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Different Nonideality Relationships, Different Databases and Their Effects on Modeling Precipitation from Concentrated Solutions Using Numerical Speciation Codes

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FIGURE

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NOMENCLATURE

(Dimensions given below are typical dimensions. Sometimes different units are used in the text.)

Roman symbols

a_i	The thermodynamic activity of substance i, dimensionless.
K_{sp}	The solubility product, $(mol/L)^n$
L	Liter.
M	Molar. Refers to the molarity of a solution, e.g., 1.0 M is a 1.0 molar solution.
pK_{sp}	The negative of the logarithm of the solubility product.
n	The sum of the exponents in the solubility product.
x	The amount of Ca^{++} ion precipitating as $Ca(OH)_2$ in Precipitation Problems #1-#3, mol/L.
y	The amount of Ca^{++} ion precipitating as $CaSO_4 \cdot 2H_2O$ in Precipitation Problem #3, mol/L.

Greek symbols

α	x_{real}/x_{ideal} in discussion of Precipitation Problems #1, #2, and #3, and in Appendix C.
β	y_{real}/y_{ideal} in discussion of Precipitation Problem #3 and in Appendixes C and D.
γ_i	The activity coefficient of substance i, L/mol.
ξ	A combination of activity coefficients. In Precipitation Problems #1 and #2, $\xi = \gamma_{Ca++}\gamma^2_{OH-}$. In Precipitation Problem #3, $\xi = \sqrt{\gamma_{SO4--}} / \gamma_{OH-}$.

Subscripts

i	Relating to substance i or to the i^{th} component in a reaction.
ideal	Relating to an ideal solution, or calculated using ideal-solution theory.
real	Relating to a real solution, or calculated using real-solution theory.
0	Initial value or entering value before precipitation occurs. Also, the value for the first term in a Taylor series expansion or an ideal-solution value.

Superscripts

+	An ion with a single positive charge.
++	An ion with a double positive charge.
-	An ion with a single negative charge.
--	An ion with a double negative charge.

Other Symbols

[ ]	Concentration, mol/L
*	In the title or suffix of a computer file, the asterisk stands for any title or suffix.
	Titles of computer codes are entirely capitalized, titles of computer files appear in bold-faced type.

ACRONYMS

D-H	Debye-Hückel.
LLNL	Lawrence Livermore National Laboratory.
RHS	Right-hand side of an equation or expression.
w.r.t.	with respect to

GLOSSARY

Anhydrite	The mineral calcium sulfate ($CaSO_4$) without water of hydration.
Antarcticite	The mineral $CaCl_2 \cdot 6H_2O$.
Glauberite	The mineral $Na_2Ca(SO_4)_2$.
Gypsum	Hydrated calcium sulfate, $CaSO_4 \cdot 2H_2O$.
Halite	Native salt, NaCl.
Mirabilite	Hydrated sodium sulfate, $Na_2SO_4 \cdot 10H_2O$.
Portlandite	The mineral calcium hydroxide, $Ca(OH)_2$.
Thenardite	The mineral sodium sulfate, Na_2SO_4.

DIFFERENT NONIDEALITY RELATIONSHIPS, DIFFERENT DATABASES AND THEIR EFFECTS ON MODELING PRECIPITATION FROM CONCENTRATED SOLUTIONS USING NUMERICAL SPECIATION CODES

by

Lee F. Brown and Michael H. Ebinger

ABSTRACT

Four simple precipitation problems are solved to examine the use of numerical equilibrium codes. The study emphasizes concentrated solutions, assumes both ideal and nonideal solutions, and employs different databases and different activity-coefficient relationships. The study uses the EQ3/6 numerical speciation codes. The results show satisfactory material balances and agreement between solubility products calculated from free-energy relationships and those calculated from concentrations and activity coefficients. Precipitates show slightly higher solubilities when the solutions are regarded as nonideal than when considered ideal, agreeing with theory. When a substance may precipitate from a solution dilute in the precipitating substance, a code may or may not predict precipitation, depending on the database or activity-coefficient relationship used. In a problem involving a two-component precipitation, there are only small differences in the precipitate mass and composition between the ideal and nonideal solution calculations. Analysis of this result indicates that this may be a frequent occurrence. An analytical approach is derived for judging whether this phenomenon will occur in any real or postulated precipitation situation. The discussion looks at applications of this approach. In the solutes remaining after the precipitations, there seems to be little consistency in the calculated concentrations and activity coefficients. They do not appear to depend in any coherent manner on the database or activity-coefficient relationship used. These results reinforce warnings in the literature about perfunctory or mechanical use of numerical speciation codes.

I. EXECUTIVE SUMMARY

This work examines using numerical equilibrium codes to solve concentrated-solution precipitation problems. The work computes compositions and amounts precipitating from solution together with solution compositions in equilibrium with precipitates using different thermodynamic databases and different activity coefficient relationships. The consistency of thermodynamic databases is perhaps the greatest source of uncertainty in numerical calculations of chemical equilibria. Perhaps the next greatest weakness in these calculations lies in the evaluation of activity coefficients. Thus this study investigates the two largest sources of uncertainty in numerical calculations of this type. The EQ3/6 numerical speciation codes are the model programs implemented in this work.

The study solves four simple problems, each emphasizing different aspects of precipitation from solution. The first problem involves precipitation of a single substance from a concentrated solution. The second problem concerns a single substance precipitating from a solution dilute in the precipitating species but concentrated in other ions. In the third problem, simultaneous precipitation of two substances from a concentrated solution occurs. The fourth problem envisions evaporation of almost all the water from the supernatant liquids remaining after the predicted precipitation in the previous problem.

There are six approaches to solving each problem. Two use different solubility-product sources for ideal-solution calculations. Two acknowledge nonideality and employ different activity-coefficient relationships and the same thermodynamic database. The final two acknowledge nonideality and use the same activity-coefficient relationship but different databases.

The results of the first problem give a precipitate amount approximately the same for both ideal and nonideal-solution calculations, as expected. The nonideal-solution calculations predict a slightly greater solubility of the precipitate, again as expected. Some calculations solving the second problem predict precipitation, some do not, with no noticeable consistency. The nonideal-solution calculations solving the third problem predict amounts of both precipitates approximately equal to those predicted by the ideal-solution calculations. There appears to be little agreement in the calculated ion concentrations and activity coefficients in the supernatant solutions. The results of the fourth problem show wide variation in the precipitate amounts, showing the weaknesses of using numerical speciation codes to predict results of evaporation campaigns without extensive knowledge of the system.

Combinations of activity coefficients and ion concentrations can yield situations where ideal-solution calculations can predict precipitate amounts from nonideal solutions. An analytical approach to comparing ideal and nonideal precipitation predictions gives a method for forecasting whether ideal precipitation predictions will be valid for nonideal solutions.

The lack of consistency in the calculated ion concentrations and activity coefficients and their apparent lack of dependence in any coherent manner on database or activity-coefficient relationships reinforce warnings in the literature about the use of numeric speciation codes without extensive knowledge of the system.

II. GOAL OF INVESTIGATION

As mentioned below in Section IV.C, numerical equilibrium computer codes have some inherent uncertainties. Perhaps the greatest uncertainty is the dependence of the results on the particular thermodynamic database being used. Another uncertainty results from the choice of activity-coefficient relationships for use in a code. It is the goal of this study to investigate how use of different thermodynamic databases and activity-coefficient relationships can influence the results of modeling different precipitation scenarios. The situations studied are simple, so interpretation of the results is unambiguous. Concentrated solutions are emphasized in this work.

III. METHODS USED IN THIS STUDY

This study uses the numerical speciation code embodied in the EQ3/6 programs. As presently distributed, these codes have embedded within them several databases and different activity-coefficient relationships. They are thus well adapted to this investigation.

The study solves four different precipitation problems. Each problem emphasizes different aspects of the precipitation process. Particular characteristics of both the precipitate and the resulting solution in equilibrium with the precipitate are determined. The study solves each problem using six different approaches. Two of the approaches assume ideal solutions, and solve the problems by simple algebra. The algebraic solutions to each problem are based on different values of the solubility products, obtained from different, but still supposedly reliable, sources.

For each problem, the four solutions that include nonideality use the thermodynamic speciation codes EQ3/6. Embedded in the codes' software are five thermodynamic databases. Three of these were chosen for this study, and Section IV.D below discusses these. Two approaches use one of these databases, but employ different relationships for calculating activity coefficients. Another activity-coefficient relationship is used with each of the other two databases. Thus each problem is solved using three databases and three activity-coefficient relationships.

Section V presents statements of the problems. Appendix A repeats the problem statements, and gives examples of the algebraic solutions for ideal-solution situations.

IV. NUMERICAL EQUILIBRIUM OR THERMODYNAMICS SPECIATION CODES

A. Overview of Numerical Equilibrium Codes.

The last 30-plus years have seen the creation of many numerical computer codes for calculating chemical equilibria in multiple-species and multiple-phase systems. In the 20 years following the basic work of Garrels and Thompson (1962), investigators developed many programs for this purpose. The codes are based on rigorous thermodynamics principles and use various thermodynamics approaches and numerical techniques for solution of the resulting equations. Zeleznik and Gordon (1968) give a thorough review of the principles involved and the bases of the applications. Nordstrom et al. (1979) compare the characteristics of codes popular at that time and the results of two test problems using those codes. Mangold and Tsang (1991) give a later list of some of the more popular codes. Bassett and Melchior (1990) also list some of the more popular codes and give an overview of then-current trends in developing these codes. The 10 years preceding this paper saw a significant decrease in the introduction of new codes (Bassett and Melchior op. cit.). Rather, the emphasis was on improving existing codes, expanding the databases on which they rely, making the codes portable from system to system, and easing the difficulties involved in using the codes. During the last 5 years, special-purpose computer programs, based on the source codes of the principal codes, have proliferated (Parkhurst 1996). These special-purpose codes have databases tailored to the situation being studied.

B. Calculation of Activity Coefficients.

The activity is "the tendency of a species to react" (Campbell 1970). It is substances' activities that are used to calculate equilibrium constants and solubility products. The solubility products are keys to predicting precipitation of solids from solution and dissolving the solids into solution.

The thermodynamic activity of a substance i in a solution is a_i. Use of an activity coefficient γ allows calculation of the activity of this component from its concentration, c_i:

$$a_i = \gamma_i c_i \qquad \text{(IV-1)}$$

Activity coefficients approach one at high dilution of a solution. At high dilution, the behavior of a solution approaches "ideal" solution behavior.

The first truly successful approach to calculating activity coefficients for species in ionic solutions was proposed by Debye and Hückel (1923). Their approach has been widely used and extended since its introduction. Glasstone (1946) and Lewis and Randall (1961) give good descriptions of the theory and its applications. More sophisticated treatments are also available (e.g., Mazo and Mou 1979).

While valid at low to perhaps moderate concentrations, the Debye-Hückel approach fails at high concentrations. Recent coding efforts have incorporated virial equations developed by Pitzer for activity coefficients (e.g., Pitzer 1979, 1991; Clegg and Whitfield 1991). These allow more exact calculation of activity coefficients for solutions at high concentrations.

C. Uncertainties in Numerical Equilibrium Codes

Fifteen years ago, Nordstrom et al. (1979) discussed uncertainties in the numerical codes then in use for calculating chemical equilibria in aqueous systems. Their comments remain valid today:

"The use of activity coefficients to describe the non-ideal behavior of aqueous electrolytes reflects our uncertain knowledge of ionic interactions and as a consequence we must approximate activity coefficients with semi-empirical equations."

"It is quite common for solubility product constants and complex stability constants to vary by 1 to 3 orders of magnitude (in different models)...Quite clearly this amount of uncertainty can cause large differences in the computer results and probably contributes the largest single source of error...the lack of carefully evaluated thermodynamic data will continue to be the most serious limitation for any type of chemical modeling."

"(There is an) inconsistency and inadequacy of activity coefficient equations." "Another related problem is the calculation of activity coefficients for neutral complexes. Very little reliable information is available on the activity of neutral ion pairs and since these often comprise the dominant species in aqueous systems their activity coefficients can be an important source of uncertainty."

"The fourth limitation is the assumption made about the redox state of aqueous systems. The distribution of redox species depends on what redox potential is assumed to dominate the chemical equilibrium...Imposed redox equilibria may not represent a realistic distribution of species."

What Daveler and Wolery (1992) say of the EQ3/6 codes is true of all numerical equilibrium codes. "What one can do with EQ3NR or EQ6 depends to a high degree on what is on the supporting data file and if so how the species and reactions on the data file are organized. For example, iron does not appear on the **hmw** data file, so this file can not be used to model the behavior of iron in brine-mineral systems. Similarly, uranium does not appear on the **sup** data file. Even if a chemical element does appear on a given data file, the corresponding species required for a given problem must also appear on it."

A cautionary note by Wolery (1992a) is worth repeating. "Geochemical modeling codes are not black boxes. Much of the usefulness (or lack of) that comes from their use is determined by the level of knowledge brought to bear by the user....Any results obtained by modeling calculations should be weighed against descriptive knowledge of the system being modeled."

Since the time of the earlier comments, the quality and extent of thermodynamic data in the code databases has improved. Little else has changed. These uncertainties should motivate caution and restraint in interpreting results of numerical modeling of chemical equilibria in aqueous systems.

V. THE EQ3/6 THERMODYNAMICS SPECIATION CODES

A. Attributes of the EQ3/6 Codes.

It is mentioned above in Section IV.A that many numerical equilibrium codes have been developed over the past 30 years. Among these is the EQ3/6 set of codes, originally created by T. J. Wolery (1978). The characteristics of some of the more popular codes are compared in Table 1, adapted from a similar table in Mangold and Tsang (1991). This table shows that the EQ3/6 codes encompass more possible precipitated mineral types than any of the other codes. While the data underlying Table 1 is 6-7 years old, the proliferation of codes mentioned above in Section IV.A makes a realistic updating of this table impossible. A current sampling of other codes indicates that the EQ3/6 codes still consider more precipitated mineral types than any other popular code.

Another property of the EQ3/6 codes is the ability to calculate along a reaction path, and to stop anywhere between the starting point and final equilibrium. Few codes have this capability.

The EQ3/6 codes have undergone continuous improvement since their origin. The version used for this report's calculations was 7.2 and is usable on 386 and 486 MS-DOS personal computers. Since the Mangold-Tsang table was developed, the EQ3/6 capabilities have expanded. The number of elements considered has increased from 47 to 78, the number of aqueous species from 686 to 851, of minerals from 713 to 885, and of gases from 11 to 75 (Daveler and Wolery 1992). While other codes have also improved their capabilities, EQ3/6 apparently remains the one with the highest numbers of mineral types and thus is appropriate for studying precipitation behavior.

