}$, gives the first Gran function F_{1x}, i.e.

$$F_{1(x)} = 10^{-pH_{ox}}\ (V_I+v_x) \qquad (163a)$$

$$= (v_x-V_{CO_2})\bar{C}_a\ \gamma_{H(o)} \qquad (163b)$$

Substituting corresponding measured values for v_x and pH_{ox} into Eq (163a) gives a series of values for F_{1x}; a plot of F_{1x} versus v_x constitutes the first Gran titration. Differentiating Eq (163b) with respect to v_x indicates that the first Gran titration will be a linear plot with slope $+\ \bar{C}_a\ \gamma_{H(o)}$. Furthermore, from Eq (163b), $F_{1(x)}$ is zero where $v_x = V_{CO_2}$ so that a linear extrapolation of the plot gives V_{CO_2} where the plot intersects the v_x ordinate for $F_{1(x)} = 0$.

When sulphate comprises a principal part of the ionic matrix, the buffering effects of the HSO_4^--SO_4^{2-} system are significant in the region 3 pH_o 4, and Eq (161) should be written as

$$H_2CO_3^*Alk_x = -[H^+]_x - [HSO_4]_{Tx} \qquad (164)$$

This equation can be restructured in a way useful for formulating the Gran function equation as follows: For equilibrium between the stoichiometric molalities of SO_{4T} and HSO_{4T},

$$[H^+]_x[SO_4]_{Tx}/[HSO_4]_{Tx} = K''_{Ta} \qquad (165)$$

Solving for $[HSO_4]_{Tx}$ in Eq (165), substituting into Eq (164) and simplifying

$$H_2CO_3^*Alk_x = -[H^+]_x\ (1 + [SO_4]_{Tx}/K''_{Ta}) \qquad (166)$$

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Now, in the pH region $pH_o > 3$, $[SO_4]_{Tx} >> [HSO_4]_{Tx}$ so that $[SO_4]_{Tx} \cong$ total sulphate and the term in round brackets in Eq (166), (), is closely a constant, i.e.

$$k_s = (1 + [SO_4]_T/K''_{Ta}) \tag{167}$$

and

$$H_2CO_3^*Alk = -[H^+]_x\, k_s \tag{168}$$

Equating Eqs (168 and 163a) and proceeding in exactly the same fashion as before (for a water without sulphates) gives the Gran function for a water with sulphates as

$$F_{1(x)} = 10^{-pH_{ox}}(V_I + v_x)$$

$$= (v_x - V_{CO_2})\, \gamma_{H(o)} \bar{C}_a / k_s \tag{169}$$

In this case, the slope of the Gran plot equals $\gamma_{H(o)}/k_s$, and determination $\gamma_{H(o)}$ from the slope requires that k_s first be determined as set out in Section 3.4.

(ii) Function for the titration in the pH region between the $H_2CO_3^*$ and HCO_3^- equivalence points: After adding v_x mℓ of strong acid to a sample in the region $5,8 < pH_o < 6,6$, two equations can be written down for each $H_2CO_3^*$ Alkalinity and HCO_3^- Alkalinity; one equation each in terms of weak acid species concentrations and one each in terms of strong acid added to a sample.

For $H_2CO_3^*$ Alkalinity: $[HCO_3^-]_{Tx} >> [CO_3^{2-}]_{Tx}$ and both $[H^+]_x$ and $[OH]_{Tx}$ are negligible, i.e.

$$H_2CO_3^*Alk_x = \frac{(V_{CO_2} - v_x)}{V_I + v_x}\, \bar{C}_a \cong [HCO_3]_{Tx} \tag{170}$$

For HCO_3^- Alkalinity: $[H_2CO_3^*]_x >> [CO_3]_{Tx}$ and $[H^+]_x$ and $[OH^-]_x$

are negligible, i.e.

$$HCO_3Alk_x = \frac{(V_{HCO_3} - v_x)}{V_I + v_x} \bar{C}_a \cong [H_2CO_3^*]_x \qquad (171)$$

Dividing Eq (170) by Eq (171) and substituting for $[HCO_3]_T/[H_2CO_3^*]$ from Eq (58a) gives

$$\frac{(V_{CO_2} - v_x)}{(V_{HCO_3} - v_x)} = \frac{{}_oK'_{T1}}{(H^+)_{o(x)}}$$

and, rearranging terms in this equation gives the second Gran Function, F_2, for determining $H_2CO_3^*Alk$,

$$10^{pH_{ox}} (V_{HCO_3} - v_x) = \frac{1}{{}_oK'_{T1}} (V_{CO_2} - v_x)$$

i.e.

$$F_{2(x)} = 10^{pH_{ox}} (V_{HCO_3} - v_x) \qquad (172a)$$

$$= \frac{1}{{}_oK'_{T1}} (V_{CO_2} - v_x) \qquad (172b)$$

In this case (*provided V_{HCO_3} is known, see (b) below*) values for $F_{2(x)}$ are determined by substituting observed corresponding values for v_x and pH_{ox} into Eq (172a). Differentiating Eq (172b) with respect to v_x indicates a linear plot for v_x versus $F_{2(x)}$; also from Eq (172b), linear extrapolation of the plot to $F_{2(x)} = 0$ gives $v_x = V_{CO_2}$, from which $H_2CO_3^*Alk$ can be determined, i.e.

$$H_2CO_3^*Alk = V_{CO_2} \cdot \bar{C}_a / V_I$$

This determination is not affected by sulphates present because the pH region is outside that where the SO_4-HSO_4 buffer system is significant.

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(b) Gran functions for determing HCO_3^- Alkalinity

(i) Function for the titration in the pH region below the HCO_3^- equivalence point:

The Gran function F_3 for determining the HCO_3^- Alkalinity is formulated in a fashion similar to that for F_2 for $H_2CO_3^*$ Alkalinity in Subsection (a)(ii) above, except that whereas in the previous example it was assumed that V_{HCO_3} is known, here it is assumed that V_{CO_2} is known, i.e. from Eqs (172a and 172b)

$$F_{3x} = 10^{-pH_{ox}} (V_{CO_2} - v_x) \qquad (173a)$$

$$= {}_oK'_{T1} (V_{HCO_3} - v_x) \qquad (173b)$$

Provided V_{CO_2} is known (or has been determined) it is possible to determine V_{HCO_3} (and hence the HCO_3^- Alk) as follows: Values for F_{3x} are determined by substituting corresponding observed data for pH_{ox} and v_x into Eq (173a). Differentiating Eq (173b) with respect to v_x indicates a linear plot for v_x versus $F_{3(x)}$ with slope $-{}_oK'_{T1}$; also, from Eq (173b) linear extrapolation of the plot to $F_3 = 0$ gives $V_{HCO_3} = v_x$. HCO_3 Alkalinity is then determined as

$$HCO_3Alk = V_{HCO_3} . \bar{C}_a / V_I$$

(ii) Function for the titration in the pH region above the HCO_3 equivalence point: As a check on the HCO_3 Alkalinity value determined in Subsection (b)(i) above, a fourth Gran function can be developed in the pH region above the HCO_3^- equivalence point. As in Subsection (b)(ii) above, two equations can be written down for each $H_2CO_3^*$ Alkalinity and HCO_3 Alkalinity: For $H_2CO_3^*$ Alkalinity, in the pH region of interest both

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$[HCO_3]_{Tx}$ and $[CO_3]_{Tx}$ contribute significantly to this alkalinity, whereas both $[H^+]_x$ and $[OH]_{Tx}$ are negligible, i.e.

$$H_2CO_3^*Alk_x = \frac{(V_{CO_2} - v_x)\bar{C}_a}{V_I + v_x} \cong [HCO_3]_{Tx} + 2[CO_3]_{Tx} \qquad (174)$$

For HCO_3 Alkalinity, compared with $[CO_3]_{Tx}$ the values for $[H^+]_x$, $[OH]_{Tx}$ and $[H_2CO_3]_x$ are all negligible, i.e.

$$HCO_3Alk_x \cong [CO_3]_{Tx} = \frac{(V_{HCO_3} - v_x)}{V_I + v_x}\,\bar{C}_a \qquad (175)$$

Dividing Eq (174) by Eq (175), substituting for $[HCO_3]_{Tx}/[CO_3]_{Tx}$ from Eq (58b) and rearranging terms gives the fourth Gran function, $F_{4(x)}$, as

$$F_{4(x)} = 10^{pH_{o(x)}}\,(V_{CO_2} - 2V_{HCO_3} + v_x) \qquad (176a)$$

$$= \frac{1}{{}_oK'_{T2}}\,(V_{HCO_3} - v_x) \qquad (176b)$$

Substituting values for V_{CO_2} and V_{HCO_3} determined from subsections (a)(ii) and (b)(i) respectively above into Eq (176a), and also for observed data for corresponding values of $pH_{o(x)}$ and v_x gives a series of values of $F_{4(x)}$ versus v_x. A plot of $F_{4(x)}$ versus v_x constitutes the fourth Gran titration. Differentiating Eq (187b) with respect to v_x indicates that the plot will be linear with slope $1/{}_oK'_{T2}$, and, linear extrapolation of this plot to F_{4x} equal to zero gives $V_{HCO_3} = v_x$.

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PHASE EQUILIBRIA

1. INTRODUCTION

Changes in the constitution of a water may arise either through artificial or natural means.

Artificial conditioning of water is a usual practice in water supplies to big cities and may involve softening of the water by precipitating calcium and magnesium or changing the pH, Alkalinity and calcium concentration to values that are acceptable in a potable water and minimize corrosion problems.

In artificial conditioning of high salinity waters, the objective is usually to minimize undesirable precipitation of minerals by adjusting pH and Alkalinity and calcium and magnesium concentrations.

For example, in the flash distillation process for desalination, precipitation takes place of calcium salts from the circulating water in the cooling system on the inside of the pipes carrying the cooling water. The scale acts as a thermal insulator reducing the efficiency of cooling. In electrodialysis and other processes making use of ion selective membranes, precipitation of minerals onto and within the membrane is often a problem.

Conditioning of waters by natural agencies takes place in rivers, water impoundments (both surface and underground reservoirs) and in the oceans. Examples are CO_2 exchange between water bodies and atmosphere, dissolution of minerals from a solid phase in contact with the water and abstraction of minerals from the water by precipitation.

Problems in chemical conditioning of waters can be subdivided, depending on whether the dissolved species' concentrations are established by *equilibrium* between (a) only species in the dissolved phase, (b) species in the dissolved and gas phases, (c) species in the dissolved and solid phases, and (d) species in the dissolved, gas and solid phases.

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(a) Equilibrium between Species in the Aqueous Phase

Conditioning problems involving equilibrium *only* between species in the aqueous phase usually arise under the following conditions: when a chemical dose is added to a water equilibrium between *dissolved species* (for example between H^+, $H_2CO_3^*$, HCO_3^-, and $CO_3^=$) is attained in a matter of milli-seconds. The new equilibrium between the dissolved species is reflected by the pH established. This new condition may be one of disequilibrium between species in the various phases. For example, after dosing the water may be supersaturated with respect to the solid phase $CaCO_3$. However, because the rate to attain equilibrium between phases is so very much slower than the rate to attain aqueous phase equilibrium, the aqueous phase equilibrium established at any time is independent of the solubility products with respect to any mineral. This situation is quite normal in stabilization of water supplies where the water is discharged in a slightly supersaturated state with respect to one or more minerals of calcium carbonate and precipitation occurs over the period of time that the water is in the reticulation system.

Addition of chemicals may also cause a disequilibrium between the aqueous and gas phases. In the example above, after chemical addition the partial pressure of CO_2 in the water may be greater or less than that in the gas phase. Single aqueous phase analyses will still apply in the water if the possibilities for gas exchange are negligible.

(b) Equilibrium between Species in the Aqueous and Gas Phases

Carbon dioxide either enters or leaves a water in contact with a gas phase, depending on the relative partial pressures of CO_2 in the two phases. The rate of CO_2 transfer across the gas-liquid interface depends on surface area of the water exposed to air, the degree of turbulence in the water and the difference in the CO_2 partial pressures between the water surface and the gas phase. Conditioning problems involving equilibrium between CO_2 in the aqueous and gas phases can be generally divided into two classes:

(i) Change in CO_2 Partial Pressure in the Gas Phase:
A water is in equilibrium with CO_2 in the gas phase. The partial pressure of CO_2 in the gas phase now changes, and it is necessary to determine the new equilibrium state of the water and the mass concentration of CO_2 exchanged between the two phases.
This problem often arises when water is pumped from underground.

(ii) Change in CO_2 Partial Pressure in the Aqueous Phase:
The partial pressure of CO_2 in the gas phase remains constant and a change in the equilibrium state of the water is brought about by chemical addition causing disequilibrium between the two phases. It is necessary to determine the final state of the water after equilibrium between the gas and aqueous phases is again re-established.
This problem could arise in water bodies open to the atmosphere where the CO_2 partial pressure is changed due to biological action, say photosynthesis.

In order to obtain solutions in both these classes of problems the minerals are considered to be infinitely soluble.

(c) Equilibrium between Species in the Aqueous and Solid Phases

This situation can be visualized as occurring where chemicals such as CO_2 or $Ca(OH)_2$ are added to a water to cause either dissolution from a solid phase in contact with the water or precipitation of the solid phase but with no exchange between the gas and liquid phases. For example, when CO_2 is the conditioning chemical, once the dose has been added, no further exchange between the gas and aqueous phases is allowed. The point of interest is the final saturated constitution of the water with respect to the precipitation mineral.

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Situations where this type of problem have relevance occur in water softening where it may be required to determine chemical dosing to reduce calcium and magnesium concentrations to desired values. In the short period over which conditioning occurs, exchange of CO_2 with the air usually can be ignored. In order to attain as rapid equilibrium with the solid phase as possible, a large surface area of the solid phase in contact with the water needs to be provided, for example by adding powdered $CaCO_3$. The added material forms the nucleus for precipitation, although the precipitant may not be pure calcium carbonate.

(d) Equilibrium between Species in the Aqueous, Solid and Gas Phases

Problems involving equilibrium between these three phases occur where a water is in contact with both a solid carbonate mineral and a gas phase. On addition of chemicals to a water in three phase equilibrium a condition of dis-equilibrium is immediately created with respect to both the gaseous and solid phases. The *immediate* change in state of the water (e.g. in pH and saturation states) is governed only by reactions within the aqueous phase. However, in time the water re-attains equilibrium with both the gaseous and solid phases.

The combined effects of CO_2 exchange and solid phase precipitation (or dissolution) are always to reduce the magnitude of the initially observed changes. In this respect these phase exchange phenomena act as a type of buffer which in time ameliorates the magnitude of change in pH and saturation due to chemical addition.

For example, addition of lime to a $CaCO_3$ saturated water causes an immediate increase in pH and $CaCO_3$ supersaturation. As $CaCO_3$ precipitation occurs from the supersaturated water the pH drops, thereby reducing the final pH change.

The analysis of any of these problems using the algebraic form of the equilibrium theory is extremely complex, particularly when

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ion-pairing effects are included. However, the graphical procedures developed in this monograph allow solution to be obtained simply and rapidly. The remainder of this chapter will deal with the establishment of various forms of conditioning diagrams and their use in solving problems.

2. CONCENTRATION AND MEASUREMENT UNITS

In low salinity waters, for water treatment a concentration scale widely used is the $CaCO_3$ equivalent scale; all the diagrams presented by Loewenthal and Marais (1976) for example are plotted in terms of this scale. The high salinity plots similarly could have been set out in terms of this scale but it was decided against this for it would go contrary to the recommendation of the IUPAC.

Normally the chemical analyses of a water, including Alkalinity and Acidity, will be in terms of stoichiometric molar quantities; chemical dosages similarly are estimated on the molar scale. In contrast, for basic research the molal scale has been the most convenient one, and all the research investigations into high salinity waters discussed in this presentation have been in terms of this scale. To accommodate the needs of the practicing chemist (as against those of the research chemist), in developing the computer programs to plot the various conditioning diagrams the inputs are all in terms of molar quantities. To calculate the activity coefficients of species as demanded in terms of the molar scale, it is necessary first to convert the input quantities to molal units, calculate the molal activity coefficients and then convert these activity coefficients to be on the molar scale. This applies to both the principal and trace species. The equilibrium relationships defining the carbonate system remain the same on both the molal and molar scales except the values of the equilibrium constants will differ between the two scales.

Conversion of activity coefficients and concentrations from the molal to the molar scale, and vice versa, has been set out in detail

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in Section 4.1, Chapter 2. Adjustment of the equilibrium constants from the values at infinite dilution to the apparent values (on the molar scale) is identical to that set out in Section 4.2.4, Chapter 4 for apparent constants on the molar scale except that the activity coefficients used in the conversions are now all on the molar scale. For example, for the apparent first dissociation constant of the carbonate weak acid-base system, K_1', on the molal scale

$$K_1' = K_1 \gamma_{CO_2} \cdot \gamma_w / \gamma_{HCO_3}$$

and, on the molar scale

$$K_1' = K_1 f_{CO_2} f_w / f_{HCO_3}$$

where γ_x = activity coefficient of species x on the molal scale

f_x = activity coefficient of species x on the molar scale

K_1 has the same value on both scales as it is the value at infinite dilution.

3. MASS PARAMETERS AND CHEMICAL DOSING

Generally $H_2CO_3^*$ Alkalinity (usually called Alkalinity) and observed pH (pH_o) are the weak acid-base parameters most conveniently measured and hence usually employed to define the state of a water at a particular temperature, pressure and ionic strength. Because CO_3^{2-} Acidity (usually called Acidity) like Alkalinity changes in a straight forward manner with chemical dosing, even though it cannot be measured accurately, it serves as an important ancillary parameter in conjunction with Alkalinity and true pH (pH) or observed pH (pH_o) to solve conditioning problems in the aqueous phase using the equilibrium approach. If pH (or pH_o) and Alkalinity measurements are available, Acidity always can be calculated via equilibrium equations using the appropriate equilibrium constants. Should a chemical now be added, the new Alkalinity and Acidity can be calculated by adding the changes in Alkalinity and Acidity (due to dosing)

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to the initial Alkalinity and Acidity values in the water. From these new values, the new pH (or pH_o) can be calculated using the equilibrium equations. These steps constitute the general pattern of solution for most types of chemical conditioning problems considering the aeueous phase.

The mass parameters Alkalinity and Acidity (and hence the total weak acid-base species concentration) are conservative quantities and change in a straightforward manner with chemical addition. For low salinity water the conservative aspect has been set out by Loewenthal and Marais (1976). In high salinity water where ion-pairing is significant the conservative aspect is not so clear and it is necessary to establish the conservative nature of the various forms of alkalinity and acidity.

In the low salinity approach, the respective changes in the mass parameters with chemical dosing are expressed as follows:

$$H_2CO_3^* \text{ Alk increase} = 2[CO_3^=]_{added} + [HCO_3^-]_{added} + [OH^-]_{added} - [H^+]_{added} \tag{1}$$

$$H_2CO_3^* \text{ Acidity change} = -H_2CO_3^* \text{ Alkalinity increase} \tag{2}$$

$$HCO_3^- \text{ Alk increase} = [HCO_3^-]_{added} + [OH^-]_{added} - [H^+]_{added} - [H_2CO_3^*]_{added} \tag{3}$$

$$HCO_3^- \text{ Acidity change} = -HCO_3^- \text{ Alkalinity increase} \tag{4}$$

$$CO_3^= \text{ Alk increase} = [OH^-]_{added} - [H^+]_{added} - [HCO_3^-]_{added} - 2[H_2CO_3^*]_{added} \tag{5}$$

$$CO_3^= \text{ Acidity change} = -CO_3^= \text{ Alkalinity increase} \tag{6}$$

$$C_t \text{ increase} = [CO_3^=]_{added} + [HCO_3^-]_{added} + [H_2CO_3^*]_{added} \tag{7}$$

The change in the total carbonate species concentration, ΔC_T, is directly given by the sum of all the carbonate species added

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irrespective of the proton condition the species assume in solution. Therefore Eq. (7) can be accepted as applicable to high or low salinity waters. With regard to changes in alkalinity and acidity parameters, the mass parameter considered is a net strong acid or base. The effects of addition of carbonate species on the net strong acid or base parameters are not immediately obvious. To establish the validity of Eqs. (1 to 6) in water where ion-pairing is significant, the effects of addition to water of CO_2, HCO_3^- and $CO_3^=$ must be examined.

(a) HCO_3^- Addition

X moles of $NaHCO_3$ is added to a high salinity water.

A proton balance equation for the *changes* in the various species concentrations on addition of HCO_3^- to highly saline water was developed in Eq.(86), Chapter 4, giving

$$\Delta[H_2CO_3^*] + \Delta[H^+] = \Delta[CO_3]_T + \Delta[OH]_T \qquad (8)$$

The change in the total carbonate species concentration, C_T, with chemical addition is given by Eq. (7), i.e.

$$C_T \text{ increase} = [HCO_3^-]_{added} = [Na^+]_{added}$$

or

$$[Na^+]_{added} = \Delta[CO_3]_T + \Delta[HCO_3]_T + \Delta[H_2CO_3^*] \qquad (9)$$

The changes in the values for the various forms of alkalinity and acidity are now determined using Eqs. (8 and 9).

(i) Changes in $H_2CO_3^*$ Alkalinity and $H_2CO_3^*$ Acidity:

Substituting for $\Delta[H_2CO_3^*]$ from Eq. (8) into Eq. (9) gives

$$[Na^+]_{added} = 2\Delta[CO_3]_T + \Delta[HCO_3]_T + \Delta[OH]_T - \Delta[H^+]$$

$$= \Delta\{2[CO_3]_T + [HCO_3]_T + [OH]_T - [H^+]\}$$

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i.e.

$$[Na^+]_{added} = \Delta H_2CO_3^* \text{ Alkalinity} \qquad (10)$$

and noting that $[Na^+]_{added} = [HCO_3^-]_{added}$

$[HCO_3^-]_{added} = \Delta H_2CO_3^*$ Alkalinity, which is the required equation.

(ii) Changes in $CO_3^=$ Alkalinity and $CO_3^=$ Acidity:

Substituting for $\Delta[CO_3]_T$ from Eq. (8) into Eq. (9) gives

$$\begin{aligned}[Na^+]_{added} &= 2\Delta[H_2CO_3^*] + \Delta[HCO_3]_T + [H^+] - [OH]_T \\ &= \Delta CO_3^= \text{ Acidity}\end{aligned}$$

i.e.

$$[HCO_3^=]_{added} = \Delta CO_3^= \text{ Acidity.}$$

(iii) Changes in HCO_3^- Alkalinity and HCO_3^- Acidity:

From Eq. (6), Chapter 3

$$\Delta C_T = \Delta H_2CO_3^* \text{ Alkalinity} - \Delta HCO_3 \text{ Alkalinity.}$$

Rearranging this equation:

$$\Delta HCO_3^- \text{ Alkalinity} = \Delta H_2CO_3^* \text{ Alkalinity} - \Delta C_T \qquad (11)$$

From Eqs. (7 and 10)

$$[Na^+]_{added} = \Delta C_T = \Delta H_2CO_3^* \text{ Alkalinity} \qquad (12)$$

Thus, from Eqs. (11 and 12)

$$\Delta HCO_3^- \text{ Alkalinity} = 0.$$

(b) $CO_3^=$ Addition

X moles/ℓ of Na_2CO_3 is added to a high salinity water.

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A proton balance equation for $CO_3^=$ addition to water was developed in Eq. (98), Chapter 4, giving

$$\Delta[OH]_T = \Delta[HCO_3]_T + 2\Delta[H_2CO_3^*] + \Delta[H^+] \qquad (13)$$

and from Eq. (7)

$$C_T \text{ increase} = [CO_3^=]_{added}$$

or

$$[Na^+]_{added}/2 = \Delta[CO_3]_T + \Delta[HCO_3]_T + \Delta[H_2CO_3^*] \qquad (14)$$

(i) Changes in $H_2CO_3^*$ Alkalinity and $H_2CO_3^*$ Acidity:

Substituting for $\Delta[H_2CO_3^*]$ from Eq. (13) into Eq. (14) and simplifying

$$[CO_3^=]_{added} = \Delta[CO_3]_T + \Delta[HCO_3]_T/2 + \Delta[OH]_T/2 - \Delta[H^+]/2$$

$$= \Delta H_2CO_3^* \text{ Alkalinity}/2 \qquad (15)$$

or, the change in $H_2CO_3^*$ Alkalinity, $\Delta H_2CO_3^*$ Alkalinity, equals twice the moles of $CO_3^=$ added.

(ii) Changes in HCO_3^- Alkalinity and HCO_3^- Acidity:

Substituting for $\Delta[HCO_3]_T$ from Eq. (13) into Eq. (14) and simplifying

$$[CO_3^=]_{added} = \Delta[CO_3]_T + \Delta[OH]_T - \Delta[H_2CO_3^*] - \Delta[H^+]$$

or

$$[CO_3^=]_{added} = \Delta HCO_3^- \text{ Alkalinity}.$$

(iii) Changes in $CO_3^=$ Alkalinity and $CO_3^=$ Acidity:

From Eq. (59), Chapter 3

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$2\Delta C_T = \Delta H_2CO_3^*$ Alkalinity + $\Delta CO_3^=$ Acidity

and rearranging this equation

$\Delta CO_3^=$ Acidity = $2\Delta C_T - \Delta H_2CO_3^*$ Alkalinity (16)

From Eq. (13)

$2\Delta C_T = 2[CO_3^=]_{added}$

and from Eq. (15)

$\Delta H_2CO_3^*$ Alkalinity = $2[CO_3^=]_{added}$

Substituting into Eq. (16) gives

$\Delta CO_3^=$ Acidity = 0.

(c) CO_2 Addition

The effects of addition of CO_2 to high salinity water on the various forms of alkalinity and acidity can be derived using the same methods outlined above for HCO_3^- addition and $CO_3^=$ addition giving

$\Delta H_2CO_3^*$ Alkalinity = 0

ΔHCO_3^- Alkalinity = $-[CO_2]_{added}$

$\Delta CO_3^=$ Alkalinity = $-2[CO_2]_{added}$

4. SINGLE PHASE EQUILIBRIUM DIAGRAM

The single phase equilibrium model considers only changes between carbonate species in the aqueous phase due to chemical addition. The model is based on the assumption that there is no mineral precipitation nor dissolution, and no CO_2 exchange between the water and the gas phase (air).

In Chapter 4 it was shown that provided at least two of the

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parameters of the carbonate system are measured (in addition to the total concentrations of species which form ion-pairs in solution, e.g. $SO_4^=$, Na^+, Mg^{++} and Ca^{++}), the remaining parameters can be calculated using equilibrium and mass balance relationships. Generally, $H_2CO_3^*$ Alkalinity (normally expressed by the term Alkalinity) and pH are the two parameters most conveniently measured and hence are usually employed to define the state of a water at a particular temperature, pressure and ionic strength. Because $CO_3^=$ Acidity (or simply Acidity) changes in a straightforward manner with chemical dosing, even though it cannot be readily measured, it serves as an important ancillary parameter in conjunction with the measured parameters Alkalinity and pH[†] to solve conditioning problems by equilibrium methods: If pH_o[†] and Alkalinity of a water are measured, Acidity always can be calculated using the equilibrium equations; should a chemical now be added to the water the new Alkalinity and Acidity values are calculated using Eqs. (1 and 5). From the new values of Alkalinity and Acidity, using the equilibrium equations, the new pH_o can be calculated. These steps constitute the general pattern of solution to most types of water conditioning problems.

Calculations required in carrying out the above solution procedure are impractical without graphical aids. In low salinity waters Loewenthal and Marais (1976) showed that aqueous phase conditioning problems can be quickly and simply solved with the aid of equilibrium conditioning diagrams. These diagrams have Alkalinity and Acidity as cartesian co-ordinates with a family of curves representing pH values plotted in the diagram using equilibrium and mass balance equations. Each diagram is for a water with a particular ionic strength and temperature and can be plotted by means of a digital computer.

[†] In this chapter the same terminology will be used as that in the previous chapter, i.e. pH is linked to the true hydrogen ion activity, and pH_o is linked to the operational hydrogen ion activity.

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For high salinity waters a similar form of single phase equilibrium diagram can be generated. However, because of the significance of ion-pairing in these waters, each diagram is unique to a water with a particular ionic constitution and temperature.

The interdependence between the mass parameters in high salinity waters has been graphically illustrated in Figure 12, Chapter 4. As shown earlier in this chapter these mass parameters are conservative, so that the interdependence is independent of ion-pairing, temperature and ionic strength. One can now superimpose a family of curves representing pH on this diagram. However, because pH is a function of the equilibrium equations (including ion-pairs), the pH lines are unique to a water with a particular ionic constitution and temperature. As an example, in Figure 1 are plotted lines representing pH in a diagram with Alkalinity ($H_2CO_3^*$ Alk) and Acidity ($CO_3^=$ Acidity) as co-ordinate parameters for water with the principal ionic species of seawater at 25°C.*

Development of the theoretical relationships linking Alkalinity, Acidity and pH for plotting pH lines in the aqueous phase equilibrium diagram can be approached in two ways:

(i) The equilibrium equations are utilized directly (including ion-pairing relationships). This approach, although basic, is relatively complex.

(ii) The equilibrium equation in terms of the apparent equilibrium constants, K_T' (see Chapter 4) are utilized.

In the second approach the fundamental relationships are reduced to those involving only H^+ and total weak acid species concentrations. Instead of having to solve approximately twenty four non-linear simultaneous equations for *each* calculated pH point in the diagram (as required in the first approach), in the second approach K_T' values are calculated by a simple iteration process

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*Included is the relationship for calculating pH from observed pH_0, as determined from the first Gran titration, see Section 3.3 Chapter 4.

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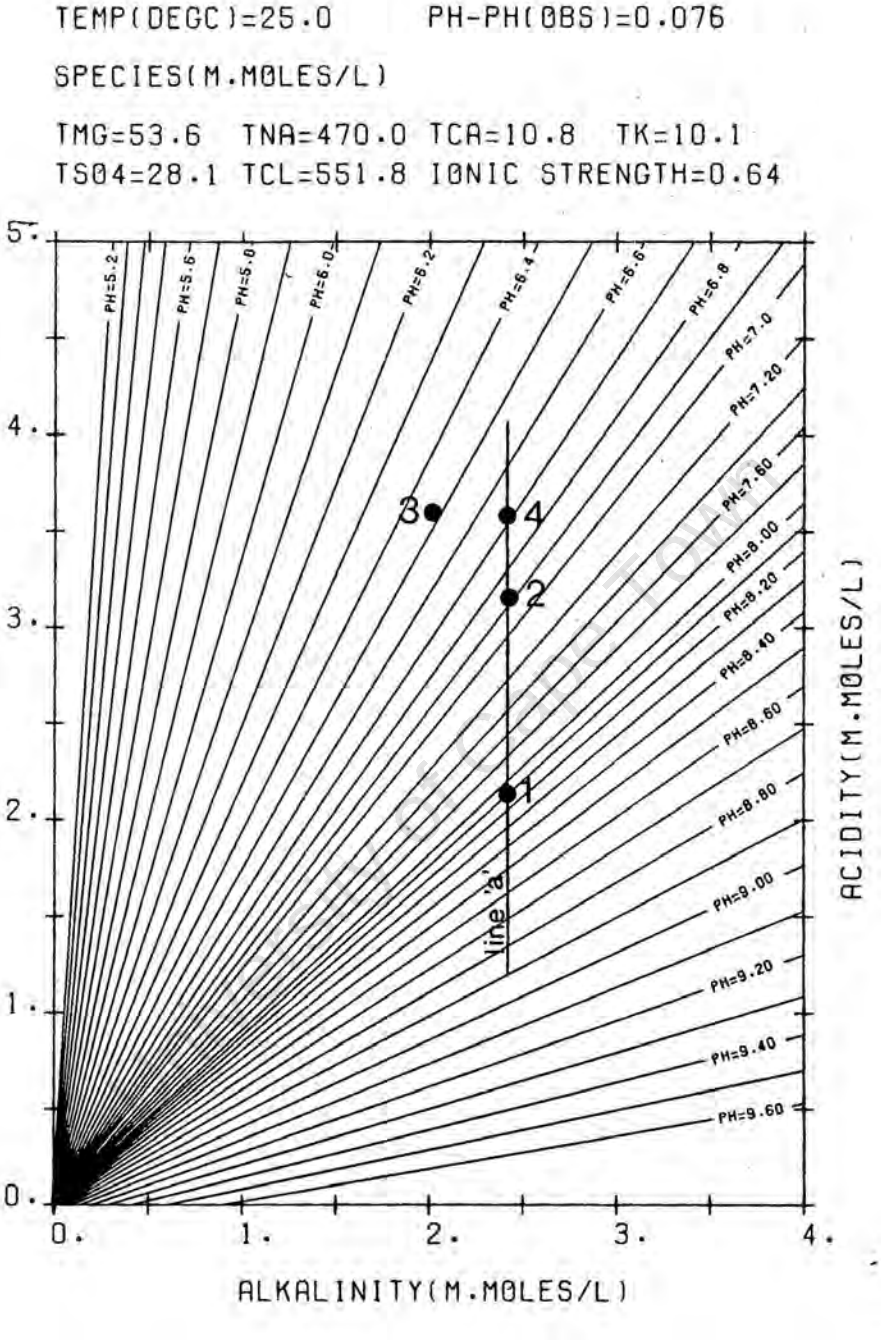

Figure 1. Single aqueous phase conditioning diagram for seawater at 25°C and 1 Atm. total pressure (Note: family of lines represent pH not pH_o).

(see Chapter 4) and pH points are calculated using only five equilibrium and mass balance equations (see below). The second approach is quite general and leads to a significant reduction in complexity and computer time.

Using the second approach, from Eqs.(57a and 57b), Chapter 4, at any particular pH:

$$[H_2CO_3^*] = (H^+)[HCO_3]_T/K'_{T1} \tag{17}$$

and

$$[CO_3]_T = K'_{T2}[HCO_3]_T/(H^+) \tag{18}$$

where K'_{T1} and K'_{T2} are apparent equilibrium constants the values of which depend on temperature, ionic strength and the degree of ion-pairing of the cations Ca^{++}, Mg^{++} and Na^+ (as shown in Eqs. (81 and 82), Chapter 4).

Substituting Eq. (17) into the equation for Acidity and simplifying gives

$$[HCO_3]_T = \frac{\text{Acidity} - [H^+] + [OH]_T}{1 + 2(H^+)/K'_{T1}} \tag{19}$$

Substituting Eq. (18) into the equation for Alkalinity gives

$$[HCO_3]_T = \frac{\text{Alkalinity} - [OH]_T + [H^+]}{1 + 2K'_{T2}/(H^+)} \tag{20}$$

Equating Eqs. (19 and 20) and simplifying gives

$$\text{Acidity} = Y.\text{Alkalinity} + (Y + 1)([H^+] - [OH]_T) \tag{21}$$

where $Y = \{1 + 2(H^+)/K'_{T1})/(1 + 2K'_{T2}/(H^+).\}$

Equation (21) is the desired equation linking (H^+) (or pH) to Alkalinity and Acidity for water with specified constant values for the *total* concentrations of calcium, magnesium, sodium, sulphate and other ions, and temperature.

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A computer program printout is listed in Supplement C for plotting the pH-Alkalinity-Acidity equilibrium diagram for the carbonate system in a high salinity water at any selected temperature. Ionic strength can either be read in directly, or it is calculated from input data for the total concentrations of principal ions, Alkalinity and pH.

4.1 Applications of Aqueous Phase Equilibrium Diagrams

Applications of the single phase Alkalinity-Acidity-pH diagram for the carbonate system has been extensively discussed by Loewenthal and Marais for low salinity waters. In high salinity waters the diagram can be utilized in almost identical fashion as with low salinity waters for solving similar types of problems. In highly saline water however, there may be two or more weak acid-base systems present. For example, seawater contains both the carbonate and borate systems. In such cases the solution procedures are still straightforward provided single phase equilibrium diagrams are available for both systems.

We shall consider the application of the aqueous phase diagram to water containing only the carbonate weak acid system. Thereafter applications to waters containing two or more weak acid systems, in particular the carbonate and borate systems in seawater, is possible using the basic theory developed here.

4.2 Carbonate System

Problems in high salinity waters in which the single phase equilibrium diagram can be used to obtain solutions can be classified as follows:

(a) Chemical dosing problems

(b) Blending problems

(c) Prediction of pH titration curves

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Solutions to these types of problems are discussed below by means of examples. The examples selected are those which bring out the principal features of chemical conditioning for the aqueous phase.

(a) Chemical Dosing Problems:

Example

Analyses of a water gives total species concentrations for calcium, magnesium, sodium and sulphate equal to those for seawater, i.e. 10,04, 54,0, 480,0 and 28,0 (all in m.moles/ℓ); Alkalinity 2,40 m.moles/ℓ, pH 8,1, $\mu = 0,7$ and temperature 25°C.

Using the single phase equilibrium diagram, Figure 1, predict Alkalinity, Acidity, C_T, pH and pH_o of the water after sequentially adding

(1) 0,5 m.moles/ℓ of CO_2

(2) 0,4 m.moles/ℓ of HCl

(3) 0,2 m.moles/ℓ of Na_2CO_3.

(1) Initial state of the water plots at Point 1 in Figure 1. The vertical ordinate value of Point 1 gives the initial Acidity in the water, i.e. Acidity 2,18 m.moles/ℓ. Referring to Eqs. (1, 5 and 6): addition of 0,5 m.moles/ℓ of CO_2 increases Acidity by 1 m.mole/ℓ and has no effect on Alkalinity, i.e.

New Alkalinity = 2,40 + 0 = 2,40 m.moles/ℓ

New Acidity = 2,18 + 1,0 = 3,18 m.moles/ℓ.

These two values plot at Point 2 in Figure 1, i.e. the new pH value is pH 6,88, and $pH_o = 6,88 - 0,08 = 6,80$.

(2) Referring to Eqs. (1,5 and 6): addition of 0,4 m.moles/ℓ of HCl increases Acidity by 0,4 m.moles/ℓ and decreases Alkalinity by 0,4 m.moles/ℓ, i.e.

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New Alkalinity = 2,40 - 0,4 = 2,00 m.moles/ℓ

New Acidity = 3,18 + 0,4 = 3,58 m.moles/ℓ.

These two values plot at Point 3 in Figure 1, i.e. the new pH value is pH 6,48, and pH_o = 6,48 - 0,08 = 6,40.

