ELEMENTS OF COMPUTER-ASSISTED THERMODYNAMIC CHEMICAL EQUILIBRIUM MODELING AS APPLIED TO WASTE TREATMENT AT COAL MINES

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Abstract

Computer-assisted thermodynamic chemical equilibrium models are useful tools for describing and understanding the reactions that occur in a chemical system.   Several models are available either free or at nominal cost. The models presently available generally are designed to compare the ion activity product with the equilibrium constant for a particular reaction.   Understanding how models calculate total dissolved activities from solute concentrations and then calculate the activities and concentrations of various aqueous species and solids is essential for selecting the best model for a particular application. Models are limited by the quality of the data in their databases and by the state of theoretical understanding of nonideal solutions.   Therefore, results from computer models must be validated through field or laboratory experiments before being accepted and used for making decisions.

Introduction

Many computerized models have been written over the years but many of these are designed for a narrow purpose.   Of the many models developed, only a few are in general use by the scientific community. Acceptance of a chemical thermodynamic equilibrium model seems to be governed by its ease of use, the extensiveness of its thermodynamic database, the breadth of the capabilities of the model, and the ease of modifying the code to suit a particular need (Mattigod, 1995).

Chemical Fundamentals

Most simply states, a model is a representation of an object or an event. A chemical equation is a model for a chemical reaction. For example, equations l-4

$$CO_{2(g)} = CO_{2(aq)} \tag{1}$$
$$CO_{2(aq)} + H_2O = H_2CO_3 \tag{2}$$
$$H_2CO_3 = H^+ + HCO_3 \tag{3}$$
$$HCO_3^- = H+ + CO_3^{2-} \tag{4}$$

represent the dissolution of gaseous carbon dioxide in water.

These equations indicate that (1) carbon dioxide gas will dissolve to some extent in water, (2) an amount of aqueous carbon dioxide will combine with an equimolar amount of water to form an equimolar amount of carbonic acid, (3) carbonic acid will dissociate in water to form hydronium and bicarbonate ions, and (4) bicarbonate ion will further dissociate (equation 4) to form another hydronium ion and carbonate ion.   When no additional information is provided, a set of chemical equations is primarily descriptive. These equations tell us what happens when carbon dioxide dissolves in water, but they don't tell us how much of each species will be present.

To determine quantities of species requires additional information, namely, an equilibrium constant for each reaction, that is, the ratio of the mathematical product of each product species activity raised to the power of the coefficient of that species in the chemical equation divided by the mathematical product of each reactant species raised to the power of its coefficient. For example, for the hypothetical reaction

$$aA + bB = cC + dD \qquad (5)$$

the equilibrium constant is

$$K_{eq} = \frac{[C]^c [D]^d}{[A]^a [B]^b} \qquad (6)$$

Equilibrium can be defined as the equality of the rates of opposing reactions. In other words, the rate of production of C and D in equation 5 by the reaction of A and B is equal to the rate of production of A and B by the reaction of C and D.

Another defmition of equilibrium can be formulated on the basis of free energy. Any system which is not at equilibrium will change spontaneously with the release of energy. At equilibrium, when the reactants and products are at the same temperature and pressure, the sum of the free energy of the products equals the sum of the free energy of the reactants. Or,

$$\Sigma \Delta G_{prod} - \Sigma \Delta G_{react} = 0 \qquad (7)$$

The standard free energy of formation of a substance is defined as the free energy change resulting from the formation of one mole of the substance from the stable elements under standard state ($25°C$ and 1 atm) conditions.

The equilibrium constant for a reaction can be calculated from the standard free-energy change of the reaction (ΔG_r°), the difference between the sum of the free energies of formation of the products less the sum of the free energies of formation of the reactants:
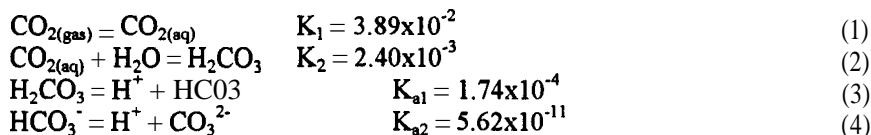
$$\Delta G_r^{\circ} = \Sigma \Delta G_r^{\circ}{}_{(prod)} - \Sigma \Delta G_r^{\circ}{}_{(react)} \qquad (8)$$

At 25°C and 1 atm pressure, the equilibrium constant is related to the standard free-energy change (in kcal) of the reaction by

$$\log K = \frac{-\Delta G_r^{o}}{1.364} \qquad (9)$$

One cau calculate equilibrium constants from standard free energies of formation, which have been tabulated by several authors.