B. Codes and Files in the EQ3/6 System.

Several documents thoroughly describe the EQ3/6 codes and give detailed descriptions of their bases (Daveler and Wolery 1992, Wolery 1992a and 1992b, Wolery and Daveler 1992). Wolery (1979) and Wolery et al. (1990) give shorter descriptions of the EQ3/6 codes, These sources may be consulted for details about the codes. Only aspects pertinent to the present work are mentioned in the next paragraphs.

The EQ3/6 software system presently consists of 3 computer codes and 19 files. The 3 codes are titled EQPT, EQ3NR, and EQ6. Of the files, the titles of 5 begin with **data0**, 5 with **data1**, and the rest have titles indicating their purpose, e.g., **input**, **output**, etc. While this study used the 3 codes, it did not use all the files. Figure 1, adapted from Wolery (1992a), shows the flow of information among the different files and codes used in this study.

The 5 files whose titles begin with **data0** contain the five databases compatible with the EQ3/6 codes. These databases are described in Table 2 and in Section D below. The **data0** files are in a form readily accessible by standard word processing software, so the user can modify these files if desired. The 5 **data1.*** files are the 5 **data0.*** files converted by the code EQPT to a form usable by the EQ3/6 codes. This setup enables the databases to be modified by the user and still be compatible with the EQ3/6 system. The present study, however, made no modifications in the databases.

The input file to the EQ3NR code specifies the problem to be processed by the EQ3/6 system. This file is titled ***.3i**. For example, we called the EQ3NR input file **caoh2a1.3i** for the first part of this study's first problem, the precipitation of $Ca(OH)_2$.

The EQ3NR code processes the input file and gives information about the species resulting from the process or situation being modeled. The information is contained in the pickup (***.3p**) and output files (***.3o**) that the code produces. For the first part of our first problem, the code titled these files **caoh2a1.3p** and **caoh2a1.3o**. Some information from these files is transferred to the input file for EQ6 (***.6i**), in this case titled **caoh2a1.6i**. EQ6 then processes the information in this input file to give the final results in output file ***.6o**, in this case **caoh2a1.6o**. As mentioned above, this processing and flow of information is illustrated in Figure 1, and described much more extensively in the works by Wolery and Daveler cited at the beginning of this section.

C. Different Relationships Available in the EQ3/6 Codes for Calculating Activity Coefficients.

The unmodified Debye-Hückel theory may be suitable only at ionic concentrations below 0.003M at the most (Frank and Thompson 1959). Because of this, the unmodified Debye-Hückel equations are not employed by the EQ3/6 codes. Davies proposed an empirical extension to Debye-Hückel theory (Wolery 1992b), and EQ3/6 offers use of the extended equation as one of the possible calculation routes.

There are reservations about the use of the Davies relationship even at low concentrations (Johnson and Pytkowicz 1979). As an alternative to the Davies equation, the EQ3/6 codes offer the use of Helgeson's (1969) "B-dot" equation. Wolery (1992b) describes the use of this equation in the EQ3/6 codes.

Even with the extensions to the Debye-Hückel theory offered by the Davies and B-dot equations, calculated activity coefficients for concentrated solutions can exhibit unacceptable levels of error. As mentioned earlier, equations developed by Pitzer appear suitable for concentrated solutions, and their use has been incorporated as an option in the EQ3/6 codes.

D. Different Databases Embedded in the EQ3/6 Codes.

Table 2 gives some characteristics of the EQ3/6 files containing the thermodynamic databases. According to Wolery (1992a), the **com** file is the largest of the 5 data files. It was developed at LLNL, drawing on many sources of data. It encompasses the broadest range of elements and species of any of the five files, taking some of its data from the other four files. As a result, there may be some lack of internal consistency. The **sup** file has a high level of internal consistency. The **nea** file has a thorough representation of the thermodynamics of uranium species.

The Pitzer equations require their own parameters, so databases particularly developed for these equations are necessary. The **pit** and the **hmw** data files are created for use with the Pitzer equations. The **pit** file covers more species, but the **hmw** file has the greater internal consistency. The latter includes mutual consistency of activity coefficient data and standard state thermodynamic data, but is limited to the set of components present in the "sea-salt" system, and is restricted to 25°C.

Wolery (1992b) and Daveler and Wolery (1992) give additional information about these database files.

E. Databases and Activity-Coefficient Relationships Used in this Study.

This study used the EQ3/6 codes to analyze precipitation from concentrated solutions. Employing the Pitzer equations in these codes would usually be the appropriate course. On the other hand, the databases available for using the Pitzer equations are not as extensive as those available to the modifications of the Debye-Hückel approach. On occasion, the only databases appropriate to a particular system may require either the Debye-Hückel approach or nothing. An indication of the errors involved in using the Debye-Hückel approach for concentrated solutions would be desirable.

This study uses four combinations of databases and activity-coefficient relationships. The Davies and B-dot equations employ the **com** database, to compare the use of these two relationships with the same database. The Pitzer equations employ the **pit** and **hmw** databases, to compare the use of these equations with different databases. The Pitzer-equations results can also be compared with those coming from using the Debye-Hückel extensions.

VI. PROBLEM STATEMENTS AND PURPOSES OF PROBLEMS

Precipitation Problem #1: Precipitation of Calcium Hydroxide (Portlandite) by Mixing Concentrated Solutions of Calcium Chloride and Sodium Hydroxide

Problem Statement. One liter of a water solution containing 500 g dissolved $CaCl_2$ is mixed at 25°C with one liter of a water solution containing 100 g dissolved NaOH. It is desired to calculate the amount of $Ca(OH)_2$ precipitating, and the types and quantities of species remaining in solution.

Purpose of Problem. This problem has a first goal of validating the EQ3/6 codes on an elementary level. In this problem, the solutions are concentrated and the calcium is in excess. Thus, almost all of the hydroxyl ion will precipitate as $Ca(OH)_2$. Solving the problem with these codes will check their ability to predict this. A second goal is to see the variation in calculated activity coefficients and ion activities resulting from using the different equations and databases embedded in the EQ3/6 codes.

Precipitation Problem #2: Possible Precipitation of Calcium Hydroxide from Mixing Dilute Solutions of Calcium Chloride and Sodium Hydroxide with a Concentrated Sodium Chloride Solution

Problem Statement. One-liter batches of three solutions are mixed together at 25°C. One liter of a water solution containing 8 g dissolved $CaCl_2$, one liter of a water solution containing 3 g dissolved NaOH, and one liter of a water solution containing 500 g dissolved NaCl are mixed together. It is desired to calculate whether $Ca(OH)_2$ precipitates, how much precipitates (if any of it does), and the types and quantities of species remaining in solution.

Purpose of Problem. The previous problem dealt with a concentrated solution. This solution is dilute in the precipitating substances, but concentrated in other ions. The goal of this problem is to check whether the use of some databases will predict precipitation, while the use of others may not. A secondary goal is the comparison of ion activities and activity coefficients calculated by the different equations and databases embedded in the EQ3/6 software.

Precipitation Problem #3: Simultaneous Precipitation of Calcium Sulfate (Gypsum) and Calcium Hydroxide (Portlandite) by Mixing Solutions of Calcium Chloride, Sodium Sulfate, and Sodium Hydroxide

Problem Statement. One-liter batches of three solutions are mixed together at 25°C. One liter of a water solution containing 500 g dissolved $CaCl_2$, one liter of a water solution containing 100 g dissolved NaOH, and one liter of a water solution containing 500 g dissolved Na_2SO_4 are all mixed together. It is desired to calculate the amounts of $Ca(OH)_2$ and $CaSO_4$ precipitating, and the types and quantities of species remaining in solution.

Purpose of Problem. This problem compares relative amounts of two precipitates, both of which should precipitate to some extent from the problem's concentrated solution. The problem also compares ion activities and activity coefficients calculated using the different equations and different databases embedded in the EQ3/6 software.

Precipitation Problem #4: Evaporation of Supernatant Solution Remaining From Simultaneous Precipitation of Calcium Hydroxide and Calcium Sulfate

Problem Statement. The supernatant solutions remaining from the precipitations in Precipitation Problem #3 are evaporated almost to dryness. It is desired to calculate the types and quantities of the substances precipitating, and the compositions of the remaining solutions.

Purpose of Problem. This problem illustrates possible differences in the predicted results of evaporation campaigns when different thermodynamic databases and different activity coefficient relationships are used to calculate the solution compositions.

VII. RESULTS

A. Precipitation Problem #1.

Table 3 presents the results from solving Precipitation Problem #1. The amounts of calcium hydroxide precipitated range from a low of 44.9 to a high of 46.3 g/L. The high value results from the ideal-solution computations, and the lower values occur when EQ3/6 is used, recognizing solution nonideality and then calculating activities. This qualitatively follows what is expected. The activity coefficients tend to be less than one under these circumstances. This results in a higher solubility of solid material, so less precipitate would be expected. The results of this problem follow the expected trend, even though some of the calculated activity coefficients are greater than one.

In spite of the higher predicted solubility of the material when nonideality is considered, almost all the possible calcium hydroxide would be expected to precipitate because of its low solubility product. The expected precipitate is observed, and thus EQ3/6 gives reasonable results for precipitate quantity in this problem no matter which relationship for calculating activity coefficients or which thermodynamic database is used.

The activity coefficients for Ca^{++} and OH^- ions show a wide variability. The coefficients for calcium range from 0.35 to 2.65 and for hydroxyl from 0.035 to 0.57. There seems to be little consistency, either among the same database using different relationships for the coefficients, or among the same relationship but using different databases.

The variability in activity coefficients is reflected in the range of ion concentrations. All the listed concentrations are dilute, so they do not differ much in absolute terms. They nevertheless exhibit significant relative differences that reinforce the uncertainties mentioned in Section IV.C.

B. Precipitation Problem #2.

Table 4 presents the results from solving Precipitation Problem #2. This is precipitation from a solution dilute in the precipitating species, but concentrated in other ions. When the solutions are assumed to be ideal, a small amount of $Ca(OH)_2$ precipitates. Since solubilities are generally higher in nonideal solutions, there should be a possibility that no precipitate is predicted when nonideality is considered in the calculations.

The table shows that three of the four nonideal equations calculate no precipitation. Only one of the two calculations using Pitzer's equations for calculating activity coefficients predicts precipitation. The other Pitzer-equation calculation (using the HMW database) predicts no precipitation, but its database shows a solubility product slightly lower than the PIT database. The lower solubility product may be the cause of the no-precipitation prediction.

The calculated ion activity coefficients do not present a coherent picture. While the activity coefficients of both the calcium and hydroxyl ions calculated using the B-dot equations are lower than those using the Pitzer equations, the activity coefficients calculated using the Davies equations are higher. These results confirm Nordstrom's 1979 warning (Section IV.C) about the "inconsistency ... of activity coefficient equations."

The difference in the precipitate masses predicted by the two ideal-solution calculations shows the significance of a small difference in solubility products. There is a 12% difference in the amounts of the two predictions, resulting from the difference in the listed solubility products. A larger difference in the listed solubility products, such as exists in the solubility products listed for $CaSO_4$ (Table 5), might mean the difference in predicting that precipitation occurs or doesn't occur.

C. Precipitation Problem #3.

Table 5 presents the results from solving Precipitation Problem #3. In this problem, gypsum [hydrated calcium sulfate or $CaSO_4 \cdot 2H_2O$] and portlandite [calcium hydroxide or $Ca(OH)_2$] were precipitated simultaneously. With one exception, the amounts of portlandite precipitated ranged from 28.6 to 29.8 g/L, and the amounts of gypsum range from 181.3 to 192.0 g/L. The exception [26.3 g/L $Ca(OH)_2$ and 197.6 g/L $CaSO_4 \cdot 2H_2O$] resulted from the unusually low $CaSO_4$ solubility product in one of the data sources used for evaluating ideal solutions.

It is of special interest that the predicted relative amounts of $Ca(OH)_2$ and $CaSO_4 \cdot 2H_2O$ did not change significantly between the ideal calculations and those that recognized the nonideality of the solutions. Let x be the amount of Ca^{++} ion that precipitated as $Ca(OH)_2$ and y the amount of Ca^{++} ion that precipitated as $CaSO_4 \cdot 2H_2O$. In the solutions to this problem, the ratio y/x ranged from 2.66 to 2.77 for the nonideal calculations. This may be compared with 2.89 for the ideal calculation. The ratios of x_{real}/x_{ideal} ranged only from 1.01 to 1.04 and y_{real}/y_{ideal} from 0.94 to 0.97. Thus, in this case, use of the ideal-solution results would have predicted realistic amounts of $Ca(OH)_2$ and $CaSO_4 \cdot 2H_2O$ precipitating. The nonideality of the solution did not change the predicted amounts of each species precipitating to a significant degree.

The results of the higher solubility in nonideal solutions can be seen again here. In all cases the calculated gypsum precipitate was less when nonideality was considered than when the solutions were assumed to be ideal. As in Precipitation Problem #1, there is a wide range of ion concentrations and activities, with little consistency observable.

D. Precipitation Problem #4.

Table 6 presents the results from solving Precipitation Problem #4. The final concentrations from Problem #3 differed, thus the starting materials of Problem #4 differed for the five cases studied. It would be expected that the amounts of the particular materials precipitated would also vary.

In the five calculations, the water, starting at 1000 g, was evaporated to 45 g H_2O. All four nonideal calculations predicted that four minerals would precipitate--portlandite [$Ca(OH)_2$], halite [NaCl], thenardite [Na_2SO_4], and glauberite [$Na_2Ca(SO_4)_2$]. No other minerals were predicted to precipitate by any of the nonideal calculations. The ideal calculation (Appendix A) therefore chose these four minerals for possible precipitation.

The major portion of the predicted precipitate is halite, being 91-94 mass % of the total precipitate in the nonideal calculations, and 97% of the precipitate from the ideal solution. This occurs because the starting solutions contained large amounts of unprecipitated sodium and chloride ions. These remained from the calcium chloride, sodium hydroxide, and sodium sulfate solutes in the original solutions that were mixed together in Problem #3. The calcium, hydroxyl, and sulfate ions had largely been removed in Problem #3's precipitation. The two calculations using the Pitzer activity-coefficient relationships predicted about 10% more halite as precipitating than the two calculations using Debye-Hückel activity-coefficient relationships.