(3) Referring to Eqs. (1,5 and 6): addition of 0,2 m.moles/ℓ of Na_2CO_3 has no effect on Acidity and increases Alkalinity by (2.0,2) = 0,4 m.moles/ℓ, i.e.

New Alkalinity = 2,00 + 0,4 = 2,4 = 2,40 m.moles/ℓ

New Acidity = 3,58 + 0 = 3,58 m.moles/ℓ.

These two values plot at Point 4 in Figure 1, i.e. the new pH value is pH 6,69, and pH_o = 6,19 - 0,08 = 6,61.

(b) Blending Problems

Example

A blend is prepared by mixing equal parts by volume of a high salinity water (the constitution of which is given in part (a) above) and a soft surface water. Determine pH of the blend. Analyses of the soft water gives Alkalinity 1,00 m.moles/ℓ, pH 6,65, μ = 0,005 and temperature 25°C.

To solve this blending problem graphically, single phase equilibrium diagrams must be plotted for each water (see Figures 1 and 2 for the high and low salinity waters respectively). To plot an equilibrium chart for the blend, the concentrations of those ions forming appreciable ion-pair species in solution must first be determined from the proportions of the waters in the blend. Considering the concentrations of these ions as negligible in the soft water (compared with the concentrations in the highly saline water), the concentrations of sodium, magnesium, calcium and sulphate in the blend are determined only from the fractional contribution of the highly saline water, i.e.

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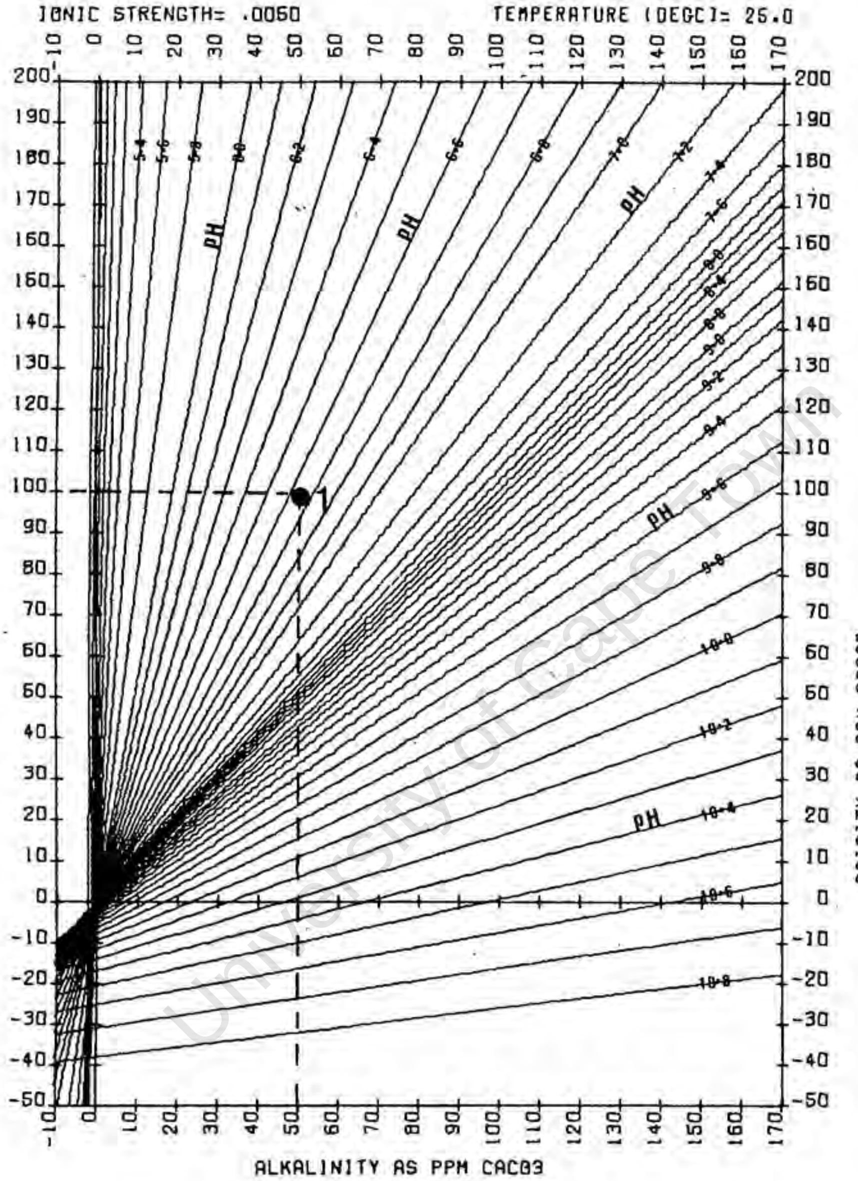

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Figure 2. Single aqueous phase conditioning chart for low salinity water, Alkalinity = 1,0 m.moles/ℓ and pH 6,65.

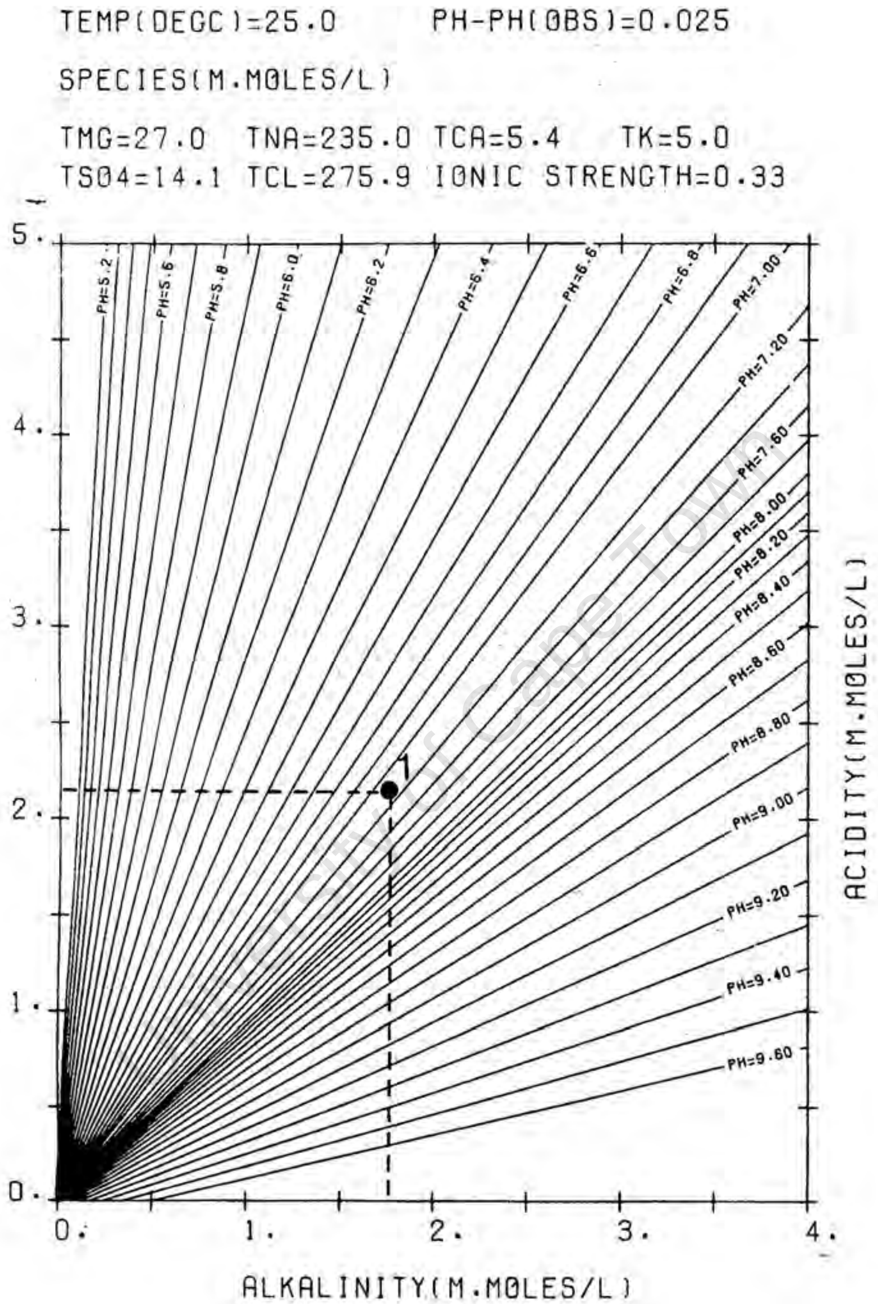

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Figure 3. Single aqueous phase conditioning diagram for seawater and low salinity water mixed 1:1 by volume.

$[Ca]_T = 10,04/2 = 5,02$ m.moles/ℓ

$[Mg]_T = 54,0/2 = 27,0$ m.moles/ℓ

$[SO_4]_T = 28,0/2 = 14,0$ m.moles/ℓ

$[Na]_T = 480,0/2 = 240,0$ m.moles/ℓ

If the ionic constitution of each water is known completely, the ionic strength of the blend can be calculated. Otherwise, ionic strength is estimated from the fractional contributions of each water. The pH of the blend is then determined as follows:

Acidity of high salinity water = 2,18 m.moles/ℓ (i.e. Acidity of Point 1 in Figure 1)

Acidity of low salinity water = 2,00 m.moles/ℓ (i.e. Acidity of Point 1 in Figure 2).

Alkalinity of blend = (2,40 + 1,00)/2 = 1,7 m.moles/ℓ

Acidity of blend = (2,18 + 2,00)/2 = 2,09 m.moles/ℓ

Referring to Figure 3: Lines representing Alkalinity and Acidity of the blend intersect at Point 1. The value of the pH line through this point gives the pH of the blend, pH = 7,10 and pH_o = 7,10 - 0,03 = 6,97.

(c) Prediction of pH Titration Curves:

By means of the aqueous equilibrium diagrams the theoretical titration curves can be predicted for addition of any of the following dosing chemicals: strong acid or base or carbonate species in the form of CO_2, HCO_3 and $CO_3^=$. These curves provide a rapid assessment of the pH response of a system to chemical dosing by either natural or artificial means.

Example

Biological action in the water given in (a) above causes CO_2 to be released into the water. Plot the theoretical curve of pH response as CO_2 is incrementally added to the water. Assume there is no CO_2 exchange with the gas phase.

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A single phase equilibrium diagram for the water is shown in Figure 1. The initial condition of the water plots at Point 1 in this diagram.

When CO_2 is added to the water, the changes in Alkalinity and Acidity are as follows:

From Eq. (2),

Alkalinity change = 0

From Eq. (5),

Acidity change = $2[CO_2]$ added.

Thus the change in state of the water is traced out along the constant Alkalinity line, Line A, in Figure 1. Intersection point of a line representing a particular pH value with Line A gives the new condition of the water after CO_2 dosing; the Acidity ordinate value of this point gives the new Acidity of the water.

The total change in Acidity gives twice the molar mass concentration of CO_2 required to effect the pH change as given by Eq.(5) i.e. ΔCO_2 = 2.Acidity moles/ℓ. Repeating this procedure for a number of decreasing pH values provides the data to plot the required titration curve (see Figure 4).

A note of caution: the titration curve as obtained here has inherent in it the assumption that the sample volume is not affected by addition of the titrant, i.e. the ionic strength of the sample is unaffected. If a relatively large volume of titrant is added in the titration of a high salinity water, the ionic strength of the sample may change significantly as the titration progresses. In this event, the dilution water used in making up the titrant should have a major ionic constitution similar to that for the high salinity water sample (Dyrssen and Sillen, 1967). Alternatively, the strength of the titrant should be such that only a small volume need be added to effect total pH change.

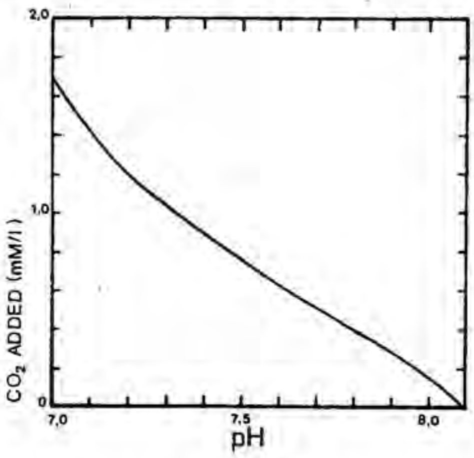

Figure 4. Addition of CO_2 to seawater which has an initial pH = 8,10 and Alkalinity = 2,20 m.moles/ℓ.

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5. AQUEOUS-GAS PHASE EQUILIBRIUM DIAGRAM

Carbon dioxide is exchanged between water and atmosphere until the CO_2 partial pressures in the two phases are equal. Consequently, in a water with a particular temperature and ionic constitution, in equilibrium with a particular partial pressure of carbon dioxide, pCO_2, in the gas phase, the carbonate species concentrations $[HCO_3]_T$ and $[CO_3]_T$ are a function only of pH; $[H_2CO_3^*]$ is independent of pH. This is illustrated in a log [species] - pH plot for $pCO_2 = 10^{-3,52}$ Atmospheres (Figure 5) as follows:

(a) Distribution $[H_2CO_3^*$

From Henry's Law for a water in equilibrium with a gas phase with a constant value for pCO_2

$$\gamma_{CO_2}[H_2CO_3^*] = K_H . pCO_2 . a_w \qquad (22)$$

where γ_{CO_2} = activity coefficient for neutral species, $H_2CO_3^*$, see Section 4.3.1, Chapter 4.

K_H = Henry's Law constant for CO_2 equilibrium between an aqueous and a gas phase and equals $10^{-1,47}$ at 25°C and one atmosphere total pressure.

Taking the logarithm of Eq. (22):

$$\log[H_2CO_3^*] = \log K_H' + \log(pCO_2) \qquad (23)$$

For $pCO_2 = 10^{-3,52}$, $[H_2CO_3^*]$ plots as a horizontal line in the log [species] - pH plot with

$$\log[H_2CO_3^*] = -3,52 - 1,54 = -5,06$$

i.e.

$[H_2CO_3^*]$ is independent of pH.

(b) $[HCO_3]_T$ with pH

From Eq. (17),

$$[HCO_3]_T = K_{T1}' [H_2CO_3^*]/(H^+) \qquad (24)$$

Substituting for $[H_2CO_3^*]$ from Eq. (22) into Eq. (24) and taking logarithms

$$\log[HCO_3]_T = \log K_H' + \log(pCO_2) - pK_{T1}' + pH \qquad (25)$$

Differentiating Eq. (25) with regard to pH

$\partial(\log[HCO_3]_T)/\partial pH = +1$ (i.e. the slope equals unity)

and from Eq. (24) at $pH = pK_{T1}'$, $[HCO_3]_T = [H_2CO_3^*]$. Hence the line representing $[HCO_3]_T$ in the diagram is plotted in Figure 5 with slope + 1 and intersecting the $[H_2CO_3^*]$ line at $pH = pK_{T1}'$, i.e. Point 1, where $pH = pK_{T1}' = 6,07$ for sea water (and $pH_o = p_oK_{T1}' = 5,995$).

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(c) $[CO_3]_T$ with pH

Solving for $[CO_3]_T$ from Eqs. (17 and 18) Chapter 4,

$$[CO_3]_T = K'_{T1}.K'_{T2}.[H_2CO_3^*]/(H^+)^2 \tag{26}$$

Substituting for $[H_2CO_3^*]$ from Eq. (22) into Eq. (26) and taking logarithms:

$$\log[CO_3]_T = \log K'_H + \log(pCO_2) - pK'_{T1} - pK'_{T2} + 2pH \tag{27}$$

From Eqs. (26 and 27), the $[CO_3]_T$ line in Figure 5 has slope + 2 and intersects the $[HCO_3]_T$ line at pH = pK'_{T2} i.e. at pH = pK'_{T2} = 9,21 for sea water (and $pH_o = p\,K'_{T2} = 9{,}135$).

The log [species] - pH plot in Figure 5 is for equilibrium between CO_2 in the aqueous and gas phases with $pCO_2 = 10^{-3,52}$ for

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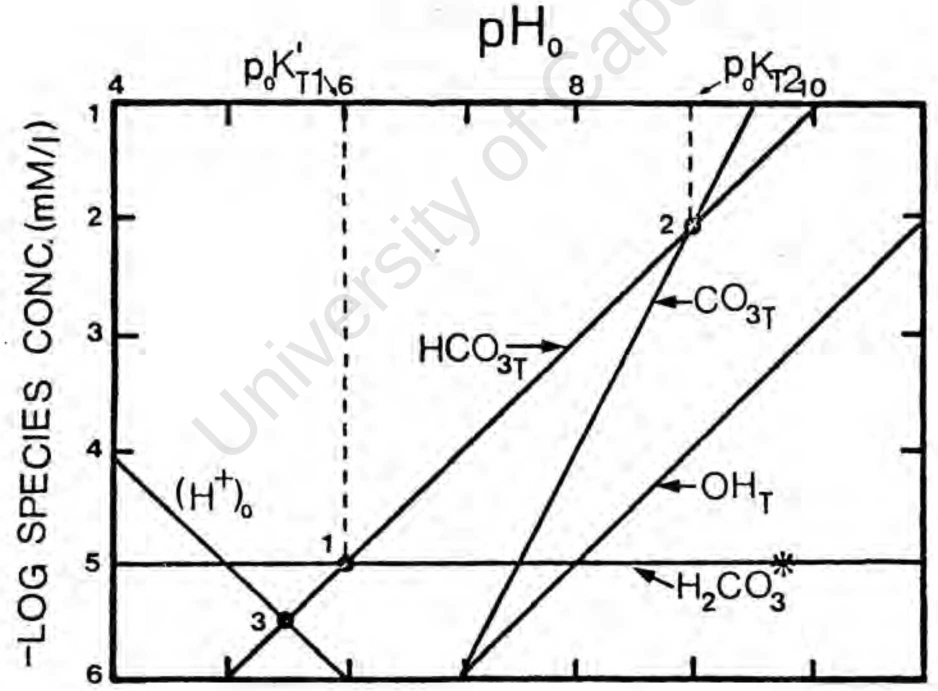

Figure 5. Distribution of stoichiometric species concentrations with pH for seawater in equilibrium with CO_2 in the air.

a water with the ionic constitution of sea water. Inherent in the diagram is the assumption that no mineral precipitation or dissolution occurs. From Figure 5 a number of interesting properties emerge for any water in equilibrium with a fixed pCO_2 value:

(1) All the carbonate species concentrations are fixed by pH.

(2) At pH values above the $H_2CO_3^*$ equivalence point, Point 3 in Figure 5 *both* $H_2CO_3^*$ Alkalinity and Acidity increase monotonically with pH.

(3) The pH at the $CO_3^=$ equivalence point is undefined. (This equivalence point was shown to occur at a pH where $[HCO_3]_T = [OH]_T$. In Figure 5 the lines representing $[HCO_3]_T$ and $[OH]_T$ both have slope + 1 and no intersection point occurs).

It is useful to compare these properties with those of the conventional log [species] - pH diagram plotted for a constant C_T: For a constant C_T, titration with a strong base decreases Acidity and increases Alkalinity (both monotonically) whereas for a constant pCO_2, titration with strong base *increases both* Alkalinity and Acidity (and vice versa for a strong acid titration). These are important points to be kept in mind when developing mathematical solution procedures to plot the respective conditioning diagrams.

5.1 Equilibrium Diagrams

In the advancement to equilibrium between CO_2 in the aqueous and gas phases, the pH in the water changes and there is a redistribution of dissolved carbonate species concentrations, i.e. a change in the dissolved CO_2 concentration occurs and more CO_2 is then exchanged with the gas phase. Although two phase equilibrium chemistry deals only with the final saturated condition, by monitoring single aqueous phase equilibrium with time, it is possible to trace qualitatively the kinetics of approach to two phase equilibrium.

The most useful parameter for the purpose is pH as it reflects the aqeuous phase equilibrium conditions almost immediately due to the rapid response characteristics of the pH probe which is not the case for pCO_2 probes and specific ion electrodes.

In the development of a graphical solution procedure, the first requirement is to develop a two phase equilibrium diagram for the system. In the previous section it was shown that values for a family of curves representing pH can be plotted in a diagram with $H_2CO_3^*$ Alkalinity and $CO_3^=$ Acidity as co-ordinate parameters. In general, any parameter could have been selected instead of pH (e.g. H^+, $CO_3^=$, HCO_3^- or $H_2CO_3^*$).

$H_2CO_3^*$ is a particularly useful parameter as it is related to pCO_2 through Henry's Law. Because of this relationship it is possible to plot a family of lines representing a range of pCO_2 values on the Alkalinity-Acidity diagram. Furthermore, the family of lines representing pCO_2 can be superimposed on the Alkalinity-Acidity plot together with pH lines, to yield a diagram for rapidly solving a wide variety of aqueous-gas phase equilibrium problems (see Figure 6).

In order to plot a family of curves representing pCO_2 in a diagram with Alkalinity and Acidity as co-ordinate, an equation linking these three parameters must first be developed. The equation for Henry's Law for CO_2 equilibrium between the gas and aqueous phases Eq. (22), can be used to solve for the total concentration (i.e. free plus ion-paired species) of bicarbonate and carbonate in a solution which is in equilibrium with a partial pressure of CO_2 equal to pCO_2 as follows:

Solving for $[H_2CO_3^*]$ in Eq. (22) and substituting into Eq. (17),

$$[HCO_3]_T = (K'_H \cdot pCO_2)K'_{T1}/(H^+) \tag{28}$$

Similarly for the carbonate species:

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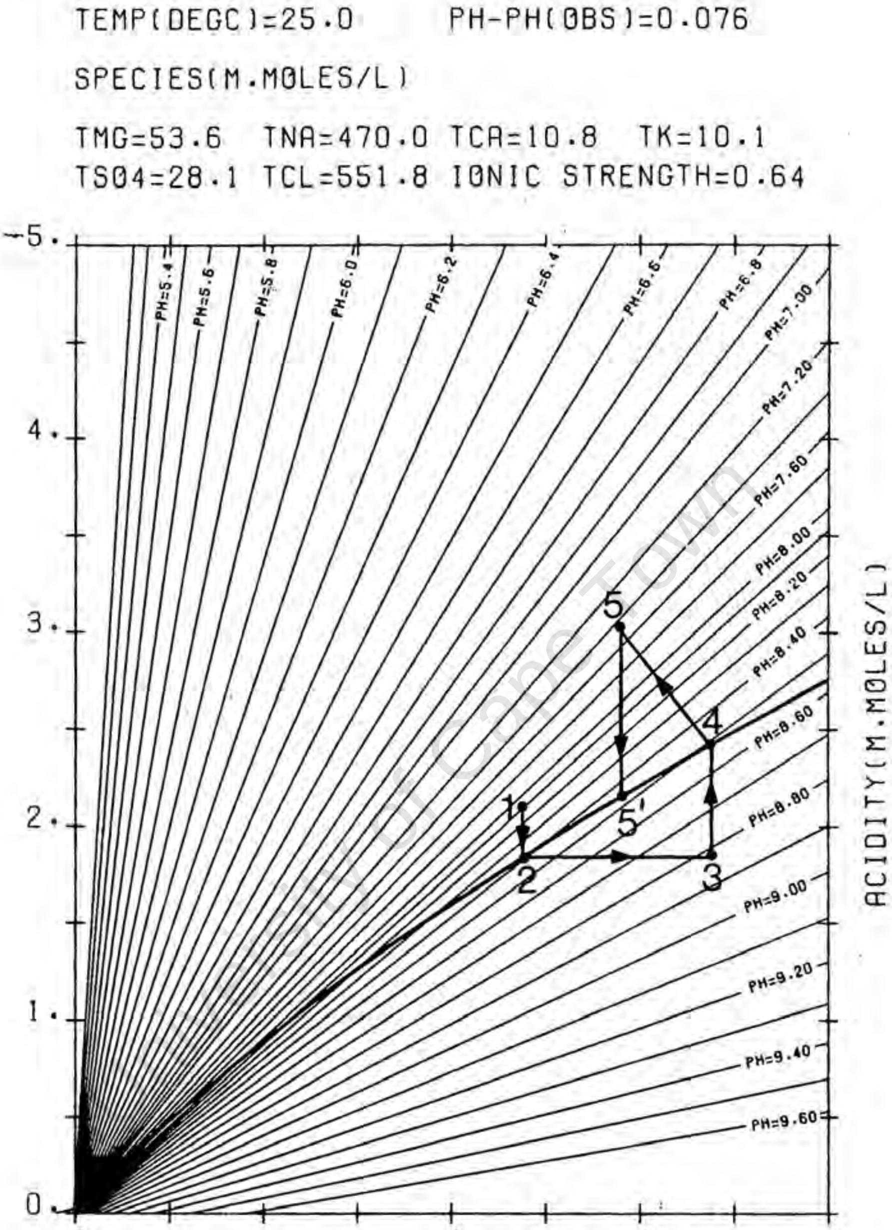

Figure 6. Chemical dosing of seawater which maintains equilibrium with CO_2 in the air.

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$$[CO_3]_T = (K_H \, pCO_2) \, K'_{T1}\text{-}K'_{T2}/(H^+)^2 \qquad (29)$$

Substituting for $[H_2CO_3^*]$ and $[HCO_3]_T$ from Eqs. (22 and 28) into the equation for Acidity, Eq.(100), Chapter 4, and simplifying

$$(H^+) = (K'_H K'_{T1} \, pCO_2 - K'_{Tw})/(\text{Acidity} - 2K'_H \, pCO_2) \qquad (30)$$

and solving for Alkalinity in terms of pCO_2 and (H^+) from Eqs. (28 and 29)

$$\text{Alkalinity} \cong \frac{2K'_H \, pCO_2 . K'_{T1} . K'_{T2}}{(H^+)^2} + \frac{K'_H \, pCO_2 \, K'_{T1}}{(H+)} + K'_{Tw} \qquad (31)$$

Substituting for (H+) from Eq. (30) into Eq. (31) gives a relationship linking Alkalinity, Acidity and pCO_2. Each chosen value of pCO_2 is represented by a line in a diagram with Alkalinity and Acidity as co-ordinates, see Figure 6.

A plot of a family of curves for a range of pH values superimposed on the 0,0003 ATM line is shown in Figure 6 for water with major ionic constitution of sea water. In Supplement C is a listing of a computer program for plotting both aqueous and aqueous-gas phase equilibrium diagrams for the carbonate system in low or high salinity waters at any temperature.

The Alkalinity - Acidity - pCO_2 - pH diagram, Figure 6, can be used to solve numerous water conditioning problems with either constant or variable partial pressure of CO_2 in the gas phase.

Example

A water with the major ionic constitution of sea water has pH 8,1 and $H_2CO_3^*$ Alkalinity 2,4 m.moles/ℓ.

(a) The water is brought to equilibrium with the air (pCO_2 = 0,0003 Atm). Determine the mass concentration of CO_2 which will be exchanged with the atmosphere and

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the final pH attained.

(b) 0,5 m.moles/ℓ of $CaCO_3$ now dissolves into the water and pCO_2 is maintained at 0,0003 Atmospheres. Determine the new state of the water.

(c) Increments of strong acid are now added to the water and equilibrium with the atmosphere is maintained. Plot the theoretical two phase equilibrium titration curve.

(a)

For clarity only the plot of the line representing equilibrium between aqueous and gas phases for $pCO_2 = 10^{-3,52} = 0,0003$ Atmospheres is shown in the Alkalinity - Acidity - pH diagram in Figure 6, line A.

The initial condition of the water (pH 8,1 and $H_2CO_3^*$ Alk = 2,40 m.moles/ℓ) plots at Point 1 in Figure 6. Point 1 plots above the pCO_2 line. CO_2 exchange between the water and gas phases will occur until the condition of the water lies on Line A.

The final two phase equilibrium condition of the water and the mass concentration of CO_2 exchange to attain this equilibrium condition are determined as follows:

Exchange of CO_2 between the air and water has no effect on Alkalinity (Eq. 1); from Eqs. (5 and 6).

$$\Delta\text{Acidity} = 2[CO_2]_{added} \qquad (32)$$

with a positive Δ denoting an increase in Acidity.

Thus, with CO_2 exchange, the point defining the condition of the water moves along the constant Alkalinity line, Line B. Intersection of Lines A and B occur at Point 2 which defines CO_2 equilibrium between aqueous and gas phases.

The Acidity change from the initial to the final condition is a measure of mass of CO_2 exchanged.

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Initial Acidity = 2,17

Final Acidity = 1,90

ΔAcidity = -0,27 m.moles/ℓ

From Eq. (32)

CO_2(added) = (-0,27)/2
= -0,13 m.moles/ℓ

i.e.

0,13 m.moles/ℓ of CO_2 is lost by the water to the air to attain CO_2 gas-aqueous phase equilibrium.

(b)

0,5 m.moles/ℓ of $CaCO_3$ now dissolves into the water which has been brought to CO_2 gas-aqueous phase equilibrium in (a) above.

This example is solved in two steps:(i) the effects of $CaCO_3$ addition on aqueous phase equilibrium are investigated, (ii) the effects of CO_2 exchange are investigated in exactly the same way as in (a) above.

(i) <u>$CaCO_3$ Dissolution</u>:

From Eq. (6), addition of $CO_3^=$ has no effect on Acidity, i.e. initial Acidity = final Acidity = 1,90 m.moles/ℓ.
From Eq. (1), the change in Alkalinity is as follows:

ΔAlk = 2.$[CO_3]_{added}$
= (2.0,5) = 1,0 m.moles/ℓ

New Alk = (2,40 + 1,0) = 3,4 m.moles/ℓ

Lines representing Alkalinity 3,4 and Acidity 1,90 intersect at Point 3 in Figure 6. The new pH is therefore pH 8,83, i.e. pH_o = 8,83 - 0,08 = 8,75.

(ii) <u>CO_2 Exchange</u>

Point 3 does not lie on the pCO_2 line, Line A, CO_2

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transfer will thus occur to bring the water to a state of CO_2 aqueous-gas phase equilibrium. Following (a) above, the final condition of the water plots at Point 4 in Figure 6, i.e. vertically above Point 3. The mass of CO_2 exchanged is calculated from Eq. (32)

$$
\begin{aligned}
[\bar{C}O_2] \text{ added} &= \Delta\text{Acidity}/2 \\
&= (2{,}45 - 1{,}90)/2 \\
&= +0{,}28 \text{ m.moles}/\ell.
\end{aligned}
$$

(c)

Plot the theoretical two phase titration curve for addition of strong acid to the sample. The initial condition of the water plots at Point 4 in Figure 6.

Addition of strong acid has the effect of decreasing Alkalinity and increasing Acidity by an amount equal to the moles of strong acid added.

The change in state of the water, *provided no CO_2 transfer occurred*, would then lie on the line at 45° up to the left and passing through Point 4, i.e. Line C.

The total titrant added to change the state of the water from Point 4 to any point on line C, equals the change in Alkalinity between Point 4 and the new point, for example, 0,5 m.moles/ℓ of strong acid will change the state of the water from Point 4 to Point 5. Point 5 does not lie on Line A so that the water is not now in aqueous-gas phase equilibrium. CO_2 exchange with the atmosphere will cause the condition of the water (defined by Point 5) to move vertically downwards (i.e. Alkalinity remains constant) until the point occurs on the two phase line, Line A, i.e. Point 5'. The value of the pH line through Point 5' gives the pH for two phase equilibrium after addition of 0,50 m.moles/ℓ of strong acid, i.e. pH 8,45 Repeating this process for a number of additions of strong acid gives the pH-alkalimetric titration curve for aqueous-gas phase equilibrium with pCO_2 = 0,0003 Atmospheres, see Figure 7.

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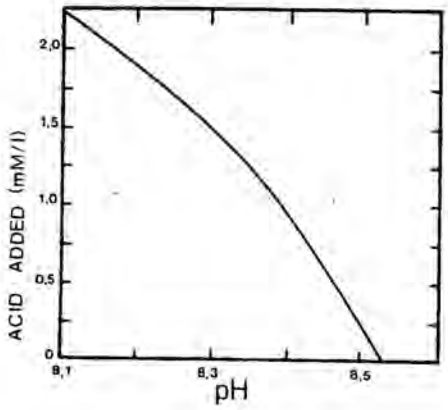

Figure 7. Strong acid titration of seawater which remains in equilibrium with CO_2 *in the air.*

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6. AQUEOUS-SOLID PHASE EQUILIBRIUM DIAGRAMS

6.1 Solubility of $CaCO_3$

Calcium carbonate may precipitate from water in one or more of three forms: calcite, aragonite and vaterite. Which of these allotropes precipitate depends on the pressure and temperature conditions, the rate at which precipitation takes place (Roques and Girou, 1974), the nature and mass of crystal seed and the presence of foreign ions.

Foreign ions may be incorporated into the crystal lattice of a precipitate provided (Krauskopf, 1967):

(i) the foreign ion has a charge and ionic radius similar to the ion which it replaces in the crystal lattice, or

(ii) there is a similarity in crystal structure between two minerals with a common ion.

An example of (i) above is the partial replacement of Mn^{++} in rhodochrosite, $MnCO_3$, by Fe^{++} to give a solid with the formula $(Fe_xMn_{1-x})CO_3$; Fe^{++} and Mn^{++} have very closely equal ionic radii of 0,75 Å and 0,80 Å respectively and these are thus able to replace one another relatively freely in many minerals, Garrels and Christ (1965). An example of (ii) above is the minerals magnesite ($MgCO_3$) and calcite ($CaCO_3$). Both crystals are in the rhombohedral class of the hexagonal crystal system and thus form an isomorphous series of magnesian calcites, $(Mg_xCa_{1-x})CO_3$. The fraction of $MgCO_3$ in the magnesian calcite crystal varies depending primarily on the ratio of Mg^{++}/Ca^{++} in aqueous phase (Winland, 1969).

6.1.1 *Aragonite and Calcite Solubility*

In order to discuss the solubilities of magnesian calcites, it is necessary first to investigate briefly the solubility of pure calcite and aragonite in water at 25°C and 1 atmosphere total pressure. Generally accepted thermodynamic constants for calcite and aragonite (Robie and Waldbaum, 1968) are:

Calcite: $\Delta G_F^o = -269{,}78$ K cal/mole, giving

$\Delta G_R^o = -11{,}38$ K cal/mole, i.e.

$pK = 8{,}34$ at 25°C

Aragonite: $\Delta G_F^o = -269{,}53$ K cal/mole, giving

$\Delta G_R^o = -11{,}13$ K cal/mole, i.e.

$pK = 8{,}16$ at 25°C

These values were determined ignoring the occurrence of the ion-pair $CaCO_3^o$. The true solubility products (i.e. those values allowing for the effects of $CaCO_3^o$) can be determined from the above data if $K_{CaCO_3^o}$ at 25°C is known. In Chapter 4 is reported measured data for the equilibrium constants (dissociation) for ion-pairing between Na^+, Ca^{++} and Mg^{++} and the carbonate species HCO_3^- and $CO_3^=$. The pK value determined for $CaCO_3^o$ at 25°C is 3,19.

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The true solubility product, K_{sp}, is then determined as follows: The value determined by Robie and Waldbaum, K_{spT}, is based on the products of stoichiometric concentrations and free species activity coefficients, i.e.

$$\gamma_{Ca} [Ca]_T . \gamma_{CO_3} [CO_3]_T = K_{spT} \tag{33}$$

$$= 10^{-8,34}$$

For the particular saturated condition where $[Ca]_T = [CO_3]_T$, Eq.(33) simplifies to

$$[Ca]_T = (K'_{spT})^{1/2} \tag{34}$$

and

$$[Ca]_T = [Ca^{++}] + [CaCO_3^o] \tag{35}$$

For $CaCO_3$ ion pairing, from Chapter 4,

$$[CaCO_3^o] = [Ca^{++}][CO_3^{=}]/K'_{CaCO_3}$$

$$= [Ca^{++}]^2/K'_{CaCO_3} \tag{36}$$

Substituting for $[Ca]_T$ and $[CaCO_3^o]$ from Eqs. (34 and 36) respectively into Eq. (35) and solving for $[Ca^{++}]$,

$$[Ca^{++}] = \{-K'_{12} + (K'^{\,2}_{CaCO_3} + 4K'^{\,1/2}_{spT} . K'_{CaCO_3})^{1/2}\}/2$$

$$= K'^{\,1/2}_{sp} \tag{37}$$

In Table 1 are compared pK_{sp} values for calcite and aragonite calculated from Eq. (37) for various assumed values of $K_{CaCO_3^o}$ using the experimentally determined values pK_{spa} (calcite) = 8,34 and pK_{spa} (aragonite) = 8,16. (The effect of temperature for these two solubility products is not discussed here).

It is evident from Table 1 that the formation of the species $CaCO_3^o$ clearly has a significant effect on the solubility products

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Table 1.

Variation in K_{sp} for calcite and aragonite at 25°C for varying values of $K_{CaCO_3^o}$

$pK(CaCO_3^o)$	1,0	2,0	3,0	3,19*
pK_{sp} (calcite)	8,34	8,35	8,39	8,41
pK_{sp} (aragonite)	8,16	8,17	8,22	8,24

* $pK(CaCO_3^o) = 3,19$ is the value at 25°C determined in Chapter 4.

of calcite and aragonite, the pK values change from 8,39 and 8,16 respectively to 8,41 and 8,24 respectively.

6.1.2 *Magnesian Calcite Solubility*

Magnesian calcites may be precipitated from aqueous solutions either as a thermodynamically stable solid phase or a meta-stable phase (Pytkowicz, 1965; Berner, 1974), or as a non-equilibrium steady state solid phase (Chave, Deffeyes, Weyl, Garrels and Thompson, 1962); the last two being transient phases. The period required for stable thermodynamic equilibrium to be attained from a transient solid phase is generally in terms of geological time. In water softening the time of residence of the seed (sludge) is relatively short. If transient phase solids are precipitated, attainment of equilibrium with respect to the stable solid phase is unlikely to occur. Thus in water treatment processes there is a greater interest in an *activity product* of the precipitate rather than a true thermodynamic solubility product.

Whereas the solubility product for the allotropes calcite and aragonite has been firmly established, (see Table 1), no firm values have been established to date for magnesian calcites. This

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probably stems from difficulties associated with solubility measurements of these calcites.

Solubility measurements of magnesian calcites usually are carried out by means of either precipitation or dissolution experiments utilising batch tests. In precipitation experiments the solution must be seeded with calcite or magnesian calcite crystals. As precipitation proceeds the $(Mg^{++})/(Ca^{++})$ ratio changes in the bulk solution resulting in the formation of crystal layers of differing composition. Consequently the crystal varies in composition from the surface inwards making it extremely difficult to determine the crystal composition corresponding to a particular $(Mg^{++})/(Ca^{++})$ ratio in the aqueous phase. Furthermore, the solid precipitated may not be in true equilibrium with the solution. According to Berner (1975), thermodynamic equilibrium is only attained between the solid and aqueous phases by cation exchange process long after precipitation has occurred.