The reason for the Pitzer calculations predicting more halite precipitating than the Debye-Hückel calculations is not clear. In spite of the different relationships and different databases, the ionic concentrations in the water are not radically different, nor are the calculated activity coefficients. The principal difference in the calculations seems to be the larger number of aqueous species considered in the Debye-Hückel calculations; the amounts of these species remaining in the water appear to make the difference in the amounts of halite precipitated. This reinforces the warning of Daveler and Wolery (1992) about results of calculations depending heavily upon the species present in the databases used.

The greater percentage of halite in the precipitate from the ideal solution results from the lower concentrations of the calcium, sodium, and sulfate ions in the starting solution for Problem #4. Nonidealities in the Problem #3 solutions caused higher concentrations of these ions in the Problem #4 starting solutions for the nonideal calculations. The amounts of portlandite, thenardite, and glauberite predicted to precipitate from the ideal solution are therefore much lower than the amounts of these minerals predicted to precipitate from the nonideal solutions. However, the amount of halite predicted to precipitate from the ideal solution is within the range of the amounts predicted by the nonideal calculations. Here again is observed the phenomenon of the ideal calculation predicting well the amount of a concentrated substance precipitating from a significantly nonideal solution.

The amounts of portlandite, thenardite, and glauberite predicted to precipitate differ significantly even among the nonideal calculations. In the nonideal calculations, the high value of portlandite is 46% above the low value, the high value of thenardite is 44% above the low value, and the high value of glauberite is over twice the low value. There seems to be no consistency among the calculations as to which produces high or low values, or whether the causes lie in species considered, equations used, or databases involved.

There is also a wide variation among the ion concentrations and activity coefficients. Here the variations among the results from using the Pitzer activity-coefficient relationships are less than the variations among the results using the two Debye-Hückel-based relationships. The Pitzer relationships are supposed to be more appropriate for concentrated solutions, and they show that quality here.

E. Mass Balances.

Table 7 presents mass balances on important elements for all four precipitation problems. The mass balances compare the calculated masses of particular elements in the final products with the masses of these elements initially specified. Tables 3-6 do not list all species considered in the calculations for the different problems, so values in these tables cannot be used for mass balances. Table 7 contains all the species involving the relevant elements considered in the calculations.

In Precipitation Problem #1, the calcium mass balances agree to within 1 in the fourth significant figure, displaying excellent agreement. In Precipitation Problem #2, the calcium mass balances agree to within 2 in the fourth significant figure, again showing excellent agreement.

Precipitation Problem #3 required more extensive calculations than either #1 or #2, so some error accumulation or some slippage in convergence would be expected. Table 7 shows that in this problem, the calcium mass balances agreed to within 8 in the fourth significant figure and the sulfur balances agreed to within 1 in the third significant figure. These levels of agreement are regarded as satisfactory.

Some of the mass balance agreements in Precipitation Problem #4 are not as good as those of the first three problems, sometimes differing in the second significant figure. While all four calcium mass balances agree within 1%, the sodium masses differ by up to 17%, the sulfur masses by up to 7%, and the chlorine masses by up to 16%. These numbers raise questions concerning the reliability of the code's predicted results for this problem. These results also show that mass balances can occasionally show difficulties in a speciation code's predictions.

F. Solubility Products

Ideally, all the values of the solubility products for a particular species should be identical. However, in Section IV.C above, it is noted that variation of solubility products among different models can be significant and occasionally drastic. For example, the $CaSO_4$ solubility products from the two sources used for ideal-solution calculations in Precipitation Problem #3 differ by a factor of 7.8. The two $Ca(OH)_2$ solubility products from the same sources are closer--they differ by 17%.

One test, therefore, of the consistency of different thermodynamic databases is the consistency of their solubility products for a given species. In this area the EQ3/6 calculations show excellent agreement among the solubility products of the different species. The solubility products using the COM database should be identical for all the $Ca(OH)_2$ precipitations in Precipitation Problems #1, #2, and #3, and they are. The same is true for the COM-calculation solubility products for $CaSO_4$ in Problem #3.

The solubility products for calculations using the PIT and HMW databases for both $Ca(OH)_2$ and $CaSO_4$ should be close to the solubility products for the two species using the COM database, and they are. The solubility products using the PIT database are essentially identical with those calculated using the COM database. The HMW database is supposed to be the most internally consistent of all the databases used by EQ3/6. The solubility products from calculations using the HMW database differ from those using the PIT database by 78% and 26% for $Ca(OH)_2$ and $CaSO_4$, respectively. This keeps them well within a factor of two, which is close to agreement for solubility products.

The free energies of formation for the constituents involved in the problems of this report are identical in the **data0.com** and **data0.pit** files. Thus, it is not surprising that the solubility products calculated using these databases are also identical. However, the solubility products calculated in the tables are slightly different than the solubility products listed in the databases. The solubility products listed in the databases agree with solubility products hand calculated from the database values of the free energies. The differences between the solubility products calculated from the concentrations and activity coefficients and the ones listed in the databases are small; they do not exceed 0.11 in the log K_{sp} values. The difference is perhaps caused by the convergence criteria of the calculations. Appendix B presents a sample calculation of log K_{sp} from a database listing of the free energies.

VIII. DISCUSSION

A. Comparison of Differences in Predicted Concentrations with Accuracy of Models and Data.

In Precipitation Problems #1, #2, and #3, the ion concentrations differ significantly for the various situations even though the amounts precipitated do not vary by large amounts. An outstanding example of this occurs in Problem #1, where the OH^- concentrations calculated using the Pitzer equations with different databases differ by more than a factor of three. It is important to compare these differences with those that might be expected to result from data reproducibility and model accuracy.

The paper by Harvie et al. (1984) states that their model matches experimental data within 10% in most cases. This work is the basis of the **hmw** database, and this database is the most internally consistent of those used in this study. As mentioned earlier, this database includes mutual consistency of activity coefficient data and standard state thermodynamic data. It also has a limited set of components and is restricted to 25°C, both of which could lead to improved accuracy.

Thus the 10% maximum difference between model and data is probably the best attainable at present. Differences in predictions somewhat greater than this should probably not be regarded as significant. Differences in predictions by factors of 2 or 3, however, are well beyond the reported range of agreement of models and data, and these again reinforce the warnings about the uses of these codes quoted in Section IV.C.

B. Approximate Invariance of the Amounts of $Ca(OH)_2$ Precipitated in Problem #1 but not in Problem #2.

1. The approximate invariance of the amounts of $Ca(OH)_2$ precipitated in Problem #1.

Table 3 shows that the precipitation amounts of $Ca(OH)_2$ predicted by the ideal-solution calculations closely approximate the precipitation amounts predicted by the nonideal-solution calculations. This is to be expected, since the solutions were concentrated in the calcium and hydroxyl ions, and most of these ions would precipitate as $Ca(OH)_2$ because of the low value of the solubility product. An analytical approach can support this intuition. Let

$x \equiv$ the moles of Ca precipitating. Then

$$K_{sp} = [Ca^{++}]\,[OH^-]^2 \quad \text{(ideal)} \quad , \tag{VIII-1}$$

$$K_{sp} = \gamma_{ca}[Ca^{++}]\,\gamma_{OH}^2[OH^-]^2 \quad \text{(real)} \quad , \tag{VIII-2}$$

$$K_{sp} = ([Ca^{++}]_0 - x_{ideal})([OH^-]_0 - 2x_{ideal})^2 \quad , \tag{VIII-3}$$

$$K_{sp} = \gamma_{Ca}([Ca^{++}]_0 - x_{real})\,\gamma_{OH}^2([OH^-]_0 - 2x_{real})^2 \quad , \text{ and} \tag{VIII-4}$$

$$\gamma_{Ca}([Ca^{++}]_0 - x_{real})\,\gamma_{OH}^2([OH^-] - 2x_{real})^2 = ([Ca^{++}]_0 - x_{ideal})([OH^-]_0 - 2x_{ideal})^2 \quad . \tag{VIII-5}$$

Let $\alpha \equiv x_{real} / x_{ideal}$, then (VIII-6)

$$\gamma_{Ca}\gamma_{OH}^2([Ca^{++}]_0 - \alpha x_{ideal})([OH^-]_0 - 2\alpha x_{ideal})^2 = ([Ca^{++}]_0 - x_{ideal})([OH^-] - 2x_{ideal})^2 \quad . \tag{VIII-7}$$

Let $\xi \equiv \gamma_{Ca}\gamma_{OH}^2$, then (VIII-8)

$$([Ca^{++}]_0 - \alpha x_{ideal})([OH^-] - 2\alpha x_{ideal})^2 = ([Ca^{++}]_0 - x_{ideal})([OH^-]_0 - 2x_{ideal})^2 / \xi \quad . \tag{VIII-9}$$

Equation (VIII-9) is an equation that is cubic in α. It may be solved for α to yield an expression of the form

$$\alpha = f(\xi) \tag{VIII-10}$$

Equation (VIII-10) may be expanded in a Taylor series around ξ_0:

$$\alpha \approx \alpha(\xi_0) + \left[\left. \frac{d\alpha}{d\xi} \right|_{\xi_0} \right] (\xi - \xi_0) + \frac{1}{2} \left[\left. \frac{d^2\alpha}{d\xi^2} \right|_{\xi_0} \right] (\xi - \xi_0)^2 + \ldots \tag{VIII-11}$$

The derivative of α may be found without the trouble of solving Eq. (VIII-9) explicitly for α. Taking derivatives of both sides of Eq. (VIII-9) w.r.t. ξ:

$$-([OH^-]_0 - 2\alpha x)^2 (x_{ideal}) \frac{d\alpha}{d\xi} - ([Ca^{++}]_0 - \alpha x_{ideal})(2)([OH^-]_0 - 2\alpha x_{ideal})(2x_{ideal}) \frac{d\alpha}{d\xi}$$

$$= - ([Ca^{++}]_0 - x_{ideal})([OH^-]_0 - 2x_{ideal})^2 / \xi^2 \quad . \qquad \text{(VIII-12)}$$

Solving for the derivative:

$$\frac{d\alpha}{d\xi} = \frac{([Ca^{++}]_0 - x_{ideal})([OH^-]_0 - 2x_{ideal})^2}{\xi^2([OH^-]_0 - 2\alpha x_{ideal})^2 \, (x_{ideal}) + ([Ca^{++}]_0 - \alpha x_{ideal}) \, (2) \, ([OH^-]_0 - 2\alpha x_{ideal}) \, (2x_{ideal})} \quad . \qquad \text{(VIII-13)}$$

Let $\xi_0 = 1$. Then $\alpha(\xi_0) = 1$, and the first two terms of the Taylor series reduce to

$$\alpha \approx 1 + \frac{([Ca^{++}]_0 - x_{ideal})([OH^-]_0 - 2x_{ideal})}{([OH^-]_0 - 2x_{ideal}) \, x_{ideal} + ([Ca^{++}]_0 - x_{ideal})(2)(2x_{ideal})} (\xi - 1) \quad . \qquad \text{(VIII-14)}$$

In Problem #1, $2x \approx [OH^-]_0$. Thus the numerator of the second term on the RHS of Eq. (VIII-14) is approximately zero. This makes α close to one, which means that the amount precipitated from the real solution is approximately equal to that predicted to precipitate by the ideal-solution calculation.

2. The significant variations in the amounts of $Ca(OH)_2$ precipitated in Problem #2. In Problem #2, $2x \neq [OH^-]_0$. Using Eq. (VIII-13) and values from Appendix A (the section on Problem #2) gives a value for $d\alpha/d\xi|_{\xi 0=1}$ of 0.686. This high value for the derivative indicates that nonidealities must be considered when predicting the amount of $Ca(OH)_2$ that will precipitate. The results of Problem #2 bear this out.

What Section 1 shows analytically is that in a solution highly concentrated in ions that are likely to precipitate, most of the material is predicted to precipitate regardless of whether an ideal solution is assumed or not. The previous paragraph shows analytically that a more realistic model than the ideal solution is needed to predict correctly the amount that precipitates when the solution is not concentrated in the precipitating ions. These two aspects of precipitation behavior would normally be expected. The above analyses thus provide support for what is intuitive.

Section A treated single-component precipitation. Section B immediately below and Appendix C apply this same approach to multicomponent precipitation. They derive standards for detecting situations where ideal-solution theory can be used to predict the amounts precipitated, and situations where ideal-solution theory cannot be used for this purpose. In multicomponent precipitation, the results are not intuitively obvious.

C. Approximate Invariance of the Amounts of $Ca(OH)_2$ and $CaSO_4 \bullet 2H_2O$ Precipitated in Problem #3.

1. The approximate invariance of the amount of $Ca(OH)_2$ precipitated in Problem #3. In Precipitation Problem #3, the ideal-solution calculations matched with reasonable accuracy the amounts of both gypsum and portlandite predicted to precipitate by the nonideal-solution calculations. This is reminiscent of the general chemistry truism that inclusion of nonideality in an equilibrium calculation often does not alter the calculated equilibrium concentrations significantly (e.g., Campbell 1970).

Appendix C studies this situation from a general point of view. In the general chemistry truism, the observation's cause is straightforward. The activity coefficients in the ratio that composes the equilibrium constant can approximately cancel out, and often do. The same can be true when precipitation occurs, as Appendix C discusses. However, there is another reason that ideal-solution calculations can predict well the amounts precipitated from nonideal solutions. Appendix C shows there are combinations of activity coefficients and concentrations that result in good prediction of precipitate amounts using the ideal solution approximation to a non-ideal solution. Appendix C also presents an approach that can predict when this effect takes place. The following paragraphs apply Appendix C's approach to the simultaneous precipitation of gypsum and portlandite in Precipitation Problem #3.