In dissolution experiments magnesian calcites formed in life process (i.e. the carbonate skeletal materials of marine organisms) are used (Chave *et al*, 1962; Plummer and Mackenzie, 1974). These carbonates have the merit that the crystal constitution is relatively homogeneous, i.e. the ratio of magnesium to calcium in the lattice is constant. However, dissolution experiments present the problem of incongruent precipitation coexisting with the dissolution process, that is, the magnesian calcite dissolves and either aragonite or pure calcite or a different magnesian calcite precipitates. This behaviour results in a steady state situation being established (i.e. a condition of non equilibrium) between the dissolving and precipitating minerals. Again a misinterpretation of true thermodynamic equilibrium is possible due to the kinetics of ion-exchange equilibrium. For this reason it is preferable to speak in terms of *activity products* rather than equilibrium solubility products.

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Chave *et al* (1962) reported steady state pH values attained in batch dissolution experiments on magnesian calcites of known composition in distilled water at a partial pressure of $P_{CO_2} = 1$ atmosphere and temperature 25°C. In order to obtain solubility products from Chave *et al's* data, Winland (1969) postulated that for a solution in stable or meta stable equilibrium with respect to a magnesian calcite, a dynamic state exists between the solid phase and Mg^{++}, Ca^{++} and carbonic species in the aqueous phase which he formulates as:

$$(1-x)(Ca^{++}) + x(Mg^{++}) + (CO_3^=) \rightleftarrows (Ca^{1-x}Mg^{x}CO_3)_s$$

i.e.

$$(Ca^{++})^{1-x}(Mg^{++})^{x}(CO_3^=) = K_{spm} \tag{38}$$

where

K_{spm} = the activity product for magnesian calcite, which varies with x

x = the mole fraction of $MgCO_3$ in the lattice, i.e.

$$x = (MgCO_3)_s/\{(CaCO_3)_s + (MgCO_3)_s\}$$

$$= (Mg)_s/\{(Ca)_s + (Mg)_s\} \tag{39}$$

Subscript 's' denotes solid species.

Using the data of Chave *et al*, Winland calculated the activity product values for K_{spm} versus X (Table 2). Similar calculations on Chave *et al's* data made by Plummer and Mackenzie (1974) and by ourselves, are also listed in Table 2.

Whereas Plummer and Mackenzie's and our values correspond closely, those of Winland show discrepancy. The reason for this difference is not clear. Perhaps Winland did not use free ion species concentrations, but even if K_{spm} values are recalculated using total ion species concentrations his values are still significantly different.

When Chave *et al* reported their results they stated that the data were not necessarily obtained from congruent precipitation and hence would probably give rise to minimum solubilities (i.e. maximum pK_{spm} values). Plummer and Mackenzie performed similar batch dissolution experiments to those of Chave *et al*, but attempted to identify the congruent phase of dissolution by monitoring the pH changes throughout the experimental period. By examination of the pH time plot they state they were able to identify the congruent phase and by extrapolating these phase data to time infinity they estimated the solubility products using Eq. (38)(see Table 2). They state that their procedures possibly give rise to maximum solubility values (i.e. minimum pK_{spm} values). Hence the true pK_{spm} values probably lie between the maximum values calculated from Chave *et al's* data and the minimum values of Plummer and Mackenzie.

Table 2.

Comparison of activity products, pK_{spm}, for various magnesian calcites at 25°C and total atmospheric pressure

Mole fraction $MgCO_3$ in magnesian calcite	Winland[2]	Data from Chave *et al*[1] calculated by Plummer & Mackenzie[3]	This monograph	Data from Plummer & Mackenzie[4]	Data[5] used in this monograph
0	8,35	8,35	8,35	8,49	8,40
0,50	8,22	8,45	8,35	8,35	8,31
0,10	8,02	8,40	8,25	8,00	8,23
0,15	7,84	8,15	8,08	7,70	8,14

1. Chave *et al* (1962)
2. Winland (1969)

3 and 4. Plummer and MacKenzie (1974)

5. Interpolated from the values reported by 3 and 4 above (see Figure 8.

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The data plotted in Figure 17 for calcite and magnesian calcite solubility indicate the wide variability between values reported. Nevertheless, the data do show the distinct trend of decrease in pK_{spm} with increase in mole fraction of $MgCO_3$ in the solid. In general, the pK_{spm} values reported by Plummer and Mackenzie are lower than those calculated from Chave *et al*, which is consistent with their respective experimental procedures as discussed above. However, the pK value for calcite measured by Plummer and Mackenzie (i.e. pK (calcite) = 8,49) is exceptionally *high* compared with the generally accepted value given in Table 1, i.e. pK(calcite) = 8,41 at 25°C. We can offer no explanation for this apparent inconsistency.

Activity products for magnesian calcite were obtained by linear interpolation from the data shown in Figure 8 using the data of Plummer and Mackenzie (1974) and Chave *et al* (1962) as interpolated

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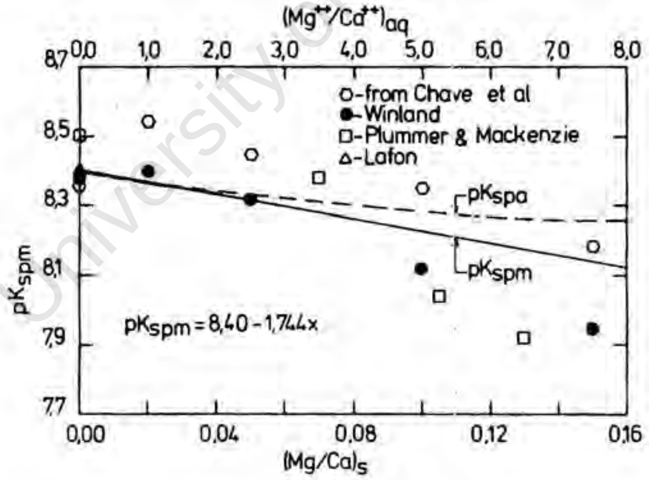

Figure 8. Dependence of magnesian calcite solubility product and the ratio of Mg to Ca in the solid phase on the ratio Mg to Ca in the aqueous phase.

by Plummer and Mackenzie (1974)

$$pK_{spm} = 8{,}41 - 1{,}744x \tag{40}$$

where

x is the mole fraction of $MgCO_3$ in the magnesian calcite lattice.

The form in which Eq.(40) is expressed is inconvenient for algebraic manipulations. Equation (40) can be transformed to be in terms of (Ca^{++}) and $(CO_3^{=})$ formulating the activity product as an apparent one

$$(Ca^{++})(CO_3^{=}) = \frac{K_{spm}}{\{(Mg^{++})/(Ca^{++})\}^x} = K_{spa} \tag{41}$$

where K_{spa} = the apparent $CaCO_3$ activity product.

An estimate of x in Eq. (41) can be made by considering isomorphism and partitioning phenomena (Krauskopf, 1967): since Mg^{++} can fit into the calcite crystal structure, when calcite is precipitated from a solution containing Mg^{++} ions, the Mg^{++} ions distribute themselves between the solid and aqueous phase, Winland (1969),

$$(CaCO_3)_s + (Mg^{++}) \rightleftarrows (Ca^{++}) + (MgCO_3)_s$$

thus for equilibrium (again not necessarily true equilibrium),from the above reaction

$$\frac{(Ca^{++})(Mg)_s}{(Mg^{++})(Ca)_s} = D \tag{42}$$

where

D = an 'equilibrium' constant also referred to as a distribution coefficient for partioning.

This equation is reformulated below into the usual form of partitioning equations

$$(Mg)_s/(Ca)_s = D\{(Mg^{++})/(Ca^{++})\} \tag{43}$$

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Winland measured the distribution coefficient for partitioning of Mg^{++} between calcite and the aqueous phase by precipitating calcite in the presence of Mg^{++}. The method of effecting precipitation was to raise the temperature of unseeded solutions containing calcium, magnesium and carbonate species. He reported that for initial $(Mg^{++})/(Ca^{++})$ ratios from 0,025 to 5,3, the partition coefficient $D = 0,02$.

Berner (1975), using a similar method of precipitation as that adopted by Winland, reported that the magnesium content of the calcite precipitated was highly variable. He concluded that the results of Winland do not reflect true equilibrium between the solid and aqueous phases and proposed that true equilibrium is only attained with cation exchange between the precipitate and aqueous phase subsequent to precipitation.

In the experiments reported by Benjamin (1977) on the kinetics of precipitation of $CaCO_3$ in the presence of Mg^{++}, the precipitation was initiated by adding pure calcite seed in batch tests. Crystallographic analyses of the precipitated mass showed that only calcite and *no aragonite* was precipitated and that up to ten percent of the mass precipitated was magnesium carbonate. These observations indicate that precipitation must have occurred as a magnesian calcite overgrowth on the calcite seed. On the basis of the partitioning coefficient of Winland, it was then found that a hypothesis could be formed which predicts the precipitation kinetics very well. Although this kinetic investigation does not reflect the true equilibrium conditions, on balance it does appear to support Winland's partitioning hypothesis. It is clear that research into this aspect is required.

For the purposes of plotting a two phase conditioning diagram for magnesian calcite, a value for D in Eq. (43) is required. Accepting Winland's observations, x in Eq. (41) can be calculated and an activity product for magnesian calcite, K_{spm}, can be written in terms of only the dissolved species concentrations.

From Eq. (39):

$$x = (Mg)_s/\{(Mg)_s + (Ca)_s\}$$

i.e.

$$x = 1/\{1 + (Ca)_s/(Mg)_s\} \qquad (44)$$

Incorporating the distribution coefficient from Eq. (43) with D = 0,02 into Eq. (44) and reducing:

$$x = 1\{1 + 50\ (Ca^{++})/(Mg^{++})\} \qquad (45)$$

that is, the fraction of $MgCO_3$ in the crystal depends only on the ratio of (Mg^{++}) to (Ca^{++}) in the aqueous phase.

Knowing x, and hence K_{spm} (from Eq. (40)), it is thus possible to calculate K_{spa} from Eq. (41). The corresponding pK_{spa} values calculated are plotted versus x and $(Mg^{++})/(Ca^{++})$ ratio in Figure 8.

6.2 Aqueous solid phase diagram.

Two phase equilibrium, between the solid phase calcite and the aqueous phase for the carbonate system, has been extensively discussed by Loewenthal and Marais (1976). They restricted their exposition to low salinity waters, i.e. waters in which ion-pairing effects can be taken as negligible. Equilibrium interrelationships between Alkalinity, pH and Ca^{++} for calcite saturation were presented in a graphical form by plotting lines representing each of these three parameters in a diagram with co-ordinate parameters Acidity and $(Alk-Ca^{++})$ called the Modified Caldwell-Lawrence Diagram. To conform to the convention usual in water treatment, the concentrations were all expressed in the equivalent form, in terms of $CaCO_3$. The plots reflected ionic strength and temperature effects, but as ion-pairing was considered negligible, the *total calcium* concentration was equal to the concentration of the free calcium species, $[Ca^{++}]$.

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When considering high salinity waters it is possible to construct similar diagrams but the treatment needs to take into consideration a number of factors which can generally be neglected in low salinity waters:

(1) The calcium lines are expressed in terms of total calcium concentration, $[Ca]_T$, instead of the free concentration, $[Ca^{++}]$. Whereas in low salinity waters the molarity equals the free concentration, in high salinity waters $[Ca^{++}]$ may be significantly different from $[Ca]_T$ due to the effects of ion-pairing of calcium with carbonate species, sulphate and hydroxide. The choice of plotting lines representing $[Ca]_T$ is made for the following reasons: (i) where significant calcium ion-pairing occurs in a water, the calcium parameter measured is usually $[Ca]_T$ unless a specific ion electrode is used, in which case (Ca^{++}) is measured. Of course it is possible to plot the diagram in terms of (Ca^{++}); (ii) with $CaCO_3$ precipitation, the molar mass of $CaCO_3$ precipitated equals the *change* in $[Ca]_T$, not the change in (Ca^{++}).

(2) Magnesium concentration is incorporated implicitly in the diagram. In the low salinity diagram, precipitation of $Mg(OH)_2$ can be treated in a diagram completely independent of the Modified Caldwell-Lawrence Diagram as it depends only on pH, ionic strength and temperature. In high salinity waters this is no longer possible; firstly, Mg^{++} ion pairs with carbonate, sulphate and hydroxide species and secondly, the activity product for magnesian calcite depends in part on the ratio of $(Mg^{++})/(Ca^{++})$ in solution. Consequently, magnesium concentration is implicitly linked to each parameter incorporated in the Modified Caldwell-Lawrence Diagram; the plot loses its generality and is unique to a particular water.

(3) Whereas in low salinity waters it is accepted that $CaCO_3$ precipitates as a pure calcite, in waters with high magnesium concentrations the precipitate will be either magnesian calcite or

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aragonite, or a mixture of these, depending upon the $(Mg^{++})/(Ca^{++})$ ratio in solution, the rate of precipitation, temperature and whether sufficient time has elapsed for ion-exchange equilibria to be established. At present it is not possible to specify exactly which form will be precipitated so that it may be necessary to plot diagrams for each of the three forms of calcium carbonate, depending on the objective of the investigation. In a desalination dosing problem for example, where the intention is to ensure that no calcium carbonate precipitation will occur, it may be desirable to use a diagram incorporating the least soluble form of $CaCO_3$.

An example of a Modified Caldwell-Lawrence Diagram for high salinity water is shown for aragonite in Figure 9.

In plotting the diagram all concentrations are expressed in the molar form. Although it is possible to develop the theory in terms of equivalent concentrations, because the application of the diagram can extend over several disciplines in which the equivalent form (expressed as $CaCO_3$) is not so common, it was decided that the development is best expressed in terms of molarites. As a consequence, the parameter $(Alk-Ca^{++})$ (in the equivalent form for low salinity water) now becomes $(Alk-2[Ca]_T)$ in the molar form.

In low salinity water it was possible to find explicit relationships linking either $[Ca^{++}]$ or Alkalinity or pH to $(Alk-Ca^{++})$ and Acidity. These relationships were used to plot lines representing constant values for Ca^{++}, Alkalinity and pH in the Modified Caldwell-Lawrence Diagram. In high salinity waters this has not been found possible. Solutions have to be obtained by successive approximation operating on the set of equations governing the state of the water.

Calculations to plot lines representing values of each of the parameters Alkalinity, pH and $[Ca]_T$ in the two phase diagram now involve simultaneously solving nineteen equilibria equations, i.e. Eq. (41) and Eqs (34 to 42 and 60a to 60c) Chapter 4,

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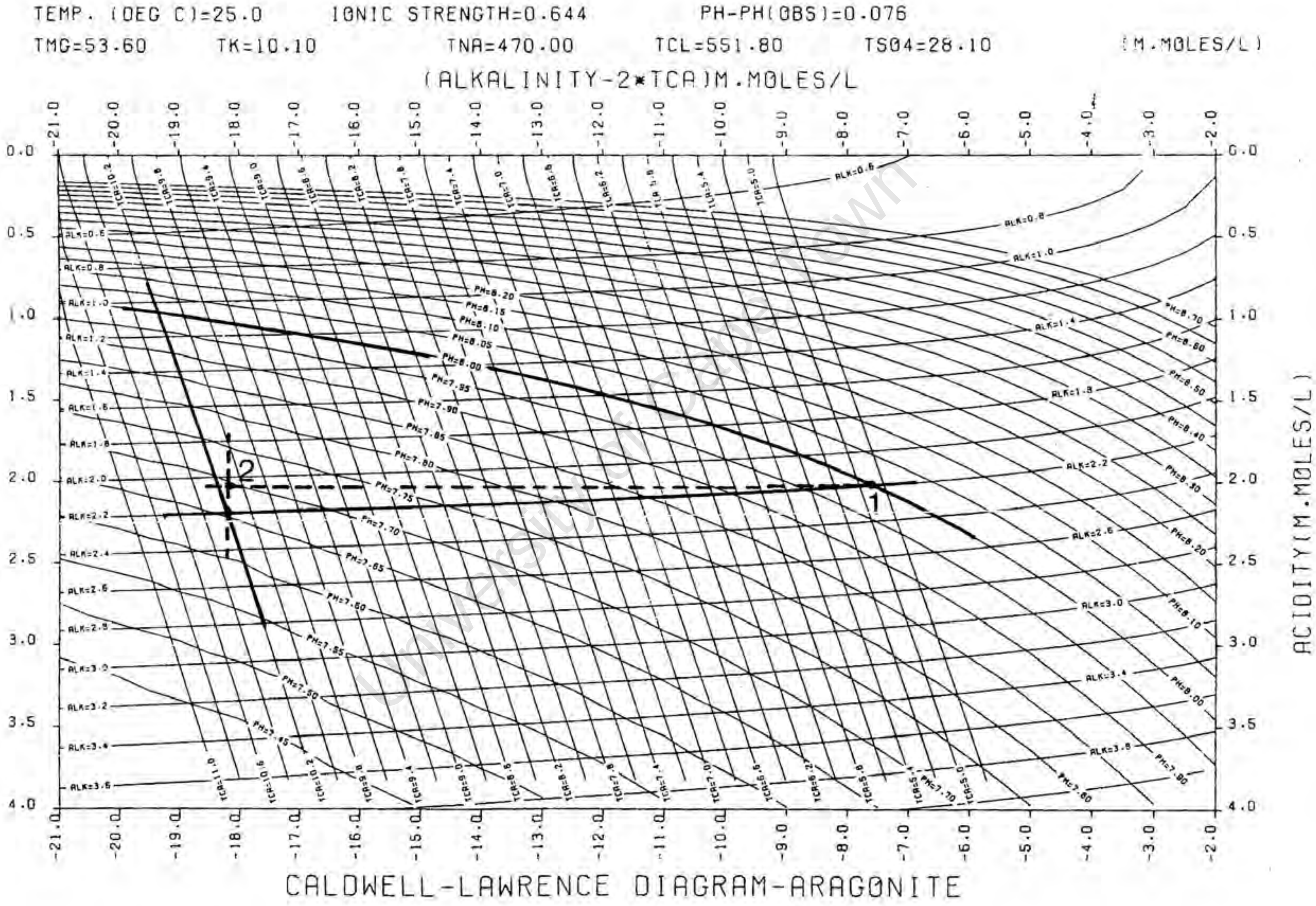

Figure 9. *Point 2 defines the aragonite saturation state for seawater with Alk = 2,20, pH 8,00 and* Ca_T *= 10,2 m.moles/ℓ.*

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and seven mass balance equations, Eqs.(44 to 48, 92 and 100) Chapter

These twenty-five simultaneous equations incorporate thirtytwo independent variables, i.e. values for five parameters must be specified so that the remainder can be calculated. The five parameters for which values are specified are the total analytical concentrations for $[SO_4]_T$, $[Na]_T$, $[K]_T$ and $[Mg]_T$ and values for any *two* of the parameters Alkalinity, Acidity, $[Ca]_T$, (Alk-2$[Ca]_T$) and pH depending on which family of lines is to be plotted in the diagram. For example, when calculating species concentrations to plot lines representing $[Ca]_T$, the extra two specified values will be for $[Ca]_T$ and [Acidity]; to plot lines representing pH the extra two specified values will be for pH and (Alk-2$[Ca]_T$). When calculating species concentrations in order to plot lines representing Alkalinity values, the choice of the extra two known parameters will depend on the particular section of the Alkalinity line to be plotted. For the horizontal sections (see Figure 9), the two extra independent parameters are Alkalinity and (Alk-2$[Ca]_T$) and for the vertical sections, Alkalinity and Acidity.

Solutions to the twenty-five simultaneous equations are obtained by a method of successive approximation. For example, to plot a pH line: the pH and a chosen value of (Alk-2$[Ca]_T$) are prescribed and it is required to calculate the corresponding Acidity value. A value is assumed for $[CO_3^=]$ and all species concentrations are calculated for this assumed value, in particular, values are calculated for (Alk-2$[Ca]_T$). The calculated value for (Alk-2$[Ca]_T$) is compared with the prescribed value for this parameter; the assumed value for $[CO_3^=]$ is then sequentially adjusted until the calculated and prescribed values for (Alk-2$[Ca]_T$) agree to four significant figures. This calculation procedure is repeated for a particular pH value and a range of (Alk-2$[Ca]_T$) values to give the corresponding Acidity values. A plot of the corresponding Acidity and (Alk-2$[Ca]_T$) values in the diagram traces a line representing the chosen value of pH in the two phase equilibrium

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diagram. This procedure is then repeated for a family of pH lines. Plots for lines representing families of Alkalinity and $[Ca]_T$ values are obtained using a similar procedure.

To plot a complete two phase equilibrium diagram the twenty-five simultaneous equations have to be solved a number of thousand times. Considering that the computer time to calculate values to plot each point in the diagram is about three seconds, using the above technique, the calculation time for a complete diagram usually is well over an hour, which is obviously impractical. To reduce the calculation time, the calculation procedure was modified to calculate in terms of total weak acid species concentrations using the apparent dissociation constants K_T' (as developed in Chapter 4). The same solution procedure of successive approximation is then used. Solutions by the two methods were identical, but the calculation time is reduced approximately twenty-five times, so that the time to calculate a complete diagram is between three and four minutes.

Supplement D includes a print out of a computer program to plot a conditioning diagram for a water with a particular temperature and major ionic species constitution for saturation with respect to calcite, aragonite or magnesian calcite. The scale and co-ordinate limits to the diagram, thermodynamic data for equilibrium constants and the values of the pH, Alkalinity and total calcium lines to be plotted are selected by the user and included as input data to the program together with the ionic constitution of the water.

An important aspect of the model concerns the magnesium concentration. At high pH values the solubility product for brucite, $Mg(OH)_2$, may be exceeded. If one considered brucite as infinitely soluble, at high pH values the concentration of the ion-pair $MgOH^+$ could exceed the input value to Alkalinity. This situation is obviously unacceptable as $[MgOH^+]$ is only a component of Alkalinity and where its value exceeds Alkalinity no solution to the model is possible. For this reason, together with the fact that the model is also used for determining chemical dosages to soften

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water to a desired magnesium concentration, the magnesium content in the water is assumed as equal to the input $[Mg]_T$ value, unless the $Mg(OH)_2$ solubility product is exceeded. When this solubility product is exceeded, $[Mg^{++}]$ is assumed equal to that value for saturation with respect to brucite.

6.3 Application of aqueous solid phase equilibrium diagram

The two phase equilibrium diagram for the calcium carbonate system has numerous applications in the elucidation of problems encountered in high ionic strength waters. These include:

(1) A qualitative and quantative estimation of the saturation state of a water with respect to either calcite, aragonite or magnesian calcite.

(2) Estimation of the mass concentrations of chemicals (e.g. CO_2, $CO_3^=$ or strong acid or base) required to adjust the water to some desired saturation state.

(3) Estimation of chemical dosage requirements in water softening.

The saturation state of a water with respect to calcite, aragonite and magnesian calcite can be estimated quickly and simply graphically. Lines representing measured values of Alkalinity, total calcium and pH are identified in the relevant equilibrium diagram. If these three lines all intersect at a point in the diagram, the water is just saturated with respect to the mineral under consideration. If not, the water is either over- or undersaturated. Graphical procedures for estimating the magnitude of over- or undersaturation are the same as those set out by Loewenthal and Marais (1976) for low ionic strength waters. Direct application of the diagram to single aqueous phase problems is not absolutely correct; this can be appreciated as follows: single

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aqueous phase equilibrium is given in the diagram by the point of intersection between lines representing pH, Alkalinity and Acidity. The value of the $[Ca]_T$ line through this intersection point represents the calcium value for which the interrelationship was determined. For under- and supersaturated waters, the calcium concentration in the water will differ from the value of the $[Ca]_T$ line through the single aqueous phase intersection point. Thus, for measured pH and Alkalinity values, the corresponding Acidity determined in the diagram will be in error insofar as the effects of incorrect calcium ion-pair concentrations on the calculated value for Acidity are concerned. The error introduced, however, usually is negligible.

Applications of the two phase equilibrium diagram to various problems arising in high salinity waters are best described by example.

Example

Analyses of a high salinity water (corresponding to sea water without the borate system) give $[Cl^-] = 0{,}5311$ moles/ℓ, $[SO_4]_T = 0{,}0284$ moles/ℓ, $[Na]_T = 0{,}4687$ moles/ℓ, $[Mg]_T = 0{,}054$ moles/ℓ, $[Ca]_T = 0{,}0102$ moles/ℓ, Alkalinity 2,20 m.moles/ℓ, pH 8,00 and temperature 25°C.

(a) Determine the saturation state of the water with respect to aragonite, calcite and magnesian calcite.

(b) 0,1 m.moles/ℓ of CO_2 is added to the system, determine the new saturation state of the water with respect to aragonite.

(c) Plot a diagram indicating the mass of $CaCO_3$ to be precipitated (or dissolved) to saturation with respect to aragonite with pH if:

(i) Acidity remains constant (i.e. the cause of change in the constitution of the water arises from $CaCO_3$ precipitation or dissolution),

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(ii) Alkalinity remains constant (i.e. the cause of change in the constitution of the water results from CO_2 addition or abstraction).

(a) *Solution*

Conditioning diagrams for aragonite, calcite and magnesian calcite are shown in Figures 9, 10 and 11 respectively. Each diagram was plotted for the chemical constitution of the synthetic sea water.

Calcite: Referring to Figure 10 for two phase equilibrian with respect to pure calcite: Lines representing measured values for Alkalinity, $[Ca]_T$ and pH do not intersect in a point. Thus the water is not just saturated with respect to pure calcite. (As indicated earlier in this chapter, because Mg^{++} is present, magnesian calcite would be the form of calcite precipitate and *not* pure calcite. However, this example is chosen purely for illustrative purposes). The saturation state of the water and mass concentration of $CaCO_3$ which will either dissolve or precipitate to calcite saturation are calculated as follows in Figure 10:

(i) Lines representing Alkalinity 2,2 m.moles/ℓ and pH 8,0 intersect at Point 1. This point defines single aqueous phase equilibrium of the dissolved carbonate species. The vertical ordinate value of Point 1 gives the Acidity of the water, i.e. Acidity 2,05 m.moles/ℓ.

(ii) The value of the calcium line through Point 1, $[Ca_T] <$ 5,0 m.moles/ℓ, is the required calcium content for calcite saturation at pH 8,0. Comparing this required calcium value with the measured calcium value, $[Ca_T] =$ 10,2 m.moles/ℓ, indicates that the water is oversaturated with respect to calcite.

The mass of $CaCO_3$ which will precipitate with time and the final saturated state with respect to calcite are estimated as follows:

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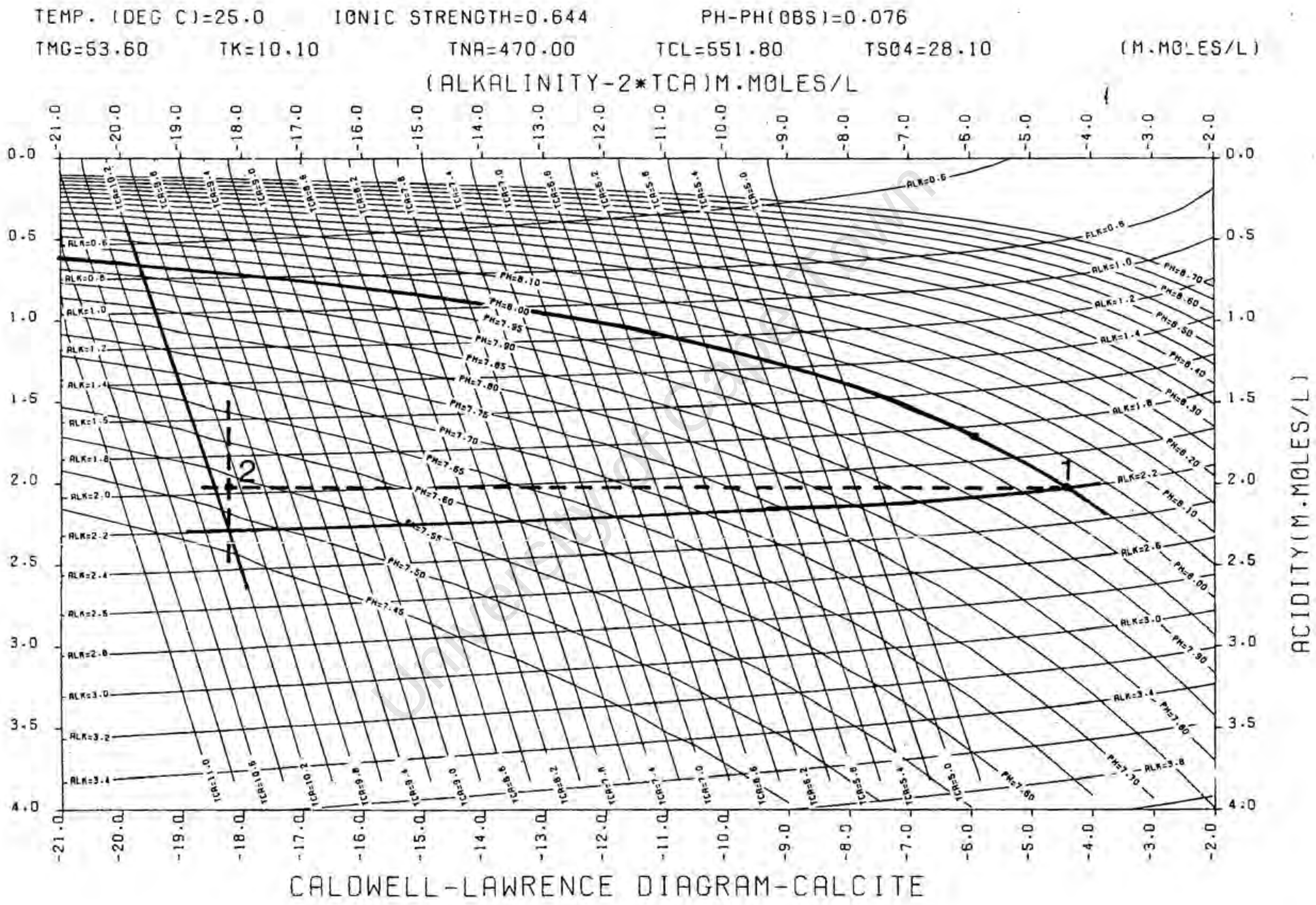

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Figure 10. *Point 2 defines the calcite saturation state for seawater with Alk = 2,20, pH 8,00 and Ca_T = 10,2 m.moles/ℓ.*

(i) Both Acidity and (Alk-2$[Ca_T]$ values remain constant with $CaCO_3$ precipitation, thus Initial Acidity = Final Acidity = 2,05 m.moles/ℓ. Initial (Alk-2$[Ca_T]$ = Final (Alk-2$[Ca_T]$ = 18,20 m.moles/ℓ. The ordinate lines for these values intersect at Point 2 in Figure 10.

(ii) The final saturated state with respect to calcite that the water would attain with time is given by values of the lines for Alkalinity, $[Ca_T]$ and pH through Point 2, i.e.

Alk = 1,97 m.moles/ℓ, $[Ca_T]$ = 10,09 and pH 7,57.

(iii) The mass of calcite which would be precipitated if the solution were to attain pure calcite saturation is given by the *change* in either $[Ca]_T$ or half the change in Alkalinity

$CaCO_3$ precipitated (calcite) = 0,5 (2,20 - 1,97)
= 10,20 - 10,09
= 0,11 m.moles/ℓ

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Aragonite: Referring to Figure 9 for two phase equilibrium with respect to aragonite: Exactly the same procedure as in (a) above can be adopted in Figure 9 for aragonite saturation state. The final saturated state (with respect to aragonite) which the water could attain with time is given by the Alkalinity, $[Ca]_T$ and pH lines through Point 2, i.e. Alkalinity = 2,04 m.moles/ℓ, $[Ca]_T$ = 10,12 m.moles/ℓ and pH 7,70.

The mass concentration of aragonite which can ultimate precipitate from the water is again given by either the change in total calcium or one half the change in Alkalinity, i.e.

$CaCO_3$ precipitated (aragonite) = 0,08 m.moles/ℓ.

Magnesian Calcite: Using the same procedure as above for calcite and aragonite saturation, in Figure 11 for magnesian calcite saturation, the final saturated state which the water would attain with time is given by the values of the Alkalinity, $[Ca]_T$ and pH lines through Point 2 in Figure 11, i.e. Alkalinity = 2,00 m.moles/ℓ, $[Ca]_T$ = 10,10 m.moles/ℓ and pH = 7,58.

The mass concentration of $CaCO_3$ precipitated to saturation is 0,10 m.moles/ℓ.

(b) *Solution*

0,10 m.moles/ℓ of CO_2 is added to the water, estimate the new saturation state of the water with respect to:

Aragonite: The changes in Alkalinity and Acidity with chemical dosing are determined from Eqs. (1 and 6), i.e.

$$\Delta Alk = 0$$

$$\Delta Acidity = 2(0,10)$$

$$= 0,2 \text{ m.moles/ℓ}$$

thus

New Alk = original Alk = 2,20 m.moles/ℓ

New Acidity = original Acidity + ΔAcidity

= 2,05 + 0,2 = 2,25 m.moles/ℓ

The new pH in the water is given by the value of the pH line through the intersection point of the lines representing the new values for Alkalinity and Acidity, i.e. Point 3 in Figure 9 giving pH = 7,63. The value of the $[Ca]_T$ line through Point 3 is $[Ca]_T$ > 10,2 m.moles/ℓ, which exceeds the actual total calcium concentration in the water. This indicates that the water is now undersaturated with respect to aragonite.

The aragonite saturated condition which the water can attain

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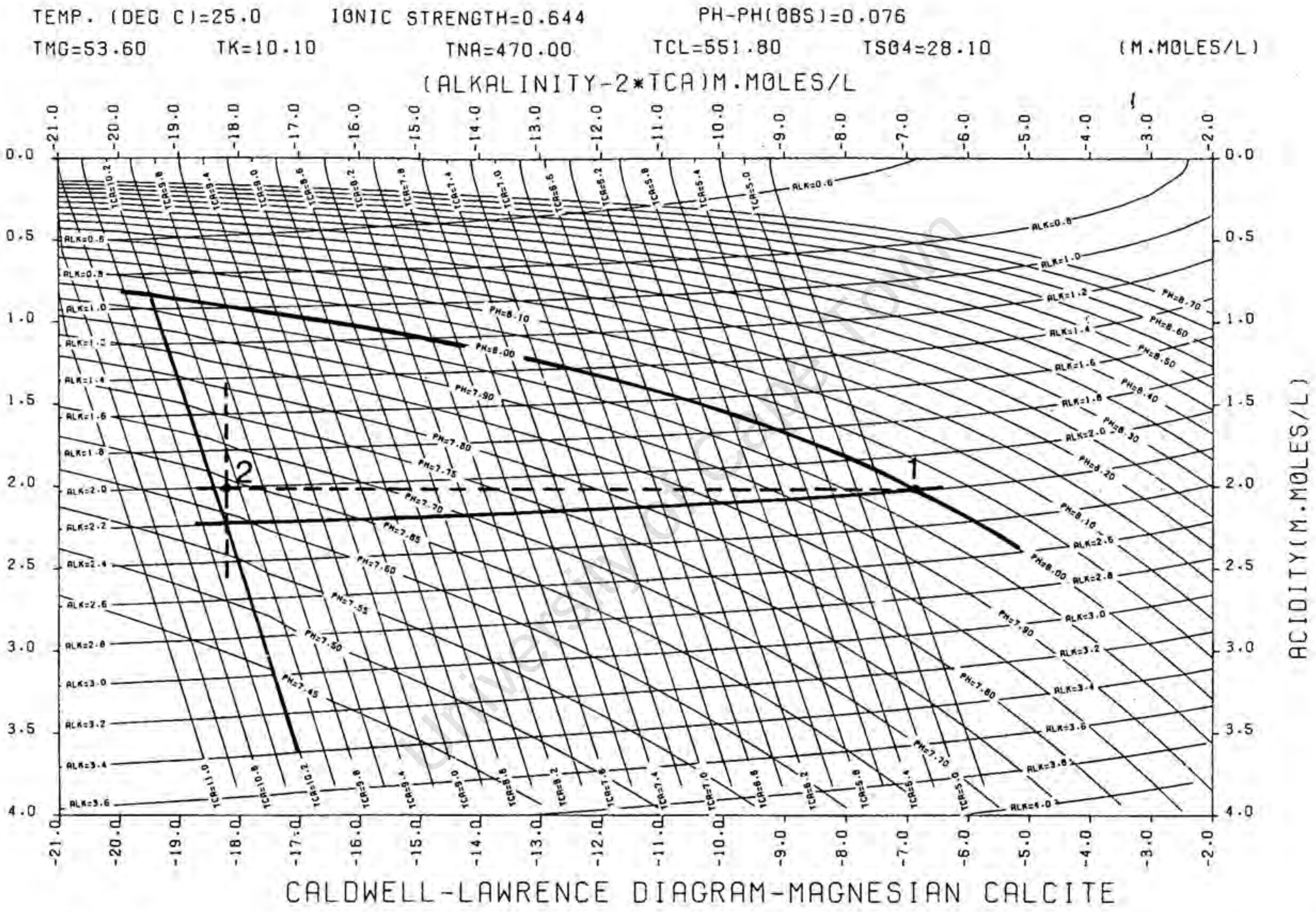

Figure 11. *Point 2 defines the magnesian calcite saturation state for seawater with Alk = 2,20, pH 8,00 and* Ca_T *= 10,2 m.moles/ℓ.*

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with time (provided there is a source of solid $CaCO_3$) is determined as in (a) above as the values of the Alkalinity, $[Ca]_T$ and pH lines through Point 4 in Figure 9, i.e. Alkalinity 2,22, $[Ca]_T = 10{,}21$ (both in m.moles/ℓ) and pH 7,65.

The mass concentration of aragonite which can dissolve into the undersaturated water is given by either (i) the difference between the measured $[Ca]_T$ in the water and the value of the $[Ca]_T$ line through Point 4, or (ii) one half the difference between the measured Alkalinity and the value of the Alkalinity line through Point 4 (see Eq. (1)), i.e.

$$
\begin{aligned}
CaCO_3 \text{ (aragonite) dissolving} &= \text{Final } [Ca]_T - \text{Initial } [Ca]_T \\
&= 10{,}21 - 10{,}20 \\
&= 0{,}5 \text{ (Final Alk - Initial Alk)} \\
&= 0{,}5\ (2{,}22 - 2{,}20) \\
&= 0{,}01 \text{ m.moles}/\ell .
\end{aligned}
$$

(c) *Solution*

Plot the mass of $CaCO_3$ to be precipitated or dissolved to *aragonite* saturation with pH when:

(i) Acidity remains constant:

When $CaCO_3$ precipitates from (or dissolved into) a water, Acidity remains constant, i.e. from Eq. (6) abstraction or addition of $CO_3^=$ does not affect the Acidity. Changes in the aragonite transient saturation state with pH can be traced as follows, using Figure 9.

Intersection point of lines representing pH values with the line representing Acidity in the water, Acidity = 2,02 m.moles/ℓ, gives the Alkalinity values in the water as $CaCO_3$ dissolution or precipitation occurs. The difference between each of these Alkalinity values and the Alkalinity value for aragonite saturation (i.e. the value of the Alkalinity line through Point 2, Alkalinity = 2,04 m.moles/ℓ) gives one half of the mass concentration of $CaCO_3$ to be precipitated to aragonite saturation.

A plot of the mass of $CaCO_3$ to be dissolved or precipitated to aragonite saturation with pH is shown in Figure 12. The plot indicates that at pH 7,70 the water is just saturated with respect to aragonite. As pH increases above pH 7,70, the mass of $CaCO_3$ to be precipitated also increases and vice versa for decreasing pH values below pH 7,70. If the water is in contact with a source of solid aragonite, one can consider the mass of $CaCO_3$ to be precipitated (or dissolved) to saturation as a measure of the driving force in the water to attain the saturated pH value of 7.70. Figure 12 thus represents a simple push-pull mechanism to aragonite saturation pH, pH 7,70, for a constant Acidity. The plot is valid only for the constant Acidity value of 2,02 m.moles/ℓ, i.e. if Acidity changes to some new value due to CO_2 transfer the same type of plot can be made for the new Acidity value.

(ii) Alkalinity remains constant (i.e. CO_2 is added to or abstracted from the water):

When CO_2 is added or abstracted from a water the effects on Alkalinity and Acidity are as follows: Alkalinity is unaffected, provided no $CaCO_3$ precipitation or dissolution occurs (see Eq.(1)); Acidity changes by twice the molar mass of CO_2 added or abstracted (see Eq. (6)).

For each Acidity value there is a particular pH in the water defining single aqueous phase equilibrium and given by the value of the pH line through the intersection point of the lines representing Acidity and the constant Alkalinity 2,20 m.moles/ℓ (i.e. Points 1 to 5 in Figure 13. Furthermore, for each of the Acidity values and the initial values of $[Ca]_T$ and Alkalinity (equal to 10,2 and 2,20 m.moles/ℓ respectively) there is a particular aragonite saturated condition given by the intersection point of lines

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concentrations from 2,20 and 10,2 m.moles/ℓ respectively. Figure 13 indicates that for each pH value (i.e. each Acidity value) the saturated pH differs and is given by the values of the pH lines through Points 1' to 5' and therefore one *cannot* consider the driving force as being that to change the pH from pH 7,70 as the example (i) above.

The problems discussed above (and variations of these problems) can be solved algebraically, as shown by Stumm and Morgan (1972), but for low salinity waters only. The graphical approach presented here is applicable to both low and high salinity water and has the merit of giving one a visual assessment of the behavioral characteristics of the system parameters.

In the general theory for the carbonate system in the aqueous phase (Chapter 3), it was shown that only two parameters pertaining to the system need to be measured to define the system. Usually the two parameters are pH and Alkalinity. However, if an instrument is available to measure the partial pressure of dissolved carbon dioxide, $pCO_2(aq)$, this parameter can be substituted for one of the two above. The reason why this is possible is that $[H_2CO_3^*]$ in the aqueous phase is lineraly related to $pCO_2(aq)$, (see Eq.(2)). As a consequence, in the Modified Caldwell-Lawrence Diagram it is possible to plot lines of $[Ca]_T$ together with a combination of any two of the parameters pH, $pCO_2(aq)$ and Alkalinity. Each combination will define the system completely. The choice of a particular combination will depend only on its suitability for solving problems. Of course, it is also valid to plot all three parameters on the same diagram, but this makes the diagram difficult to read.

7. THREE PHASE EQUILIBRIUM (AQUEOUS, SOLID AND GAS PHASES)

Earlier in this chapter it was shown that for two phase equilibrium between molecularly dissolved CO_2 in the aqueous phase and a partial

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pressure of CO_2 in the gas phase, pH is a function of one mass parameter only (see Figure 5). Thus, for a water with a particular temperature and ionic constitution in equilibrium with CO_2 in the gas phase, the pH established is related to the measured Alkalinity. For example, referring to Figure 6, for a synthetic sea water at 25°C containing only the carbonate weak acid system in equilibrium with the air (with pCO_2 = 0,0003 Atmospheres) and Alkalinity = 2,20 m.moles/ℓ: intersection point of the lines representing pCO_2 0,0003 Atmospheres and Alkalinity 2,20 m.moles/ℓ defines the equilibrium state of the water, the value of the pH line through this point gives the predicted pH, i.e. pH = 8,20. Alkalinity may be replaced as the independent parameter by any of the mass parameters of the carbonate system (i.e. C_T or Acidity). This chosen mass parameter together with the partial pressure of CO_2 in the air, pCO_2, automatically define the pH for CO_2 equilibrium between the aqueous and gas phases.

Lines representing three phase equilibrium between the aqueous, solid and gas phases can be plotted in the Modified Caldwell-Lawrence Diagram with close approximation, as follows:

Referring to Figure 6, the line representing a particular pCO_2 value is defined by a set of $H_2CO_3^*$ Alkalinity and $CO_3^=$ Acidity values (or a set of any *two* of the parameters Alkalinity, Acidity, C_T and pH). From Figure 6, a plot of Alkalinity and Acidity values for pCO_2 equal to 0,0003 Atmospheres is made in the Modified Caldwell-Lawrence Diagram, see Line A in Figure 15. Line A traces the condition for approximate two phase equilibrium between CO_2 in the gas phase (pCO_2 = 0,0003 Atmospheres) and carbonate species in the aqueous phase. If the line representing $[Ca]_T$ intersects the point defining aqueous-gas phase equilibrium on Line A, the water is in three phase equilibrium.

Line A, as plotted above, is only approximate because the relationship linking pCO_2, Alkalinity and Acidity in Figure 14 is for a constant $[Ca]_T$ value, whereas the relationship between Alkalinity

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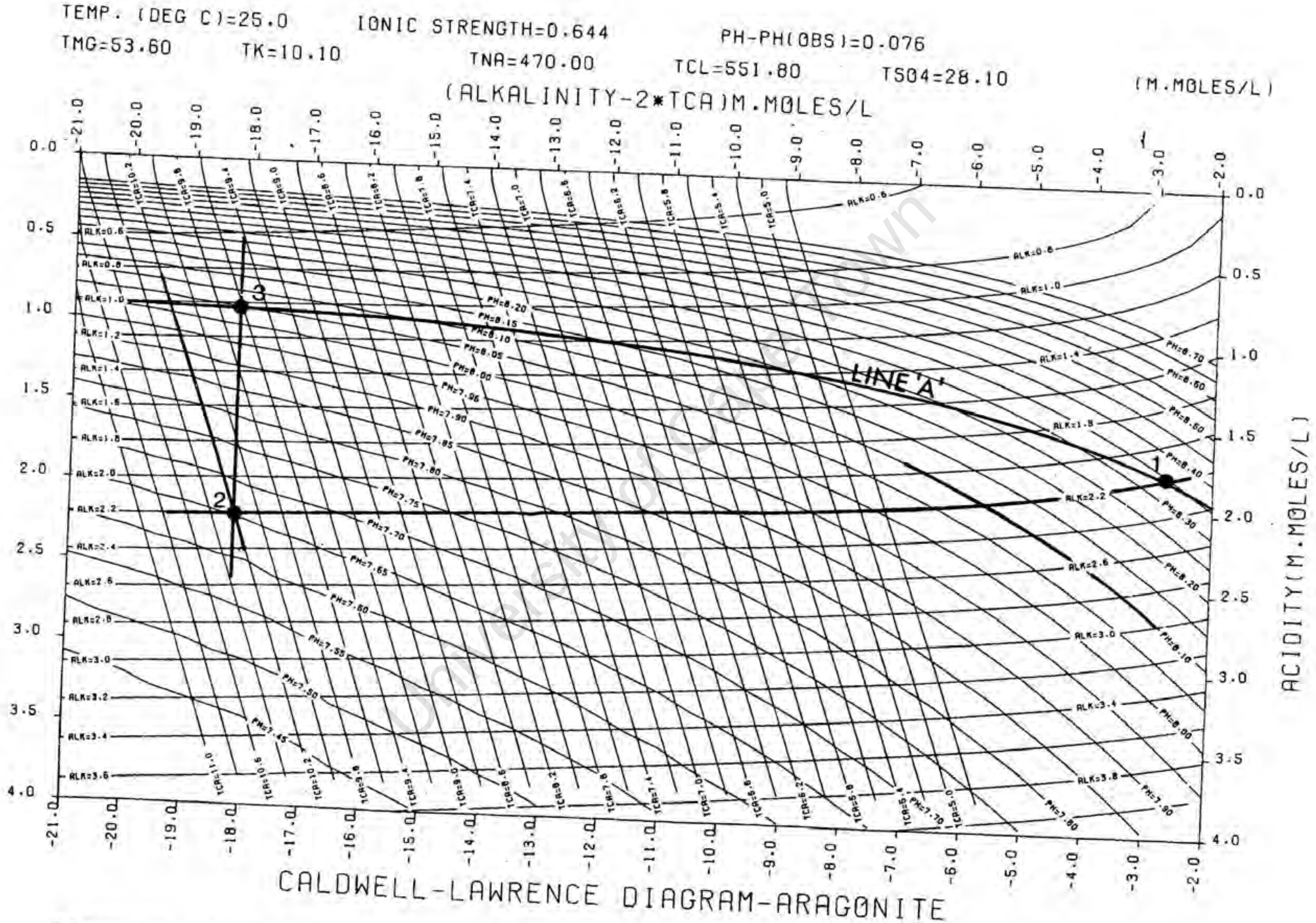

Figure 15. Line 'A' represents equilibrium between CO_2 in the air and seawater.

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and Acidity in the Modified Caldwell-Lawrence Diagram incorporates the variable $[Ca]_T$ value for $CaCO_3$ solubility. However, for all practical purposes the error is negligible. An exact solution to plot a family of curves of pCO_2 values in the gas phase, with Acidity and $(Alk-2[Ca]_T)$ as coordinates, is included as a subprogram in the computer program listing for the Modified Caldwell-Lawrence Diagram in Supplement D.

If a water is saturated with respect to the solid phase (say aragonite), but not in equilibrium with the gas phase, CO_2 transfer will take place between the aqueous and gas phases until equilibrium is established. In attaining equilibrium between the gas and aqueous phases, the water now becomes either super- or undersaturated with respect to the solid phase (aragonite) depending on whether CO_2 is expelled or absorbed by the water respectively.

In any water (either saturated or undersaturated with respect to $CaCO_3$) *which is seeded with solid* $CaCO_3$ and brought to equilibrium with respect to CO_2 in the gas phase, the *three phase equilibrium* condition which the water ultimately attains is given by the intersection point of the $(Alk-2[Ca]_T)$ ordinate value which remains constant with the pCO_2 line for the gaseous phase. The molar mass of CO_2 exchanged with the gas phase is given by the change in Acidity of the water between the initial and final condition. If the acidity change is positive, CO_2 is absorbed by the water to CO_2 equilibrium and *vice versa* for a negative change in Acidity. The molar mass of $CaCO_3$ precipitated from (or dissolved into) the water is given by the change in the total dissolved calcium concentration. These aspects were considered in detail by Loewenthal and Marais in their monograph on low salinity waters; as the graphical applications in high salinity waters are identical to those in low salinity waters the reader is referred to their work on low salinity conditioning diagrams for any further clarification which may be required.

If borate and carbonate weak acid systems are present, the borate system acts as a pH buffer which tends to reduce pH changes with chemical dosing. Consequently, the mass of $CaCO_3$ precipitated or dissolved to saturation is enhanced compared with values calculated considering the carbonate system only. In so far as equilibrium between the aqueous and gas phases is concerned, the buffering effect of the borate system causes an increase in the molar mass of CO_2 ~~to~~ be exchanged to equilibrium. These effects can be determined by using the aqueous phase borate diagram in conjunction with the carbonate system diagrams. The interaction between the borate and carbonate systems is essentially a single phase problem even though the problem for the carbonate system might be for two or three phase equilibria.

The buffering effect of the borate system in sea water is relatively small compared with that of the carbonate system, hence in discussing the carbonate system equilibrium changes, for simplicity the borate system has been neglected.

7.1 Application to Sea Water (Carbonate System Only)

The three phase diagram, Figure 15, is of particular interest in its application to natural water bodies. These waters are rately in equilibrium with respect to either the solid or gas phases; the pH continually fluctuates as (i) CO_2 is either given off or taken up by microorganisms and CO_2 exchange occurs with the gas phase, and (ii) solid $CaCO_3$ is either removed from or dissolved into the water. The pH fluctuations in such a water body are a measure of the response of the system to CO_2 exchange with both the microorganisms and the gas phase, and $CaCO_3$ precipitation and dissolution. An example of such a system is the diurnal and seasonal fluctuation of pH in the surface waters of the oceans.

Sillen (1961) and Garrels (1965) suggested that in terms of *geological time* precipitation and ion exchange phenomena of the *silicate system* plays the central rôle in pH establishment and

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buffering of the oceans. They hypothesize that both the $CaCO_3$ saturation state of the oceans and the pCO_2 established in the atmosphere are a response to the pH established in the long term by the silicate system. However, whereas geologists are primarily concerned with the long term paleohistory of the oceans, oceanographers need to consider shorter time periods in their studies of biological productivity, gas exchange across the sea surface and precipitation of solid species from the water mass (Pytkowicz, 1965). These short term changes are manifested by continual fluctuations in the observed pH of the seas, between pH 7,8 and 8,3, and these are most likely the response to a simple 'push and pull' mechanism afforded by the carbonate system.

In the surface layers of the sea a number of chemical processes may operate simultaneously, i.e. CO_2 exchange with the atmosphere, CO_2 release or uptake by organisms and $CaCO_3$ dissolution or abstraction. These processes can be subdivided into two general classes of problems: (1) due to some action the pH of the water rises or falls. How will CO_2 exchange with the atmosphere effect the changes to equilibrium assuming no $CaCO_3$ precipitation or dissolution occurs? Obviously the water may be (or become) super- or undersaturated with respect to $CaCO_3$ solid so that a changing precipitation or dissolution potential is set up as CO_2 exchange occurs with the atmosphere. (2) Due to some action the pH in the water rises or falls. How will $CaCO_3$ precipitation or dissolution effect the changes to equilibrium with respect to aragonite assuming that no CO_2 exchange occurs either due to biota or with the air. In the process of advancement to aragonite saturation a changing *potential* for CO_2 exchange with the atmosphere will be set up due to the non-equilibrium between the aqueous and gas phases.

Example

Illustrate graphically the driving forces acting on the pH of the surface layers sea water (without the borate system) as CO_2

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exchange occurs with the atmosphere but *no* mineral precipitation or dissolution occurs. Assume that the Alkalinity (i.e. $H_2CO_3^*$ Alkalinity) remains constant and equal to 2,20 m.moles/ℓ and that aragonite is the stable solid phase of $CaCO_3$.

Referring to Figure 15:
Line A represents a partial pressure of CO_2, pCO_2, equal to that in the atmosphere, i.e. 0,0003 Atmospheres. Intersection point of the line representing Alkalinity 2,20 m.moles/ℓ with Line A occurs at Point 1. The pH and Acidity values of this point give the values of these parameters at equilibrium between aqueous and gas phases, i.e. pH = 8,35 and Acidity = 1,74 m.moles/ℓ.

Two 'push-pull' mechanisms will be acting on the pH (a) that due to pCO_2 disequilibrium between air and water and (b) that due to super- or undersaturation with respect to aragonite due to changes in Acidity resulting from CO_2 exchange between the aqueous and gas phases, i.e. one expects pH to fluctuate between the Points 2 and 1 in Figure 15, $7,65 < pH < 8,35$ or $7,59 < pH_c < 8,27$.

(a) Driving Force Afforded by CO_2 Exchange

Alkalinity remains unchanged with CO_2 transfer provided no mineral precipitation/dissolution occurs. The points of intersection of lines representing pH values (for pH values above and below pH = 8,35) with the Alkalinity line 2,20 define transient states to CO_2 equilibrium, i.e. Points 2, 3, ... 5 in Figure 16. The difference in Acidity between the saturated equilibrium condition, Point 1 with Acidity 1,74 m.moles/ℓ, and the Acidity of each of the transient points gives the molar mass of CO_2 to be exchanged between the two phases to saturation. A plot of the mass of CO_2 to be exchanged to saturation with pH for each of these transient points is shown in Figure 17. Note that for increasing and decreasing pH values above and below pH 8,35 the driving force to saturation increases monotonically.

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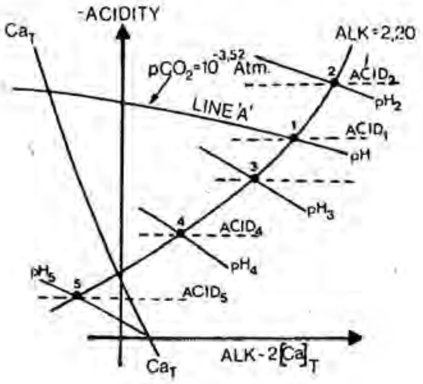

Figure 16. Determination of 'driving potentials' to gas phase and solid phase (aragonite) equilibrium for seawater with constant fixed Alkalinity using the Modified Caldwell-Lawrence diagram.

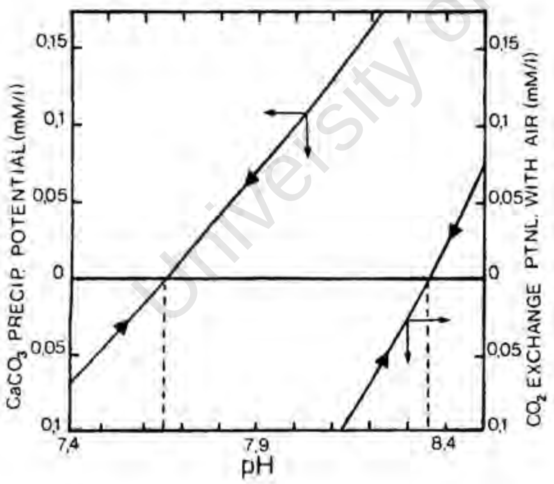

Figure 17. 'Driving potentials' to CO_2 equilibrium with the air and aragonite saturation for seawater with a constant fixed Alkalinity = 2,20 m.moles/ℓ.

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(b) Driving Force Afforded by $CaCO_3$ non-saturation due to CO_2 Exchange

The precipitation aspect for each Acidity value was discussed in detail in a previous example in this chapter. A plot of the potential molar mass of $CaCO_3$ that can be precipitated to aragonite saturation with pH is shown in Figure 17 for constant $H_2CO_3^*$ Alkalinity = 2,20 m moles/ℓ.

Considering each effect separately, the pH would tend to the point where the function (driving force) is zero. Considered conjointly, the pH would tend to a point where some function of these two functions tends to zero. This combined function, which will be influenced principally by the kinetics of each process, is likely to have its minimum between the two zero values. The plots therefore indicate that the pH in the surface waters of the sea is likely to be established in the region pH 7,65 to 8,35.

Example

Illustrate graphically the driving forces acting on the pH in the surface waters of the sea (neglecting the borate system) as $CaCO_3$ saturation is attained with respect to aragonite, i.e. constant Acidity conditions. Assume that the pCO_2 in the air is 0,0003 atmospheres, initial Alkalinity is 2,20 m.moles/ℓ and the initial Acidity 2,01 m.moles/ℓ.

As in Example 1, two 'push-pull' mechanisms will be acting on the pH: (a) that due to super- or undersaturation with respect to aragonite and (b) that due to pCO_2 disequilibrium due to changes in Alkalinity resulting from $CaCO_3$ abstraction/dissolution.

(a) Driving Force on pH Due to $CaCO_3$ Abstraction/dissolution

With abstraction of $CaCO_3$ from the water, the Acidity remains constant and equals the initial Acidity value. The molar mass of $CaCO_3$ to be precipitated to aragonite saturation for Acidity = 2,01 m.moles/ℓ with pH was determined in a previous example and is shown

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plotted in Figures 12 and 18.

(b) Driving Force Afforded by pCO_2 Disequilibrium Due to Changes in Alkalinity Resulting from $CaCO_3$ Precipitation

For each of the transient states to aragonite saturation shown in Figure 19, i.e. Points 1', 2' ... 5', there exists a unique Alkalinity value which is given by the Alkalinity line passing this transient condition. Intersection of lines representing each of these transient Alkalinity values with the line representing pCO_2 0,0003 Atmospheres occurs at Points 1, 2, ... 5 in Figure 19. The difference in Acidity between the Points 1' and 1, 2' and 2, ... 5' and 5 gives twice the molar mass of CO_2 to be exchanged with the atmosphere to attain equilibrium between dissolved and atmospheric CO_2. A plot of these mass concentrations with pH is shown in Figure 18. This plot represents the driving force acting on pH due to CO_2 disequilibrium with the air as $CaCO_3$ precipitates (or dissolves) from the surface layers of the sea.

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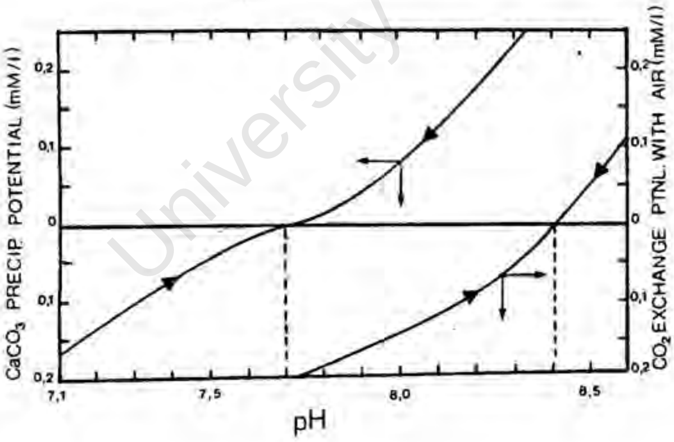

Figure 18. 'Driving potentials' to aragonite saturation and CO_2 equilibrium with the air for seawater with constant fixed Acidity = 2,0 m.moles/ℓ.

In a similar fashion to the reasoning adopted in Example 1, the pH is likely to be established in the region pH 7,70 to 8,30.

If the buffer effects of the borate system were also considered, then the pH for aragonite saturation would *increase* to some value around pH 7,85 and the pH for pCO_2 equilibrium would decrease to a value of about pH 8,15 thereby narrowing down the pH range in which one expects the pH of surface seawater to be.

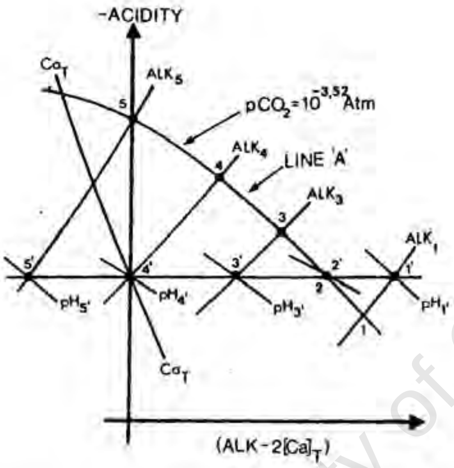

Figure 19. Determination of 'driving potentials' to gas phase and solid phase (aragonite) equilibrium for seawater with constant fixed Acidity using the Modified Caldwell-Lawrence diagram.

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8. APPLICATION TO WATER SOFTENING

Softening and 'hardening' of a water are often required in water treatment. Softening implies removal of the divalent metallic cations Ca and Mg by precipitation as $CaCO_3$ and $Mg(OH)_2$ respectively by addition of OH^- and/or CO_3^{2-}, or by addition of HCO_3^- for a water with negative Acidity. Hardening of a water implies increasing the calcium and (perhaps) the carbonate content; it is achieved either by addition of CO_2 or a strong acid to a water plotting in the positive Acidity region of the Modified Caldwell-Lawrence diagram and in contact with solid $CaCO_3$.

8.1 Softening vector diagrams

Softening and hardening dosage calculations are always carried out for water in aqueous-solid phase equilibrium. For $CaCO_3$ softening, the water will be saturated with respect to $CaCO_3$ both before and after addition of a dosing chemical. That is, one moves from an initial saturated condition before dosing to a final saturated condition after dosing, represented by a point in the diagram.

Usually, the initial state of the water will be either over or undersaturated with respect to $CaCO_3$ and the final state desired may also be an under or slightly oversaturated one with respect to $CaCO_3$. Consequently, before the softening or hardening calculations *per se* can be carried out, the state of the water must be brought to one of saturation with respect to $CaCO_3$. Similarly, after softening or hardening additional dosages must be added to bring the water to the required over or undersaturated state. These calculations are ancilliary to the softening-hardening dosage calculations and are performed assuming single aqueous phase equilibrium. (These have been discussed briefly earlier in this chapter and extensively so by Loewenthal and Marais, 1976).

Returning to the dosage calculations for softening, when a water is saturated with respect to $CaCO_3$, then, in the Modified Caldwell-Lawrence diagram the total calcium, Alkalinity and pH lines describing this state will cross at a point. If the appropriate chemical for softening is added (for example, in the positive Acidity region adding either $Ca(OH)_2$ or Na_2CO_3, and in the negative Acidity region adding either CO_2 or Na_2CO_3) the final state will be at a different point in the diagram, the three lines representing the softened water again crossing at a point.

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Simple rules can be derived whereby the movement of the saturated equilibrium point can be calculated. The position in the diagram of the final point relative to the initial point is described by a vector of magnitude and direction depending on the mass and type of chemical added. For rapid utilization of the diagram, to adjust a water from one saturated state to another, it is convenient to develop a softening vector diagram, or a two phase direction format diagram. The format diagram gives the direction and distance which a point representing a $CaCO_3$ saturated water in the conditioning diagram moves when adding a specific type and mass of chemical dose, see Figure 20. The direction format diagram is developed as follows:

X m.moles/ℓ of each of the following chemicals are added to water saturated with respect to $CaCO_3$, i.e. (i) $Ca(OH)_2$, (ii) CO_2, (iii) Ca^{2+}, (iv) CO_3^{2-}, (v) HCO_3^-, (vi) OH^- and (vii) H^+.

(i) Addition of X m.moles/ℓ of $Ca(OH)_2$:

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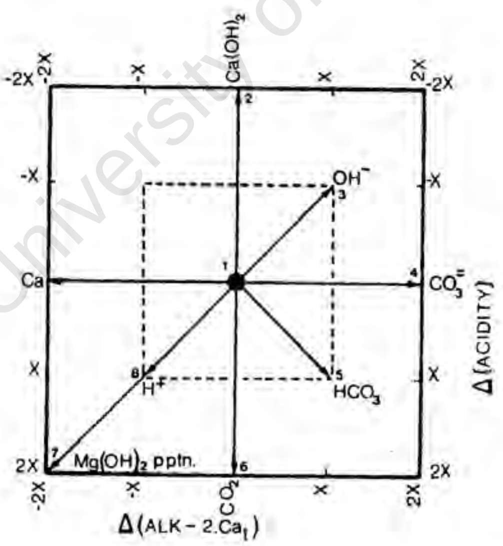

Figure 20: Vector diagram to be used with the Caldwell-Lawrence Diagram for addition of X m.moles/ℓ of chemical to water remaining saturated with respect to $CaCO_3$ (Valid provided Caldwell-Lawrence Diagram is plotted with equal ordinate scales).

Addition of X m.moles/ℓ of $Ca(OH)_2$ to a water has the following effects on Ca_T, Alk, Acidity and Alk-2[Ca_T],

$\Delta[Ca_T] = X$

From Eq (1)

$\Delta Alk - 2\Delta[Ca_T] = 2X - 2X = 0$

and, from Eq (6)

$\Delta Acidity = -2X$

Suppose Y m.moles/ℓ of $CaCO_3$ dissolves into (or precipitates from) the water such that the solution remains saturated with respect to $CaCO_3$

$\Delta Ca_T = Y$

$\Delta Alk = 2Y$

i.e.

$\Delta Alk - 2\ Ca_T = 2Y - 2Y = 0$

and

$\Delta Acidity = 0$

The overall effects on (Alk - 2.Ca_T) and Acidity are

$\Delta(Alk - 2[Ca]_T) = 0$

$\Delta Acidity = -2X$

Thus, adding X m.moles/ℓ lime to a saturated water moves the point describing the water in the Modified Caldwell-Lawrence diagram, Point 1 in Figure 20, vertically by 2X units to Point 2 provided Acidity and (Alk - 2$[Ca]_T$) have equal scales in the diagram.

(ii) Addition of X m.moles/ℓ of CO_2:

The overall effects on Acidity and (Alk-2$[Ca]_T$) of adding X m.moles/ℓ of CO_2 to a water which remains saturated with

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respect to $CaCO_3$ are

ΔAcidity = 2X

and

$\Delta(Alk-2[Ca]_T) = 0$

Thus, addition X m.moles/ℓ of CO_2 to such a saturated water moves the point describing the water in the Caldwell-Lawrence diagram, Point 1 in Figure 20, vertically down by 2X units to Point 6 provided that Acidity and $(Alk-2[Ca]_T$ have equal scales in the diagram.

(iii) Addition of X m.moles/ℓ of Ca^{2+}:

The effects on Acidity and $(Alk-2[Ca]_T$ on addition X m.moles/ℓ Ca^{2+} (for example by addition $CaCl_2$) to a water saturated with respect to $CaCO_3$ are

ΔAcidity = 0

and

$\Delta(Alk-2[Ca]_T = -2X$

Thus, adding X m.moles/ℓ of Ca^{2+} to a saturated water moves the point describing the water in the Caldwell-Lawrence diagram, Point 1 in Figure 20, horizontally to the left by 2X units to Point 9 provided Acidity and $(Alk-2[Ca]_T$ have equal scales in the diagram.

(iv) Addition of X m.moles/ℓ of CO_3^{2-}:

The effects on Acidity and $(Alk-2[Ca]_T$ of addition X m.moles/ℓ CO_3^{2-} (for example Na_2CO_3) to a water saturated with respect to $CaCO_3$ are

ΔAcidity = 0

$\Delta(Alk-2[Ca]_T) = 2X$

Thus, adding X m.moles/ℓ of CO_3^{2-} to a saturated water moves

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the point describing the water in the Caldwell-Lawrence diagram, Point 1 Figure 20, horizontally to the right by 2X units to Point 4.

(v) Addition ox X m.moles/ℓ of HCO_3^-:

The effects on Acidity and (Alk-2$[Ca]_T$ of addition X m.moles/ℓ of HCO_3^- to a water remaining saturated with respect to $CaCO_3$ are

ΔAcidity = X

Δ(Alk-2$[Ca]_T$)= X

Thus, adding X m.moles/ℓ of HCO_3^- to a saturated water moves the point describing the water in the Caldwell-Lawrence diagram, Point 1 Figure 20, forty five degrees down to the right $(2X^2)^{\frac{1}{2}}$ units to Point 5 provided that Acidity and (Alk-2$[Ca]_T$) have equal scales in the diagram.

(vi) Addition of X m.moles/ℓ of OH^-:

The effects on Acidity and (Alk-2$[Ca]_T$ of adding X m.moles/ℓ OH^- to a water remaining saturated with respect to $CaCO_3$ are

ΔAcidity = -X

Δ(Alk-2$[Ca]_T$) = X

Thus, adding X m.moles/ℓ of OH^- to a saturated water moves the point describing the water in the Caldwell-Lawrence diagram, Point 1 Figure 20, forty five degrees upwards to the right $(2X^2)^{\frac{1}{2}}$ units to Point 3 provided Acidity and (Alk-2$[Ca]_T$ have equal scales in the diagram.

(vii) Addition of X m.moles/ℓ of H^+:

The effects on Acidity and (Alk-2$[Ca]_T$ of adding X m.moles/ℓ of H^+ to a water remaining saturated with respect to $CaCO_3$ are

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ΔAcidity = X

$\Delta(\text{Alk-}2[\text{Ca}]_T) = -X$

Thus, adding X m.moles/ℓ of H^+ to a saturated water moves the point describing the water in the Caldwell-Lawrence diagram, Point 1 in Figure 20, forty five degrees downwards to the left by $(2X^2)^{\frac{1}{2}}$ units to Point 8 provided Acidity and $(\text{Alk-}2[\text{Ca}]_T)$ have equal scales in the diagram.

The application of the above derivations to calcium softening (or hardening) using the Caldwell-Lawrence diagram is summarized below:

(i) The state of a saturated water plots as a point in the conditioning diagram.

(ii) Addition of various chemicals to a saturated water in contact with $CaCO_3$ moves the point in the diagram, describing the saturation state, a specific distance and direction depending on the mass and type of chemical added.

(iii) Choosing Acidity and $(\text{Alk-}2[\text{Ca}]_T)$ to have equal scales in the diagram, Figure 20 gives the vectorial movement which a saturated equilibrium point in the conditioning diagram moves due to addition of the specific chemicals.

8.2 Magnesium softening

For softening purposes the maximum concentration of free magnesium in water is assumed to be governed by the solubility of brucite, $Mg(OH)_2$. That is, at saturation with respect to brucite,

$$[Mg^{2+}]_S[OH^-]^2 = K'_{Mg(OH)_2} \tag{46}$$

where $[Mg^{2+}]_S$ = concentration of free Mg^{2+} at saturation with respect to brucite

$K'_{Mg(OH)_2}$ = apparent solubility product for brucite

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and, solving for $[Mg^{2+}]_s$ in Eq (46)

$$[Mg^{2+}]_S = \frac{K'_{Mg(OH)_2} \cdot (H+)^2}{(K'_w)^2} ,$$

$$= K'_{Mg(OH)_2} 10^{-2pH}/(K'_w)^2 \qquad (47)$$

From Eq (47), for a particular ionic medium the maximum concentration of *free* Mg^{2+} depends only on pH. However, in water softening one is interested in dosage estimation to reduce the *total* magnesium concentration (i.e. free plus ion paired species) to some desired value. The link between pH and total magnesium for a water saturated with respect to $Mg(OH)_2$ is established as follows:

Where the total carbonate species in solution are very much less than the total magnesium concentration, i.e. $[Mg]_T >> C_T$, the influence of magnesium carbonate and bicarbonate ion pairs on $[Mg]_T$ is negligible, i.e.

$$[Mg]_T \cong [Mg^{2+}]_S \ (1 + [SO_4^{2-}]/K'_{MgSO_4} + [OH^-]/K'_{MgOH}) \qquad (48)$$

Substituting for $[Mg^{2+}]_S$ from Eq (47) into Eq (48)

$$[Mg]_{TS} = \{K'_{Mg(OH)_2} . 10^{-2pH}/(K'_w)^2\}.\{1+[SO_4^{2-}]/K'_{MgSO_4} + 10^{pH}.K'_w/K'_{MgOH}\} \qquad (49)$$

where $[Mg]_{TS}$ = total magnesium in solution at saturation with respect to brucite.

From Eq (49), for a water with a particular principal ionic matrix, $[Mg]_T$ is a function only of pH, and it is possible to plot a nomograph of $[Mg]_T$ versus pH for $Mg(OH)_2$ saturation, see Figure 21. Utilization of this nomograph together with the Caldwell-Lawrence diagram supplies the means of dosage estimation for

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magnesium softening. The equations for plotting the lines representing pH, Alkalinity, $[Ca]_T$ and pCO_2 in the Modified Caldwell-Lawrence diagram each contain a $[Mg]_T$ term, but there is a restriction on the value for this term: provided the water is undersaturated with respect to $Mg(OH)_2$ the input value for $[Mg]_T$ is inserted into the equations, if however $Mg(OH)_2$ solubility is exceeded, the saturated value for $[Mg]_T$ needs to be used. This is necessary not only for use in magnesium softening, but also because the plots of the families of curves for Alkalinity, total calcium and pH include the effects of $MgOH^-$ ion pairing. The species $MgOH^-$ contributes to both Alkalinity and Acidity, consequently unless $MgOH^-$ concentration is limited by $Mg(OH)_2$ solubility, in the high pH regions the untenable situation may arise where $[MgOH^-]$ exceeds the input values for Alkalinity and Acidity.

Precipitation of $Mg(OH)_2$ from a supersaturated water (which remains saturated with respect to $CaCO_3$) can be depicted by a vector in the Caldwell-Lawrence diagram in the same fashion as addition of other dosing chemicals depicted in Figure 20, as follows:

X m.moles/ℓ of $Mg(OH)_2$ is *precipitated* from a water which remains saturated with respect to $CaCO_3$,

ΔAcidity = 2X

ΔAlk = -2X

$\Delta[Ca]_T$ = 0

i.e.

$\Delta(Alk-2[Ca]_T) = -2X$

Suppose Y m.moles/ℓ of $CaCO_3$ dissolves into (or precipitates from) the water such that the water remains saturated with respect to $CaCO_3$ during the $Mg(OH)_2$ precipitation process

ΔAcidity = 0

ΔAlk = 2Y

$\Delta[Ca]_T$ = Y

i.e.

$\Delta Alk-2.[Ca]_T = 0$

The overall effects on the coordinate parameters are

$\Delta(Alk-2[Ca]_T = -2X$

and

ΔAcidity = 2X

Thus, precipitation of X m.moles/ℓ of $Mg(OH)_2$ from a $CaCO_3$ saturated water moves the point describing the water in the Caldwell-Lawrence diagram, Point 1 in Figure 20, forty five degrees down to the left by $(8X^2)^{\frac{1}{2}}$ units to point 7 provided Acidity and $(Alk-2[Ca]_T)$ have equal scales in the diagram.