Let x be the amount of Ca^{++} ion that precipitates as $Ca(OH)_2$ and let y be the amount of Ca^{++} ion that precipitates as $CaSO_4{\bullet}2H_2O$. A relationship for x in terms of y may be obtained from a ratio of the solubility-product relationships. For the ideal calculations of this problem,

$$\frac{[Ca^{++}]([OH^-]_0 - 2x_{ideal})^2}{[Ca^{++}]([SO_4^{--}]_0 - y_{ideal})} = \frac{K_{sp[Ca(OH)2]}}{K_{sp[CaSO4]}} \quad . \tag{VIII-15}$$

Canceling where appropriate and solving for x yields

$$x_{ideal} = \tfrac{1}{2}\left\{[OH^-]_0 - \left[\frac{K_{sp[Ca(OH)2]}}{K_{sp[CaSO4]}}([SO_4^{--}]_0 - y_{ideal})\right]^{\frac{1}{2}}\right\} \quad . \tag{VIII-16}$$

For a real or nonideal solution the analog of Eq. (VIII-15) is

$$\frac{(\gamma_{Ca^{++}})\,[Ca^{++}](\gamma_{OH^-})^2([OH^-]_0 - 2x_{real})^2}{(\gamma_{Ca^{++}})[Ca^{++}](\gamma_{SO_4^{--}})([SO_4^{--}]_0 - y_{real})} = \frac{K_{sp[Ca(OH)2]}}{K_{sp[CaSO4]}} \quad , \tag{VIII-17}$$

and solving Eq. (VIII-17) for x gives the analog of Eq. (VIII-16) for real or nonideal solutions:

$$x_{real} = \tfrac{1}{2}\left\{[OH^-]_0 - \frac{\gamma_{SO_4^{--}}^{\frac{1}{2}}}{\gamma_{OH^-}}\left[\frac{K_{sp[Ca(OH02]}}{K_{sp[CaSO4]}}([SO_4]_0 - y_{real})\right]^{\frac{1}{2}}\right\} \quad . \tag{VIII-18}$$

Since almost all the calcium ion is precipitated in both the ideal and real-solution calculations, the approximation

$$x + y \approx [Ca^{++}]_0 \tag{VIII-19}$$

is valid. Solving this approximation for y and substituting it into Eqs. (VIII-16) and (VIII-18) give the implicit equations for x:

$$x_{ideal} \approx {}^1\!/_2 \left\{ [OH^-]_0 - \left[\frac{K_{sp[Ca(OH)2]}}{K_{sp[CaSO4]}} ([SO_4^{--}]_0 - [Ca^{++}]_0 + x_{ideal}) \right]^{1/2} \right\} \quad . \qquad \text{(VIII-20)}$$

and

$$x_{real} \approx {}^1\!/_2 \left\{ [OH^-]_0 - \frac{\gamma_{SO_4^{--}}^{1/2}}{\gamma_{OH^-}} \left[\frac{K_{sp[Ca(OH)2]}}{K_{sp[CaSO4]}} ([SO_4^{--}]_0 - [Ca^{++}]_0 + x_{real}) \right]^{1/2} \right\} \quad . \qquad \text{(VIII-21)}$$

What is of interest here are the two ratios x_{real}/x_{ideal} and y_{real}/y_{ideal}. To ease the algebra, we follow the guide of Appendix C and let $\alpha \equiv x_{real}/x_{ideal}$, $\beta \equiv y_{real}/y_{ideal}$, and $\xi \equiv \sqrt{\gamma_{SO4--}} / \gamma_{OH-}$. First consider α. From Eqs. (VIII-20) and (VIII-21),

$$\alpha \approx \frac{[OH^-]_0 - \xi \left[\frac{K_{sp[Ca(OH)2]}}{K_{sp[CaSO4]}} ([SO_4^{--}]_0 - [Ca^{++}]_0 + x_{real}) \right]^{1/2}}{[OH^-]_0 - \left[\frac{K_{sp[Ca(OH2)]}}{K_{sp[CaSO4]}} ([SO_4^{--}]_0 - [Ca^{++}]_0 + x_{ideal}) \right]^{1/2}} \quad . \qquad \text{(VIII-22)}$$

Substituting the RHS of $x_{real} \equiv \alpha x_{ideal}$ for x_{real} on the RHS of Eq. (VIII-22)'s numerator gives

$$\alpha \approx \frac{[OH^-]_0 - \xi \left[\frac{K_{sp[Ca(OH)2]}}{K_{sp[CaSO4]}} ([SO_4^{--}]_0 - [Ca^{++}]_0 + \alpha x_{ideal}) \right]^{1/2}}{[OH^-]_0 - \left[\frac{K_{sp[Ca(OH)2}}{K_{sp[CaSO4]}} ([SO_4^{--}]_0 - [Ca^{++}]_0 + x_{ideal}) \right]^{1/2}} \quad . \qquad \text{(VIII-23)}$$

This development assumes that the ideal calculations have been carried out, and the only unknowns in the above equation are α and ξ. The equation is implicit in α and can be written

$$\alpha \approx \alpha(\xi) \qquad \text{(VIII-24)}$$

Expanding this in a Taylor series gives

$$\alpha \approx \alpha(\xi_0) + \left[\left. \frac{d\alpha}{d\xi} \right|_{\xi_0} \right] (\xi - \xi_0) + \frac{1}{2} \left[\left. \frac{d^2\alpha}{d\xi^2} \right|_{\xi_0} \right] (\xi - \xi_0)^2 + \ldots \qquad \text{(VIII-25)}$$

Let $\xi_0 = 1$. Then solution of Eq. (VIII-23) for α gives

$$\alpha(\xi_0) = 1 \quad . \qquad \text{(VIII-26)}$$

This is equivalent to asking what happens if the effects of the activity coefficients cancel. The obvious answer is that $\alpha(\xi_0{=}1)$ should equal one, which it does.

If the second-order and higher terms in Eq. (VIII-25) are small, they may be ignored. When this occurs, Eq. (VIII-25) becomes

$$\alpha \approx 1 + \left[\left. \frac{d\alpha}{d\xi} \right|_{\xi_0} \right] (\xi - 1) \quad . \qquad \text{(VIII-27)}$$

The denominator of the RHS of Eq. (VIII-23) equals $2x_{ideal}$. Using this equality and taking derivatives of both sides of Eq. (VIII-23) yields

$$\frac{d\alpha}{d\xi} \approx \frac{1}{2x_{ideal}} \left\{ - [(K_{sp[Ca(OH)2]} / K_{sp[CaSO4]})([SO_4^{--}]_0 - [Ca^{++}]_0 + \alpha x_{ideal})]^{1/2} \right.$$

$$\left. - \tfrac{1}{2} \left[\frac{K_{sp[Ca(OH)2]}}{K_{sp[CaSO4]}} ([SO_4^{--}]_0 - [Ca^{++}]_0 + \alpha x_{ideal}) \right]^{-1/2} \left[\frac{K_{sp[Ca(OH)2]}}{K_{sp[CaSO4]}} \right] (x_{ideal}) \frac{d\alpha}{d\xi} \right\} \quad . \qquad \text{(VIII-28)}$$

Solving for $d\alpha/d\xi$ and setting ξ_0 equal to 1 is the next step. Setting ξ_0 equal to 1 makes α equal to 1; the first square-root term on the RHS of Eq. (VIII-14) equals $[OH^-]_0 - 2x_{ideal}$ when α equals 1. Implementing this gives

$$\frac{d\alpha}{d\xi}\Big|_{\xi 0=1} \approx - \frac{2([OH^-]_0 - 2x_{ideal})^2}{x_{ideal}[4([OH^-]_0 - 2x_{ideal}) + K_{sp[Ca(OH)2]} / K_{sp[CaSO4]}]} \quad , \qquad \text{(VIII-29)]}$$

and

$$\alpha \approx 1 - \left[\frac{2([OH^-]_0 - 2x_{ideal})^2}{x_{ideal}[4([OH^-]_0 - 2x_{ideal}) + K_{sp[Ca(OH)2]} / K_{sp[CaSO4]}]} \right] (\xi - 1) \quad . \qquad \text{(VIII-30)}$$

This is the equation that tells to what extent nonideality of Problem #3's mixture will affect the amount of calcium hydroxide precipitated. The term in brackets on the RHS of the equation is a sensitivity factor; it gives the sensitivity of the amount of $Ca(OH)_2$ precipitated to the nonideality of the solution. More precisely, it gives the sensitivity of the amount of $Ca(OH)_2$ precipitated to a ratio of activity coefficients.

Evaluating the terms in Eq. (VIII-29) for Precipitation Problem #3, using values for the ideal calculation taken from Appendix A, gives

$$\alpha \approx 1 - \left[\frac{2[0.833 - (2)(0.386)]^2}{(0.386)\,\{4[0.833 - (2)(0.386)] + 4.68\text{x}10^{-6} / 7.1\text{x}10^{-5}\}} \right] (\xi - 1) \quad . \qquad \text{(VIII-31)}$$

Carrying out the indicated arithmetic yields

$$\alpha \approx 1 - (0.062)(\xi - 1) \quad . \qquad \text{(VIII-32)}$$

For Problem #3, therefore, the sensitivity factor for calcium hydroxide precipitation equals 0.062. With a sensitivity factor this small, it is not likely that nonideality will affect the amount of calcium hydroxide precipitated to any marked extent. Using values of the calculated activity coefficients listed in Table 4, values of the factor $\xi - 1$ range from -0.12 to -0.68, resulting in values of α ranging from 1.01 to 1.04. This correctly predicts the observed range of 1.01 to 1.04.

2. The approximate invariance of the amount of $CaSO_4 \bullet 2H_2O$ precipitated in Problem #3. A similar procedure, only solving for the y's instead of the x's in the early steps, can produce an equation for y_{ideal}/y_{real} or β analogous to Eq. (VIII-30):

$$\beta \approx 1 + \left[\frac{(2)([SO_4^{--}]_0 - y_{ideal})}{y_{ideal}\{1 + 4[(K_{sp[CaSO4]} / K_{sp[Ca(OH)2]})([SO_4^{--}]_0 - y_{ideal})]^{1/2}\}} \right] (\xi - 1) \quad . \qquad \text{(VIII-33)}$$

Appendix D presents the complete derivation of this equation. The derivation is the analog for the y's of Eqs. (VIII-15) to (VIII-28). Equation (VIII-33) is the equation that tells to what extent nonideality of Problem #3's mixture will affect the amount of gypsum precipitated. The term in brackets on the RHS of the equation gives the sensitivity of the amount of $CaSO_4 \bullet 2H_2O$ precipitated to the nonideality of the solution or, more precisely, to the ratio of the relevant activity coefficients.

Evaluating the terms in Eq. (VIII-33) for Precipitation Problem #3, using values for the ideal calculation taken from Appendix A, gives

$$\beta \approx 1 + \left[\frac{(2)(1.173 - 1.115)}{(1.115)\,\{1 + (4)\,[(7.1\text{x}10^{-5} / 4.68\text{x}10^{-6})(1.173 - 1.115)]^{1/2}\}} \right] (\xi - 1) \quad . \qquad \text{(VIII-34)}$$

Carrying out this arithmetic gives

$$\beta \approx 1 + (0.022)(\xi - 1) \quad . \qquad \text{(VIII-35)}$$

This says that the sensitivity factor for gypsum precipitation is 0.022 for Problem #3. This factor is even smaller than that for calcium hydroxide precipitation. As above, this size of sensitivity factor says it is not likely that nonideality will affect the amount of gypsum precipitated to any marked extent. Using the factors of -0.12 and -0.68 that multiply ξ-1 predicts that the values of β should range from 1.00 to 0.98. The observed values of 0.97 to 0.94 are smaller but still in the same range. However, the differences here show that using Eq. (VIII-35), and by implication Eq. (VIII-27), does not necessarily give a quantitative value of the change in α or β when taking nonideality into account.

D. General Applications of the Sensitivity Factors.

1. Qualitative and quantitative aspects. The sensitivity factors derived above depend only upon ideal-solution properties. The examples given above and in Appendix C show that if the factors are sufficiently small, nonidealities will not significantly affect the amount or composition of the precipitate of sparingly soluble substances from a particular solution. Thus, frequently ideal-solution calculations can be used with confidence to predict precipitation results from nonideal solutions. This would be particularly valuable in situations where the information needed for calculating activity coefficients is unavailable.

If, however, the sensitivity factors are not small, the examples above and in Appendix C say that nonideality must be considered in calculations predicting precipitate amount and composition.

The sensitivity factors derived above and in Appendix C cannot be used quantitatively to predict precipitate composition and amount when the ideal-solution calculations will be inaccurate. The differences between the values of α and β predicted by the sensitivity factors and actually calculated can be significant. The truncation of the Taylor series after the first term introduces inaccuracy and diminishes its quantitative predictive ability. Nevertheless, the examples demonstrate the qualitative ability of the sensitivity factor to predict when ideal-solution theory can and cannot be used to predict precipitation composition and amount.

2. Future directions. The development of the sensitivity-factor principles presented above and in Appendix C concerned only one and two-component precipitate systems. An obvious need is the extension of this development to multicomponent systems with precipitates of three and more components.

It may also be possible to improve the accuracy of the sensitivity factors by numerically determining the higher derivatives using appropriate numerical speciation codes.

IX. CONCLUSIONS

Numerical speciation codes satisfy the simple qualitative consistency tests posed by four elementary equilibrium problems. Precipitates show higher solubilities when solutions are regarded as nonideal than when they are considered ideal. When substances possess low solubilities, codes predict almost complete precipitation. Both of these qualitative aspects agree with expectations and chemical theory. The EQ3/6 codes exhibited this behavior, and this conclusion assumes that other codes reflect the quality of the EQ3/6 codes.

Numerical speciation codes also satisfy some simple quantitative consistency tests posed by the four elementary equilibrium problems. Solubility products are identical when they are derived from the same database, and numerically close when they stem from different databases. For three of the four problems tested, mass balances checked with high accuracy. Calculations converge to values of concentration and activity coefficient which give solubility products close to those listed in the databases and those calculated from Gibbs free energy data. Like the previous conclusion, the EQ3/6 codes exhibited this behavior, and it is assumed that other codes reflect this quality.

On occasion, elemental mass balances based on the numerical results may not agree, indicating possible inaccuracies in the calculated final compositions. The phenomenon was observed in calculating precipitation from supernatant solutions, and this may be an important consideration in evaporation campaigns. An unsatisfactory mass balance can serve as an indicator of unreliability in a speciation code's predictions.

The predictions of the calculations carried out in solving the four problems illustrate warnings that exist in the literature about the use of numerical speciation codes. There were wide and unpredictable differences in the concentrations and activities of the various ions in the supernatant solutions. These resulted in significant differences in amounts precipitated in the problem modeling an evaporation campaign (Problem #4).

There are circumstances where a combination of concentrations and activity coefficient ratio allow ideal-solution theory to predict precipitation from nonideal solutions with reasonable accuracy. These circumstances can exist even when activity coefficients do not approximately cancel out in the pertinent relationships. Whether these circumstances exist for a particular situation can be predicted by suitable calculations.