Example: Analyses on a water from Graaff-Reinett, S. Africa, gives [Alkalinity] = 5,6, $[SO_4]_T$ = 2,97, $[Cl^-]$ = 15,5, $[Mg]_T$ = 5,11, $[Ca]_T$ = 3,86 (all in m.moles/ℓ) and pH 7,4. It is required to estimate the lime and Na_2CO_3 dosages to soften the water to $[Mg]_T$ = 3,0 m.moles/ℓ and $[Ca]_T$ = 1,5 m.moles/ℓ. Temperature = 25°C.

Solution:

A plot of the lines representing Ca_T = 3,86, Alk = 5,60 and pH = 7,20 (the initial condition of the water) is shown in Figure 21 and indicates that the raw water is supersaturated with respect to $CaCO_3$. In the presence of solid $CaCO_3$ the water should attain $CaCO_3$ saturation represented by Point 1 in Figure 21, with Acidity = 7,0 and $Alk-2[Ca]_T = -2.12$.

In practice the calcium and magnesium softening are carried out in the same reactor, however for the purposes of estimating chemical dosage requirements it is convenient to consider calcium and magnesium softening separately.

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(a) Magnesium softening:

Referring to the nomograph $[Mg]_T$-pH nomograph in Figure 21, for a final desired $[Mg]_T$ concentration equal to 3,0 m.moles/ℓ the pH (after $Mg(OH)_2$ precipitation) must be pH = 10,25. The point in Figure 21 representing the condition of the water *after* $Mg(OH)_2$ precipitation has occurred, Point 3, is established as follows: Precipitation of 2,11 m.moles/ℓ of $Mg(OH)_2$ from solution changes $(Alk\text{-}2[Ca]_T)$ by - 4,22 m.moles.

Initial $(Alk\text{-}2[Ca_T]) = 5{,}60 - 2.3{,}86 = -2{,}12$

$(Alk\text{-}2[Ca]_T)$ after $Mg(OH)_2$ precipitation $= -2{,}12 - 4{,}22$
$= -6{,}34$

The intersection point of lines representing $(Alk\text{-}2[Ca]_T = -6{,}34$ and pH = 10,25 occurs at Point 3 and is the condition of the water after $Mg(OH)_2$ has precipitated.

Estimation of the lime requirements to bring about magnesium softening: Addition of $Ca(OH)_2$ to the water saturated with respect to $CaCO_3$ causes the point describing the water to move vertically upwards in the diagram (see Figure 20), a distance of twice the m.moles of $Ca(OH)_2$ added, i.e. addition of lime causes Point 1 to move vertically in Figure 21. The condition of the water *before* $Mg(OH)_2$ precipitation occurs but after the required $Ca(OH)_2$ dosage has been applied, Point 2, is established by the intersection point of the $(Alk\text{-}2[Ca]_T$ line through Point 1 and the line at 45° *upwards* to the right through Point 3, i.e. if lime is applied such that Point 1 moves to Point 2, then spontaneous precipitation of $Mg(OH)_2$ will move Point 2 at 45° downwards to the left (see Figure 20).

$$\text{Lime dosage} = 0{,}5\ (\text{Acidity}_1 - \text{Acidity}_2)$$
$$= 0{,}5\ (+\ 7{,}0 + 4{,}22)$$
$$= 5{,}61 \text{ m.moles}/\ell$$

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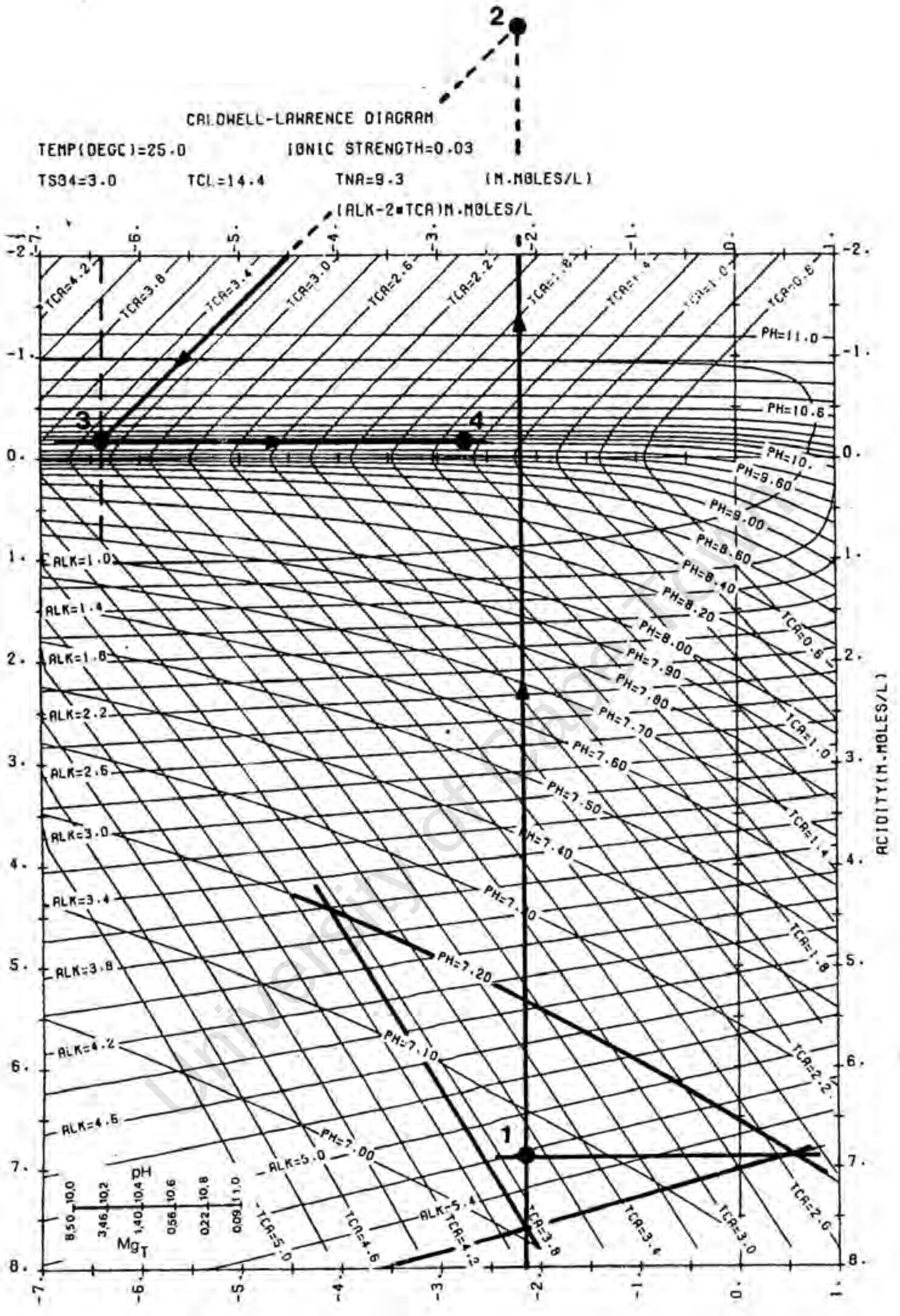

Figure 21: Dosage estimation for calcium and magnesium softening using lime and Na_2CO_3

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(b) Calcium softening:

From the direction format diagram, addition of $CO_3^=$ moves a point describing saturation horizontally to the right a distance twice the m.moles of $CO_3^=$ added. The required final Ca_T is 1,5 m.moles/ℓ. Intersection of $[Ca]_T = 1,5$ and the horizontal line through Point 3 occurs at Point 4. The Na_2CO_3 dosage is therefore one half the distance between Points 3 and 4, i.e.

$$Na_2CO_3 \text{ dosage} = (-2,8 + 6,34)/2$$
$$= 2,27 \text{ m.moles/ℓ}.$$

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2. Input data

The input data to the program are in stoichiometric quantities on either the molal or molar scale; the output correspondingly will be on the same scale as the input.

Input data is inserted in free format on three cards as follows:

Card 1: Read in concentration scale to be used (i.e. either molal or, molar) by assigning an integer value to the logical unit number variable KZ. If the molal scale is used, KZ is assigned the integer value (plus) one, 1; if the molar scale is used, KZ is assigned the integer value (minus) one, -1.

Card 2: Read in stoichiometric concentrations (on the scale selected in Card 1) of principal species comprising the ionic matrix in the following order: total Na, total Mg, total Ca, total K, total Cl and total SO_4. If a species is not present the value 0.0 must be inserted.

Card 3: Read in the stoichiometric concentrations (on the scale selected in Card 1) of the principal salt species comprising the matrix in the following order: NaCl, Na_2SO_4, $MgCl_2$, $MgSO_4$, $CaCl_2$, $CaSO_4$, KCl and K_2SO_4. (This input is necessary to allow determination of non-ideal volumetric effects). If a salt is not present, the value 0.0 must be inserted.

To illustrate, a synthetic seawater has the following composition (on the molal scale): NaCl = 0,418; Na_2SO_4 = 0,0284; $MgCl_2$ = 0,0540; $CaCl_2$ = 0,0108; KCl = 0,0101

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Card 1: 1

Card 2: 0.474B0.054B0.0108B0.0101B0.557B0.0284

Card 3: 0.418B0.0284B0.054B0.0B0.0108B0.0B0.0101B0.0

Note: B denotes a blank space.

3. Assumptions in activity coefficient determinations

(i) Neutral ion paired species have activity coefficients equal to unity.

(ii) CO_{2aq} has an activity coefficient dependent only on ionic strength, μ, as $ln\gamma_{CO_{2aq}} = 0,22\mu$.

(iii) Singly charged ion paired species have activity coefficients equal to that for Na^+.

(iv) Activity coefficient for Cl^- is determined assuming Cl^- has zero primary hydrated water.

(v) Cs^+ does not ion pair with SO_4^{2-}, CO_3^{2-}, HCO_3^- and OH^-.

4. Calculation procedure

Determinations of activity coefficients are always on the *molal* scale in the subroutine program SUBROUTINE ACTIVE. If the input to the program is on the molar scale the subroutine program first converts the data onto the molal scale, the entities are calculated on this scale and converted back onto the molar scale (the concentration scale of the input). Output from the main program is always on the same scale as the input.

The calculation procedure for activity coefficients and free and ion paired species concentrations is an iterative one involving successive approximation (within the subroutine program) as follows:

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(i) The Davies equation together with the input principal stoichiometric species concentrations are used to estimate initial ionic strength and starting values for the mono- and divalent ionic species activity coefficients.

(ii) Ion pairing constants are adjusted for activity coefficient effects to give apparent equilibrium constants for ion pairs.

(iii) Free and ion paired species concentrations are determined from mass balance considerations.

(iv) Ionic strength is recalculated based on the species concentrations determined in (iii) above.

(v) Mean activity coefficients for free species, the water component and Cl^- are determined using Eqs. (27, 29 and 52) Chapter 3, respectively.

(vi) Single free ionic activity coefficients, γ_m, for the cations Mg^{2+}, Ca^{2+}, Na^+, K^+ and Cs^+ (and H^+) are calculated from γ_{Cl} and the mean activity coefficients of the chloride salts of each of these cation species (γ_{MCl_x}) assuming no ion pairing between Cl^- and the cation species, from

$$\gamma_M = (\gamma_{MCl_x}\pm)^{1+x}/\gamma_{Cl}^x$$

(vii) Single free ionic activity coefficients of the anions (γ_A) for SO_4^{2-}, OH^-, HCO_3^- and CO_3^{2-} are calculated from γ_{Cs} and the mean activity coefficients for the cesium salts of each of these anion species ($\gamma_{Cs_xA}\pm$) assuming no ion pairing between Cs^+ and each of the anion species, from,

$$\gamma_A = (\gamma_{Cs_xA}\pm)^{1+x}/\gamma_A$$

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(viii) The procedure from (ii) to (vii) is repeated until successive values for the ionic strength agree to within four significant figures.

(ix) Calculate the stoichiometric single and mean activity coefficients from the stoichiometric and free concentrations and the free activity coefficients.

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```
C       ******************************************
C       THIS PROGRAM DETERMINES STOICHIOMETRIC
C       AND  SINGLE ION ACTIVITY COEFFICIENTS
C       AND CONCS. ON THE MOLAL OR MOLAR SCALE
C       FOR 25DEGC. AND 1ATM. TOTAL PRESSURE.
C       ********************************************
      REAL NACL,NA2SO4,MGCL2,KCL,K2SO4,MGSO4
C       ********************************
      COMMON ACCA,ACMG,ACH,ACNA,ACSO4,ACK,
     .ACNAS,ACKSO,ANASOT,ACHCO3,ACOH,ACCO3,TACCCL,
     .TACMCL,ACLT,TACCSO,TACMG,TACCA,TACNA,TACSO4,
     .TACNC,TACKCL,TACNSO,TAMGSO,TACKSO,AHCL,AKCL,
     .ANACL,ACACL2,AMGCL,AK2SO4,ANA2SO,AMGSO,ACASO,
     .TMG,TCA,TNA,TK,TCL,TSO4,FMG,FNA,FCA,FSO4,
     .CNASO,CNA2SO,TACK,FK,CKSO4,CK2SO4,CCASO,
     .CMGSO,ACCO2,NACL,NA2SO4,MGCL2,MGSO4,CACL2,
     .CASO4,KCL,K2SO4,U1,SLOPE,CBA,AH2O,AW,ACHOP,
     .KZ
C      *********************************
C      READ IN CONCENTRATION UNITS TO
C      BE USED
C      KZ=1(MOLAL SCALE)
C      KZ=-1(MOLAR SCALE)
C      **********************************
      READ(5,10)KZ
C      **********************************
C      ************************************
C      READ CONC. OF TOTAL NA,MG,CA,K,CL,SO4
C      IN MOLAL/MOLAR UNITS.
C      ***********************************
      READ(5,10)TNA,TMG,TCA,TK,TCL,TSO4
   10  FORMAT()
   15  FORMAT()
C      *************************************
C      READ IN CONC. OF SALT SPECIES MAKING UP THE
C      SOLUTION IN MOLAL/MOLAR UNITS
C      *********************************
      READ(5,15)NACL,NA2SO4,MGCL2,MGSO4,CACL2,CASO4,KCL,K2SO4
C      *********************************
C      CALCULATE ACTIVITY COEFFICIENTS
C      IN SUBROUTINE ACTIVE.
C      ********************************
      SLOPE=1.
      CBA=1.
      CALL ACTIVE
      WRITE(6,3001)
 3001  FORMAT(30X,'***************************')
      IF(KZ)3002,3002,3004
 3002  WRITE(6,3003)
 3003  FORMAT(30X,'ALL UNITS ON THE MOLAR SCALE')
      GO TO 3006
 3004  WRITE(6,3005)
 3005  FORMAT(30X,'ALL UNITS ON THE MOLAL SCALE')
 3006  WRITE(6,3007)
 3007  FORMAT(30X,'***************************',///)
C      **************************
      WRITE(6,3011)
 3011  FORMAT(28X,'WHERE SPECIES DO NOT MAKE UP',
     ./,1H ,27X,'THE PRINCIPAL IONIC MATRIX',
```

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```
    ./,1H ,27X,'THEIR TRACE ACTIVITY COEFFICIENT',
    ./,1H ,27X,'VALUES ARE DETERMINED')
     WRITE(6,304)
304   FORMAT(//1X,'****************************'
    .'*********')
     WRITE(6,305)
305   FORMAT(1X,'STOICHIOMETRIC SPECIES CONCENTRATION')
     WRITE(6,306)
306   FORMAT(1X,'****************************'
    .'********',//)
     WRITE(6,310)
310   FORMAT(3X,'TMG',7X,'TCA',7X,'TNA',8X,'TK',8X,'TCL',
    .7X,'TSO4')
     WRITE(6,320)TMG,TCA,TNA,TK,TCL,TSO4
320   FORMAT(6E10.4,/,/,/)
     WRITE(6,321)
321   FORMAT(1X,'***************************'
    .'***************')
     WRITE(6,330)
330   FORMAT(1X,'FREE AND ION PAIRED SPECIES CONCENTRATIONS')
     WRITE(6,331)
331   FORMAT(1X,'****************************'
    .'*************',//)
     WRITE(6,340)
340   FORMAT(4X,'MG',8X,'CA',7X,'NA',8X,'SO4',6X,'NASO4',
    .5X,'NA2SO4',8X,'K',6X,'KSO4',6X,'K2SO4',7X,'CASO4'
    .,4X,'MGSO4',4X,'CL')
     WRITE(6,350)FMG,FNA,FCA,FSO4,CNASO,CNA2SO,FK,CKSO4,
    .CK2SO4,CCASO,CMGSO,TCL
350   FORMAT(12E10.4,/,/,/)
     WRITE(6,351)
351   FORMAT(1X,'*****************************'
    .'***********')
     WRITE(6,360)
360   FORMAT(1X,'FREE SPECIES SINGLE ION ACTIVITY COEFF.')
     WRITE(6,361)
361   FORMAT(1X,'*****************************'
    .'**********',//)
     WRITE(6,370)
370   FORMAT(2X,'MG',4X,'CA',4X,'SO4',3X,'H+',5X,'NA+',3X,
    .'K+',2X,'NASO4',2X,'KSO4',2X,'CL',4X,'H2O',4X,
    .'HCO3',3X,'CO3',2X,'OH',/)
     WRITE(6,380)ACMG,ACCA,ACSO4,ACH,ACNA,ACK,ACNAS,
    .ACKSO,ACLT,AH2O,ACHCO3,ACCO3,ACOH
380   FORMAT(13(1X,F5.3),/,/,/)
     WRITE(6,381)
381   FORMAT(1X,'****************************'
    .'**************')
     WRITE(6,385)
385   FORMAT(1X,'STOICHIOMETRIC SINGLE ION ACTIVITY COEFF.')
     WRITE(6,386)
386   FORMAT(1X,'*****************************'
    .'************',//)
     WRITE(6,390)
390   FORMAT(2X,'MG',4X,'CA',5X,'SO4',2X,'NA',4X,'K',6X,'CL')
     WRITE(6,400)TACMG,TACCA,TACSO4,TACNA,TACK,ACLT
400   FORMAT(1X,6(F5.3,1X),/,/,/)
     WRITE(6,401)
401   FORMAT(1X,'*************************'
```

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```
     .'*******************')
  402  CONTINUE
      WRITE(6,410)
  410  FORMAT(1X,'MEAN STOICHIOMETRIC SPECIES ACTIVITY COEFF.')
      WRITE(6,411)
  411  FORMAT(1X,'**************************'
     .'**********************',//)
      WRITE(6,420)
  420  FORMAT(2X,'NACL',2X,'KCL',1X,'NA2SO4',2X,'K2SO4',
     .1X,'MGSO4',1X,'CASO4',1X,'MGCL2',1X,'CACL2')
      WRITE(6,430)TACNC,TACKCL,TACNSO,TACKSO,TAMGSO,
     .TACCSO,TACMCL,TACCCL
  430  FORMAT(8(1X,F5.3))
      WRITE(6,431)
  431  FORMAT(//1X,'************************************')
      WRITE(6,432)
  432  FORMAT(1X,'MEAN FREE ACTIVITY COEFFICIENTS')
      WRITE(6,433)
  433  FORMAT(1X,'*******************'
     .'****************',//)
      WRITE(6,434)
  434  FORMAT(2X,'HCL',3X,'NACL',3X,'KCL',
     .2X,'MGCL2',1X,'CACL2',1X,'MGSO4',
     .1X,'CASO4',1X,'K2SO4',1X,'NA2SO4')
      WRITE(6,435)AHCL,ANACL,AKCL,AMGCL,ACACL2,
     .AMGSO,ACASO,AK2SO4,ANA2SO
  435  FORMAT(9(1X,F5.3))
      STOP
      END
```

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```
      SUBROUTINE ACTIVE
C      ********************************
C      THIS SUB-PROGRAM DETERMINES:
C      (1)FREE AND STOICHIOMETRIC SINGLE
C         ION ACTIVITY COEFFICIENTS.
C      (2)MEAN FREE AND STOICHIOMETRIC
C         ACTIVITY COEFFICIENTS.
C      (3)DISTRIBUTION OF FREE AND ION
C         -PAIRED SPECIES CONCENTRATIONS.
C      *********************************
      REAL K32,K33,K34,K35,K36,K37,NACL,NA2SO4,
     .MGCL2,MGSO4,KCL,K2SO4
C      **********************************
      COMMON ACCA,ACMG,ACH,ACNA,ACSO4,ACK,
     .ACNAS,ACKSO,ANASOT,ACHCO3,ACOH,ACCO3,TACCCL,
     .TACMCL,ACLT,TACCSO,TACMG,TACCA,TACNA,TACSO4,
     .TACNC,TACKCL,TACNSO,TAMGSO,TACKSO,AHCL,AKCL,
     .ANACL,ACACL2,AMGCL,AK2SO4,ANA2SO,AMGSO,ACASO,
     .TMG,TCA,TNA,TK,TCL,TSO4,FMG,FNA,FCA,FSO4,
     .CNASO,CNA2SO,TACK,FK,CKSO4,CK2SO4,CCASO,
     .CMGSO,ACCO2,NACL,NA2SO4,MGCL2,MGSO4,CACL2,
     .CASO4,KCL,K2SO4,U1,SLOPE,CBA,AH2O,AW,ACHOP,
     .KZ
C      ********************************
C      ADJUST MOLAR UNITS TO MOLAL UNITS
C      *********************************
      IF(KZ)16,16,17
   16  SUMQ=16.61*NACL+26.8*KCL+14.5*MGCL2
     .+17.8*CACL2+11.52*NA2SO4+32.*K2SO4
     .-7.0*MGSO4-4.0*CASO4
      CONNX=1.-(SUMQ/1000)
      TNA=TNA/CONNX
      TK=TK/CONNX
      TCA=TCA/CONNX
      TMG=TMG/CONNX
      TSO4=TSO4/CONNX
      TCL=TCL/CONNX
      NACL=NACL/CONNX
      KCL=KCL/CONNX
      MGCL2=MGCL2/CONNX
      CACL2=CACL2/CONNX
      MGSO4=MGSO4/CONNX
      CASO4=CASO4/CONNX
      NA2SO4=NA2SO4/CONNX
C      ****************************************
C      CALC. APPROX. IONIC STRENGTH,U1
C       ***************************************
   17  U1=2*(TMG+TCA+TSO4)+0.5*(TNA+TK+TCL)
C      ***************************************
C      SET INITIAL ACTIVITY COEFF. VALUES
C      FROM THE DAVIES EQ.(AC1 AND AC2)
C      ***********************************
      AC1=-0.509*((U1**0.5)/(1+U1**0.5)-0.2*U1)
      AC2=4*AC1
      AC1=10.**AC1
      AC2=10.**AC2
      ACN22=1.0
      ACN21=1.0
      ACCA=AC2
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```
      ACMG=AC2
      ACSO4=AC2
      ACNA=AC1
      ACK=AC1
      ACNAS=AC1
      ACKSO=AC1
      MM=0
C       ******************************
C       FIX SULPHATE ION PAIRING CONSTANTS
C       K33=K(MGSO4),K32=K(CASO4),K34=K(NASO4)
C       K35=K(KSO4),K36=K(NA2SO4),K37=K(K2SO4)
C       ********************************
       K32=0.0037
       K33=0.004
       K34=0.27
       K35=0.43
       K36=0.10
       K37=0.14
      CI=U1
C
      DO 200 J=1,3
C       **********************************
C       CALC. ACCURATE VALUES FOR ACTIVITY
C       COFFICIENTS
C       **********************************
      IF(MM-1)20,25,25
20     N=1
25     LL=0
      NN=1
30     FSO4=TSO4
35     FFCA=(ACCA*ACSO4)/(ACN22*K32)
      FCA=TCA/(1+FFCA*FSO4)
      FFMG=(ACMG*ACSO4)/(ACN22*K33)
      FMG=TMG/(1+FFMG*FSO4)
      FFK=(ACK*ACSO4)/(ACKSO*K35)
      FFFK=(ACK**2.)*ACSO4/(K37*ACN21)
      FFNA=(ACNA*ACSO4)/(ACNAS*K34)
      FFFNA=(ACNA**2.)*ACSO4/(K36*ACN21)
      IF(FSO4)36,36,37
36     FNA=TNA
      FK=TK
      GO TO 38
37     FNA=-(1+FFNA*FSO4)+((1+FFNA*FSO4)**2.+8.*TNA*FFFNA
     .*FSO4)**0.5
      FNA=FNA/(4.*FFFNA*FSO4)
      FK=-(1+FFK*FSO4)+((1+FFK*FSO4)**2.+8.*TK*FFFK*FSO4)
     .**0.5
      FK=FK/(4.*FFFK*FSO4)
38     TTSO4=FSO4*(1+FFCA*FCA+FFMG*FMG+FFNA*FNA+FFK*FK+
     .FFFNA*FNA**2.+FFFK*FK**2.)
      IF(TTSO4-TSO4)50,75,40
40     IF(NN-1)45,45,65
45     FSO4=0.1*FSO4
      GO TO 35
50     IF(NN-1)55,55,60
55     FRACT=FSO4
60     FSO4=FSO4+FRACT
      NN=2
      GO TO 35
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 65    FSO4=FSO4-FRACT
      FRACT=FRACT*0.1
      FSO4=FSO4+FRACT
      IF(LL-4)70,75,75
 70    LL=LL+1
      GO TO 35
 75    CONTINUE
      CNASO=(ACSO4)*FNA*FSO4/(K34)
      CNA2SO=(ANASOT**3.)*(FNA**2.)*FSO4/(K36*ACN21)
      CKSO4=(ACK*ACSO4*FK*FSO4)/(ACNA*K35)
      CK2SO4=((ACK**2.)*(ACSO4*FSO4)*(FK**2.))/(K37*ACN21)
      U1=2*(FMG+FCA+FSO4)+0.5*(FNA+TCL+FK+CNASO+CKSO4)
      CCASO=(ACCA*ACSO4*FCA*FSO4)/(ACN22*K32)
      CMGSO=(ACMG*ACSO4*FMG*FSO4)/(ACN22*K33)
      IF(MM-1)80,100,100
 80    AC1=-.509*((U1**0.5)/(1+U1**0.5)-0.2*U1)
      AC2=4*AC1
      AC1=10.**AC1
      AC2=10.**AC2
      ACCA=AC2
      ACMG=AC2
      ACSO4=AC2
      ACNA=AC1
      ACK=AC1
      ACNAS=AC1
      ACKSO=AC1
      ACN22=1.0
      ACN21=1.0
      N=N+1
      IF(N-3)25,100,100
 100   CONTINUE
      MM=MM+1
C
C      ACCURATE CALCULATION OF ACTIVITY COEFFICIENTS
C
      SUMMQ=-TCA*1.81-TMG*2.0-FNA*.48+FSO4*1.6+TCL*1.4+
     .0.1*TK+1.6*(CNASO+CNA2SO+CKSO4)
      SUMMH=FCA*7.05+FMG*8.12+FNA*2.4+FSO4*0.0+CMGSO*4.0+
     .CCASO*3.0+CNASO*2.4+CKSO4*0.0+1.01*FK+CNA2SO*3.8
      SUMM=FMG+FCA+TCL+FSO4+CMGSO+FNA+CNASO+CNA2SO+FK
     .+CKSO4+CK2SO4
C
C      CALCULATE MEAN ACTIVITY COEFF. FOR HCL(TRACE)
C
      Q=(18.07+1.424*U1**0.5)/18
      HO=4.09
      H=HO-0.0009*U1**1.5+0.000015*U1**3
      QO=1.
      AT=TCL+TSO4
      CT=TNA+FMG+FCA+TK
      AOH=3.79+(TCL*1.81+TSO4*2.15)/AT
      AOCL=1.81+(FMG*3.89+FCA*3.85+TNA*3.14+TK*2.54)/CT
      B1=0.328
      AEL=(-0.5853*U1**0.5)*(1/(1+B1*AOH*U1**0.5)+1/(1+
     .B1*AOCL*U1**0.5))
      B2=0.018
      AHE1=B2*Q*(SUMMQ+SUMMH-SUMM)/(2*(1+B2*SUMMQ))
      AHE2=((H-2)/2)*LOG(1+B2*SUMMQ)
      AHE3=(H/2)*LOG(1-B2*SUMMH)
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      AHE4=(QO-Q)/2+(HO-H)/2+LOG((Q+H)/(QO+HO))+(15)*(HO-H
     .+(FNA*0.00028+FK*0.00034+FMG*0.0004+FCA*0.0004)*U1)
      X=B2*SUMMH
      AHE5=0.5*NACL*(0.75*0.104/(U1**0.5))*(0.41-X)
      AHE6=0.5*KCL*(0.75*0.104/(U1**0.5))*(0.2-X)
      AHE7=0.5*NA2SO4*(0.75*0.676/((U1*3)**0.5))*(0.534-X)
      AHE8=0.5*MGSO4*(0.75*0.714/((U1*4)**0.5))*(0.76-X)
      AHE9=0.5*MGCL2*(0.75*.286/((U1*3)**0.5))*(0.65-X)
      AHE10=0.5*CACL2*(0.75*.309/((U1*3)**0.5))*(0.62-X)
      AHE11=0.5*K2SO4*(0.75*0.694/((U1*3)**0.5))*(0.377-X)
      AHET=AEL+AHE1+AHE2-AHE3+AHE4-AHE5-AHE6-AHE7-AHE8-
     .AHE9-AHE10-AHE11
      AHET=AHET+(0.048+0.005*FNA)*FNA+0.054*FK+0.042*FMG
     .**2.+(0.094-0.059*FCA)*FCA
      AHET=EXP(AHET)
C
C      CALCULATE MEAN ACTIVITY COEFF. FOR NACL
C
      EXQ=Q
      EXH=H
      Q=(16.61+1.5*1.868*U1**0.5+0.096*U1)/18.+0.0027*U1
      QO=0.923
      H=2.4-0.00014*U1**2
      HN=H
      QN=Q
      HO=2.40
      AONA=3.14+(TCL*1.81+TSO4*2.15)/AT
      AEL=(-0.5853*U1**0.5)*(1/(1+B1*AONA*U1**0.5)+1/(1+
     .B1*AOCL*U1**0.5))
      B2=0.018
      ANA1=AHE1*Q/EXQ
      ANA2=AHE2*(H-2)/(EXH-2)
      ANA3=AHE3*H/EXH
      ANA4=(QO-Q)/2+LOG((Q+H)/(QO+HO))+15.*(HO-H
     .+(FNA*0.00028+FK*0.00034+FMG*0,0004+FCA*0.0004)*U1)
      ANA5=AHE5
      ANA6=AHE6
      ANAT=AEL+ANA1+ANA2+ANA4-ANA3-ANA5-AHE6-AHE7-AHE8-AHE9
     .-AHE10-AHE11
      ANAT=ANAT-0.008*FK+0.022*TMG
      ACNAT=EXP(ANAT)
C
C      CALCULATE MEAN ACT. COEFF. FOR CSOH
C
      EXQ=Q
      EXH=H
      HCSOH=3.95
      Q=(17.7+1.5*1.868*U1**0.5)/18.
      QO=17.7/18.
      AOCS=1.55+(TCL*1.81+TSO4*2.15)/AT
      AOOH=AOCL-1.81+4.6
      AEL=(-0.5853*U1**0.5)*(1./(1.+B1*AOCS*U1**0.5)
     .+1./(1.+B1*AOOH*U1**0.5))
      ACS1=ANA1*Q/EXQ
      ACS2=ANA2*(HCSOH-2)/(EXH-2)
      ACS3=ANA3*HCSOH/EXH
      ACS4=(QO-Q)/2+LOG((Q+HCSOH)/(QO+HCSOH))
      ACSOH=AEL+ACS1+ACS2-ACS3+ACS4-AHE5-AHE6-AHE7-AHE8
     .-AHE9-AHE10-AHE11
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```
      ACSOH=EXP(ACSOH)
C
C      CALCULATE MEAN ACTIVITY COEFF. FOR KCL
C
      H=HCSOH
      EXQ=Q
      EXH=H
      QO=1.489
      Q=(26.8+1.5*1.868*U1**0.5)/18
      HO=1.01
      H=1.01-0.00017*U1**2.
      HK=H
      QK=Q
      AOK=2.50+(TCL*1.81+TSO4*2.15)/AT
      AEL=(-0.5853*U1**0.5)*(1/(1+B1*AOK*U1**0.5)+1/(1+
     .B1*AOCL*U1**0.5))
      AK1=ACS1*Q/EXQ
      AK2=ACS2*(H-2)/(EXH-2)
      AK3=ACS3*H/EXH
      AK4=(QO-Q)/2+LOG((Q+H)/(QO+HO))+15.*(HO-H
     .+(FNA*0.00028+FK*0.00034+FMG*0.0004+FCA*0.0004)*U1)
      AKT=AEL+AK1+AK2-AK3+AK4-ANA6-AHE7-AHE8-AHE9-AHE10
     .-AHE11-ANA5
      AKT=AKT+(-0.0295+0.0045*FNA)*FNA-0.032*FMG-0.045*FCA
      ACKT=EXP(AKT)
C
C      CALCULATE MEAN ACTIVITY COEFF. FOR CSCL
C
      EXQ=Q
      EXH=H
      Q=(39.15+2.802*U1**0.5)/18+0.013*U1
      QO=2.175
      HO=0.2
      H=0.2-0.00015*U1**2.
      AOCS=1.55+(TCL*1.81+TSO4*2.15)/AT
      AEL=(-0.5853*U1**0.5)*(1/(1+B1*AOCS*U1**0.5)
     .+1/(1+B1*AOCL*U1**0.5))
      ACSCL1=AK1*Q/EXQ
      ACSCL2=AK2*(H-2)/(EXH-2)
      ACSCL3=(H/2)*LOG(1-B2*SUMMH)
      ACSCL4=(QO-Q)/2+LOG(Q/QO)+15.*(
     .HO-H+(FNA*0.00028+FK*0.00034+FMG*0.0004+FCA*0.0004)
     .*U1)
      ACSCLT=AEL+ACSCL1+ACSCL2+ACSCL4-ANA5-ANA6-ACSCL3
     .-AHE7-AHE8-AHE9-AHE10-AHE11
      ACSCLT=EXP(ACSCLT)
C
C      CALCULATE MEAN ACT. COEFF. FOR CSHCO3
C
      EXQ=Q
      EXH=H
      Q=(30.0+1.5*1.868*U1**0.5)/18.
      QO=1.667
      HO=0.5
      H=HO-0.00015*U1**0.5
      AOHCO=2.08+AOCL-1.81
      AEL=(-0.5853*U1**0.5)*(1./(1+B1*AOCS*U1**0.5)
     .+1./(1+B1*AOHCO*U1**0.5))
      ACSHC1=ACSCL1*Q/EXQ
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      ACSHC2=ACSCL2*(H-2)/(EXH-2)
      ACSHC3=(H/2)*LOG(1-B2*SUMMH)
      ACSHC4=(QO-Q)/2+LOG((Q+H)/(QO+HO))+15.*(HO-H
     .+(FNA*0.00028+FK*0.00034+(FMG+FCA)*0.0004)*U1)
      ACSHCT=AEL+ACSHC1+ACSHC2-ACSHC3+ACSHC4-ANA5-ANA6
     .-AHE7-AHE8-AHE9-AHE10-AHE11
      ACSHCT=EXP(ACSHCT)
C
C      CALCULATE MEAN ACTIVITY COEFF. FOR MGCL2
C
      EXQ=Q
      EXH=H
      Q=(14.5+1.5*5.15*(U1/3)**0.5)/18
      QO=0.806
      HO=8.12
      H=HO-0.00185*(U1/3)**2
      HM=H
      QM=Q
      AOMG=AOH+0.10
      AEL=(-0.3902*U1**0.5)*(4/(1+B1*AOMG*U1**0.5)+2/(1+
     .B1*AOCL*U1**0.5))
      AMGCL1=ACSHC1*Q*2/(EXQ*3)
      AMGCL2=((H-3)/3.)*LOG(1+B2*SUMMQ)
      AMGCL3=(H/3.)*LOG(1-B2*SUMMH)
      AMGCL4=(QO-Q)/3+(HO-H)/3+LOG((Q+H)/(QO+HO))+10*(HO-H)
     .+10.*(FMG*0.0012+FCA*0.0012+FK*0.001+FNA*0.00084)*U1
      AMGCL5=2*AHE9
      AMGCLT=AEL+AMGCL1+AMGCL2-AMGCL3+AMGCL4-2*(ANA5+ANA6
     .+AHE7+AHE8+AHE9+AHE10+AHE11)
      AMGCLT=AMGCLT+(0.033-0.008*FNA)*FNA
      AMGCLT=EXP(AMGCLT)
C
C      CALCULATE MEAN ACTIVITY COEFF. FOR CACL2
C
      EXQ=Q
      EXH=H
      Q=(17.78+9*(U1/3)**0.5)/18
      QO=0.988
      HO=7.05
      H=7.05-0.00180*(U1/3)**2
      HC=H
      QC=Q
      AOCA=AOMG-0.05
      AEL=(-0.3902*U1**0.5)*(4/(1+B1*AOCA*U1**0.5)+2/(1+
     .B1*AOCL*U1**0.5))
      ACACL1=AMGCL1*Q/EXQ
      ACACL2=AMGCL2*(H-3)/(EXH-3)
      ACACL3=AMGCL3*H/EXH
      ACACL4=(QO-Q)/3+(HO-H)/3+LOG((Q+H)/(QO+HO))+10*(HO-H)
     .+10.*((FMG+FCA)*0.0012+FK*0.00104+FNA*0.00084)*U1
      ACACLT=AEL+ACACL1+ACACL2-ACACL3+ACACL4-2*(ANA5+ANA6
     .+AHE7+AHE8+AHE9+AHE10+AHE11)
      ACACLT=ACACLT+0.017*FNA
      ACACLT=EXP(ACACLT)
C
C      CALCULATE MEAN ACTIVITY COEFF. FOR CS2SO4
C
      EXQ=Q
      EXH=H
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      Q=(56.68+14.55*(U1/3)**0.5)/18.
      QO=3.149
      H=0.4-0.00015*U1**2.
      HO=0.4
      AOSO4=AOCL-1.81+2.05
      AOCS=1.55+(TCL*1.81+TSO4*2.05)/AT
      AEL=(-0.3902*U1**0.5)*(4/(1+B1*AOSO4*U1**0.5)
     .+2/(1+B1*AOCS*U1**0.5))
      ACSSO1=ACACL1*Q/EXQ
      ACSSO2=ACACL2*(H-3)/(EXH-3)
      ACSSO3=ACACL3*H/EXH
      ACSSO4=(QO-Q)/3+LOG((Q+H)/(QO+H))+10.*
     .(HO-H+((FCA+FMG)*0.0012+FK*0.00104+(FNA)*0.00084)*U1)
      ACSSOT=AEL+ACSSO1+ACSSO2-ACSSO3+ACSSO4-2*(ANA5+ANA6
     .+AHE7+AHE8+AHE9+AHE10+AHE11)
      ACSSOT=EXP(ACSSOT)
C
C      CALCULATE MEAN ACT. COEFF. FOR CS2CO3
C
      EXQ=Q
      EXH=H
      Q=(37.+14.55*(U1/3)**0.5)/18.
      QO=2.056
      HO=0.8
      H=HO-0.00015*U1**0.5
      AOCO3=AOSO4-2.15+1.95
      AEL=(-0.3902*U1**0.5)*(4./(1+B1*AOCO3*U1**0.5)
     .+2./(1+B1*AOCS*U1**0.5))
      ACSCO1=ACSSO1*Q/EXQ
      ACSCO2=ACSSO2*(H-3)/(EXH-3)
      ACSCO3=ACSSO3*H/EXH
      ACSCO4=(QO-Q)/3+LOG((Q+H)/(QO+HO))+10.*
     .(HO-H+((FCA+FMG)*0.0012+FK*0.001+FNA*0.00084)*U1)
      ACSCOT=AEL+ACSCO1+ACSCO2-ACSCO3+ACSCO4-2*(ANA5+ANA6
     .+AHE7+AHE8+AHE9+AHE10+AHE11)
      ACSCOT=EXP(ACSCOT)
C      DETERMINE SINGLE ION ACTIVITY COEFF. FOR CL
C
      EXH=H
      EXQ=Q
      Q=(25.2+((2.*U1)**0.5)/(1.+B1*AOCL*U1**0.5)+1.05*U1)
     ./18.
      QO=1.40
      H=0.0
      HO=H
      AEL=(-1.1706*U1**0.5)/(1.+B1*AOCL*U1**0.5)
      ACL1=ACSCO1*3.*Q/EXQ
      ACL2=-LOG(1+0.018*SUMMH)
      ACL3=0.0
      ACL4=(QO-Q)+LOG(Q/QO)
      ACLT=AEL+ACL1+ACL2+ACL3+ACL4-AHE5-AHE6-AHE7-AHE8-AHE9
     .-AHE10-AHE11
      ACLT=EXP(ACLT)
C
C      DETERMINE SINGLE ION ACTIVITY COEFF. FOR FREE SPECIES
C
      ACCA=((ACACLT)**3)/(ACLT**2)
      ACMG=((AMGCLT)**3)/(ACLT**2)
      ACH=((AHET)**2)/(ACLT)
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      ACNA=((ACNAT)**2)/(ACLT)
      ACS=((ACSCLT)**2.)/ACLT
      ACSO4=(ACSSOT**3.)/(ACS**2.)
      ACK=((ACKT)**2)/(ACLT)
      ACNAS=ACNA
      ACKSO=ACNA
      ANASOT=((ACNA**2.)*ACSO4)**0.333
      ACHCO3=(ACSHCT**2.)/ACS
      ACOH=(ACSOH**2.)/ACS
      ACCO3=(ACSCOT**3.)/(ACS**2.)
      ACCO2=EXP(U1*0.22)
  200  CONTINUE
C     ******************************************
C      CALCULATE ACT. COEFF.FOR WATER COMPONENT
C     *******************************************
      AOCAT=(FMG*3.89+FCA*3.85+TNA*3.14+TK*2.54)
     ./CT
      AOAN=(TCL*1.81+TSO4*2.00)/AT
      AOH2=AOCAT+AOAN
      ZZ=B1*AOH2*(U1)**0.5
      Z1=((1+ZZ)-(1./(1+ZZ))-2*LOG(1+ZZ))*3./((ZZ)**3.)
      HEL=B2*1.1706*0.666*((U1)**1.5)*Z1
      AK1=B2*(SUMMQ+SUMMH-SUMM)/(1+B2*SUMMQ)
      AK2=LOG((1-B2*SUMMH)/(1+B2*SUMMQ))
      DHDM1=B2*(0.00028*FNA**2)*U1
      DHDM2=B2*(0.00034*FK**2)*U1
      DHDM3=B2*(0.0036*FCA**2)*U1
      DHDM4=B2*(0.0037*FMG**2)*U1
      AK3=(AK2+30.)*(DHDM1+DHDM2+DHDM3+DHDM4)
      AK4=DHDM1*(QN+HN-2)/(QN+HN)+DHDM2*(QK+HK-2)/(QK+HK)
     .+DHDM3*(QC+HC-3)/(QC+HC)+DHDM4*(QM+HM-3)/(QM+HM)
      DQDM1=(B2*0.75*0.104*FNA**2)/(U1**0.5)
      DQDM2=(B2*0.75*0.104*FK**2)/(U1**0.5)
      DQDM4=(B2*0.75*0.286*FMG**2)/((U1/3.)**0.5)
      DQDM3=(B2*0.75*0.393*FCA**2)/((U1/3.)**0.5)
      FR=B2*(NACL*HN*2/(QN+HN)+KCL*HK*2/(QK+HK)
     .+TMG*HM*3/(QM+HM)+TCA*HC*3/(QC+HC))
      AK5=FR*(DQDM1+DQDM2+DQDM3+DQDM4)
      AK6=DQDM1*(QN+HN-2)/(QN+HN)+DQDM2*(QK+HK-2)/(QK+HK)
     .+DQDM3*(QC+HC-3)/(QC+HC)+DQDM4*(QM+HM-3)/(QM+HM)
      AW=HEL+AK1+AK2-AK3-AK4+AK5+AK6
      AW=AW-B2*(3*TMG*(-0.011*2*TK+0.007*2*TNA)+
     .3*TCA*(-0.015*2*TK)+2*TNA*(-0.009*2*TK))
      AW=EXP(AW)
      AH2O=AW
C      *****************************************
C      DETERMINE STOICHIOMETRIC MEAN AND SINGLE
C      ION ACTIVITY COEFFICIENTS
C      *****************************************
      IF(TNA)300,232,233
  232  FFNA=1.
      GO TO 234
  233  FFNA=FNA/TNA
  234  IF(TK)300,235,236
  235  FFK=1.
      GO TO 237
  236  FFK=FK/TK
  237  IF(TMG)300,238,239
  238  FFMG=1.
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      GO TO 240
 239   FFMG=FMG/TMG
 240   IF(TCA)300,241,242
 241   FFCA=1.
      GO TO 243
 242   FFCA=FCA/TCA
 243   IF(TSO4)300,244,245
 244   FFSO4=1.
      GO TO 246
 245   FFSO4=FSO4/TSO4
 246   TACMCL=((ACMG*FFMG)*(ACLT**2.))**0.333
      TACCCL=((ACCA*FFCA)*(ACLT**2.))**0.333
      TACCSO=(ACCA*FFCA*ACSO4*FFSO4)**0.5
      TACMG=ACMG*FFMG
      TACCA=ACCA*FFCA
      TACNA=ACNA*FFNA
      TACK=ACK*FFK
      TACSO4=ACSO4*FFSO4
      TACNC=(ACNA*FFNA*ACLT)**0.5
      TACKCL=(ACK*FFK*ACLT)**0.5
      TACNSO=(((ACNA*FFNA)**2.)*(ACSO4*FFSO4))**0.333
      TAMGSO=(ACMG*FFMG*ACSO4*FFSO4)**0.5
      TACKSO=(((ACK*FFK)**2.)*(ACSO4*FFSO4))**0.333
      AHCL=(ACH*ACLT)**0.5
      AKCL=(ACK*ACLT)**0.5
      ANACL=(ACNA*ACLT)**0.5
      ACACL2=(ACCA*(ACLT)**2.)**0.333
      AMGCL=(ACMG*(ACLT)**2.)**0.333
      AK2SO4=(ACSO4*(ACK)**2.)**0.333
      ANA2SO=(ACSO4*(ACNA)**2.)**0.333
      AMGSO=(ACSO4*ACMG)**0.5
      ACASO=(ACSO4*ACCA)**0.5
 300   CONTINUE
 C     ********************************
 C     DETERMINE OPERATIONAL ACTIVITY
 C     COEFFICIENT FOR H+,ACHOP.
 C     ********************************
      IF(KZ)250,250,3001
 3001  CK12=(10.**(-0.59))/ACCA
      CK13=(10.**(-0.53))/ACMG
      CK14=(10.**(0.55))/(ACNA**2.)
      CKHSO4=10.**(-1.99)
      CON=ACHCO3/(1+FNA/CK14+FMG/CK13+FCA/CK12)
      CON2=(1+(ACH*ACSO4*FSO4)/(CKHSO4*CON))
      ACHOP=SLOPE*CON2/CBA
 C     ***************************
 C     CONVERT UNITS TO MOLAR SCALE
 C     ***************************
      IF(KZ)250,250,301
 250   ACCA=ACCA/CONNX
      ACMG=ACMG/CONNX
      ACCO2=ACCO2/CONNX
      ACH=ACH/CONNX
      ACNA=ACNA/CONNX
      ACSO4=ACSO4/CONNX
      ACK=ACK/CONNX
      ACNAS=ACNAS/CONNX
      ACKSO=ACKSO/CONNX
      ANASOT=ANASOT/CONNX
```

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```
      ACHCO3=ACHCO3/CONNX
      ACOH=ACOH/CONNX
      ACCO3=ACCO3/CONNX
      TACMCL=TACMCL/CONNX
      TACCCL=TACCCL/CONNX
      ACLT=ACLT/CONNX
      TACCSO=TACCSO/CONNX
      TACMG=TACMG/CONNX
      TACCA=TACCA/CONNX
      TACNA=TACNA/CONNX
      TACSO4=TACSO4/CONNX
      TACNC=TACNC/CONNX
      TACKCL=TACKCL/CONNX
      TACK=TACK/CONNX
      TACNSO=TACNSO/CONNX
      TAMGSO=TAMGSO/CONNX
      TACKSO=TACKSO/CONNX
      TMG=TMG*CONNX
      TCA=TCA*CONNX
      TNA=TNA*CONNX
      TK=TK*CONNX
      TCL=TCL*CONNX
      TSO4=TSO4*CONNX
      FMG=FMG*CONNX
      FNA=FNA*CONNX
      FCA=FCA*CONNX
      FSO4=FSO4*CONNX
      CNASO=CNASO*CONNX
      CNA2SO=CNA2SO*CONNX
      FK=FK*CONNX
      CKSO4=CKSO4*CONNX
      CK2SO4=CK2SO4*CONNX
      CCASO=CCASO*CONNX
      CMGSO=CMGSO*CONNX
      AHCL=(ACH*ACLT)**0.5
      AKCL=(ACK*ACLT)**0.5
      ANACL=(ACNA*ACLT)**0.5
      ACACL2=(ACCA*(ACLT)**2.)**0.333
      AMGCL=(ACMG*(ACLT)**2.)**0.333
      AK2SO4=(ACSO4*(ACK)**2.)**0.333
      ANA2SO=(ACSO4*(ACNA)**2.)**0.333
      AMGSO=(ACSO4*ACMG)**0.5
      ACASO=(ACSO4*ACCA)**0.5
C      ******************************
C      DETERMINE OPERATIONAL ACTIVITY
C      COEFFIENT FOR H+,ACHOP.
C      *******************************
      CK12=(10.**(-0.59))/ACCA
      CK13=(10.**(-0.53))/ACMG
      CK14=(10.**(0.55))/(ACNA**2.)
      CKHSO4=10.**(-1.99)
      CON=ACHCO3/(1+FNA/CK14+FMG/CK13+FCA/CK12)
      CON2=(1+(ACH*ACSO4*FSO4)/(CKHSO4*CON))
      ACHOP=SLOPE*CON2/CBA
  301  CONTINUE
      RETURN
      END
```

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1. Objectives

This program is concerned with the carbonate system in highly saline waters in which the principal ionic matrix is comprised of one or more of the salts NaCl, Na_2SO_4, KCl, K_2SO_4, $MgCl_2$ $MgSO_4$, $CaCl_2$ and $CaSO_4$. The following are determined:

(i) The relationship between 'true' pH and the operational pH, pH(0).

(ii) The operational stoichiometric apparent equilibrium constants for the carbonate system, i.e. $p_oK'_{T1}$ and $p_oK'_{T2}$.

(iii) The distribution of free and ion paired carbonate and hydroxide species concentrations with pH(0) on either the molal or molar scale.

(iv) The distribution of free species and ion paired species buffer capacities with pH(0).

(v) The distribution of the stoichiometric species buffer capacities with pH(0).

2. Input data

The input data to the program are in stoichiometric quantities on either the molal or molar scale; the output correspondingly will be on the same scale, i.e. either molal or molar scale.

Card 1: Read in the concentration scale to be used (i.e. either molal or molar) by assigning an integer value to the logical unit number variable KZ. If the molal scale is used, KZ is assigned the integer value (plus) one, 1; if the molar scale is used, KZ is assigned the integer value (minus) one, -1.

Card 2: Read in the stoichiometric concentrations (in floating point on the scale selected in Card 1) of the species comprising the principal ionic matrix in the following order: total Na, total Mg, total Ca, total K, total Cl,

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total SO_4. The data are entered in free format, and, where a species is not present, the value 0.0 must be inserted.

Card 3: Read in the stoichiometric concentrations (in floating point on the scale selected in Card 1) of the salts comprising the principal ionic matrix in the following order: NaCl, Na_2SO_4, $MgCl_2$, $MgSO_4$, $CaCl_2$, $CaSO_4$, KCl, K_2SO_4. The data are entered in free format, and, where a salt is not present the value 0.0 must be inserted.

Card 4: Read in the total carbonate weak acid-base species concentration (in floating point on the scale selected in Card 1).

Card 5: Read in the data to determine the residual liquid junction potential effects on pH. The data required are the measured slope of the first Gran titration (i.e. the titration carried out in the region $3,0 < pH < 3,8$, SLOPE) and the concentration (in floating point on the scale selected in Card 1) of strong acid used in the titration (an example is given below of such a Gran titration and determination of SLOPE). These data are entered in free format.

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3. Calculation procedures

The calculations are carried out assuming a constant ionic medium, that is, the distribution of *principal species* comprising the ionic matrix is assumed independent of pH. (Distribution of minor species, i.e. carbonate weak acid-base species vary with pH but this has negligible effect on the ionic strength). The calculation procedure is as follows:

(i) Determine mean and single ion free and stoichiometric activity coefficients and distribution of free and ion paired *principal* species concentrations (on the scale selected). This determination is carried out within the subroutine program SUBROUTINE ACTIVE as described in Supplement A.

(ii) Weak acid equilibrium constants are adjusted to the apparent and apparent stoichiometric form using Eqs. (60a and 60b, and 57a and 57b) Chapter 4, respectively.

(iii) For each pH value of interest the stoichiometric carbonate species concentrations are determined from the input C_T value using Eqs. (52, 57a and 57b) Chapter 4.

(iv) The free and ion paired weak acid-base species concentrations are determined from the free cation species concentrations (determined in (i) above), the stoichiometric carbonate species concentrations (determined in (iii) above) and Eqs. (50 and 51), Chapter 4; the respective buffer capacities from Eqs. (135 and 138) Chapter 4.

An example of a plot of the output for seawater is shown in the text in Figures 5 and 13, Chapter 4.

4. Determination of SLOPE from a Gran titration

The Gran function F, for the strong acid titration in the region 3,0 < pH < 3,8 was determined in Section 6.2.4, Chapter 4 as

$$F_{1(x)} = 10^{-pH_{o(x)}} \cdot (V_1 + \nu_x) \qquad \text{(B1)}$$

where $pH_{o(x)}$ = operational pH after adding ν_x mℓ of standard strong acid.

V_1 = initial volume of sample in mℓ.

$F_{1(x)}$ = value of the first Gran function after addition of ν_x mℓ of standard strong acid.

In Section 3.4 Chapter 4 the theory linking the slope of the Gran titration function F_1 to the operational activity coefficient $\gamma_{H(o)}$ is presented. An example of the experimental determination of SLOPE from a strong acid titration of seawater is set out below. The observed operational pH values after adding increments of strong acid (molarity = 0,1056) to a sample of seawater with initial volume V_1 = 487,0 mℓ is set out in Table B.1 below. Also listed in this table are the corresponding values for $F_{1(x)}$ determined using Eq. (B1).

Table B.1 Determination of Gran function values $F_{1(x)}$ from the strong acid titration (molarity 0,1056) of a 487,0 mℓ sample of seawater.

ν_x mℓ	$V_1 + \nu_x$ mℓ	pH_o	$F_{1(x)}$
0,0	487,0		
11,40	498,40	4,111	0,0386
11,60	498,60	3,984	0,0517
11,80	498,80	3,880	0,0658
12,00	499,00	3,792	0,0806
12,20	499,20	3,716	0,0960
12,40	499,40	3,652	0,1113
12,60	499,60	3,593	0,1275
12,80	499,80	3,541	0,1438
13,00	500,00	3,495	0,1599

A plot of ν_x versus $F_{1(x)}$ (from Table B.1) is shown plotted in Figure B.1. The measured slope = 0,0815.

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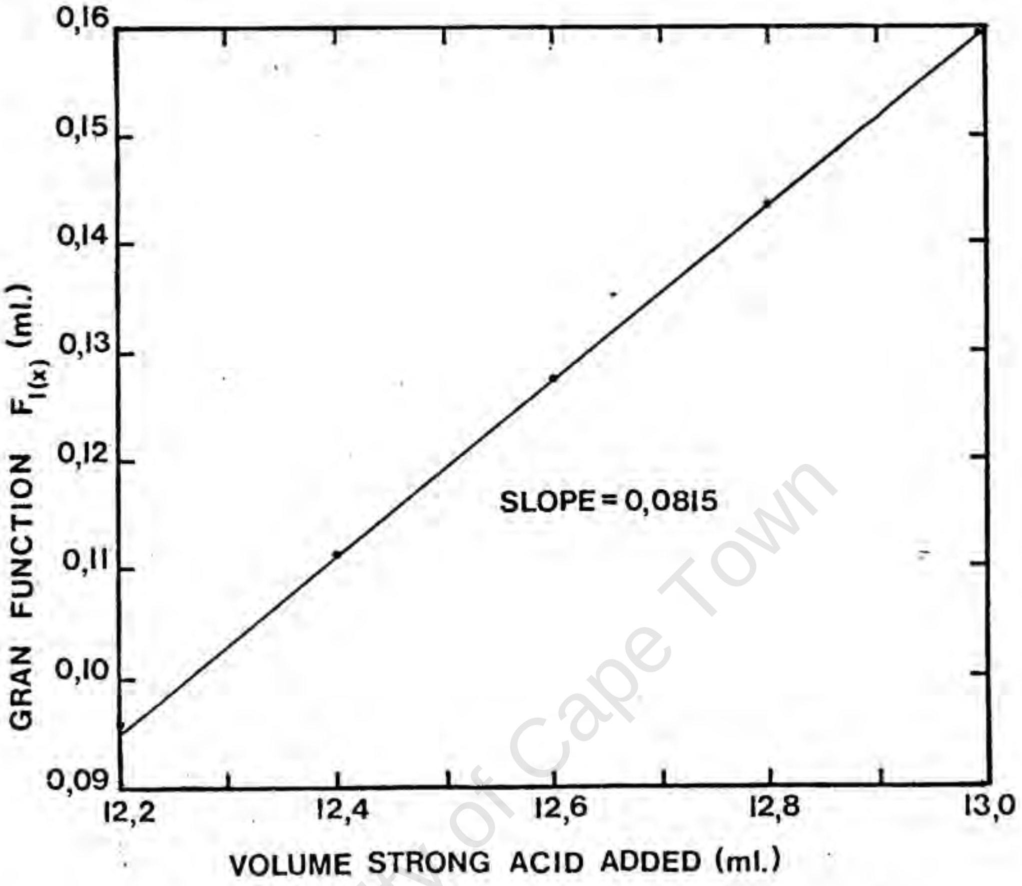

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Figure B.1: *First Gran titration plot for 487,0 mℓ seawater titrated with standard strong acid, molarity 0,1056.*

Distribution of Species with pH

```
C      THIS PROGRAM DETERMINES:
C          (1)THE RELATIONSHIP BETWEEN TRUE PH
C             AND OPERATIONAL PH,PHO.
C          (2)THE APPARENT STOICHIOMETRIC
C             OPERATIONAL EQUILIBRIUM CONSTANTS
C             FOR THE CARBONATE SYSTEM.
C          (3)THE DISTRIBUTION OF LOG SPECIES
C             CONCENTRATION WITH PHO
C          (4)DISTRIBUTION OF SPECIES BUFFER
C             CAPACITY WITH PHO.
C      *****************************************
      REAL KW,KMGCO,KMGHC,KCACO,KCAHC,KNAHC,
     .KNACO,KMGOH,KCAOH,KOT1,KDO1,KDO2,KOT2,K1,K2
     .,MGHC,MGCO,MGOH,NAHC,NACO,NACL,NA2SO4,MGCL2,
     .MGSO4,KCL,K2SO4
      COMMON ACCA,ACMG,ACH,ACNA,ACSO4,ACK,
     .ACNAS,ACKSO,ANASOT,ACHCO3,ACOH,ACCO3,TACCCL,
     .TACMCL,ACLT,TACCSO,TACMG,TACCA,TACNA,TACSO4,
     .TACNC,TACKCL,TACNSO,TAMGSO,TACKSO,AHCL,AKCL,
     .ANACL,ACACL2,AMGCL,AK2SO4,ANA2SO,AMGSO,ACASO,
     .TMG,TCA,TNA,TK,TCL,TSO4,FMG,FNA,FCA,FSO4,
     .CNASO,CNA2SO,TACK,FK,CKSO4,CK2SO4,CCASO,
     .CMGSO,ACCO2,NACL,NA2SO4,MGCL2,MGSO4,CACL2,
     .CASO4,KCL,K2SO4,U1,SLOPE,CBA,AH2O,AW,ACHOP,
     .KZ
      DIMENSION PHO(50)
C      ********************************
C      READ IN CONCENTRATION UNITS
C      TO BE USED
C      KZ=1(MOLAL SCALE)
C      KZ=-1(MOLAR SCALE)
C      ********************************
      READ(5,10)KZ
C      *********************************
C      READ IN PRINCIPAL IONIC SPECIES
C      IN MOLAL/MOLAR UNITS
C      *********************************
      READ(5,10)TNA,TMG,TCA,TK,TCL,TSO4
C      *********************************
C      READ IN PRINCIPAL SALT SPECIES
C      IN THE SOLUTION(MOLAL UNITS)
C      *********************************
      READ(5,10)NACL,NA2SO4,MGCL2,MGSO4,CACL2,
     .CASO4,KCL,K2SO4
C      **********************************
C      READ IN TOTAL CARBONATE SPECIES
C      CONCENTRATION IN MOLAL/MOLAR UNITS
C      ***********************************
      READ(5,10)CT
C      ***********************************
C      READ IN SLOPE OF FIRST GRAN TITRATION
C      AND MOLALITY/MOLARITY OF TITRANT.
C      ************************************
      READ(5,10)SLOPE,CBA
 10    FORMAT( )
C      ********************************
C      DETERMINE ACTIVITY COEFFICIENTS
C      IN SUBROUTINE 'ACTIVE'
C      *********************************
```

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```
      CALL ACTIVE
      ACHC=ACHCO3
      ACCO=ACCO3
      ACO2=ACCO2
      ACN=1.
      FNAS=FNA
      FCAS=FCA
      FMGS=FMG
      FKS=FK
      AW=AH2O
C      **********************************
C      ADJUST EQUILIBRIUM CONSTANTS FOR
C      ACTIVITY COEFFICIENT EFFECTS
C      ***********************************
      K1=10**(-6.352)
      K2=10**(-10.329)
      KW=10**(-14.0)
      KMGCO=10**(-2.92)
      KMGHC=10**(-0.53)
      KCACO=10**(-3.16)
      KCAHC=10**(-0.59)
      KNACO=10**(-0.85)

      KNAHC=10**(0.55)
      KMGOH=10**(-2.08)
      KCAOH=10**(-1.38)
C
      KMGCO=KMGCO*ACN/(ACMG*ACCO)
      KMGHC=KMGHC*ACNA/(ACMG*ACHC)
      KCACO=KCACO*ACN/(ACCA*ACCO)
      KCAHC=KCAHC*ACNA/(ACCA*ACHC)
      KNAHC=KNAHC*ACN/(ACNA*ACHC)
      KNACO=KNACO*ACNA/(ACCO*ACNA)
      KMGOH=KMGOH*ACNA/(ACMG*ACOH)
      KCAOH=KCAOH*ACNA/(ACCA*ACOH)
C
C      ***********************************
C      CALCULATE OPERATIONAL APPARENT AND
C      APPARENT (BOTH STOICHIOMETRIC)
C      EQUILIBRIUM CONSTANTS.
C      ************************************
      DIFF=-LOG10(ACH)+LOG10(ACHOP)
      KDO1=K1*AW*ACCO2*(ACHOP/ACH)/ACHC
      KDO2=K2*ACHC*(ACHOP/ACH)/ACCO
C
      Y=(1+(FMGS/KMGHC)+(FCAS/KCAHC)+FNAS/KNAHC)
      Z=(1+(FMGS/KMGCO)+(FCAS/KCACO)+(FNAS/KNACO))
C
      CCT=-LOG10(CT)
      KOT1=KDO1*Y
      KOT2=KDO2*Z/Y
      OK1=-LOG10(KDO1)
      OK2=-LOG10(KDO2)
      OKT1=-LOG10(KOT1)
      OKT2=-LOG10(KOT2)
      WRITE(6,16)
16     FORMAT(30X,'*************************')
      IF(KZ)17,17,19
17     WRITE(6,18)
```

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```
18     FORMAT(30X,'MOLAR CONCENTRATION UNITS')
      GO TO 21
19     WRITE(6,20)
20     FORMAT(30X,'MOLAL CONCENTRATION UNITS')
21     WRITE(6,22)
22     FORMAT(30X,'*************************')
      WRITE(6,230)
230    FORMAT(///1X,'*********************'
     .'*****************')
      WRITE(6,231)
231    FORMAT(1X,'STOICHIOMETRIC SPECIES '
     .,'CONCENTRATIONS')
      WRITE(6,232)
232    FORMAT(1X,'************************'
     .'**************',//)
      WRITE(6,233)CT,TNA,TMG,TCA,TK,TCL,TSO4
233    FORMAT(2X,'TOTAL CARBONATE (CT)=',E9.3,
     ./,1H ,1X,'TOTAL SODIUM (TNA)=',E9.3,
     ./,1H ,1X,'TOTAL MAGNESIUM (TMG)=',E9.3,
     ./,1H ,1X,'TOTAL CALCIUM (TCA)=',E9.3,
     ./,1H ,1X,'TOTAL POTASSIUM (TK)=',E9.3,
     ./,1H ,1X,'TOTAL CHLORIDE (TCL)=',E9.3,
     ./,1H ,1X,'TOTAL SULPHATE (TSO4)=',E9.3)
      WRITE(6,234)
234    FORMAT(///1X,'************************'
     .'***********************')
      WRITE(6,235)
235    FORMAT(1X,'RELATIONSHIP BETWEEN PH,PH,'
     .'AND OPERATIONAL PH,PHO')
      WRITE(6,236)
236    FORMAT(1X,'*****************************'
     .'*******************',//)
      WRITE(6,237)DIFF
237    FORMAT(1X,'PH-PHO=',F5.3)
      WRITE(6,23)
23     FORMAT(///1X,'*****************************'
     .'******************************************')
      WRITE(6,24)
24     FORMAT(1X,'OPERATIONAL STOICHIOMETRIC'
     .' EQUILIBRIUM CONSTANTS FOR THE '
     .'CARBONATE SYSTEM')
      WRITE(6,25)
25     FORMAT(1X,'********************************'
     .'**************************************')
      WRITE(6,26)OKT1
26     FORMAT(///1X,'PK1=',F6.3)
      WRITE(6,27)OKT2
27     FORMAT(//1X,'PK2=',F6.3)
      WRITE(6,28)
28     FORMAT(////1X,'*********************************'
     .'**************')
      WRITE(6,29)
29     FORMAT(1X,'PH(OPERATIONAL) VERSUS LOG SPECIES '
     .,'CONCENTRATION')
      WRITE(6,30)
30     FORMAT(1X,'*************************************'
     .,'**************')
      WRITE(6,31)
31     FORMAT(//3X,'PHO',4X,'CO2',5X,'HCO3',3X,'MGHCO3',
```

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```
     .2X,'CAHCO3',2X,'NAHCO3',3X,'THCO3',3X,'MGCO3',3X,
     .'CACO3',3X,'NACO3',4X,'CO3',4X,'TCO3',5X,'OH',5X,
     .'CAOH',4X,'MGOH',/)
C
C      ********************************
C      CALCULATE LOG SPECIES VALUES FOR
C      INPUT PH AND TOTAL CARBONATE SPECIES
C      CONCENTRATION.
C      *********************************
      PHO(1)=4.0
      DO 50 I=1,30
      HO=10**(-PHO(I))
      H=HO*(ACH/ACHOP)
      OH=(KW/H)/ACOH
      CO3T=CT/((HO**2.)/(KOT1*KOT2)+1.+HO/KOT2)
      HCO3T=CT/((HO/KOT1)+1+(KOT2/HO))
      CO3=CO3T/Z
      HCO3=HCO3T/Y
      CO2=HO*HCO3T/KOT1
      MGOH=FMGS*OH/KMGOH
      CAOH=FCAS*OH/KCAOH
      OHT=OH+MGOH+CAOH
      MGHC=LOG10(FMGS*HCO3/KMGHC)
      MGCO=LOG10(FMGS*CO3/KMGCO)
      CAHC=LOG10(FCAS*HCO3/KCAHC)
      CACO=LOG10(FCAS*CO3/KCACO)
      NAHC=LOG10(FNAS*HCO3/KNAHC)
      NACO=LOG10(FNAS*CO3/KNACO)
      MGOH=LOG10(FMGS*OH/KMGOH)
      CAOH=LOG10(FCAS*OH/KCAOH)
      CO3=LOG10(CO3)
      HCO3=LOG10(HCO3)
      CO2=LOG10(CO2)
      OH=LOG10(OH)
      CO3T=LOG10(CO3T)
      HCO3T=LOG10(HCO3T)
      WRITE(6,32)PHO(I),CO2,HCO3,MGHC,CAHC,NAHC,HCO3T,MGCO,
     .CACO,NACO,CO3,CO3T,OH,CAOH,MGOH
 32    FORMAT(15F8.3,/)
      PHO(I+1)=PHO(I)+0.2
 50    CONTINUE
      E=2.30258
C      *********************************
C      DETERMINE THE DISTRIBUTION OF BUFFER
C      CAPACITIES OF FREE AND ION PAIRED
C      SPECIES WITH PH
C      **********************************
      WRITE(6,51)
 51    FORMAT(///1X,'************************'
     .'***************')
      WRITE(6,52)
 52    FORMAT(1X,'PH(OPERATIONAL) VERSUS BUFFER'
     .' CAPACITY')
      WRITE(6,53)
 53    FORMAT(1X,'**************************'
     .'*************')
      WRITE(6,54)
 54    FORMAT(///45X,'BUFFER CAPACITY OF SPECIES',/)
      WRITE(6,55)
```

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```
 55      FORMAT(2X,'PHO',8X,'CO2',6X,'CO2',4X,'MGHCO3',3X,
       .'CAHCO3',3X,'NAHCO3',4X,'HCO3',5X,'HCO3',4X,'MGCO3',
       .4X,'CACO3',4X,'NACO3',5X,'H2O')
        WRITE(6,56)
 56     FORMAT(10X,'(TOTAL)',3X,'(FREE)',29X,'(TOTAL)',3X,
       .'(FREE)')
        PHO(1)=4.0
        DO 100 I=1,30
        HO=10**(-PHO(I))
        H=HO*(ACH/ACHOP)
        OH=(KW/H)/ACOH
        CO3T=CT/((HO**2.)/(KOT1*KOT2)+1.+HO/KOT2)
        HCO3T=CT/((HO/KOT1)+1.+(KOT2/HO))
        CO3=CO3T/Z
        HCO3=HCO3T/Y
        CO2=HO*HCO3T/KOT1
        MGOH=FMGS*OH/KMGOH
        CAOH=FCAS*OH/KCAOH
        OHT=OH+MGOH+CAOH

        BTH2O=E*(H+OHT)
        BTH2C=(E*CO2*HCO3T)/CT
        BTHC=(E*HCO3T*CO3T)/(CT)
        BH2C=E*CO2*HCO3/CT
        BHC=E*HCO3*CO3/CT
        BHCCA=(E*CO2*FCAS*HCO3)/(KCAHC*CT)
        BHCMG=(E*CO2*FMGS*HCO3)/(KMGHC*CT)
        BHCNA=(E*CO2*FNAS*HCO3)/(KNAHC*CT)
        BCOCA=(E*HCO3T*FCAS*CO3)/(KCACO*CT)
        BCOMG=(E*HCO3T*FMGS*CO3)/(KMGCO*CT)
        BCONA=(E*HCO3T*FNAS*CO3)/(KNACO*CT)
        WRITE(6,60)PHO(I),BTH2C,BH2C,BHCMG,BHCCA,BHCNA,BTHC,
       .BHC,BCOMG,BCOCA,BCONA,BTH2O
 60      FORMAT(12E9.3,/)
        PHO(I+1)=PHO(I)+0.2
 100    CONTINUE
        STOP
        END
```

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1. Objectives

This program is concerned with conditioning diagrams for the carbonate system considering either equilibrium between dissolved carbonate species in the aqueous phase only, or, equilibrium between dissolved carbonate species in the aqueous phase and carbon dioxide in the gas phase. The program plots:

(i) a family of curves representing *true* pH values in a diagram with Alkalinity and Acidity as co-ordinates for single aqueous phase equilibrium, and/or

(ii) a family of curves representing partial pressure of CO_2 (in a gas phase) for equilibrium between carbonate species in the aqueous phase and CO_2 in the gas phase in a diagram with Alkalinity and Acidity as co-ordinates.

Plots for either low salinity or high salinity solutions can be made. Low salinity can be accepted if $\mu < 0,1$. For such waters residual liquid junction potential effects on pH are negligible so that $pH \simeq pH(0)$. For high salinity waters cognizance is taken of residual liquid junction potential effects on pH, but to do this the program requires data from a Gran titration to determine this effect (see Supplement B for an example of a Gran titration).

For both high and low salinity waters plots are valid only for 25°C and one atmosphere total pressure.

The plotting program, which forms part of the main program is written specifically for the CALCOMP plot subroutine.

2. Input data

The unit of concentration for the input data to the program is the *molar scale*. The input data is inserted into the program as follows:

Data Card 1: Read in the stoichiometric concentrations in moles/ℓ of the species comprising the principal ionic matrix in the following order total Na,

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total Mg, total Ca, total K, total Cl and total SO_4. The data is read in free format, and, where a species is not present, the value 0.0 must be inserted.

Data Card 2: Read in the stoichiometric concentrations of the salts comprising the principal ionic matrix in moles/ℓ in the following order: NaCl, Na_2SO_4, $MgCl_2$, $MgSO_4$, $CaCl_2$, $CaSO_4$, KCl and K_2SO_4. The data are inserted in free format. If a salt is not present 0.0 must be inserted.

Data Card 3: Read in the number of pH lines and pCO_2 lines to be plotted (NPH and NPCO respectively) in integer format. If no pCO_2 (or pH) lines are to be plotted, enter the value 'zero', i.e. 0 (an integer).

Data Card 4: Read in data for defining the type of diagram to be plotted by assigning values to the *integer* variables LAG and SOFT as follows:

LAG = 1, only pH lines are plotted in the diagram

LAG = 0, both pH and pCO_2 lines are plotted

LAG = -1, only pCO_2 lines are plotted

SOFT = 1, a plot for low salinity water for which pH approximates operational pH

SOFT = -1, a plot for a high salinity water for which the relationship between pH and pH(0) must be determined.

For example, if lines representing only pH are wanted in the diagram for seawater (a high salinity water), then values for LAG and SOFT to be entered into this data card must be 1 and -1 respectively, i.e.

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Card 4: 1B-1. Where B indicates a blank space.

Data Card 5: Read in the ordinate limits to the diagram, i.e. the maximum Alkalinity and Acidity ordinate values (in m.moles/ℓ), MAXALK and MAXACD respectively; these data are entered onto a card in free format. For example, if the maximum Alkalinity and Acidity volumes are 4,0 and 6,0 m.moles/ℓ respectively, Data Card 5 will be as follows:

4.0B6.0 Where B indicates a blank space.

Data Card 6: This card is inserted for high salinity waters. Read in the data to determine the residual liquid junction potential effects on pH. The data required here are the measured slope of the first Gran titration (i.e. the titration carried out in the region $3 < pH < 3,8$, SLOPE, and the concentration (molarity) of standard strong acid used in this titration, CBA). If the diagram to be plotted is for a low salinity water, (i.e. SOFT = 1 in Data Card 4), this card is omitted from the input data. (See Supplement B, Section 4 for an example of a Gran titration).

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Data Cards for pH values

If lines representing pH are to be plotted in the diagram, i.e. LAG equals either 1 or 0 on Data Card 4, then pH values are entered one value per card, starting with the lowest pH value and entered in order of *increasing pH values;* if LAG = -1 then no pH lines are plotted and no pH data cards are entered.

Data Cards for pCO_2 values

If lines representing partial pressure of CO_2 are to be plotted in the diagram, i.e. LAG = 0 or -1 in Data Card 4, then pCO_2 values are entered one value per card starting with the highest pCO_2 value and entered in order of decreasing pCO_2 values; if LAG = 1, no pCO_2 lines are plotted and no pCO_2 data cards are entered.

3. Calculation procedure to plot pH and pCO_2 lines

The calculation procedure to plot pH and/or pCO_2 lines in the diagram is as follows:

(i) Activity coefficients and the principal species concentrations are determined as set out in Supplement A using the subroutine program, SUBROUTINE ACTIVE. For this purpose the input concentrations (on the molar scale) are converted first to the molal scale and activity coefficients (on the molal scale) are calculated; these activity coefficients (and species concentrations) are then converted back to the molar scale (the unit of concentration used in the main program).

(ii) Stoichiometric apparent equilibrium constants K'_{T1} and K'_{T2} (on the molar scale) are calculated by the same procedure as described in Supplement B.

(iii) For a fixed input value of pH and a series of selected values for Acidity the corresponding Alkalinity values are calculated using Eq. (21), Chapter 5.

(iv) For a particular pH value, a plot of the paired Alkalinity and Acidity values traces a line representing pH in the Alkalinity-Acidity axis.

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(v) Procedures in (iii) and (iv) are repeated for all the input pH values.

(vi) For pCO_2 lines: for a fixed input value for pCO_2, determine $[H_2CO_3^*]$ using Eq. (22), Chapter 5: for this value of $[H_2CO_3^*]$ and a series of selected values for Alkalinity corresponding values are determined for Acidity as follows:

For the input value of pCO_2 (i.e. $[H_2CO_3^*]$) determine (H^+) as

$$(H^+) = \{-B + (B^2 - 4AC)^{\frac{1}{2}}\}/2A$$

where

$$A = 1/f_H$$

$$B = \text{Alkalinity} - 2[H_2CO_3^*]$$

$$C = K'_{T1}\ [H_2CO_3^*] - K'_{Tw}$$

For the input values of pCO_2 and Alkalinity and the value for (H^+) determined above, calculate the corresponding Acidity value, i.e.

$$\text{Acidity} = 2[H_2CO_3^*]\{1+K'_{T1}/(H^+) + K'_{T2}/(H^+)^2\} - \text{Alkalinity}$$

(vii) For a particular pCO_2 value, a plot of the paired Alkalinity and Acidity values traces a line representing pCO_2 in the Alkalinity-Acidity axes.

(viii) Procedures (vi) and (vii) are repeated for all the input pH values.

4. Output from program

The output from this program is a plot via either a drum or plane table plotter. An example of such a plot for seawater is shown in Figure 6, Chapter 5. Note that each plot is headed with the relationship linking true and operational pH, and the principal ionic matrix species concentrations.

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```
C     *********************************************
C     PROGRAM TO PLOT LINES REPRESENTING PH OR
C     PH AND PCO2 OR ONLY PCO2 VERSUS ALKALINITY AND
C     ACIDITY.
C     (ALL UNITS ON THE MOLAR SCALE)
C     *********************************************
C
      CHARACTER*4 MSG
      REAL K11,K12,K13,K14,K21,K22,K23,K24,K41,K33,
     -K32,K34,KS,K42,K43,KH,KMG,KHSO4,NACL,NA2SO4,
     .MGCL2,MGSO4,KCL,K2SO4,MAXALK,MAXACD
      DOUBLE PRECISION FRACT,H
      COMMON ACCA,ACMG,ACH,ACNA,ACSO4,ACK,
     .ACNAS,ACKSO,ANASOT,ACHCO3,ACOH,ACCO3,TACCCL,
     .TACMCL,ACLT,TACCSO,TACMG,TACCA,TACNA,TACSO4,
     .TACNC,TACKCL,TACNSO,TAMGSO,TACKSO,AHCL,AKCL,
     .ANACL,ACACL2,AMGCL,AK2SO4,ANA2SO,AMGSO,ACASO,
     .TMG,TCA,TNA,TK,TCL,TSO4,FMG,FNA,FCA,FSO4,
     .CNASO,CNA2SO,TACK,FK,CKSO4,CK2SO4,CCASO,
     .CMGSO,ACCO2,NACL,NA2SO4,MGCL2,MGSO4,CACL2,
     .CASO4,KCL,K2SO4,U1,SLOPE,CBA,AH2O,AW,ACHOP,
     .KZ
      DIMENSION PH(50),ACID(500),PKK(50),
     -ALK(500),PCO(50),MSG(5)
      DATA MSG /'PLS ','LOAD',' P1-','BK/I','5   '/
C     **********************************************
C     READ IN CONC. OF MAJOR IONS IN
C     THE SOLUTION (MOLES/L)
C     *********************************************
      READ(5,2)TMG,TNA,TCL,TCA,TSO4,TK
C     ******************************************
C     READ IN CONCENTRATIONS OF SALTS MAKING
C     UP THE SOLUTION (MOLES/L)
C     ******************************************
      READ(5,2)NACL,NA2SO4,MGCL2,MGSO4,CACL2,CASO4,
     .KCL,K2SO4
C     ***********************************************
C     DATA FOR NUMBER OF LINES TO BE PLOTTED
C     NPH=NO. OF PH LINES
C     NPCO=NO. OF CO2 PARTIAL PRESSURE LINES
C     ********************************************
      READ(5,2)NPH,NPCO
C     *******************************************
C     READ IN DIAGRAM TO BE PLOTTED
C     LAG=1 ONLY PH LINES ARE PLOTTED
C     LAG=0 BOTH PH AND PCO2 LINES ARE PLOTTED
C     LAG=-1 ONLY PCO2 LINES ARE PLOTTED
C     SOFT=1 LOW SALINITY WITH ION PAIRING
C     SOFT=-1 HIGH SALINITY WITH ION PAIRING
C     *******************************************
      READ(5,2)LAG,SOFT
C     *********************************************
C     DATA FOR DIAGRAM LIMITS (IN M.MOLES/L)
C     MAXALK=MAXIMUM ALKALINITY VALUE
C     MAXACD=MAXIMUM ACIDITY VALUE
C     **********************************************
      READ(5,2)MAXALK,MAXACD
2     FORMAT()
C     ****************************************
```