X. ACKNOWLEDGMENTS

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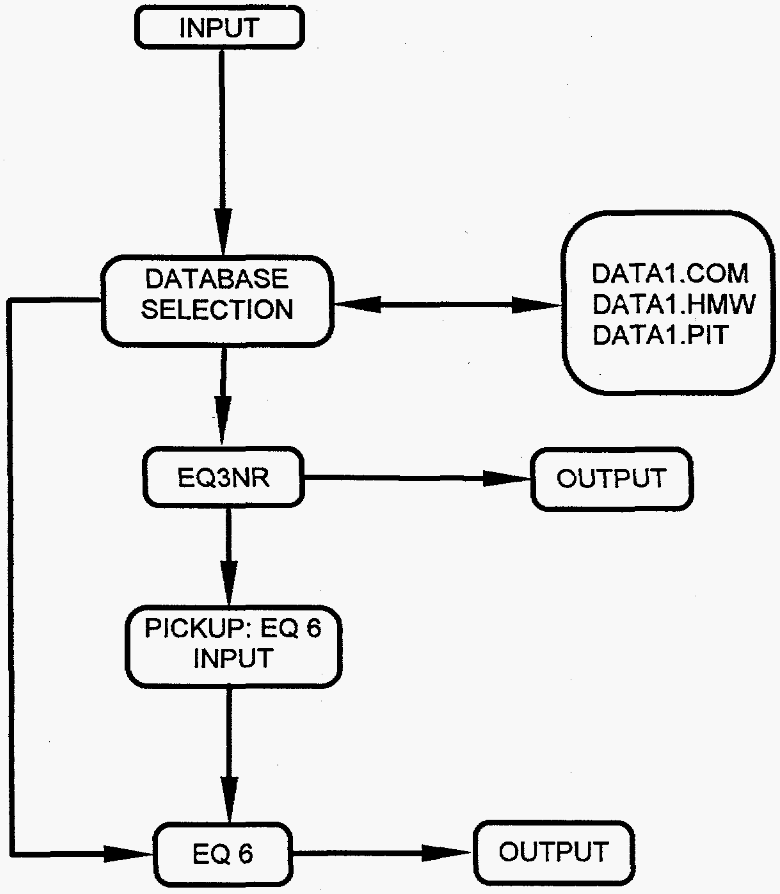

Figure 1. The flow of information among the computer codes EQPT, EQ3NR, and EQ6. This figure is modified from a more detailed diagram in Wolery (1992a). The codes and files depicted here are the ones relevant to this study. For the complete information flow among the EQ3/6 codes, Wolery's manual should be consulted.

Table 1. MAJOR CHARACTERISTICS OF CHEMICAL EQUILIBRIA CODES[(a)]

Code Name	Elements	Aqueous Species	Organics	Gases	Redox Elements	Precip./ Dissoln. Minerals	Activity Coeff.
ECHEM	>34	>520	no	7	>38	>340	Davies & D-H
EQUILIB	26	200	no	7	9	186	D-H
EQ3/6	47	686	<10	11	>25	713	D-H, Davies & Pitzer
MINTEQ	31	373	no	3	8	328	D-H & Davies
PHREEQE	19	120	yes	3	3	21	Davies, neutral species & Pitzer
SOILCHEM	47	1853	889	3	11	250	Davies & D-H
TRANSCHEM	100	300	50	50	10	50	Bromley-Zemaitis & Pitzer
WATEQ4F	30	245	12	2	7	321	Truesdell-Jones, D-H & Davies

(a) Adapted from a table presented by Mangold and Tsang (1991).

Table 2. MAJOR CHARACTERISTICS OF THE EQ3/6 DATA FILES[a]

File Name (Suffix)	**com**	**sup**	**nea**	**pit**	**hmw**
Source	GEMBOCHS (LLNL)[b]	SUPCRT92[c]	NEA draft report[d]	Pitzer (1979)	Harvie, Møller, & Weare
(1984)					
Activity Coefficient Relationship	Extended Debye-Hückel	Extended Debye-Hückel	Extended Debye-Hückel	Pitzer's Equations	Pitzer's Equations
Temperature Limits	0-300°C	0-300°C	0-300°C	0-100°C	25°C
Number of Chemical Elements	78	69	32	52	9
Number of Basis Species	147	105	50	62	13
Number of Aqueous Species	852	315	158	68	17
Number of Pure Minerals	886	130	188	381	51
Number of Solid Solutions	12	0	0	0	0
Number of Gas Species	76	16	76	38	3

(a) Adapted from a table in Wolery (1992a).

(b) GEMBOCHS is a software code developed at Lawrence Livermore National Laboratory.

(c) The **sup** data file is based entirely on SUPCRT92 (Johnson, Oelkers, and Helgeson 1992).

(d) The **nea** data file is based on a database developed as part of the Thermochemical Data Base project of the Nuclear Energy Agency of the Organization for Economic Cooperation and Development. The first volume of a projected series reporting these data has appeared (Wanner and Forest 1992).

Table 3. RESULTS FROM SOLVING PRECIPITATION PROBLEM #1– PRECIPITATION OF PORTLANDITE FROM A CONCENTRATED SOLUTION

Database	Ideal Soln. #1(a)	Ideal Soln. #2(b)	COM, Davies	COM, B-dot	PIT	HMW
The Precipitate:						
Amt. $Ca(OH)_2$ ppt., g/L	46.3	46.3	45.43	45.44	45.91	44.93
x_{real}/x_{ideal}			0.98	0.98	0.99	0.97
The liquid:						
pH	11.2	11.3	11.4	11.7	11.8	11.9
$[Ca^{++}]$, mol/L	1.628	1.628	0.624	1.150	1.633	1.647
$[OH^{-}]$, mol/L	0.0017	0.0018	0.0026	0.0055	0.0119	0.0381
γ_{Ca++}	1.000	1.000	2.653	0.347	2.255	2.211
γ_{OH-}	1.000	1.000	0.566	0.550	0.0842	0.0349
$pK_{sp[Ca(OH)2]}$ (fr. concs. & γs			5.44	5.44	5.44	5.19
$pK_{sp[Ca(OH)2]}$ (fr. databases)	5.33	5.26	5.21(c)	5.21(c)	5.21(c)	5.19(c)

(a) Using solubility products from Lide (1993).

(b) Using solubility products from Dean (1992).

(c) Calculated from standard free energies of formation in database.

Table 4. RESULTS FROM SOLVING PRECIPITATION PROBLEM #2--POSSIBLE PRECIPITATION OF PORTLANDITE

Database	Ideal Soln. #1(a)	Ideal Soln. #2(b)	COM, Davies	COM, B-dot	PIT	HMW
<u>The Precipitate</u>:						
Amt. $Ca(OH)_2$ ppt., g/L	0.350	0.310	0.0	0.0	0.348	0.0
x_{real}/x_{ideal}			0	0	0.99	0
<u>The liquid</u>:						
pH	12.1	12.2	12.3	12.2	12.6	12.6
$[Ca^{++}]$, mol/L	0.0193	0.0195	0.0133	0.0189	0.0193	0.0240
$[OH^-]$, mol/L	0.0156	0.0166	0.0228	0.0284	0.0397	0.0491
γ_{Ca++}	1.000	1.000	1.08	0.234	0.594	0.492
γ_{OH-}	1.000	1.000	0.580	0.284	0.451	0.423
$pK_{sp[Ca(OH)2]}$ (fr. concs. & γ's)			(c)	(c)	5.44	(c)
$pK_{sp[Ca(OH)2]}$ (fr. databases)	5.33	5.26	5.21(d)	5.21(d)	5.21(d)	5.19(d)

(a) Using solubility products from Lide (1993).

(b) Using solubility products from Dean (1992).

(c) Solubility products cannot be calculated from solute concentrations and activity coefficients because no precipitation occurs.

(d) Calculated from standard free energies of formation in database.

Table 5. RESULTS FROM SOLVING PRECIPITATION PROBLEM #3--SIMULTANEOUS PRECIPITATION OF GYPSUM AND PORTLANDITE

Database	Ideal Soln. #1(a)	Ideal Soln. #2(b)	COM, Davies	COM, B-dot	PIT	HMW
The Precipitate:						
Amt. $Ca(OH)_2$ ppt., g/L	28.6	26.3	28.9	28.8	29.8	29.3
Amt. gypsum ppt., g/L	192.0	197.6	185.9	181.3	184.1	184.7
x_{real}/x_{ideal}			1.01	1.01	1.04	1.02
y_{real}/y_{ideal}			0.97	0.94	0.96	0.96
The liquid:						
pH	12.8	13.1	12.2	12.3	12.2	12.3
$[Ca^{++}]$, mol/L	0.00123	0.00036	0.0137	0.0443	0.0314	0.0354
$[OH^{-}]$, mol/L	0.061	0.124	0.0242	0.0321	0.0312	0.0462
$[SO_4^{--}]$, mol/L	0.058	0.026	0.00867	0.0402	0.108	0.104
γ_{Ca++}	1.000	1.000	1.37	0.249	0.626	0.538
γ_{OH-}	1.000	1.000	0.576	0.569	0.438	0.398
γ_{SO4--}	1.000	1.000	0.255	0.0929	0.0199	0.0170
$pK_{sp[Ca(OH)2]}$ (fr. concs. & γ's)			5.44	5.43	5.44	5.19
$pK_{sp[Ca(OH)2]}$ (fr. databases)	5.33	5.26	5.21(c)	5.21(c)	5.21(c)	5.19(c)
$pK_{sp[CaSO4]}$ (fr. concs. & γ's)			4.38	4.39	4.37	4.47
$pK_{sp[CaSO4]}$ (fr. databases)	4.15	5.04	4.31(c)	4.31(c)	4.31(c)	4.36(c)

(a) Using solubility products from Lide (1993).

(b) Using solubility products from Dean (1992).

(c) Calculated from standard free energies of formation in database.

Table 6. RESULTS FROM SOLVING PRECIPITATION PROBLEM #4-- EVAPORATION OF WATER FROM SUPERNATANT SOLUTIONS RESULTING FROM PROBLEM #2

Amounts of precipitates and water are per liter of original solution.

Database	Ideal Soln. [(a)]	COM, Davies	COM, B-dot	PIT	HMW
The Precipitate:					
Portlandite $[Ca(OH)_2]$, g	0.088	1.46	1.11	1.00	1.45
Halite [NaCl], g	162.2	154.2	147.4	167.8	168.2
Thenardite $[Na_2SO_4]$, g	4.08	7.54	5.25	5.95	5.85
Glauberite $[Na_2Ca(SO_4)_2]$, g	0.165	3.81	8.05	5.00	4.40
The liquid:					
pH	14.1	13.2	13.2	13.6	13.7
H_2O, g	45.2[(b)]	45.2	45.2	45.2	45.2
$[Na^+]$, mol/L	7.66	4.75	7.19	6.99	6.97
$[Ca^{++}]$, mol/L	0.0	0.00017	0.00267	0.00067	0.00146
$[Cl^-]$ mol/L	5.03	4.33	6.49	5.57	5.44
$[OH^-]$, mol/L	1.30	0.0574	0.0860	0.0955	0.142
$[SO_4^{--}]$, mol/L	0.642	0.00331	0.0799	0.665	0.697
γ_{Na+}	1.000	3.41	1.55	1.86	1.84
γ_{Ca++}	1.000	21.82	0.654	3.55	2.43
γ_{Cl-}	1.000	0.548	0.533	0.533	0.532
γ_{OH-}	1.000	0.548	0.533	0.411	0.301
γ_{SO4--}	1.000	0.562	0.0496	0.00438	0.00447

Table 6 (cont.)

Database	Ideal Soln.[a]	COM, Davies	COM, B-dot	PIT	HMW
<u>The liquid (cont.)</u>:					
$pK_{sp[Ca(OH)2]}$ (fr. concs. & γ's)		5.44	5.44	5.44	5.19
$pK_{sp[Ca(OH)2]}$ (fr. databases)	5.21[c]	5.21[c]	5.21[c]	5.21[c]	5.19[c]
$pK_{sp[NaCl]}$ (fr. concs. & γ's)		-1.59	-1.59	-1.59	-1.57
$pK_{sp[NaCl]}$ (fr. databases)	-1.59	-1.59[c]	-1.59[c]	-1.59[c]	-1.57[c]
$pK_{sp[Na2SO4]}$ (fr. concs. & γ's)		0.31	0.31	0.31	0.29
$pK_{sp[Na2SO4]}$ (fr. databases)	0.31	0.31[c]	0.31[c]	0.31[c]	0.29[c]
$pK_{sp[Na2Ca(SO4)2]}$ (fr. concs. & γ's)		5.47	5.47	5.47	5.25
$pK_{sp[Na2Ca(SO4)2]}$ (fr. databases)	5.47	5.47[c]	5.47[c]	5.47[c]	5.24[c]

(a) Using solubility products from the COM database.

(b) This value assumed to match results of EQ3/6 runs.

(c) Calculated from standard free energies of formation in database.

Table 7. MASS BALANCES

All quantities are in moles. Total amounts calculated to be entering or leaving are underlined. In theory, the amount of a particular ion entering should agree with the sum of the amounts of that ion leaving.

Database	COM, Davies	COM, B-dot	PIT	HMW
Precipitation Problem #1 Portlandite Precipitation				
Calcium Balance:				
Ca^{++} in entering $CaCl_2$ solution	4.505	4.505	4.505	4.505
Calcium in precipitated $Ca(OH)_2$	1.226	1.227	1.239	1.213
Ca^{++} ion in final solution	1.248	2.300	3.267	3.293
$CaCl^+$ in final solution	0.552	0.305		
$CaCl_2(aq)$	1.439	0.640		
$CaOH^+$ in final solution	0.041	0.034		
Total calcium in final forms	4.506	4.506	4.506	4.506
Precipitation Problem #2 Possible Portlandite Precipitation				
Calcium Balance:				
Ca^{++} in entering $CaCl_2$ solution	0.07208	0.07208	0.07208	0.07208
Calcium in precipitated $Ca(OH)_2$			0.01410	
Ca^{++} ion in final solution	0.03979	0.05680	0.05799	0.07206
$CaCl^+$ in final solution	0.00920	0.00515		
$CaCl_2(aq)$	0.01667	0.00601		
$CaOH^+$ in final solution	0.00644	0.00413		
Total calcium in final forms	0.07209	0.07209	0.07209	0.07206

Table 7 (cont.)