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```
C     READ SLOPE OF FIRST GRAN TITRATION(SLOPE)
C     AND MOLARITY OF STANDARD ACID (CBA)
C     ***************************************
     IF(SOFT)50,50,55
50    READ(5,2)SLOPE,CBA
     GO TO 56
55    SLOPE=1.
     CBA=1.
56    CONTINUE
C     ***************************************
C     READ IN PH VALUES (ONE/CARD)
C     IN ASCENDING ORDER.
C     ********************************************
     IF(LAG)1003,1002,1002
1002 CONTINUE
     DO 10 I=1,NPH
     READ(5,2)PH(I)
  10 CONTINUE
1003 CONTINUE
C     ********************************************
C     ********************************************
C     *********************************************
C     READ IN PCO2 VALUES (ATMOSPHERES),
C     ONE VALUE/CARD
C     *********************************************
     IF(LAG)1001,1001,1004

1001 CONTINUE
     DO 14 I=1,NPCO
     READ(5,2)PCO(I)
  14 CONTINUE
1004 CONTINUE
C     ***********************************************
C     ENTER IN PK VALUES AT 25DEGC. FOR
C     DISSOCIATION REACTIONS: (1)H2CO3,(2)HCO3,(3)CASO4
C     (4)NASO4-,(5)MGSO4,(6)NAHCO3,(7)NACO3-,(8)MGHCO3+,
C     (9)MGCO3,(10)CAHCO3+,(11)CACO3,(12)MGOH+,(13)CAOH+,
C     (14)H2O,(15)CALCITE KSP,(16)MG(OH)2 KSP,(17)ARAGONITE
C     ********************************************
     PKK(1)=6.352
     PKK(2)=10.329
     PKK(3)=2.41
     PKK(4)=0.60
     PKK(5)=2.38
     PKK(6)=-0.55
     PKK(7)=0.85
     PKK(8)=0.53
     PKK(9)=2.92
     PKK(10)=0.59
     PKK(11)=3.16
     PKK(12)=2.08
     PKK(13)=3.16
     PKK(14)=14.0
     PKK(15)=8.41
     PKK(16)=10.41
     PKK(17)=8.24
     T=25.
C     *****************************************
C     CALL SUBROUTINE 'ACTIVE' TO CALCULATE
```

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```
      GO TO 75
70     ALJ=0.0
75     CONTINUE
C      *******************************************
C      INITIATE PLOT ROUTINE AND LABLE DIAGRAM
C      ********************************************
      CALL PLOTS(0,0,0)
      CALL OPMES(20,MSG)
      CALL PAGSIZ(60.,60.)
      CALL FACTOR(5.0)
      TMX=MAXALK*2.+1.
      NTMX=IFIX(TMX)
      TMY=MAXACD*2.+1.
      NTMY=IFIX(TMY)
      CALL PLOT(3.,3.,-3)
      Y=0.0
      X=-0.5
      DO 100 I=1,NTMX
      X=X+0.5
      CALL SYMBOL(X,Y,0.1,3,0.,-2)
100    CONTINUE
      Y=-0.5
      X=MAXALK
      DO 110 I=1,NTMY
      Y=Y+0.5
      CALL SYMBOL(X,Y,0.1,3,0.,-2)
110    CONTINUE
      X=MAXALK+0.5
      Y=MAXACD
      DO 120 I=1,NTMX
      X=X-0.5
      CALL SYMBOL(X,Y,0.1,3,0.,-2)
120    CONTINUE
      X=0.0
      Y=MAXACD+0.5
      DO 130 I=1,NTMY
      Y=Y-0.5
      CALL SYMBOL(X,Y,0.1,3,0.,-2)
130    CONTINUE
      TMX=MAXALK+1.
      NTMX=IFIX(TMX)
      TMY=MAXACD+1
      NTMY=IFIX(TMY)
      AALK=-1.
      Y=-0.2
      DO 140 I=1,NTMX
      AALK=AALK+1.
      X=AALK
      CALL NUMBER(X,Y,0.1,AALK,0.,0)
140    CONTINUE
      X=(MAXALK/2.)-1.
      Y=-0.5
      CALL SYMBOL(X,Y,0.1,21HALKALINITY(M.MOLES/L),0.,21)
      AACID=-1.
      X=-0.25
      DO 150 I=1,NTMY
      AACID=AACID+1.
      Y=AACID
      CALL NUMBER(X,Y,0.1,AACID,0.,0)
```

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```
150   CONTINUE
     X=MAXALK+0.3
     Y=(MAXACD)/2.-0.9
     CALL SYMBOL(X,Y,0.1,18HACIDITY(M.MOLES/L),90.,18)
     Y=MAXACD+1.1
     X=0.0
     CALL SYMBOL(X,Y,0.1,11HTEMP(DEGC)=,0.,11)
     CALL NUMBER(999.0,999.0,0.1,T,0.,1)
     X=2.0
     CALL SYMBOL(X,Y,0.1,11HPH-PH(OBS)=,0.,11)
     CALL NUMBER(999.0,999.0,0.1,ALJ,0.,3)
     Y=Y-0.3
     X=0.0
     CALL SYMBOL(X,Y,0.1,18HSPECIES(M.MOLES/L),0.,18)
     Y=Y-0.3
      CALL SYMBOL(X,Y,0.1,4HTMG=,0.,4)
     CALL NUMBER(999.0,999.0,0.1,TMG,0.,1)
     X=1.0
     CALL SYMBOL(X,Y,0.1,4HTNA=,0.,4)
     CALL NUMBER(999.0,999.0,0.1,TNA,0.,1)
     X=2.0
     CALL SYMBOL(X,Y,0.1,4HTCA=,0.,4)
     CALL NUMBER(999.0,999.0,0.1,TCA,0.,1)
     X=3.0
     CALL SYMBOL(X,Y,0.1,3HTK=,0.,3)
     CALL NUMBER(999.0,999.0,0.1,TK,0.,1)
     Y=Y-0.2
     X=0.0
     CALL SYMBOL(X,Y,0.1,5HTSO4=,0.,5)
     CALL NUMBER(999.0,999.0,0.1,TSO4,0.,1)
     X=1.0
     CALL SYMBOL(X,Y,0.1,4HTCL=,0.,4)
     CALL NUMBER(999.0,999.0,0.1,TCL,0.,1)
     X=2.
     CALL SYMBOL(X,Y,0.1,15HIONIC STRENGTH=,0.,15)
     CALL NUMBER(999.0,999.0,0.1,U,0.,2)
     LL=-1
     AK1=K11*(1.+FCA/K12+FMG/K13+FNA/K14)
     AK2=K21*(1.+FCA/K22+FMG/K23+FNA/K24)*K11/AK1
C     *******************************************
C     CALCULATIONS TO PLOT LINES REPRESENTING
C     INPUT VALUES FOR PH(NOT OPERATIONAL)
C     *******************************************
     IF(LAG)710,490,490
490   DO 600I=1,NPH
     PPH=PH(I)
     PHM=(-LOG10(AK1)-LOG10(AK2))/2.
     HA=(10.**(-PH(I)))*10.**3.
     H=HA/AH
     OH=K41/H
     OHT=OH*(1.+FMG/K43+FCA/K42)
     IF(LL)500,500,550
500   ACID(1)=MAXACD
     CON=(2*AK2/H+1)/(2*H/AK1+1.)
     ALK(1)=(ACID(1)+OHT-H)*CON-H+OHT
     IF(MAXALK-ALK(1))510,520,520
510   LL=1
     GO TO 550
520   IF(PPH-PHM)530,530,540
```

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```
530   ALK(2)=0.
     CON=(2*H/AK1+1)/(2*AK2/H+1.)
     ACID(2)=(ALK(2)-OHT+H)*CON+H-OHT
     GO TO 580
540   ACID(2)=0.0
     CON=(2*AK2/H+1)/(2*H/AK1+1.)
     ALK(2)=(ACID(2)+OHT-H)*CON-H+OHT
     GO TO 580
550   ALK(1)=MAXALK
     CON=(2*H/AK1+1.)/(2*AK2/H+1.)
     ACID(1)=(ALK(1)-OHT+H)*CON+H-OHT
     IF(ACID(1))610,610,555
555   IF(PPH-PHM)560,560,570
560   ALK(2)=0.0
     CON=(2*H/AK1+1)/(2*AK2/H+1)
     ACID(2)=(ALK(2)-OHT+H)*CON+H-OHT
     GO TO 580
570   ACID(2)=0.0
     CON=(2*AK2/H+1.)/(2*H/AK1+1)
     ALK(2)=(ACID(2)+OHT-H)*CON-H+OHT
     GO TO 580
580   CALL PLOT(ALK(1),ACID(1),3)
     CALL PLOT(ALK(2),ACID(2),2)
600   CONTINUE
610   CONTINUE
C     ****************************************
C     CALCULATIONS TO PLOT LINES REPRESENTING
C     INPUT VALUES FOR PARTIAL PRESSURE OF CO2
C     *****************************************
     IF(LAG)710,710,850
710   KH=1./10.**1.47
     DO 840 J=1,NPCO
     H2CO3=(KH*PCO(J)*AH2O/ACO2)*10.**3.
     LL=1
     LM=1
     ALK(1)=MAXALK
     TM=10.*MAXALK+1.
     NTM=IFIX(TM)
     DO 820 I=1,NTM
     TALK=ALK(I)
     H=10.**3.
     OH=K41/H
     OHT=OH*(1.+FMG/K43+FCA/K42)
     NN=1
     MM=1
715   AALK=H2CO3*AK1*(1/H+2*AK2/(H**2.))+OHT-H
     IF(AALK-TALK)720,780,740
720   IF(NN-1)730,730,770
730   H=0.1*H
     GO TO 715
740   IF(NN-1)750,750,760
750   FRACT=H
760   H=H+FRACT
     NN=2
     GO TO 715
770   H=H-FRACT
     FRACT=0.1*FRACT
     H=H+FRACT
     IF(MM-4)775,775,780
```

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```
775    MM=MM+1
      GO TO 715
780    ACID(I)=H2CO3*(2.+AK1/H)+H-OHT
      IF(ACID(I)-MAXACD)800,800,790
790    LM=LM+1
      GO TO 810
800    IF(ACID(I))825,825,810
810    LL=LL+1
      ALK(I+1)=ALK(I)-0.1
820    CONTINUE
825    XPAGE=ALK(LM)
      YPAGE=ACID(LM)
      CALL PLOT(XPAGE,YPAGE,3)
      DO 830 I=LM,LL
      XPAGE=ALK(I)
      YPAGE=ACID(I)
      CALL PLOT(XPAGE,YPAGE,2)
830    CONTINUE
840    CONTINUE
850    CONTINUE
      CALL PLOT(0,0,999)
      STOP 'END OF PROGRAM,PLOT SENT TO CALCOMP'
      END
```

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1. Objectives

This program plots the Modified Caldwell-Lawrence Diagram for

(i) families of curves representing true pH, total calcium at saturation with respect to $CaCO_3$, $[Ca]_T$, and Alkalinity, Alk, in a diagram with coordinates Acidity and (Alkalinity -2. total calcium), i.e. (Alk -2 $[Ca]_T$), or,

(ii) families of curves representing partial pressures of CO_2, pCO_2, total calcium at saturation with respect to $CaCO_3$ and Alkalinity in a diagram with coordinates Acidity and (Alk - 2 $[Ca]_T$).

The selected calcium carbonate mineral for $CaCO_3$ saturation can be selected as either calcite or aragonite or magnesian calcite. With each plot a separate nomograph is drawn of pH (true) versus total magnesium for $Mg(OH)_2$, i.e. brucite, saturation.

It should be noted that the diagrams above are valid for 25°C and 1 Atm. total pressure only.

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2. Input data

The unit of concentration for the input data is the molar scale.The input data is inserted in free format.

Data Card 1: Read in the stoichiometric concentrations in moles/ℓ (in floating point) of the species comprising the principal ionic matrix in the following order: total Na, total Mg, total Ca, total K, total Cl and total SO_4. The data are inserted in free format, and, where a species is not present, the value 0.0 must be inserted. An example of this card is set out in Supplement A.

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Data Card 2: Read in the stoichiometric concentrations of salts (in floating point) comprising the principal ionic matrix (on the molar scale, i.e. moles/ℓ) in the following order: NaCl, Na_2SO_4, $MgCl_2$, $MgSO_4$, $CaCl_2$, $CaSO_4$, KCl, K_2SO_4. The data are entered on one card in free format, and, where the species is not present, the value 0.0 must be inserted. (The reason for this card, and an example, is set out in Supplement A).

Data Card 3: Read in the number each of pH, total calcium, Alkalinity and pCO_2 lines to be plotted, i.e. NPH, NCA, NALK and NPCO respectively in integer form. If no pH or pCO_2 lines are to be plotted, enter the value 'zero', i.e. 0 (integer). For example, if 20 pH lines, 24 total calcium lines, 16 Alkalinity lines and no pCO_2 lines are to be plotted, values are entered as follows:

Data Card 3: 20B24B16B0
Where B indicates a blank space.

Data Card 4: Read in the data for defining the type of diagram to be plotted by assigning values to integer variables LAG, LUG, LC and SOFT as follows:

(i) LC defines which lines are to be plotted in the diagram, i.e.

LC = 1, plots the conventional Modified Caldwell-Lawrence diagram, i.e. lines representing pH, total calcium and Alkalinity.

LC = 2, plots lines representing total calcium, Alkalinity and pCO_2.

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(ii) LAG and LUG define the pricipitation mineral, i.e. calcite, aragonite, or magnesian calcite as follows:

LAG = 1, LUG = 1, calcite is the precipitation mineral

LAG = 2, LUG = 2, aragonite is the precipitation mineral

LAG = 1, LUG = 2, magnesian calcite is the precipitation mineral.

(iii) SOFT defines the relationship between pH and operational pH, pH(0):

SOFT = 1, pH = pH(0) is assumed, i.e. a low salinity water with $\mu \leq 0{,}1$.

SOFT = -1, pH ≠ pH(0) i.e. $\mu > 0{,}1$. In this case the relationship between pH and pH(0) is determined from the data of a Gran titration (inserted in Data Card 6) as set out in Supplement B.

Values for these integers are entered in the data in the following order: LC, LAG, LUG, SOFT. For example, for seawater where one wants the conventional Caldwell-Lawrence diagram (i.e. lines for TCA, pH and Alkalinity), LC = 1, with the mineral phase Aragonite, i.e. LAG = 2, LUG = 1 and activity coefficients are to be determined using the subroutine program SUBROUTINE ACTIVE, SOFT = -1, i.e

Card 4: 1B2B1B-1
Where B indicates a blank space.

Data Card 5: Read in the diagram limits in floating point, i.e. the maximum and minimum values (in m.moles/ℓ) for

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(Alk-2 $[Ca]_T$)and for Acidity: MAXAMC, MINAMC and MAXACD, MINACD respectively. For example, if maximum and minimum values for (Alk-2 $[Ca]_T$) are -3,00 m.moles/ℓ and -21,0 m.moles/ℓ respectively, and maximum and minimum Acidity values are 4,0 and 0,0 m.moles/ℓ respectively:

Card 5: -3.0B-21.0B4.0B0.0
Where B indicates a blank space.

Data Card 6: This card must be inserted for all high salinity plots (i.e. for SOFT = -1 in Card 4) and includes the data to determine the residual liquid junction potential effects on pH. The data required are the measured slope of the first Gran titration (i.e. the titration carried out in the region $3,0 < pH < 3,8$) SLOPE, and the molar concentration of strong acid used in this titration, CBA. These data are inserted in free format as follows:

Card 6: SLOPEbCBA
Where b denotes a blank space.

If the diagram to be plotted is for a low salinity water (i.e. SOFT = 1 in Data Card 4) this card is omitted from the input data.

Data Cards for pH values (optional)

If lines representing pH are to be plotted in the diagram, i.e. LC = 1 (in Data Card 4), then pH values are entered in floating point one value per card up to NPH cards (see Data Card 3) starting with the lowest value and entered in order of increasing pH values. If no pH lines are to be plotted (NPH = 0 in Card 3 and LC = 2 in Card 4) no data cards are submitted for pH.

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Data Cards for total calcium values

These data are entered (in floating point) one value per card (in m.moles/ℓ) starting with the lowest value and entered in order of increasing total calcium values. The number of data to be inserted is given by NCA (Card 3).

Data Cards for Alkalinity values

These data are inserted (in floating point) one value per card (in m.moles/ℓ) starting with the lowest value and entered in order of *increasing* Alkalinity values. The number of data to be read in is given by NALK (Card 3).

Data Cards for pCO_2 values

If lines representing pCO_2 are to be plotted in the diagram, i.e. LC = 2 in Data Card 4, these data are entered (in floating point) one value per card starting with the highest value and entered in order of *decreasing* pCO_2 values. The data are read in Atmospheres and the number of data to be read is given by NPCO (Card 3).

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3. Calculations procedures to plot pH, Alkalinity, total calcium and pCO_2 lines

(a) Activity coefficients (for free species): Activity coefficients are determined as set out in Supplement A using a subroutine program, SUBROUTINE ACTIVE. For this purpose in the subroutine program the input principal species concentrations (on the molar scale) are converted first to the molal scale and activity coefficients (on the molal scale) are calculated; before return to the main program these activity coefficients (and the input principal species

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concentrations) are converted back to the molar scale (the unit of concentration for inputs and outputs in the main program).

(b) Equations to plot lines representing pH, Alkalinity, total calcium, $[Ca]_T$, and partial pressure of CO_2, pCO_2: The equations to plot lines representing pH, Alkalinity, $[Ca]_T$ and pCO_2 in the Modified Caldwell-Lawrence diagram, for a high salinity water in which significant ion pairing occurs, are similar to those for low salinity water, except that equilibrium constants used within these equations are now formulated in the apparent stoichiometric form, see Eqs. (59a, 59b and 59c), Chapter 4.

(i) Equations for pH lines

The corresponding high salinity equations for plotting pH lines in the Caldwell-Lawrence diagram (taking due account of ion pairing) are as follows:

Put $X = (Alk-2[Ca]_T)$
and $Y =$ Acidity
The equations (in the stoichiometric molar form) for plotting pH lines are now

$$[HCO_3]_T = \{-B \pm (B^2 - 4AC)^{\frac{1}{2}}\}/2A \qquad (S4.1)$$

where
$A = (-1-2K''_{T2}/[H^+])$
$B = (X-K''_{Tw}/[H^+] + [H^+])$
$C = 2K'_{Ts}[H^+]/K''_{T2}$
and

$$\text{Acidity} = 2[H^+][HCO_3]_T/K''_{T1} + [HCO_3]_T + [H^+] - K'_{Tw}/[H^+] \qquad (S4.2)$$

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Substituting Eq. (S4.1) into Eq. (S4.2) gives an equation linking the parameters $[H^+]$ (and hence pH) with Acidity and (Alk-2$[Ca]_T$). Choosing a number of values for (Alk-2$[Ca]_T$) (i.e. X) for a fixed selected pH (i.e. $[H^+]$) the corresponding values for Acidity are calculated. Plotting these corresponding values of Acidity and (Alk-2 $[Ca]_T$) in the diagram traces a line for a selected pH value.

(ii) <u>Equations for total calcium lines, $[Ca]_T$</u>: The corresponding high salinity equations for plotting $[Ca]_T$ lines in the Caldwell-Lawrence diagram (taking due account of ion pairing) are as follows:

$$(\text{Alk-}2[Ca]_T) = (2K'_{Ts}/[Ca]_T) + [HCO_3]_T + (K''_{Tw}K'_{Ts})/(K''_{T2}[Ca]_T [HCO_3]_T) - (K''_{T2}[Ca]_T[HCO_3]_T/K'_{Ts}) \qquad (S4.3)$$

where $[HCO_3]_T$ in the above equation is determined for a particular Acidity and $[Ca]_T$ values from the cubic equation in $[HCO_3]_T$, i.e.

$$\frac{2K''_{T2}[Ca]_T[HCO_3]_T^3}{K''_{T1}\ K'_{Ts}} + [HCO_3]_T^2(1+K''_{T2}[Ca]_T/K'_{Ts}) - \text{Acidity}.[HCO_3]_T - K''_{Tw}.K'_{Ts}/(K''_{Ts}.[Ca]_T) = 0 \qquad (S4.4)$$

For a fixed chosen value of $[Ca]_T$ and a range of values for Acidity: the cubic equation in $[HCO_3]_T$, Eq. (S4.4), has only one real root which can be calculated by an iterative procedure of successive approximation: substituting this $[HCO_3]_T$ value into Eq. (S4.3) gives the (Alk-2$[Ca]_T$) value corresponding to each Acidity value. Plotting the corresponding (Alk-2$[Ca]_T$ and Acidity values traces a line for $[Ca]_T$ in the diagram.

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(iii) Equations for Alkalinity lines: Alkalinity lines plot in the Modified Caldwell-Lawrence diagram as curves each with two horizontal limbs joined by a vertical section (see Figure 21, Chapter 5). To plot the horizontal section accurately, for some input Alkalinity values, Acidity values are calculated for corresponding selected (Alk-2 $[Ca]_T$ values. For the vertical section of the curve (Alk-2$[Ca]_T$) values are calculated for corresponding selected Acidity values.

Equation for horizontal section of Alkalinity line: The corresponding high salinity equations for plotting the horizontal section of the Alkalinity lines in the Caldwell-Lawrence diagram (taking due account of ion pairing) are as follows:

$$\text{Acidity} = 2[H^+]Z/K''_{T1} + Z + [H^+] - K''_{tw}/[H^+] \qquad (S4.5)$$

$$\text{where } Z = \frac{2K'_{Ts}\,[H^+]}{K''_{T2}\{\text{Alk} + (\text{Alk}-2[\text{Ca}]_T)\}}$$

and

$$[H^+] = \{-B \pm (B^2 - 4A.C)^{\frac{1}{2}}\}/2A \qquad (S4.6)$$

$$\text{where } A = \{2K'_{Ts} - K''_{T2}(X-\text{Alk})\}/\{K''_{T2}(X-\text{Alk})\}$$

$$X = (\text{Alk}-2[\text{Ca}]_T)$$

$$B = \{4K''_{Ts}.K'_{Ts}/(X-\text{Alk})\}-\text{Alk}$$

$$C = K''_{tw}$$

Substituting for $[H^+]$ from Eq. (S4.6) into Eq. (S4.5) gives an equilibrium equation for Acidity in terms of Alkalinity and (Alk-2$[Ca]_T$).

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For a chosen value of Alkalinity and a series of values of (Alk-2$[Ca]_T$), the corresponding Acidity values are calculated. Plotting the corresponding values for Acidity and (Alk-2$[Ca]_T$) traces a line representing the horizontal section of the Alkalinity curve in the Caldwell-Lawrence diagram.

Equation for vertical section of Alkalinity line: The corresponding high salinity equations for plotting the vertical section of the Alkalinity lines in the Caldwell-Lawrence diagram (taking due account of ion pairing) are as follows:

$$\text{Acidity} - (2W[HCO_3]_T/K''_{T1} + [HCO_3]_T + W - K''_{Tw}/W = 0 \qquad (S4.7)$$

where $W = (2K''_{T2}[HCO_3]_T + K''_{Tw})/(\text{Alk} - [HCO_3]_T)$

and

$$(\text{Alk}-2[Ca]_T) = \text{Alk} - 2K'_{Ts}W/(K''_{T2}[HCO_3]_T) \qquad (S4.8)$$

Equation (S4.7) is quadratic in $[HCO_3]_T$. For a fixed chosen value of Alkalinity and a series of values for Acidity the corresponding $[HCO_3]_T$ are determined and hence a series of values for (Alk-2$[Ca]_T$) from Eq. (S4.8). Plotting the corresponding Acidity and (Alk-2$[Ca]_T$) values traces the vertical section of the Alkalinity line in the Modified Caldwell-Lawrence diagram. The change over from the horizontal to the vertical line plots takes place when the slope of the horizontal line increases above 15° of the slope curvature to prevent (Alk-2$[Ca]_T$) increment value to project beyond the vertical curve.

(iv) Equations for partial pressure of CO_2 (pCO_2) lines:

The corresponding high salinity equations for plotting pCO_2 lines in the Caldwell-Lawrence diagram taking due

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account of ion pairing) are as follows:

$$\text{Alk-}2[\text{Ca}]_T = \frac{2K''_{T2}.K''_{T1}\ K'_H\ pCO_2}{[H^+]^2} + \frac{K''_{T1}\ K'_H\ pCO_2}{[H^+]} + \frac{K''_{Tw}}{[H^+]}$$

$$- (2K'_{Ts}[H^+]^2)/(K''_{T2}\ K''_{T1}\ K'_H\ pCO_2) \qquad (S4.9)$$

and

$$\text{Acidity} = 2K'_H.pCO_2 + K''_{T1}.K'_H\ pCO_2/[H^+] + [H^+] - K''_{Tw}/[H^+] \qquad (S4.10)$$

For fixed selected values for pCO_2, and a series of values for (Alk-2$[Ca]_T$) are series of values for $[H^+]$ (determined by successive approximation) are determined from Eq. (S4.9), and hence a series of values for Acidity are determined from Eq. (S4.10). Plotting the corresponding values for (Alk-2$[Ca]_T$) and Acidity traces a line respresenting the selected pCO_2 value in the Caldwell-Lawrence diagram.

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```
C      *************************************************
C      PROG. TO PLOT THE MODIFIED CALDWELL-LAWERENCE DIAG.
C           FOR MULTI-PHASE HIGH SALINITY CONDITIONS
C           (ALL UNITS ON THE MOLAR SCALE)
C      **************************************************
C
      CHARACTER*4 MSG
      REAL K11,K12,K13,K14,K21,K22,K23,K24,K41,K33,
     -K32,K34,KW,K42,K43,KS,KMG,KHSO4,MGCL2,MGSO4,
     -MAXAMC,MINAMC,MAXACD,MINACD,KC,NACL,NA2SO4,KCL
     -,K2SO4
      COMMON ACCA,ACMG,ACH,ACNA,ACSO4,ACK,
     .ACNAS,ACKSO,ANASOT,ACHCO3,ACOH,ACCO3,TACCCL,
     .TACMCL,ACLT,TACCSO,TACMG,TACCA,TACNA,TACSO4,
     .TACNC,TACKCL,TACNSO,TAMGSO,TACKSO,AHCL,AKCL,
     .ANACL,ACACL2,AMGCL,AK2SO4,ANA2SO,AMGSO,ACASO,
     .TMG,TCA,TNA,TK,TCL,TSO4,FMG,FNA,FCA,FSO4,
     .CNASO,CNA2SO,TACK,FK,CKSO4,CK2SO4,CCASO,
     .CMGSO,ACCO2,NACL,NA2SO4,MGCL2,MGSO4,CACL2,
     .CASO4,KCL,K2SO4,U1,SLOPE,CBA,AH2O,AW,ACHOP,
     .KZ
      DOUBLE PRECISION FRACT,FCO3,H,FOH
      DIMENSION PH(50),AMC(1000),ACID(1000),CA(50),PKK(50),
     -ALK(50),PCO(50),S(1000),MSG(5)
     .,PHM(25),TTMG(25)
      DATA MSG /'PLS ','LOAD',' P1-','BK/I','5   '/
C      **********************************
C      READ IN CONC. OF MAJOR IONS IN
C      THE WATER IN MOLES/L.
C      ******************************************
C      ***************************************
      READ(5,2)TNA,TMG,TCA,TK,TCL,TSO4
C      ***************************************
C      READ IN CONCETRATION OF SALTS MAKING
C      UP THE PRINCIPAL IONIC MATRIX(MOLES/L)
C      ***************************************
      READ(5,2)NACL,NA2SO4,MGCL2,MGSO4,CACL2,
     .CASO4,KCL,K2SO4
C      ****************************************
C      DATA FOR NUMBER OF LINES TO BE PLOTTED
C      NPH=NO. OF PH LINES
C      NCA=NO. OF CA LINES
C      NALK=NO. OF ALK LINES
C      NPCO=NO. OF CO2 PARTIAL PRESSURE LINES
C      *************************************
      READ(5,2)NPH,NCA,NALK,NPCO
C      *****************************************
C      SELECT DIAGRAM TO BE PLOTTED AND
C      PRECIPITATION MINERAL AND METHOD
C      FOR DETERMINING ACTIVITY COEFF.
C
C      LC=1 (CONVENTIONAL MODIFIED CADWELL-LAWERANCE
C           DIAG.,A PLOT OF PH,TCA,ALK.)
C
C      LC=2 (MOD.C-L DIAG PLOTTING ONLY ALK AND PCO2 LINES)
C
C      CALCITE(LAG=1,LUG=1),ARAGONITE(LAG=2,LUG=1),MAGNESIUM
C      CALCITE(LUG=2)
C
C      SOFT=1.?LOW SALINITY:PH=PH(O)!
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C      SOFT=-1.?HIGH SALINE:PH#PH(O)!
C      ********************************************
      READ(5,2)LC,LAG,LUG,SOFT
C      ********************************************
C      DATA FOR DIAGRAM LIMITS (IN M.MOLES/L)
C      MAXAMC=MAX.(ALK-2*TCA)(FOR EXAMPLE-4.)
C      MINAMC=MIN.(ALK-2*TCA)(FOR EXAMPLE-20.)
C      MAXACD=MAX. ACIDITY VALUE (FOR EXAMPLE 5.0)
C      MINACD=MIN. ACIDITY VALUE (FOR EXAMPLE-0.5)
C      **********************************************
      READ(5,2)MAXAMC,MINAMC,MAXACD,MINACD
C      **********************************************
C      ****************************************
C      READ SLOPE OF FIRST GRAN TITRATION(SLOPE)
C      AND MOLARITY OF STANDARD STRONG ACID(CBA)
C      *******************************************
      IF(SOFT)8,8,9
8     READ(5,2)SLOPE,CBA
C      ********************************************
C      READ IN PH VALUES (ONE/CARD)
C      IN ASCENDING ORDER.
C      *********************************************
9      SLOPE=1.
      CBA=1.
      IF(LC-1)1002,1002,1003
1002 CONTINUE
      DO 10 I=1,NPH
      READ(5,2)PH(I)
  10 CONTINUE
1003 CONTINUE
C      ********************************************
C      READ IN CALCIUM VALUES IN ASCENDING ORDER
C      ONE VALUE/CARD (M.MOLES/L)
C      **********************************************
      DO 11 I=1,NCA
      READ(5,2)CA(I)
  11 CONTINUE
C      *********************************************
C      READ IN ALKALINITY VALUES IN ASCENDING ORDER,
C      ONE VALUE/CARD (M.MOLES/L)
C      *******************************************
      DO 12 I=1,NALK
      READ(5,2)ALK(I)
  12 CONTINUE
C      *********************************************
C      READ IN PCO2 VALUES (ATMOSPHERES),
C      ONE VALUE/CARD
C      *********************************************
      IF(LC-1)1004,1004,1001

1001 CONTINUE
      DO 14 I=1,NPCO
      READ(5,2)PCO(I)
  14 CONTINUE
1004 CONTINUE
C      *********************************************
      T=25.
      TA=273.+T
      TR=298.
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```
C       READ IN PK VALUES AT 25DEGC. FOR
C       DISSOCIATION REACTIONS: (1)H2CO3,(2)HCO3,(3)CASO4
C       (4)NASO4-,(5)MGSO4,(6)NAHCO3,(7)NACO3-,(8)MGHCO3+,
C       (9)MGCO3,(10)CAHCO3+,(11)CACO3,(12)MGOH+,(13)CAOH+,
C       (14)H2O,(15)CALCITE KSP,(16)MG(OH)2 KSP,(17)ARAGONITE
C       ********************************************
      PKK(1)=6.352
      PKK(2)=10.329
      PKK(3)=2.41
      PKK(4)=0.60
      PKK(5)=2.38
      PKK(6)=-0.55
      PKK(7)=0.85
      PKK(8)=0.53
      PKK(9)=2.92
      PKK(10)=0.59
      PKK(11)=3.16
      PKK(12)=2.08
      PKK(13)=1.38
      PKK(14)=14.0
      PKK(15)=8.41
      PKK(16)=10.41
      PKK(17)=8.24
C       *****************************************
C       CALCULATE ACTIVITY COEFFTS. FROM
C       SUBROUTINE 'ACTIVE'
C       ****************************************
      KZ=-1
      CALL ACTIVE
      ANM=1.
      ACO2=ACCO2
      AH=ACH
      AHCO3=ACHCO3
      AH2O=AW
      ACO3=ACCO3
      AOH=ACOH
      AMG=ACMG
      ANA=ACNA
      ACA=ACCA
      HAF=ACHOP
      U=U1
      U1=U1**0.5
      ASO4=ACSO4
C       *******************************************
C       CONVERT MOLES/L TO M.MOLES/L
C       ****************************************
      TCA=TCA*1000
      TMG=TMG*1000
      TSO4=TSO4*1000
      TCL=TCL*1000
      TK=TK*1000
      TNA=TNA*1000
C       *************************************************
C       ADJUST K VALUES TO INCORPORATE ACTIVITY COEFFICIENTS
C       AND TO BE IN THE M.MOLAR FORM
C       *************************************************
      K11=(10.**(-1.*PKK(1)))*ACO2*AH2O*10.**3./(AH*AHCO3)
      K21=(10.**(-1.*PKK(2)))*AHCO3*10.**3/(AH*ACO3)
      K41=(10.**(-1.*PKK(14)))*AH2O*10.**6./(AH*AOH)
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     K12=(10.**(-1.*PKK(10)))*10.**3./ACA
     K22=(10.**(-1.*PKK(11)))*ANM*10.**3./(ACA*ACO3)
     K32=(10.**(-1.*PKK(3)))*ANM*10.**3./(ACA*ASO4)
     K42=(10.**(-1.*PKK(13)))*ANA*10.**3./(ACA*AOH)
     K13=(10.**(-1.*PKK(8)))*10.**3./AMG
     K23=(10.**(-1.*PKK(9)))*ANM*10.**3./(AMG*ACO3)
     K33=(10.**(-1.*PKK(5)))*ANM*10.**3./(AMG*ASO4)
     K43=(10.**(-1.*PKK(12)))*ANA*10.**3./(AMG*AOH)
     K14=(10.**(-1.*PKK(6)))*ANM*10.**3./(ANA**2.)
     K24=(10.**(-1.*PKK(7)))*ANA*10.**3./(ANA*ACO3)
     K34=(10.**(-1.*PKK(4)))*ANA*10.**3./(ANA*ASO4)
     KS=(10.**(-1.*PKK(15)))*10.**6./(ACA*ACO3)
     KMG=(10.**(-1.*PKK(16)))*10.**9./(AMG*AOH**2.)
     KHSO4=(10.**(-1.99))
     KMG=(0.0175*T)+9.97
     KMG=(1./10.**KMG)*(10.**9.)/(AMG*AOH**2.)
     CKS=KS
     SKS=(10.**(-1.*PKK(17)))*10.**6./(ACA*ACO3)
C     **********************************
C     CALCULATE RESIDUAL LIQUID JUNCTION
C     EFFECTS ON PH.
C     ***********************************
     IF(SOFT)4990,4990,4991
4990  HAFL=-ALOG10(HAF)
     AHL=-ALOG10(AH)
     ALJ=AHL-HAFL
     GO TO 4993
4991  ALJ=0.0
4993  CONTINUE
C
C     INITIATE PLOT ROUTINE AND LABLE DIAGRAM
C
     CALL PLOTS(0,0,0)
     CALL OPMES(20,MSG)
     CALL PAGSIZ(60.,60.)
     CALL FACTOR(3.0)
     IF(SOFT)7999,7900,7900
7999  CALL PLOT(1.0,1.0,-3)
     CALL PLOT(0.0,21.0,2)
     CALL PLOT(29.8,21.0,2)
     CALL PLOT(29.8,0.0,2)
     CALL PLOT(0.0,0.0,2)
     CALL SYMBOL(1.5,20.5,.28,14HTEMP. (DEG C)=,0.,14)
     CALL NUMBER(999.0,999.0,.28,T,0.,1)
     CALL SYMBOL(8.0,20.5,.28,15HIONIC STRENGTH=,0.,15)
     CALL NUMBER(999.0,999.0,.28,U,0.,3)
     CALL SYMBOL(16.0,20.5,.28,11HPH-PH(OBS)=,0.,11)
     CALL NUMBER(999.0,999.0,.28,ALJ,0.,3)
     CALL SYMBOL(1.5,19.8,.28,4HTMG=,0.,4)
     CALL NUMBER(999.0,999.0,.28,TMG,0.,2)
     CALL SYMBOL(5.5,19.8,.28,3HTK=,0.,3)
     CALL NUMBER(999.0,999.0,.28,TK,0.,2)
     CALL SYMBOL(10.5,19.8,.28,4HTNA=,0.,4)
     CALL NUMBER(999.0,999.0,.28,TNA,0.,2)
     CALL SYMBOL(15.,19.8,.28,4HTCL=,0.,4)
     CALL NUMBER(999.0,999.0,.28,TCL,0.,2)
     CALL SYMBOL(19.5,19.8,.28,5HTSO4=,0.,5)
     CALL NUMBER(999.0,999.0,.28,TSO4,0.,2)
     CALL SYMBOL(25.0,19.8,.28,11H(M.MOLES/L),0.,11)
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```
      CALL SYMBOL(10.0,19.0,.35,
     .27H(ALKALINITY-2*TCA)M.MOLES/L,0.,27)
      CALL SYMBOL(29.0,6.5,.35,18HACIDITY(M.MOLES/L),90.
     .,18)
      CALL SYMBOL(7.0,1.1,0.42,
     .26HCALDWELL-LAWRENCE DIAGRAM-,0.,26)
      IF(LUG.EQ.2)CALL SYMBOL(999.,999.,0.42,
     .17HMAGNESIAN CALCITE,0.,17)
      IF(LAG.EQ.2.AND.LUG.EQ.1)CALL SYMBOL(999.,999.,
     -0.42,9HARAGONITE,0.,9)
      IF(LAG.EQ.1.AND.LUG.EQ.1)CALL SYMBOL(999.,999.,
     -0.42,7HCALCITE,0.,7)
      CALL SYMBOL(6.2,0.4,0.28,
     -46HEQUILIBRIUM LINES FOR CALCIUM, ALKALINITY AND ,0.,
     .46)
      IF(LC.EQ.1)CALL SYMBOL(999.,999.,0.28,2HPH,0.,2)
      IF(LC.EQ.2)CALL SYMBOL(999.,999.,0.28,
     -20HCO2 PARTIAL PRESSURE,0.,20)
      CALL PLOT(2.0,3.0,-3)
      CALL PLOT(0.0,14.5,2)
      CALL PLOT(25.0,14.5,2)
      CALL PLOT(25.0,0.0,2)
      CALL PLOT(0.0,0.0,2)
      TX=MAXAMC-MINAMC
      DX=25.0/TX
      TY=MAXACD-MINACD
      DY=14.5/TY
      XPAGE=-(MINAMC*DX)
      YPAGE=MAXACD*DY
      CALL PLOT(XPAGE,YPAGE,-3)
      NDIV=2*IFIX(TY)+1
      XPAGE=MAXAMC*DX
      YP=MINACD-0.5
      DO 8000 IK=1,NDIV
      YP=YP+0.5
      YPAGE=-(YP*DY)
      XPAGE=XPAGE+0.07
      CALL SYMBOL(XPAGE,YPAGE,0.14,13,90.,-1)
      XPAGE=XPAGE+0.23
      CALL NUMBER(XPAGE,YPAGE,0.21,YP,0.,1)
      XPAGE=XPAGE-0.3
 8000 CONTINUE
      XPAGE=MINAMC*DX
      YP=YP+0.5
      DO 8001 IK=1,NDIV
      YP=YP-0.5
      YPAGE=-(YP*DY)
      XPAGE=XPAGE-0.07
      CALL SYMBOL(XPAGE,YPAGE,0.14,13,90.,-1)
      XPAGE=XPAGE-1.03
      CALL NUMBER(XPAGE,YPAGE,0.21,YP,0.,1)
      XPAGE=XPAGE+1.1
 8001 CONTINUE
      NDIV=IFIX(TX)+1
      YPAGE=-(MINACD*DY)
      XP=MAXAMC+1.
      DO 8002 IK=1,NDIV
      XP=XP-1.
      XPAGE=XP*DX
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```
      YPAGE=YPAGE+0.07
      CALL SYMBOL(XPAGE,YPAGE,0.14,13,0.,-1)
      YPAGE=YPAGE+0.13
      CALL NUMBER(XPAGE,YPAGE,0.21,XP,90.,1)
      YPAGE=YPAGE-0.2
 8002 CONTINUE
      XP=XP-1.
      YPAGE=-(MAXACD*DY)
      DO 8003 IK=1,NDIV
      XP=XP+1.
      XPAGE=XP*DX
      YPAGE=YPAGE-0.07
      CALL SYMBOL(XPAGE,YPAGE,0.14,13,0.,-1)
      YPAGE=YPAGE-1.03
      CALL NUMBER(XPAGE,YPAGE,0.21,XP,90.,1)
      YPAGE=YPAGE+1.1
 8003 CONTINUE
      IF(MAXAMC.GT.0..AND.MINACD.LT.0.)CALL SYMBOL(0.,
     .0.,.5,3,0.,-1)
      GO TO 4994
 7900  CONTINUE
      XMAX=MAXAMC
      XMIN=MINAMC
      YMAX=-MINACD
      YMIN=-MAXACD
      XPAGE=-XMIN+2.
      YPAGE=MAXACD+2.
      CALL PLOT(XPAGE,YPAGE,-3)
      TMX=2*(XMAX-XMIN)+1
      TMY=2*(YMAX-YMIN)+1
      NTMX=IFIX(TMX)
      NTMY=IFIX(TMY)
      XPAGE=XMIN-0.5
      YPAGE=YMIN
      CALL PLOT(XMIN,YMIN,3)
      DO 7910 I=1,NTMX
      XPAGE=XPAGE+0.5
      CALL SYMBOL(XPAGE,YPAGE,0.1,3,0.,-2)
 7910  CONTINUE
      YPAGE=YPAGE-0.5
      DO 7911 I=1,NTMY
      YPAGE=YPAGE+0.5
      CALL SYMBOL(XPAGE,YPAGE,0.1,3,0.,-2)
 7911  CONTINUE
      XPAGE=XPAGE+0.5
      DO 7912 I=1,NTMX
      XPAGE=XPAGE-0.5
      CALL SYMBOL(XPAGE,YPAGE,0.1,3,0.,-2)
 7912  CONTINUE
      YPAGE=YPAGE+0.5
      DO 7913 I=1,NTMY
      YPAGE=YPAGE-0.5
      CALL SYMBOL(XPAGE,YPAGE,0.1,3,0.,-2)
 7913  CONTINUE
      CALL PLOT(XMIN,0.,3)
      XPAGE=XMIN-0.5
      DO 7914 I=1,NTMX
      XPAGE=XPAGE+0.5
      CALL SYMBOL(XPAGE,0.0,0.1,3,0.,-2)
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```
 7914  CONTINUE
      CALL PLOT(0.,YMAX,3)
      YPAGE=YMAX+0.5
      DO 7915 I=1,NTMY
      YPAGE=YPAGE-0.5
      CALL SYMBOL(0.0,YPAGE,0.1,3,0.,-2)
 7915  CONTINUE
      TMY=YMAX-YMIN+1
      TMX=XMAX-XMIN+1
      NTMY=IFIX(TMY)
      NTMX=IFIX(TMX)
      CALL PLOT(XMIN,YMIN,3)
      AMCA=MINAMC-1.
      YPAGE=YMIN-0.32
      DO 7916 I=1,NTMX
      AMCA=AMCA+1.
      XPAGE=AMCA
      CALL NUMBER(XPAGE,YPAGE,0.1,AMCA,90.,0)
 7916  CONTINUE
      XPAGE=XMAX+0.1
      AACID=MAXACD+1.
      DO 7917 I=1,NTMY
      AACID=AACID-1.
      YPAGE=-AACID
      CALL NUMBER(XPAGE,YPAGE,0.1,AACID,0.,0)
 7917  CONTINUE
      YPAGE=(YMAX+YMIN)/2.-0.9
      XPAGE=XMAX+0.5
      CALL SYMBOL(XPAGE,YPAGE,0.1,18HACIDITY(M.MOLES/L),
     .90.,18)
      YPAGE=YMAX+0.05
      AMCA=MAXAMC+1.
      DO 7918 I=1,NTMX
      AMCA=AMCA-1.
      XPAGE=AMCA
      CALL NUMBER(XPAGE,YPAGE,0.1,AMCA,90.,0)
 7918  CONTINUE
      XPAGE=(XMAX+XMIN)/2.-2.5
      YPAGE=YMAX+1.3
      CALL SYMBOL(XPAGE,YPAGE,0.1,
     .25HCALDWELL-LAWRENCE DIAGRAM,0.,25)
      XPAGE=XMIN
      YPAGE=YPAGE-0.3
      CALL SYMBOL(XPAGE,YPAGE,0.1,11HTEMP(DEGC)=,0.,11)
      CALL NUMBER(999.0,999.0,0.1,T,0.,1)
      XPAGE=XPAGE+2.5
      CALL SYMBOL(XPAGE,YPAGE,0.1,15HIONIC STRENGTH=,0.,15)
      CALL NUMBER(999.0,999.0,0.1,U,0.,2)
      YPAGE=YPAGE-0.3
      XPAGE=XMIN
      CALL SYMBOL(XPAGE,YPAGE,0.1,5HTSO4=,0.,5)
      CALL NUMBER(999.0,999.0,0.1,TSO4,0.,1)
      XPAGE=XPAGE+1.5
      CALL SYMBOL(XPAGE,YPAGE,0.1,4HTCL=,0.,4)
      CALL NUMBER(999.0,999.0,0.1,TCL,0.,1)
      XPAGE=XPAGE+1.5
      CALL SYMBOL(XPAGE,YPAGE,0.1,4HTNA=,0.,4)
      CALL NUMBER(999.0,999.0,0.1,TNA,0.,1)
      XPAGE=XPAGE+1.5
```

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```
      CALL SYMBOL(XPAGE,YPAGE,0.1,11H(M.MOLES/L),0.,11)
      XPAGE=(XMAX+XMIN)/2.-1.
      YPAGE=YPAGE-0.3
      CALL SYMBOL(XPAGE,YPAGE,0.1,20H(ALK-2*TCA)M.MOLES/L,
     .0.,20)
      XPAGE=XMIN-0.32
      AACID=MINACD-1.
      DO 7919 I=1,NTMY
      AACID=AACID+1.
      YPAGE=-AACID
      CALL NUMBER(XPAGE,YPAGE,0.1,AACID,0.,0)
 7919  CONTINUE
      DX=1.
      DY=1.
 4994  IF(LAG-1)4995,4995,4996
 4996 KS=SKS
 4995 CONTINUE
      KW=K41
C      ***************************************************
C      CALCULATIONS FOR PH LINES
C      BDIFF=INCREMENTAL CHANGE IN (ALK-2*TCA)M.MOLES/L
C      ***************************************************
      FM=AH
      IF(LC-1)5026,5026,5027
 5026 CONTINUE
      WRITE(6,3)
      DO 100 I=1,NPH
      H=(1./(10.**PH(I)))*(10.**3.)/AH
      AMC(1)=MINAMC
      FOH=KW/H
      LM=1
      DO 90 J=1,1000
      MM=1
      LL=1
      FCO3=10.
      CONST=(10.**6)/(ACA*ACO3)
      IF(LUG-1)16,16,1600
 1600 KS=CKS
   16 FCA=KS/FCO3
      FSO4=TSO4
   17 FMG=TMG/(1.+FSO4/K33)
      FNA=TNA/(1.+FSO4/K34)
      TTSO4=FSO4*(1.+FMG/K33+FCA/K32+FNA/K34)
      IF(TTSO4-TSO4)20,20,18
   18 FSO4=FSO4*0.9
      GO TO 17
   20 FFMG=KMG/(FOH)**2.
      IF(FFMG-FMG)30,40,40
   30 FMG=FFMG
      FSO4=TSO4
   31 FNA=TNA/(1.+FSO4/K34)
      TTSO4=FSO4*(1.+FMG/K33+FCA/K32+FNA/K34)
      IF(TTSO4-TSO4)40,40,35
   35 FSO4=FSO4*0.9
      GO TO 31
   40 CONTINUE
      AK1=K11*(1.+FCA/K12+FMG/K13+FNA/K14)
      AK2=K21*(1.+FCA/K22+FMG/K23+FNA/K24)*K11/AK1
      TCO3=FCO3*(1.+FCA/K22+FMG/K23+FNA/K24)
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```
      GMOH=FMG*FOH/K43
      CAOH=FCA*FOH/K42
      FHCO3=H*FCO3/K21
      TCA=FCA*(1.+FSO4/K32+FCO3/K22+FHCO3/K12+FOH/K42)
      THCO3=TCO3*H/AK2
      H2CO3=H*THCO3/AK1
      AALK=2.*TCO3+THCO3+FOH+GMOH+CAOH
      TOH=FOH+GMOH+CAOH
      Y=AALK-2.*TCA
      IF(LUG-1)42,42,41
   41 XX=1./(1.+50.*FCA/FMG)
      PKS=8.4-1.744*XX
      KS=(1./10.**PKS)/((FMG/FCA)**XX)
      KS=KS*CONST
   42 IF(Y-AMC(J))60,80,50
   50 IF(LL-1)55,55,65
   55 FCO3=0.1*FCO3
      GO TO 16
   60 IF(LL-1)61,61,62
   61 FRACT=FCO3
   62 FCO3=FCO3+FRACT
      LL=2
      GO TO 16
   65 MM=MM+1
      IF(4-MM)80,80,70
   70 FCO3=FCO3-FRACT
      FRACT=0.1*FRACT
      FCO3=FCO3+FRACT
      GO TO 16
   80 ACID(J)=2.*H2CO3+THCO3+H-TOH
      Y=AMC(J)
      IF(ACID(1)-MAXACD)811,100,100
  811 IF(ACID(1)-MINACD)5027,812,812
  812 IF(ACID(J)-MAXACD)81,91,91
   81 IF(Y-MAXAMC)82,91,91
   82 AMC(J+1)=AMC(J)+0.5
      LM=LM+1
   90 CONTINUE
   91 XPAGE=AMC(1)*DX
      YPAGE=-(ACID(1)*DY)
      CALL PLOT(XPAGE,YPAGE,3)
      WRITE(5,4)PH(I)
      IF(ACID(LM)-MAXACD)93,93,92
   92 LM=LM-1
   93 DO 96 J=1,LM
      XPAGE=AMC(J)*DX
      YPAGE=-(ACID(J)*DY)
      CALL PLOT(XPAGE,YPAGE,2)
   96 CONTINUE
  100 CONTINUE
C      ****************************************************
C      CALCULATIONS FOR CALCIUM LINES
C      ****************************************************
 5027 CONTINUE
      WRITE(6,5)
      ACID(1)=MINACD
      DO 250 I=1,NCA
      TCA=CA(I)
      WRITE(5,4)CA(I)
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```
      ACID(1)=MINACD
      LM=1
      LO=1
      DO 200 J=1,1000
      MM=0
      LL=0
      H=1./(10.**4.)
  105 FOH=KW/H
      FSO4=TSO4
  110 FNA=TNA/(1.+FSO4/K34)
      FCA=TCA/(1.+FSO4/K32)
      FMG=TMG/(1.+FSO4/K33)
      TTSO4=FSO4*(1.+FNA/K34+FCA/K32+FMG/K33)
      IF(TTSO4-TSO4)130,130,120
  120 FSO4=0.9*FSO4
      GO TO 110
  130 FFMG=KMG/(FOH**2.)
      IF(FFMG-FMG)125,125,135
  125 FMG=FFMG
      FSO4=TSO4
  126 FNA=TNA/(1.+FSO4/K34)
      FCA=TCA/(1.+FSO4/K32)
      TTSO4=FSO4*(1.+FNA/K34+FCA/K32+FMG/K33)
      IF(TTSO4-TSO4)135,135,131
  131 FSO4=0.9*FSO4
      GO TO 126
  135 CONTINUE
      LLL=0
  140 AK1=K11*(1.+FCA/K12+FMG/K13+FNA/K14)
      AK2=K21*(1.+FCA/K22+FMG/K23+FNA/K24)*K11/AK1
      IF(LUG-1)142,142,141
  141 XX=1./(1.+50.*FCA/FMG)
      PKS=8.4-1.744*XX
      KS=(1./10.**PKS)/((FMG/FCA)**XX)
      KS=KS*CONST
  142 FCO3=KS/FCA
      TCO3=FCO3*(1.+FCA/K22+FMG/K23+FNA/K24)
      THCO3=TCO3*H/AK2
      FHCO3=FCO3*H/K21
      H2CO3=THCO3*H/AK1
      GMOH=FMG*FOH/K43
      CAOH=FCA*FOH/K42
      FCA=TCA/(1.+FSO4/K32+FCO3/K22+FHCO3/K12+FOH/K42)
      LLL=LLL+1
      IF(LLL-3)140,140,150
  150 AACID=2.*H2CO3+THCO3+H-FOH-CAOH-GMOH
      IF(AACID-ACID(J))170,185,160
  160 IF(LL-1)161,161,175
  161 H=0.1*H
      GO TO 105
  170 IF(LL-1)171,171,172
  171 FRACT=H
  172 H=H+FRACT
      LL=2
      GO TO 105
  175 MM=MM+1
      IF(4-MM)185,185,180
  180 H=H-FRACT
      FRACT=0.1*FRACT
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```
           H=H+FRACT
           GO TO 105
      185  AALK=2.*TCO3+THCO3+FOH+GMOH+CAOH
           AMC(J)=AALK-2.*TCA
           IF(ACID(J))1801,186,186
     1801   IF(AMC(J)-MAXAMC)1803,1802,1802
     1802  LO=LO+1
           GO TO 190
     1803   IF(AMC(J)-MINAMC)1804,1804,190
     1804   AMC(J)=MINAMC
           GO TO 190
     186    IF(ACID(J)-MAXACD)187,201,201
     187    IF(AMC(J)-MINAMC)1870,188,188
     1870   AMC(J)=MINAMC
           GO TO 190
     188    IF(AMC(J)-MAXAMC)190,201,201
      190  LM=LM+1
           IF(ACID(J)-0.3)191,192,192
      191  ACID(J+1)=ACID(J)+0.04
           GO TO 200
      192  ACID(J+1)=ACID(J)+0.25
      200  CONTINUE
      201  XPAGE=AMC(LO)*DX
           YPAGE=-(ACID(LO)*DY)
           CALL PLOT(XPAGE,YPAGE,3)
           LM=LM-1
           DO 206 J=LO,LM
           XPAGE=AMC(J)*DX
           YPAGE=-(ACID(J)*DY)
           CALL PLOT(XPAGE,YPAGE,2)
      206  CONTINUE
      250  CONTINUE
     C      ********************************************
     C      CALCULATIONS TO PLOT ALKALINITY LINES
     C      ********************************************
           LUC=0
           WRITE(6,6)
           DO 650 I=1,NALK
           LDAC=0
           LADC=0
           LML=1
           LM=1
           LMM=1
           LZZ=1
           IF(LUC-1)251,251,252
      251  AMC(1)=MINAMC
           GO TO 253
      252  ACID(1)=MAXACD
           LMM=2
      253  CONTINUE
           DO 599 J=1,1000
      254  LL=0
           MM=0
           IF(LMM-2)258,350,350
     C      *********************************************
     C      CALCULATION FOR HORIZONTAL SECTION
     C      OF ALK. LINE
     C      *********************************************
      258  H=1./(10.**3.)
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```
      KKK=1
      TCA=(ALK(I)-AMC(J))/2
  259 FSO4=TSO4
  260 FNA=TNA/(1.+FSO4/K34)
      FCA=TCA/(1.+FSO4/K32)
      FMG=TMG/(1.+FSO4/K33)
      TTSO4=FSO4*(1.+FNA/K34+FCA/K32+FMG/K33)
      IF(TTSO4-TSO4)280,280,270
  270 FSO4=0.9*FSO4
      GO TO 260
  280 FOH=KW/H
      FFMG=KMG/(FOH**2.)
      IF(FFMG-FMG)285,285,296
  285 FMG=FFMG
      KKK=2
      FSO4=TSO4
  286 FNA=TNA/(1.+FSO4/K34)
      FCA=TCA/(1.+FSO4/K32)
      TTSO4=FSO4*(1.+FNA/K34+FCA/K32+FMG/K33)
      IF(TTSO4-TSO4)295,295,290
  290 FSO4=0.95*FSO4
      GO TO 286
  295 CONTINUE
  296 LLL=0
  300 AK1=K11*(1.+FCA/K12+FMG/K13+FNA/K14)
      AK2=K21*(1.+FCA/K22+FMG/K23+FNA/K24)*K11/AK1
      IF(LUG-1)3002,3002,3001
 3001 XX=1./(1.+50.*FCA/FMG)
      PKS=8.4-1.744*XX
      KS=(1./10.**PKS)/((FMG/FCA)**XX)
      KS=KS*CONST
 3002 FCO3=KS/FCA
      TCO3=FCO3*(1.+FCA/K22+FMG/K23+FNA/K24)
      THCO3=TCO3*H/AK2
      FHCO3=FCO3*H/K21
      H2CO3=THCO3*H/AK1
      GMOH=FMG*FOH/K43
      CAOH=FCA*FOH/K42
      TOH=FOH+GMOH+CAOH
      TC=2.*TCO3+THCO3
      FSO4=TSO4
  301 IF(KKK-1)3020,3020,3030
 3020 FMG=TMG/(1.+FSO4/K33+FCO3/K23+FHCO3/K13+FOH/K43)
 3030 FCA=TCA/(1.+FSO4/K32+FCO3/K22+FHCO3/K12+FOH/K42)
      FNA=TNA/(1.+FSO4/K34+FCO3/K24+FHCO3/K14)
      TTSO4=FSO4*(1.+FCA/K32+FMG/K33+FNA/K34)
      IF(TTSO4-TSO4)309,309,302
 302   FSO4=FSO4*0.9
      IF(KKK-1)3020,3020,3030
  309 LLL=LLL+1
      IF(LLL-3)300,310,310
  310 AALK=2.*TCO3+THCO3+TOH-H
      IF(AALK-ALK(I))325,340,320
  320 IF(LL-1)321,321,330
  321 H=0.1*H
      GO TO 259
  325 IF(LL-1)326,326,327
  326 FRACT=H
  327 H=H+FRACT
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```
      LL=2
      GO TO 259
  330 MM=MM+1
      IF(4-MM)340,340,335
  335 H=H-FRACT
      FRACT=0.1*FRACT
      H=H+FRACT
      GO TO 259
  340 ACID(J)=2.*H2CO3+THCO3+H-TOH
      PPH=-1.*ALOG10(H*FM)
      HH=H
      IF(AMC(J)-MAXAMC)3407,600,600
 3407 IF(ACID(J)-MINACD)600,600,3406
 3406 IF(ACID(1)-MAXACD)3402,3402,3401
 3401 LUC=2
      ACID(1)=MAXACD
      GO TO 350
 3402 IF(LM-1)343,343,3403
 3403 S(J)=ACID(J-1)-ACID(J)
      IF(LACD)3413,3413,3400
 3413 IF(LM-2)343,343,3404
 3404 IF(S(J)-1.1*S(J-1))3400,3400,344
 3400 IF(ACID(J)-MINACD)600,600,341
  341 IF(AMC(J)-MAXAMC)343,600,600
  343 IF(ACID(J)-1.0)344,3430,3430
C
C      SET (ALK-CA) DELTA VALUE
C
 3430  IF(SOFT)3432,3431,3431
 3431  DAMC=0.1
      GO TO 3433
 3432  DAMC=0.5
 3433 AMC(J+1)=AMC(J)+DAMC
      GO TO 598
  344 CONTINUE
C      *********************************************
C      CALCULATIONS TO PLOT VERTICAL
C      SECTIONS OF ALK. LINE
C      *********************************************
  350 LMM=2
      LL=0
      LACD=LACD+1
      LZ=0
      MM=0
      CT=(ACID(J)+ALK(I))/2.
      IF(LM-1)3503,3503,3502
 3502 PPH=PPH+0.03
      H=(1./(10.**PPH))/FM
      FRACT=H/10.
      LL=2
      GO TO 352
 3503 H=1./10.**3.
  352 FOH=KW/H
      LZZ=1
      LLL=1
  354 FSO4=TSO4
  355 FNA=TNA/(1.+FSO4/K34+FCO3/K24+FHCO3/K14)
      FCA=TCA/(1.+FSO4/K32+FCO3/K22+FHCO3/K12+FOH/K42)
      FMG=TMG/(1.+FSO4/K33+FCO3/K23+FHCO3/K13+FOH/K43)
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      TTSO4=FSO4*(1.+FNA/K34+FCA/K32+FMG/K33)
      IF(TTSO4-TSO4)365,365,360
  360 FSO4=FSO4*0.9
      GO TO 355
  365 FFMG=KMG/(FOH**2.)
      IF(FFMG-FMG)366,370,3650
 3650 LZZ=1
      GO TO 370
  366 FMGG=FMG
      FMG=FFMG
      LZZ=2
  367 FSO4=TSO4
 3670 FNA=TNA/(1.+FSO4/K34+FCO3/K24+FHCO3/K14)
      FCA=TCA/(1.+FSO4/K32+FCO3/K22+FHCO3/K12+FOH/K42)
      TTSO4=FSO4*(1.+FNA/K34+FCA/K32+FMG/K33)
      IF(TTSO4-TSO4)370,370,368
  368 FSO4=0.9*FSO4
      GO TO 3670
  370 TOH=FOH*(1.+FCA/K42+FMG/K43)
      AK1=K11*(1.+FCA/K12+FMG/K13+FNA/K14)
      AK2=K21*(1.+FCA/K22+FMG/K23+FNA/K24)*K11/AK1
      TCO3=CT/(1.+H/AK2+H**2./(AK1*AK2))
      FCO3=TCO3/(1.+FCA/K22+FMG/K23+FNA/K24)
      H2CO3=(FCO3*H**2.)/(K11*K21)
      FHCO3=(H*FCO3)/K21
      THCO3=FHCO3*(1.+FCA/K12+FMG/K13+FNA/K14)
      IF(LUG-1)372,372,371
  371 XX=1./(1.+50.*FCA/FMG)
      PKS=8.4-1.744*XX
      KS=1./(10.**PKS)/((FMG/FCA)**XX)
      KS=KS*CONST
  372 FCA=KS/FCO3
      TCA=FCA*(1.+FSO4/K32+FCO3/K22+FHCO3/K12+FOH/K42)
      IF(LLL-3)376,376,385
  376 LLL=LLL+1
      GO TO 354
  385 AACID=2.*H2CO3+THCO3+H-TOH
      GMOH=FOH*FMG/K43
      AALK=2.*TCO3+THCO3+TOH-H
      CAOH=FOH*FCA/K42
      TTOH=FOH+CAOH
      TC=2.*TCO3+THCO3
      IF(LZZ-1)389,389,3851
 3851 IF(TTOH-GMOH)3960,389,389
  389 IF(AALK-ALK(I))390,398,392
  390 IF(LL-1)391,391,395
  391 H=0.1*H
      GO TO 352
  392 IF(LL-1)393,393,394
  393 FRACT=H
  394 H=H+FRACT
      LL=2
      GO TO 352
  395 IF(2-MM)398,398,396
  396 MM=MM+1
      H=H-FRACT
      FRACT=0.1*FRACT
      H=H+FRACT
      GO TO 352
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```
3960 IF(AALK-ALK(I))3963,398,3961
3961 IF(LL-1)3962,3962,3966
3962 H=0.95*H
     GO TO 352
3963 IF(LL-1)3964,3964,3965
3964 FRACT=0.04*H
     LL=2
3965 H=H+FRACT
     GO TO 352
3966 IF(LZ-4)3967,398,398
3967 LZ=LZ+1
     H=H-FRACT
     FRACT=0.1*FRACT
     H=H+FRACT
     GO TO 352
 398 FHCO3=FCO3*H/K21
     PPH=-1.*ALOG10(H*FM)
     HH=H
     TCA=FCA*(1.+FCO3/K22+FHCO3/K12+FSO4/K32+FOH/K42)
     AMC(J)=ALK(I)-2.*TCA
 399 IF(ACID(J)-MINACD)600,600,400
 400 IF(AMC(J)-MAXAMC)405,600,600
C     *************************************************
C     SET ACIDITY DELTA VALUE
C     **************************************************
405   IF(AMC(J)-MINAMC)600,406,406
 406 DACID=0.04
     ACID(J+1)=ACID(J)-DACID
     GO TO 598
 598 LM=LM+1
 599 CONTINUE
 600 CONTINUE
     IF(AMC(LM)-MAXAMC)602,602,601
 601 LM=LM-1
     GO TO 6020
602   IF(AMC(LM)-MINAMC)6010,6020,6020
6010  AMC(LM)=MINAMC
6020 XPAGE=AMC(1)*DX
     YPAGE=-(ACID(1)*DY)
     CALL PLOT(XPAGE,YPAGE,3)
     WRITE(5,4)ALK(I)
     DO 610 J=1,LM
     XPAGE=AMC(J)*DX
     YPAGE=-(ACID(J)*DY)
     CALL PLOT(XPAGE,YPAGE,2)
 610 CONTINUE
 611 CONTINUE
 650 CONTINUE
C     *************************************************
C     CALCULATIONS TO PLOT CO2 PARTIAL PRESSURE LINES
C     *************************************************
     IF(LC-1)801,801,651
 651 CONTINUE
     WRITE(6,7)
     KC=1./10.**1.47
     DO 800 I=1,NPCO
     H2CO3=KC*PCO(I)*10.**3.
     LM=1
     MM=0
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      LL=0
      AMC(1)=MINAMC
      DO 790 J=1,1000
      LL=0
      MM=0
      FCO3=10.
  698 H=((K11*K21*H2CO3)/FCO3)**0.5
      FCA=KS/FCO3
      FSO4=TSO4
  699 FNA=TNA/(1.+FSO4/K34)
      FMG=TMG/(1.+FSO4/K33)
      TTSO4=FSO4*(1.+FCA/K32+FMG/K33+FNA/K34)
      IF(TTSO4-TSO4)761,761,760
  760 FSO4=0.9*FSO4
      GO TO 699
  761 FOH=KW/H
      IF(FFMG-FMG)762,765,765
  762 FMG=FFMG
  763 FNA=TNA/(1.+FSO4/K34)
      TTSO4=FSO4*(1.+FCA/K32+FMG/K33+FNA/K34)
      IF(TTSO4-TSO4)764,765,765
  764 FSO4=1.1*FSO4
      GO TO 763
  765 FHCO3=H*FCO3/K21
      AK1=K11*(1.+FCA/K12+FMG/K13+FNA/K14)
      AK2=K21*(1.+FCA/K22+FMG/K23+FNA/K24)*K11/AK1
      TCO3=FCO3*(1.+FCA/K22+FMG/K23+FNA/K24)
      IF(LUG-1)767,767,766
  766 XX=1./(1.+50.*FCA/FMG)
      PKS=8.4-1.744*XX
      KS=(1./10.**PKS)/((FMG/FCA)**XX)
      KS=KS*CONST
  767 THCO3=TCO3*H/AK2
      TOH=FOH*(1.+FMG/K43+FCA/K42)
      TCA=FCA*(1.+FSO4/K32+FCO3/K22+FHCO3/K12+FOH/K42)
      AALK=2.*TCO3+THCO3+TOH-H
      AAMC=AALK-2.*TCA
      IF(AAMC-AMC(J))770,780,768
  768 IF(LL-1)769,769,773
  769 FCO3=0.1*FCO3
      GO TO 698
  770 IF(LL-1)771,771,772
  771 FRACT=FCO3
  772 FCO3=FCO3+FRACT
      LL=2
      GO TO 698
  773 IF(3-MM)780,774,774
  774 MM=MM+1
      FCO3=FCO3-FRACT
      FRACT=0.1*FRACT
      FCO3=FCO3+FRACT
      GO TO 698
  780 ACID(J)=2.*H2CO3+THCO3+H-TOH
      IF(AMC(J)-MAXAMC)785,791,791
  785 IF(ACID(J)-MAXACD)786,791,791
  786 AMC(J+1)=AMC(J)+1.0
      LM=LM+1
  790 CONTINUE
  791 XPAGE=AMC(1)*DX
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```
      YPAGE=-(ACID(1)*DY)
      CALL PLOT(XPAGE,YPAGE,3)
      WRITE(5,4)PCO(I)
      DO 793 J=1,LM
      XPAGE=AMC(J)*DX
      YPAGE=-(ACID(J)*DY)
      CALL PLOT(XPAGE,YPAGE,2)
  793 CONTINUE
  800 CONTINUE
  801 CONTINUE
      IF(SOFT)8130,8130,9001
 9001  PHM(1)=10.0
      DO 8070 I=1,8
      H=(10.**(-PHM(I))/AH)*1000.
      OH=K41/H
      FMG=KMG/(OH**2.)
      MM=1
      NN=1
      FSO4=TSO4
 9002  FCA=TCA/(1.+FSO4/K32+OH/K42)
      FNA=TNA/(1.+FSO4/K34)
      TTSO4=FSO4*(1.+FCA/K32+FNA/K34+FMG/K33)
      IF(TTSO4-TSO4)8010,8060,9003
 9003  IF(NN-1)8005,8005,8040
 8005  FSO4=FSO4*0.1
      GO TO 9002
 8010  IF(NN-1)8020,8020,8030
 8020  FRACT=FSO4
 8030  FSO4=FSO4+FRACT
      NN=2
      GO TO 9002
 8040  FSO4=FSO4-FRACT
      FRACT=FRACT*0.1
      FSO4=FSO4+FRACT
      IF(MM-3)8050,8050,8060
 8050  MM=MM+1
      GO TO 9002
 8060  TTMG(I)=FMG*(1.+FSO4/K33+OH/K34)
      PHM(I+1)=PHM(I)+0.2
 8070  CONTINUE
      XPAGE=XMAX+2.
      YPAGE=YMAX+2.
      CALL PLOT(XPAGE,YPAGE,-3)
      NTMY=8
      XPAGE=0.0
      YPAGE=1.
      DO 8100 I=1,8
      YPAGE=YPAGE-1.
      CALL SYMBOL(XPAGE,YPAGE,0.1,3,0.,-2)
 8100  CONTINUE
      YPAGE=1.
      XPAGE=0.1
      DO 8110 I=1,8
      YPAGE=YPAGE-1.
      PHL=PHM(I)
      CALL NUMBER(XPAGE,YPAGE,0.1,PHL,0.,1)
 8110  CONTINUE
      YPAGE=1.
      XPAGE=-0.5
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      DO 8120 I=1,8
      YPAGE=YPAGE-1.
      TM=TTMG(I)
      CALL NUMBER(XPAGE,YPAGE,0.1,TM,0.,3)
 8120  CONTINUE
      XPAGE=0.7
      YPAGE=-4.
      CALL SYMBOL(XPAGE,YPAGE,0.2,2HPH,90.,2)
      XPAGE=-0.8
      YPAGE=-3.8
 8130  CONTINUE
      CALL SYMBOL(XPAGE,YPAGE,0.2,3HTMG,90.,3)
      CALL PLOT(0,0,999)
      STOP 'END OF PROGRAM, PLOT SENT TO CALCOMP'
C      *****************
C      FORMAT STATEMENTS
C      *****************
    2 FORMAT()
    3 FORMAT(1X,'LIST OF PH LINES PLOTTED'/)
    4 FORMAT(5X,F6.2)
    5 FORMAT(1X,'LIST OF CALCIUM LINES PLOTTED'/)
    6 FORMAT(1X,'LIST OF ALKALINITY LINES PLOTTED'/)
    7 FORMAT(1X,'LIST OF CO2 PARTIAL PRESSURE LINES PLOTTED'/)
      END
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