Database	COM, Davies	COM, B-dot	PIT	HMW
Precipitation Problem #3 Simultaneous Portlandite and Gypsum Precipitation				
Calcium Balance:				
Ca^{++} in entering $CaCl_2$ solution	4.505	4.505	4.505	4.505
Calcium in precipitated $Ca(OH)_2$	1.170	1.165	1.208	1.186
Calcium in precipitated $CaSO_4{\bullet}2H_2O$	3.239	3.159	3.208	3.218
Ca^{++} ion in final solution	0.041	0.133	0.0943	0.1062
$CaCl^+$ in final solution	0.012	0.013		
$CaCl_2(aq)$	0.024	0.016		
$CaOH^+$ in final solution	0.008	0.011		
Calcium in $CaSO_4(aq)$	0.016	0.016		
Total calcium in final forms	4.510	4.513	4.510	4.510
Sulfur Balance:				
Sulfur in entering Na_2SO_4 solution	3.520	3.520	3.520	3.520
Sulfur in precipitated $CaSO_4{\bullet}2H_2O$	3.239	3.159	3.208	3.218
Sulfur in SO_4^{--}	0.026	0.121	0.323	0.313
Sulfur in $NaSO^-$	0.249	0.237		
Sulfur in $CaSO_4(aq)$	0.016	0.016		
Total sulfur in final forms	3.530	3.533	3.532	3.531

Table 7 (cont.)

Database	COM, Davies	COM, B-dot	PIT	HMW
Precipitation Problem #4 Evaporation of Water				
Calcium Balance:				
Calcium in entering solution	0.03363	0.04434	0.03143	0.03541
Calcium in precipitated $Ca(OH)_2$	0.01965	0.01498	0.01344	0.01952
Calcium in precipitated $Na_2Ca(SO_4)_2$	0.01368	0.02893	0.01796	0.01582
Ca^{++} ion in final solution	0.00001	0.00022	0.00004	0.00009
$CaCl_2(aq)$ in final solution	0.00036	0.00040		
$CaSO_4(aq)$ in final solution	0.00007	0.00007		
$CaCl^+$ in final solution	0.00004	0.00006		
$CaOH^+$ in final solution	0.00004	0.00006		
Total calcium in final forms	0.03385	0.04472	0.03144	0.03543
Sodium Balance:				
Sodium in entering solution	3.3087	3.3054	3.3074	3.3070
Sodium in precipitated NaCl	2.6378	2.5218	2.8717	2.8779
Sodium in precipitated $Na_2Ca(SO_4)_2$	0.0274	0.0579	0.0359	0.0316
Sodium in precipitated Na_2SO_4	0.1062	0.0740	0.0838	0.0824
Na^+ in final solution	0.3649	0.6011	0.4502	0.4482
NaCl(aq) in final solution	0.4939	0.5380		
$NaSO_4^-$ in final solution	0.0280	0.0386		
NaOH(aq) in final solution	0.0259	0.0282		
Total sodium in final forms	3.6841	3.8596	3.4416	3.4401

Table 7 (cont.)

Database	COM, Davies	COM, B-dot	PIT	HMW
Precipitation Problem #4 Evaporation of Water (cont.)				
Sulfur Balance:				
Sulfur in entering solution	0.09711	0.11934	0.10788	0.10433
Sulfur in precipitated $Na_2Ca(SO_4)_2$	0.01368	0.02893	0.01796	0.01582
Sulfur in precipitated Na_2SO_4	0.05309	0.03699	0.04190	0.04118
SO_4^{-} ion in final solution	0.00025	0.00668	0.04283	0.04481
$NaSO_4^-$ in final solution	0.02797	0.03858		
$CaSO_4$(aq) in final solution	0.00007	0.00007		
Total sulfur in final forms	0.09507	0.11124	0.10269	0.10182
Chlorine Balance:				
Chlorine in entering solution	3.1246	3.1063	3.1233	3.1237
Chlorine in precipitated NaCl	2.6378	2.5218	2.8717	2.8779
Cl^- ion in final solution	0.3321	0.5426	0.3585	0.3497
NaCl(aq) in final solution	0.4939	0.5380		
2 x $CaCl_2$(aq) in final solution	0.0007	0.0008		
$CaCl^+$ in final solution	0.00004	0.00007		
Total chlorine in final forms	3.4646	3.6032	3.2302	3.2276

Appendix A

PROBLEM STATEMENTS OF FOUR SIMPLE PRECIPITATION PROBLEMS AND SAMPLE PROBLEM CALCULATIONS FOR IDEAL SOLUTIONS

Precipitation Problem #1

Precipitation of Calcium Hydroxide (Portlandite) by Mixing of Concentrated Solutions of Calcium Chloride and Sodium Hydroxide

Problem Statement. One liter of a water solution containing 500 g dissolved $CaCl_2$ is mixed at 25°C with one liter of a water solution containing 100 g dissolved NaOH. How much $Ca(OH)_2$ precipitates? What are the species remaining in solution, and how much is there of each species?

Data.	Atomic Weights:	Ca:	40.08
		Cl:	35.453
		H:	1.0079
		Na:	22.98977
		O:	15.9994
	Molecular Weights:	$CaCl_2$:	110.99
		NaOH:	40.00
		$Ca(OH)_2$:	74.09

Solubility Product of $Ca(OH)_2$: 4.68×10^{-6} [From Lide (1993)].

Solution #1--Using Solubility Product and Assuming an Ideal Solution.

Total volume of solution: 2 liters.

Initial molar amounts: 500/110.99 = 4.505 moles $CaCl_2$.
100/40.00 = 2.500 moles NaOH.

Molar concentrations: Sodium ion: 2.500/2.000 = 1.250 moles/liter Na^+.
Chloride ion: (4.505)(2)/2.000 = 4.505 moles/liter Cl^-.

Solubility of $Ca(OH)_2$ in water:
Reaction: $Ca^{++} + 2OH^-$ Solubility product relationship: $[Ca^{++}][OH^-]^2 = 4.68 \times 10^{-6}$.
Let x be the gram-equivalents of Ca^{++} that precipitate from one liter of solution as $Ca(OH)_2$.
Then the amounts remaining in solution are:

$[OH^-] = [OH^-]_0 - 2x$; $\{[OH^-]_0 = 1.250$ moles/liter$\}$
$[Ca^{++}] = [Ca^{++}]_0 - x$; $\{[Ca^{++}]_0 = 2.253$ moles/liter$\}$.

From the solubility product relationship:

$\{[Ca^{++}]_0 - x\}\{[OH]_0 - 2x\}^2 = 4.68 \times 10^{-6}$

Since

$2x \approx [OH]_0$, $x \approx 0.625$ moles/liter
$[Ca^{++}] \approx 2.253 - 0.625 = 1.628$ moles/liter
$[OH^-]^2 \approx 4.68 \times 10^{-6}/1.628$
$[OH^-] \approx 1.696 \times 10^{-3}$ moles/liter

The pH of the solution is $-\log[(10^{-14})/(1.696 \times 10^{-3})] = 11.2$.

An iteration of the solution procedure, using the new value of $[OH^-]$, gives a corrected value of $[OH^-]$ of 1.695×10^{-3} moles/liter. The first solution is close enough.

An ion balance on the process: The mixed solution had 2.50 moles Na^+ ions and 2.50 moles OH^- ions from the sodium hydroxide solution. The mixed solution had 4.505 moles Ca^{++} ions and 9.010 Cl^- ions from the calcium chloride solution. Essentially all the hydroxyl ions and 1.25 moles of Ca^{++} ion precipitated, leaving 3.26 moles Ca^{++} ion in the solution. The 3.26 Ca^{++} plus the 2.50 moles Na^+ ion balance the 9.01 moles Cl^- in the solution.

Amount of calcium hydroxide precipitating: 1.25 moles of Ca^{++} precipitates, which means that 1.25 moles of $Ca(OH)_2$ precipitates. $1.25 \times 74.09 = 92.6$ g of calcium hydroxide precipitates.

Precipitation Problem #2

Possible Precipitation of Calcium Hydroxide from Mixing Dilute Solutions of Calcium Chloride and Sodium Hydroxide with a Concentrated Sodium Chloride Solution

Problem Statement. One-liter batches of three solutions are mixed together at 25°C. One liter of a water solution containing 8 g dissolved $CaCl_2$, one liter of a water solution containing 3 g dissolved NaOH, and one liter of a water solution containing 500 g dissolved NaCl are mixed together. How much $CaSO_4$ precipitates? What are the species remaining in solution, and how much is there of each species?

Data.	Atomic Weights:	Ca:	40.08
		Cl:	35.453
		H:	1.0079
		Na:	22.98977
		O:	15.9994
	Molecular Weights:	$CaCl_2$:	110.99
		NaOH:	40.00
		NaCl:	58.45
		$Ca(OH)_2$:	74.09

Solubility Product of $Ca(OH)_2$: 4.68×10^{-6} [From Lide (1993)].

Solution #1--Using Solubility Product and Assuming an Ideal Solution.

Total volume of solution: 3 liters.

Initial molar amounts: $8/110.99 = 0.07208$ moles $CaCl_2$.
$3/40.00 = 0.07500$ moles NaOH.
$500/58.45 = 8.554$ moles NaCl.

Initial molar concentrations: Sodium ion: $(0.075+8.554)/3.000 = 2.876$ moles/liter Na^+.
Chloride ion: $(0.0721+8.554)/3.000 = 2.875$ moles/liter Cl^-.
Hydroxyl ion: $0.0750/3 = 0.02500$ moles/liter OH^-.
Calcium ion: $0.07208/3 = 0.02403$ moles/liter Ca^{++}.

Solubility of $Ca(OH)_2$ in $CaCl_2$-NaOH-NaCl solution:
Reaction: $Ca^{++} + 2OH^-$.
Solubility product relationship: $[Ca^{++}][OH^-]^2 = 4.68 \times 10^{-6}$.
Let x be the gram-equivalents of Ca^{++} that precipitate from one liter of solution as $Ca(OH)_2$.

Then the amounts remaining in solution are:

$[OH^-] = [OH^-]_0 - 2x$; $\{[OH^-]_0 = 0.02500$ moles/liter$\}$

$[Ca^{++}] = [Ca^{++}]_0 - x$; $\{[Ca^{++}]_0 = 0.02403$ moles/liter$\}$

From the solubility product relationship:

$$\{[Ca^{++}]_0 - x\}\{[OH]_0 - 2x\}^2 = 4.68 \times 10^{-6}$$

The approximation made in Problem #1 is not possible here. Solving this cubic equation by trial-and-error yields

$x = 0.00472$ moles/liter

$[Ca^{++}] = 0.02403 - 0.00472 = 0.01931$ moles/liter

$[OH^-] = 0.02500 - (2)(0.00472) = 0.01556$ moles/liter

The pH of the solution is $-\log[(10^{-14})/(0.01556)] = 12.1$

Amount of calcium hydroxide precipitating: 0.00472 mol/L of Ca^{++} precipitates, which means that 0.00472 mol/L of $Ca(OH)_2$ precipitates. 0.00472 x 74.09 = 0.350 g/L of calcium hydroxide precipitates, or a total of 1.049 g of calcium hydroxide precipitates from the 3 liters of solution.

Precipitation Problem #3

Simultaneous Precipitation of Calcium Sulfate (Gypsum) and Calcium Hydroxide (Portlandite) by Mixing of Solutions of Calcium Chloride, Sodium Sulfate, and Sodium Hydroxide

Problem Statement. One-liter batches of three solutions are mixed together at 25°C. One liter of a water solution containing 500 g dissolved $CaCl_2$, one liter of a water solution containing 100 g dissolved NaOH, and one liter of a water solution containing 500 g dissolved Na_2SO_4 are mixed together. How much $Ca(OH)_2$ precipitates and how much $CaSO_4$ precipitates? What are the species remaining in solution, and how much is there of each species?

Data.

Atomic Weights:	Ca:	40.08
	Cl:	35.453
	H:	1.0079
	Na:	22.98977
	O:	15.9994
	S:	32.066
Molecular Weights:	$CaCl_2$:	110.99
	NaOH:	40.00
	Na_2SO_4:	142.06
	$Ca(OH)_2$:	74.09
	$CaSO_4$:	136.14

Solubility Product of $Ca(OH)_2$: 4.68×10^{-6} [From Lide (1993)].

Solubility Product of $CaSO_4$: 7.1×10^{-5} [From Lide (1993)].

Solution #1--Using Solubility Products and Assuming an Ideal Solution.

Total volume of solution: 3 liters.

Initial molar amounts: 500/110.99 = 4.505 moles $CaCl_2$.
100/40.00 = 2.500 moles NaOH.
500/142.06 = 3.520 moles Na_2SO_4

Initial molar concentrations (before precipitation):

Calcium ion, $[Ca^{++}]_0$: 4.505/3.000 = 1.502 moles/liter Ca^{++}.
Sodium ion, $[Na^+]_0$: [2.500+(2)(3.520)]/3.000 = 3.180 moles [illegible]r Na^+.
Chloride ion, $[Cl^-]_0$: 9.010/3.000 = 3.003 moles/liter Cl^-.
Hydroxyl ion, $[OH^-]_0$: 2.500/3.000 = 0.833 moles/liter OH^-.
Sulfate ion, $[SO_4^{--}]_0$: 3.520/3.000 = 1.173 moles/liter SO_4^{--}.

Solubility of $Ca(OH)_2$ in water:
Reaction: $Ca^{++} + 2OH^-$ Solubility product relationship: $[Ca^{++}][OH$ [illegible] 4.68×10^{-6}.
Solubility of $CaSO_4$ in water:
Reaction: $Ca^{++} + SO_4^{--} \Leftrightarrow CaSO_4$
Solubility product relationship: $[Ca^{++}][SO_4] = 7.1 \times 10^{-5}$.
Let x be the gram-equivalents of Ca^{++} that precipitate from on [illegible] of solution as $Ca(OH)_2$.
Let y be the gram-equivalents of Ca^{++} that precipitate from on [illegible] of solution as $CaSO_4$.
Then the amounts remaining in solution are:

$[Ca^{++}] = [Ca^{++}]_0 - x - y$;
$[OH^-] = [OH^-]_0 - 2x$;
$[SO_4^{--}] = [SO_4^{--}]_0 - y$.

From the solubility product relationships:

$$\{[Ca^{++}]_0 - x - y\}\{[OH^-]_0 - 2x\}^2 = 4.68 \times 10^{-6}$$

and

$$\{[Ca^{++}]_0 - x - y\}\{[SO_4^{--}]_0 - y\} = 7.1 \times 10^{-5}$$

Now, since there is an excess of sulfate and hydroxyl ions over that necessary to precipitate all the calcium ions, it may be assumed that

$$x + y \approx 1.502 \quad .$$

The first factor on the LHS of the first two equations is very small, and best set equal to $[Ca^{++}]$. Thus there are three equations and three unknowns, x, y, and $[Ca^{++}]$. Solving the three equations simultaneously yields

$$[Ca^{++}] = 1.248 \times 10^{-3} \text{ moles/liter.}$$

For a better value of the quantity x + y, take $1.502-1.248 \times 10^{-3} = 1.501$. Solving the three equations again simultaneously yields

x = 0.386 moles/liter of Ca^{++} precipitated as $Ca(OH)_2$.
y = 1.115 moles/liter of Ca^{++} precipitated as $CaSO_4$.
$[OH^-]$ = 0.833 - (2)(0.386) = 0.061 moles/liter.
$[SO_4^{--}]$ = 1.173 - 1.115 = 0.058 moles/liter.

$[OH^-]$ is 0.061 M. The pH of the solution is $-\log[(10^{-14})/0.061] = 12.8$.

An ion balance on the process: The mixed solution had 12.50 moles Na^+ ions and 12.50 moles OH^- ions from the sodium hydroxide solution. The mixed solution had 4.505 moles Ca^{++} ions and 9.010 Cl^- ions from the calcium chloride solution. Essentially all the calcium and 9.010 moles of OH^- ion precipitated, leaving 3.49 moles OH^- ion in the solution. The 9.010 Cl^- plus the 3.49 moles OH^- ion balance the 12.50 moles Na^+ in the solution.

The solution gives 0.386 mol/L of Ca^{++} precipitating as $Ca(OH)_2$, which means that (0.386)(74.09) = 28.6 g/L $Ca(OH)_2$ precipitates, or (3)(28.6) = 85.8 g total $Ca(OH)_2$ precipitates from the 3-liter mixture. The solution also gives 1.115 moles/liter of Ca^{++} precipitating as $CaSO_4$, which means that (1.115)(136.14) = 151.8 g/L $CaSO_4$ precipitates, or (151.8)(3) = 455.4 g of $CaSO_4$ precipitates from the 3-liter mixture. Since the $CaSO_4$ precipitates from a water solution, it will appear as the hydrate gypsum ($CaSO_4 \bullet 2H_2O$), and the amount will be (151.8)(172.17/134.16) = 192.0 g/L gypsum precipitating.

Precipitation Problem #4

Evaporation of Supernatant Solution Remaining From Simultaneous Precipitation of Calcium Hydroxide and Calcium Sulfate

Problem Statement. The supernatant solutions remaining from the precipitations in Precipitation Problem #3 are evaporated almost to dryness. What substances precipitate in each case, and how much of each substance precipitates? What are the properties and compositions of any liquids remaining?

Data.			
Atomic Weights:	Ca:	40.08	
	Cl:	35.453	
	H:	1.0079	
	Na:	22.98977	
	O:	15.9994	
	S:	32.066	
Molecular Weights:	$CaCl_2$:	110.99	
	$Ca(OH)_2$:	74.09	
	$CaSO_4$:	136.14	
	NaCl:	58.443	
	NaOH:	40.000	
	Na_2SO_4:	142.043	
	$Na_2Ca(SO_4)_2$	278.18	
Solubility Products:	$Ca(OH)_2$:		6.19×10^{-6}
	NaCl:		38.5
	Na_2SO_4:		0.491
	$Na_2Ca(SO_4)_2$:		3.40×10^{-6}

(all from the COM database)

Solution #1--Using Solubility Products and Assuming an Ideal Solution.

When EQ3/6 was used to evaporate the water, the initial solution was one liter, and the final product solutions all contained 45.2 g of water. Assume the same amounts for the ideal calculations. Thus, the original 3 liters of solution will become 1 liter for this calculation.

Initial molar amounts:	Na^+:	(2.500+3.520*2)/3 = 3.180 moles Na^+
	Cl^-:	(4.505*2)/3 = 3.003 moles Cl^-
from	Ca^{++}:	0.00123 moles Ca^{++}
Problem	OH^-:	0.061 moles OH^-
#3	SO_4^{--}:	0.058 moles SO_4^{--}

Initial molar concentrations:	$[Na^+]_0$:	3.180/0.0452 = 70.35 mol/L
	$[Cl^-]_0$:	3.003/0.0452 = 66.44
	$[Ca^{++}]_0$:	0.00123/0.0452 = 0.0272
	$[OH^-]_0$:	0.061/0.0452 = 1.35
	$[SO_4^{--}]_0$:	0.058/0.0452 = 1.28

Equations:

$$[Na^+][Cl^-] = 38.5$$

$$[Na^+]^2[SO_4^{--}] = 0.491$$

$$[Ca^{++}][OH^-]^2 = 6.19 \times 10^{-6}$$
$$[Na^+]^2[Ca^{++}][SO_4^{--}]^2 = 3.40 \times 10^{-6}$$

Unknowns:

$w \equiv$ mol/L of Na^+ going to NaCl
$x \equiv$ mol/L of Na^+ going to Na_2SO_4
$y \equiv$ mol/L of Na^+ going to $Na_2Ca(SO_4)_2$
$z \equiv$ mol/L of Ca^{++} going to $Ca(OH)_2$

Resulting equations:

$$([Na^+]_0\text{-}w\text{-}x\text{-}y)([Cl^-]_0\text{-}w) = 38.5$$
$$([Na^+]_0\text{-}w\text{-}x\text{-}y)^2([SO_4^{--}]_0\text{-}x) = 0.491$$
$$([Na^+]_0\text{-}w\text{-}x\text{-}y)^2([Ca^{++}]_0\text{-}\tfrac{1}{2}y\text{-}z)([SO_4^{--}]_0\text{-}x)^2 = 3.40 \times 10^{-6}$$
$$([Ca^{++}]_0\text{-}\tfrac{1}{2}y\text{-}z)([OH^-]_0\text{-}2z)^2 = 6.19 \times 10^{-6}$$

Solution of system of equations: The system consists of four nonlinear algebraic equations containing four unknowns. The general approach to a system of this type involves one or more iterative optimization methods. In the present situation, however, an *ad hoc* approach is possible because of the characteristics of the problem. The unknown w is probably much larger than x or y or even $x+y$. This means that the first equation may be solved for an approximate value of w by ignoring the presence of x and y. Then, knowing an approximate value of $([Na^+]_0\text{-}w\text{-}x\text{-}y)$, the second equation may be solved for x. This may be substituted back into the first equation, which may then be solved for an improved value of w. This operation may be cycled until the best possible approximations of w and x are obtained. Then, with good approximate values of $([Na^+]_0\text{-}w\text{-}x\text{-}y)$ and $([SO_4^{--}]_0\text{-}x)$, the third equation may be solved for an approximate value of the quantity $([Ca^{++}]_0\text{-}\tfrac{1}{2}y\text{-}z)$. Having an approximate value of $([Ca^{++}]_0\text{-}\tfrac{1}{2}y\text{-}z)$ enables the fourth equation to be solved for z. The term $([Ca^{++}]_0\text{-}\tfrac{1}{2}y\text{-}z)$ then may be solved for an approximate value of y. The entire operation is repeated, using the approximate values of x and y to obtain improved values of w, x, y, and z. This cycle is repeated until no change takes place in the values of the unknowns and the equations are satisfied. During the cycles, mass constraints (e.g., $y < 2[Ca^{++}]_0$, $z < [Ca^{++}]_0$) were placed on some of the variables. Following this procedure yields the following values:

w = 61.415 mol/L
x = 1.272
y = 0.00180
z = 0.0263

This leads to the following amounts precipitating:

Portlandite:	(0.0263)(74.09)(0.0452) = 0.0881 g
Halite:	(61.415)(58.443)(0.0452) = 162.2
Thenardite:	(1.272)(142.043)(0.0452)/2 = 4.08
Glauberite:	(0.0263)(278.18)(0.0452)/2 = 0.165

and to the following amounts in solution:

$[Na^+]$:	70.35 - (61.415+1.272+0.0018) = 7.66 mol/L
$[Ca^{++}]$:	0.0272 - (½*0.0018+0.0263) = 0.0
$[Cl^-]$:	66.44 - 61.415 = 5.03
$[OH^-]$:	1.35 - 2*0.0263 = 1.30
$[SO_4^{--}]$:	1.28 - (½*1.272+0.0018) = 0.642

The amounts precipitating and the amounts in solution are recorded in Table 6.

Appendix B

SAMPLE CALCULATION OF SOLUBILITY PRODUCT FROM FREE ENERGIES OF FORMATION

This appendix calculates the solubility product of calcium sulfate from listed free energies of formation of calcium sulfate, the calcium ion, and the sulfate ion. The standard free energies of formation listed below are obtained from the EQ3/6 file **data0.hmw**.

Species	ΔG_f°
$CaSO_4$	-316.226 kcal/mol
Ca^{++}	-132.302
SO_4^{--}	-177.974

Basic relationship: $\Delta G_{rcn}^\circ = -RT\,\ell n\, K_{eq}$

Reaction: $CaSO_4 \leftrightarrow Ca^{++} + SO_4^{--}$

$$\Delta G_{rcn}^\circ = \Delta G_{f[Ca++]}^\circ + \Delta G_{f[SO4--]}^\circ - \Delta G_{f[CaSO4]}^\circ$$

$$\Delta G_{rcn}^\circ = -177.974 - 132.302 + 316.226 = 5.950 \text{ kcal/mol}$$

$$\ell n\, K = -(5.950)(1000)/[(1.987)(298.2)] = -10.04$$

$$\ell og\, K = -10.04/2.3026 = -4.361$$

The parameter pK_{sp} is equal to the negative of the logarithm of the solubility product. The above calculation makes pK_{sp} equal to 4.361. This is extremely close to the value of 4.3621 listed in the file **data0.hmw**. It also may be compared with the value of 4.47 from the EQ3/6-HMW calculations reported in Table 4 for $CaSO_4$.

Appendix C

MODELING MULTICOMPONENT PRECIPITATION FROM NONIDEAL SOLUTIONS

In Problem #3, the amounts of gypsum and portlandite predicted to precipitate by ideal-solution calculations matched reasonably well the amounts predicted to precipitate by nonideal-solution calculations. This is reminiscent of the general chemistry truism that inclusion of nonideality in an equilibrium calculation often does not alter the calculated equilibrium concentrations significantly (cf., e.g., Campbell 1970).

In the general chemistry truism, the cause is straightforward. Often, the activity coefficients in the ratio that composes the equilibrium constant approximately cancel. The same can be true of multicomponent precipitation, as is shown below in the discussion following Table C-1.

However, there is another possible cause for ideal-solution calculations to predict well the amounts precipitated from nonideal solutions when multiple substances precipitate. The following development shows there are combinations of solubility-product ratios and concentrations that will cause this to occur. It does not necessarily occur; particular combinations of solubility-product ratios and concentrations are necessary. An approach is developed below that predicts when this effect will take place.

The model solution has a cation C^+ and two anions $A1^-$ and $A2^-$. The salts CA1 and CA2 are sparingly soluble, with solubility products K_{sp1} and K_{sp2}. The cation C^+ is the limiting ion. Let x be the amount of A1 that is converted to CA1 and y be the amount of A2 that is converted to CA2. Since the salts are sparingly soluble, almost all the cation C^+ will be precipitated, and

$$x + y \approx [C^+]_0 \quad . \tag{C-1}$$

An expression for x in terms of y may be obtained from a ratio of the solubility-product relationships. For the ideal calculation of this situation,

$$\frac{[C^+]([A1^-]_0 - x_{ideal})}{[C^+]([A2^-]_0 - y_{ideal})} = \frac{K_{sp1}}{K_{sp2}} ; \frac{\mathrm{Max}\{[A1^-]_0 - [C^+]_0, 0\}}{[A2^-]_0} \le \frac{K_{sp1}}{K_{sp2}} \le \frac{[A1^-]_0}{\mathrm{Max}\{[A2^-]_0 - [C^+]_0, 0\}} \quad . \tag{C-2}$$

As seen, there is a limited range of K_{sp1}/K_{sp2} in which Eq. (C-2) is valid. When the left-hand inequality is not satisfied, no CA2 precipitates, and the solubility product relationship is not valid for $[C^+][A2^-]$. When the right-hand inequality is not satisfied, no CA1 precipitates, and the solubility product relationship is not valid for $[C^+][A1^-]$. The following development is valid only for the limited range of Eq. (C-2).

Canceling where appropriate and solving for x yields

$$x_{ideal} = [A1^-]_0 - \frac{K_{sp1}}{K_{sp2}}([A2^-]_0 - y_{ideal}) \quad . \tag{C-3}$$

For a real or nonideal solution the analog of Eq. (C-2) is

$$\frac{(\gamma_{C+})\,[C^+](\gamma_{A1-})\,([A1^-]_0 - x_{real})}{(\gamma_{C+})\,[C^+]\,(\gamma_{A2-})\,([A2^-]_0 - y_{ideal})} = \frac{K_{sp1}}{K_{sp2}}\,;$$

$$\frac{\mathrm{Max}\{([A1^-]_0 - [C^+]_0), 0\}}{[A2^-]_0} \le \frac{\gamma_{A2-}K_{sp1}}{\gamma_{A1-}K_{sp2}} \le \frac{[A1^-]_0}{\mathrm{Max}\{([A2^-]_0 - [C^+]_0), 0\}} \quad . \qquad \text{(C-4)}$$

Again, there is a limited range over which this equation is valid, and the following development applies only to this range. Solving Eq. (C-4) for x gives the analog of Eq. (C-3) for real or nonideal solutions:

$$x_{real} = [A1^-]_0 - \left[\frac{\gamma_{A2-}}{\gamma_{A1-}}\right]\frac{K_{sp1}}{K_{sp2}}\,([A2^-]_0 - y_{real}) \quad . \qquad \text{(C-5)}$$

Solving Eq. (C-1) for y and substituting it into Eqs. (C-3) and (C-5) gives the implicit equations for x_{ideal} and x_{real}:

$$x_{ideal} \approx [A1^-]_0 - \frac{K_{sp1}}{K_{sp2}}\,([A2^-]_0 - [C^+]_0 + x_{ideal}) \qquad \text{(C-6)}$$

and

$$x_{real} \approx [A1^-]_0 - \left[\frac{\gamma_{A2-}}{\gamma_{A1-}}\right]\frac{K_{sp1}}{K_{sp2}}\,([A2^-]_0 - [C^+]_0 + x_{real}) \quad . \qquad \text{(C-7)}$$

What are of interest here are the two ratios x_{real}/x_{ideal} and y_{real}/y_{ideal}. To ease the algebra, let $\alpha \equiv x_{real}/x_{ideal}$, $\beta \equiv y_{real}/y_{ideal}$, and $\xi \equiv \gamma_{A2-}/\gamma_{A1-}$. First consider α. In this simple situation, Eqs. (C-6) and (C-7) can be solved explicitly for x_{ideal} and x_{real} and the ratio set equal to α. This approach yields

$$x_{ideal} \approx \frac{[A1^-]_0 - (K_{sp1}/K_{sp2})\,([A2^-]_0 - [C^+]_0)}{1 + (K_{sp1}/K_{sp2})} \qquad \text{(C-8)}$$

and

$$x_{real} \approx \frac{[A1^-]_0 - \xi(K_{sp1}/K_{sp2})\,([A2^-]_0 - [C^+]_0)}{1 + \xi(K_{sp1}/K_{sp2})} \quad . \qquad \text{(C-9)}$$

Dividing Eq. (C-9) by Eq. (C-8) results in

$$\alpha \approx \frac{\{[A1^-]_0 - \xi(K_{sp1}/K_{sp2})([[A2^-]_0 - [C^+]_0)\}[1 + (K_{sp1}/K_{sp2})]}{\{[A1^-]_0 - (K_{sp1}/K_{sp2})([[A2^-]_0 - [C^+]_0)\}[1 + \xi(K_{sp1}/K_{sp2})]} \quad . \qquad \text{(C-10)}$$

Table C-1 presents the results of substituting various concrete values into Eq. (C-10). The first two sets of values show that α can differ significantly from one. In these two cases, $\alpha = 2$ and $\alpha = 0$. These situations represent the two extremes of the valid range of this development. In the first situation,

α is at its maximum, just at the point where no CA2 precipitates. In the second, α is at its minimum, just at the point where no CA1 precipitates.

Table C-1. EFFECTS ON x_{real}/x_{ideal} AND $d\alpha/d\xi|_{\xi0=1}$ OF CONCENTRATION, SOLUBILITY-PRODUCT RATIO, AND ACTIVITY-COEFFICIENT RATIO FOR THE PRECIPITATION MODEL

Conc. of A1	Conc. of A2	K_{sp2}/K_{sp1}	$\gamma_{c2-}/\gamma_{c1-}$ (ξ)	x_{real}/x_{ideal} (α)	$d\alpha/d\xi|_{\xi0=1}$
$2[C^+]_0$	$2[C^+]_0$	1	0.5	2	-1.5
$2[C^+]_0$	$2[C^+]_0$	1	2	0	
$2[C^+]_0$	$\frac{1}{2}[C^+]_0$	100	0.5	1.03	-1.9×10^{-4}
$2[C^+]_0$	$\frac{1}{2}[C^+]_0$	100	2	0.99	

The second two sets of values show that α can be very close to one, even when the ratio of activity coefficients (ξ) differs significantly from one. When $\xi = 1$, of course, effects of the activity coefficients cancel, the numerator and denominator of Eq. (C-10) are identical, and $\alpha = 1$. Table C-1 shows that even when effects of the activity coefficients do not cancel, α can still be very close to one. This depends on the particular combination of ion concentrations and solubility-product ratio.

Analysis creates a standard for judging whether a particular combination of ion concentrations and solubility product ratio can cause α to differ significantly from one. If $\alpha(\xi)$ is expanded in a Taylor series, then

$$\alpha \approx \alpha(\xi_0) + \left[\left. \frac{d\alpha}{d\xi} \right|_{\xi_0} \right] (\xi - \xi_0) + \tfrac{1}{2} \left[\left. \frac{d^2\alpha}{d\xi^2} \right|_{\xi_0} \right] (\xi - \xi_0)^2 + \ldots \tag{C-11}$$

Let $\xi_0 = 1$. Then solution of Eq. (C-10) for α gives

$$\alpha(\xi_0) = 1 \quad . \tag{C-12}$$

This is equivalent to asking what happens if the effects of the activity coefficients cancel. The obvious answer is that $\alpha(\xi{=}1)$ should equal one, which it does. Equation (C-11) then becomes

$$\alpha \approx 1 + \left[\left. \frac{d\alpha}{d\xi} \right|_{\xi0=1} \right] (\xi - 1) + \tfrac{1}{2} \left[\left. \frac{d^2\alpha}{d\xi^2} \right|_{\xi0=1} \right] (\xi - 1)^2 + \ldots \tag{C-13}$$

Solving Eq. (C-10) for $d\alpha/d\xi$ yields

$$\frac{d\alpha}{d\xi}=\left\{\frac{[1+(K_{sp1}/K_{sp2})]}{[A1^-]_0-(K_{sp1}/K_{sp2})([A2^-]_0-[C^+]_0)}\right\}\left\{\frac{\text{[illegible]}}{[1+\xi(K_{s\text{[illegible]}p2})^2}\right\}$$

$$\times\Big([1+\xi(K_{sp1}/K_{sp2})](-1)(K_{sp1}/K_{sp2})([A2^-]_0[\text{[illegible]})$$

$$-\{[A1^-]_0-\xi(K_{sp1}/K_{sp2})([A2^-]_0-[\text{[illegible]}(K_{sp1}/K_{sp2})\Big)\ . \qquad \text{(C-14)}$$

Table C-1 also presents the values of $d\alpha/d\xi|_{\xi0=1}$ for the cases mentioned above. It shows that with one set of concentrations and solubility-product ratios, the value of $d\alpha/d\xi|_{\xi0=1} = -1.5$. With another set of concentrations and solubility-product ratios, the value of $d\alpha/d\xi|_{\xi0=1} = -2 \times 10^{-4}$. The former situation resulted in a significant change of α, and the latter an insignificant change of α. The values of $d\alpha/d\xi|_{\xi0=1}$ of course represent the sensitivity of α to a change in ξ, and this is an indicator of when α will change noticeably if ξ is significantly different from one.

If the second-order and higher terms in Eq. (C-13) are small, they may be ignored. When this occurs, Eq. (C-13) becomes

$$\alpha \approx 1 + (d\alpha/d\xi|_{\xi0=1})(\xi-1)\ . \qquad \text{(C-15)}$$

A quick look at the values of α and the values of $d\alpha/d\xi|_{\xi0=1}$ in Table C-1 shows that Eq. (C-15) is not valid for any of the situations posed in the table. It gives changes in α from the ideal that are in the correct direction and in the correct range, but the differences reflected in the Table C-1 values for α are not predicted closely by Eq. (C-15). It appears that if Eq. (C-13) is to be used for predicting the proper value of α for a particular situation, it cannot be truncated after the first term.

The development for the ratio y_{real}/y_{ideal}, or β, follows the same path with the same qualitative results. There are particular combinations of concentrations and solubility products that give β close to 1, and an expression may be derived that tells when this will occur.

Appendix D

DERIVATION OF EQUATION (VIII-33)

The derivation begins with Eq. (VIII-15) of Section VIII.B. Again let x be the amount of Ca^{++} ion that precipitates as $Ca(OH)_2$ and y the amount of Ca^{++} ion that precipitates as $CaSO_4{\bullet}2H_2O$. This time a relationship for y in terms of x will be obtained from the ratio of the solubility-product relationships. For the ideal calculations of Precipitation Problem #3,

$$\frac{[Ca^{++}]([OH^-]_0 - 2x_{ideal})^2}{[Ca^{++}]([SO_4^{--}]_0 - y_{ideal})} = \frac{K_{sp[Ca(OH)2]}}{K_{sp[CaSO4]}} \quad . \qquad \text{(VIII-15)}$$

Canceling where appropriate and solving for y yields

$$y_{ideal} = [SO_4^{--}]_0 - \frac{K_{sp[CaSO4]}}{K_{sp[Ca(OH)2]}}([OH^-]_0 - 2x_{ideal})^2 \quad . \qquad \text{(D-1)}$$

For a real or nonideal solution the analog of Eq. (VIII-15) is

$$\frac{(\gamma_{Ca^{++}})\,[Ca^{++}](\gamma_{OH^-})^2([OH^-]_0 - 2x_{real})^2}{(\gamma_{Ca^{++}})[Ca^{++}](\gamma_{SO_4^{--}})([SO_4^{--}]_0 - y_{real})} = \frac{K_{sp[Ca(OH)2]}}{K_{sp[CaSO4]}} \qquad \text{(VIII-17)}$$

and solving Eq. (VIII-17) for y gives the analog of Eq. (D-1) for real or nonideal solutions:

$$y_{real} = [SO_4^{--}]_0 - \frac{\gamma^2_{OH-}}{\gamma_{SO4--}}\left[\frac{K_{sp[CaSO4]}}{K_{sp[Ca(OH2)]}}([OH^-]_0 - 2x_{ideal})^2\right] \quad . \qquad \text{(D-2)}$$

Since almost all the calcium ion is precipitated in both the ideal and real-solution calculations, the approximation

$$x + y \approx [Ca^{++}]_0 \qquad \text{(VIII-19)}$$

is valid. Solving this approximation for x and substituting it into Eqs. (D-1) and (D-2) gives the implicit equations for y:

$$y_{ideal} \approx [SO_4^{--}]_0 - \frac{K_{sp[CaSO4]}}{K_{sp[Ca(OH)2]}}([OH^-]_0 - 2[Ca^{++}]_0 + 2y_{ideal})^2 \qquad \text{(D-3)}$$

and

$$y_{real} \approx [SO_4^{--}]_0 - \frac{\gamma^2_{OH-}\,K_{sp[CaSO4]}}{\gamma_{SO4--}\,K_{sp[Ca(OH)2]}}([OH^-]_0 - 2[Ca^{++}]_0 + 2y_{real})^2 \quad . \qquad \text{(D-4)]}$$

This derivation concerns y_{real}/y_{ideal}, or β. As in the derivation for α, let $\xi \equiv \sqrt{\gamma_{SO4--}}/\gamma_{OH-}$. From Eqs. (D-3) and (D-4),

$$\beta \approx \frac{[SO_4^{--}]_0 - \left[\frac{1}{\xi^2}\right]\left[\frac{K_{sp[CaSO4]}}{K_{sp[Ca(OH)2]}}([OH^-]_0 - 2[Ca^{++}]_0 + 2y_{real})^2\right]}{[SO_4^{--}]_0 - \left[\frac{K_{sp[CaSO4]}}{K_{sp[Ca(OH)2]}}([OH^-]_0 - 2[Ca^{++}]_0 + 2y_{ideal})^2\right]} \quad . \tag{D-5}$$

Substituting the RHS of $y_{real} \equiv \beta y_{ideal}$ for y_{real} on the RHS of Eq. (D-5)'s numerator gives

$$\beta \approx \frac{[SO_4^{--}]_0 - \left[\frac{1}{\xi^2}\right]\left[\frac{K_{sp[CaSO4]}}{K_{sp[Ca(OH)2]}}([OH^-]_0 - 2[Ca^{++}]_0 + 2\beta\, y_{ideal})^2\right]}{[SO_4^{--}]_0 - \left[\frac{K_{sp[CaSO4]}}{K_{sp[Ca(OH)2]}}([OH^-]_0 - 2[Ca^{++}]_0 + 2y_{ideal})^2\right]} \quad . \tag{D-6}$$

This development assumes that the ideal calculations have been carried out, and that the only unknowns in the above equation are β and ξ. The equation is implicit in β and can be written

$$\beta \approx \beta(\xi) \quad . \tag{D-7}$$

Expanding this in a Taylor series gives

$$\beta \approx \beta(\xi_0) + \left[\left.\frac{d\beta}{d\xi}\right|_{\xi_0}\right](\xi - \xi_0) + \frac{1}{2}\left[\left.\frac{d^2\beta}{d\xi^2}\right|_{\xi_0}\right](\xi - \xi_0)^2 + \ldots \tag{D-8}$$

Let $\xi_0 = 1$. Then solution of Eq. (D-6) for β gives

$$\beta(\xi_0) = 1 \quad . \tag{D-9}$$

This is equivalent to asking what happens if the effects of the activity coefficients cancel. The obvious answer is that $\beta(\xi_0{=}1)$ should equal one, which it does.

If the second-order and higher terms in Eq. (D-8) are small, they may be ignored. When this occurs, Eq. (D-8) becomes

$$\beta \approx 1 + \left[\left.\frac{d\beta}{d\xi}\right|_{\xi_0}\right](\xi - 1) \quad . \tag{D-10}$$

The denominator of the RHS of Eq. (D-6) equals y_{ideal}. Using this equality and taking derivatives of both sides of Eq. (D-6) yields

$$\frac{d\beta}{d\xi} \approx \frac{-1}{y_{ideal}} \left\{ \frac{K_{sp[CaSO4]}}{K_{[Ca(OH)2]}} ([OH^-]_0 - 2[Ca^{++}]_0 + 2\beta\, y_{ideal})^2 \left(\frac{-2}{\xi^3}\right) + \frac{2}{\xi^2} \left[\frac{K_{sp[CaSO4]}}{K_{sp[Ca(OH)2]}} ([OH^-]_0 - 2[Ca^{++}]_0 + 2\beta\, y_{ideal}) \right] (2y_{ideal}) \frac{d\beta}{d\xi} \right\} \quad . \qquad \text{(D-11)}$$

Solving for $d\beta/d\xi$ and setting ξ_0 equal to 1 is the next step. Setting ξ_0 equal to 1 makes β equal to 1; the ratio of solubility products times the squared term on the RHS of Eq. (D-11) equals $[SO_4^{--}]_0 - y_{ideal}$ when β equals 1. Implementing this gives

$$\left.\frac{d\beta}{d\xi}\right|_{\xi_{0=1}} \approx \frac{(2)\,([SO_4^{--}]_0 - y_{ideal})}{y_{ideal} \left\{ 1 + 4[K_{sp[CaSO4]} / K_{sp[Ca(OH)2]})([SO_4^{--}]_0 - y_{ideal})]^{1/2} \right\}} \quad . \qquad \text{(D-12)}$$

Substituting this expression into Eq. (D-10) gives

$$\beta \approx 1 + \left[\frac{(2)([SO_4^{--}]_0 - y_{ideal})}{y_{ideal}\{1 + 4[(K_{sp[CaSO4]} / K_{sp[Ca(OH)2]})([SO_4^{--}]_0 - y_{ideal})]^{1/2}\}} \right] (\xi - 1) \quad . \qquad \text{(D-13)}$$

This is Eq. (VIII-33) in the text.

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