We are now in a position to calculate the activities of the various species that are formed with the dissolution of carbon dioxide. The equilibrium constants for reactions 1 through 4 are as follows:

$$CO_{2(gas)} = CO_{2(aq)} \qquad K_1 = 3.89 \times 10^{-2} \qquad (1)$$
$$CO_{2(aq)} + H_2O = H_2CO_3 \qquad K_2 = 2.40 \times 10^{-3} \qquad (2)$$
$$H_2CO_3 = H^+ + HCO3 \qquad K_{a1} = 1.74 \times 10^{-4} \qquad (3)$$
$$HCO_3^- = H^+ + CO_3^{2-} \qquad K_{a2} = 5.62 \times 10^{-11} \qquad (4)$$

By substituting the atmospheric partial pressure of carbon dioxide, 0.0003 atm, into equation 1, and solving the four equations, the concentrations of $CO_{2,,,,,,}$ H_2CO_3, HCO_3^-, and CO_3^{2-} are found to vary with pH as shown in Figure 1.

These calculations yield activities rather than concentrations. The activity of a species is a

measure of its effective concentration, and is usually smaller than concentration, Activity is related to concentration through the equation

$$act_i = \gamma \, c_i \tag{10}$$

where act_i is the activity of the ith species, γ is the activity coefficient, and c_i is the concentration of the ith species. The difference between activity and concentration arises because in a solution, each ion is surrounded by a shell of oppositely charged ions, which decreases the ability of the central ion to enter into chemical reactions.

In an ideal solution, the activity coefficient is equal to 1 and activity equals concentration. Real solutions are not ideal, however, so activity coefficients must be calculated for different solutes. An equation commonly used used to calculate activity coefficients is the extended **Debye-Hückel** equation,

$$-\log \gamma_i = \frac{A z_i^2 \sqrt{I}}{1 + B a_i \sqrt{I}} \tag{11}$$

where $A = 1.82 \times 10^6 (\epsilon T)^{-3/2}$, $B = 50.3 (\epsilon T)^{-\frac{1}{2}}$, and e signifies the dielectric constant of the solvent, and T is the absolute temperature of the solution.

The quantity a_i is dependent on the "effective diameter" of the ion. Values of a_i have been determined experimentally and are available in tabulated form. The symbol z_i is the ionic charge, and I is the ionic strength of the solution. The ionic strength is calculated from

$$I = \frac{1}{2} \sum m_i z_i^2 \tag{12}$$

where m_i is the molal concentration (mole/kg) of the ith ion in solution.

The extended Debye-Htickel equation is valid for ionic strengths up to about 0.05m. Other equations, such as the Guntelberg equation or the Davies equation have been developed for higher ionic strengths (Butler, 1964). The Davies equation is useful for ionic strengths up to approximately 0.5m. This ionic strength limit is satisfactory for most environmental work. Figure 2 shows a comparison of activity coefficients calculated from the Debye-Htickel, Guntelberg, and Davies equations with experimental data for several solutes. Figure 2 shows that none of the three equations matches the experimental data entirely adequately. The Pitzer equation (not shown in Figure 2) is useful for calculating activity coefficients in solutions in which the ionic strength is greater than 0.5m.

Typically, in a thermodynamic chemical equilibrium model, the activities of solutes are compared with the solubility of each potential mineral in the database. If the solubility product of some mineral in the model's database is exceeded by the ion activity product (IAP) of the dissolved constituents in the solution being modeled, the model allows the mineral to precipitate until the IAP equals the solubility product. Conversely, if a mineral is present in the solid phase and the IAP of the dissolved constituents in the model solution is less than the solubility product of the mineral, the model allows the mineral to dissolve until the IAP and the solubility product are equal.

For example, the solubility product, K_{sp}, of calcite at 25°C is 0.87×10^{-8} and is simply an equilibrium constant for the chemical reaction

$$CaCO_3 = Ca^{2+} + CO_3^{2-} \qquad\qquad K_{sp} = 0.87 \times 10^{-8} \tag{13}$$
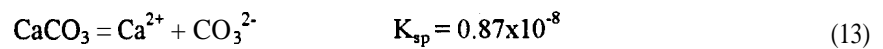
By definition, the activity of any solid is equal to 1, so the equilibrium constant for the above reaction is

$$K_{sp} = [Ca^{2+}][CO_3^{2-}] \tag{14}$$

The IAP is calculated from the activities of the dissolved mineral constituents. The saturation index is defined as $\log(IAP/K_{sp})$ for the mineral. If the saturation index is positive, the solution is supersaturated with respect to that mineral, and precipitation of the mineral is allowed by the model. If the saturation index is negative, the solution is undersaturated with respect to that mineral, and dissolution of the mineral is allowed.

Thermodynamic equilibrium models generally are organized around two major approaches. The most common approach is to base the calculations on equilibrium constants (Mattigod, 1995), as illustrated above. The second approach is called the free energy minimization approach. The second approach is not commonly used because the data required are neither as readily available nor as reliable as equilibrium constants. However, the two methods produce mathematically equivalent results.

Limitations of Chemical Equilibrium Models

Assumption of Equilibrium

Thermodynamic chemical equilibrium models assume that equilibrium has been attained in the system of interest. This may be the case in a well-stirred solution in a beaker, but it is not necessarily true for a natural system. Natural systems are subject to slow changes in solution composition due to the diffusion of solutes into or out of the system, the diffusion of gases such as oxygen or carbon dioxide into or out of the system, transport of solutes through the system because of groundwater flow, oxidation-reduction reactions, acid-base reactions, microbial activities, adsorption-desorption, and other processes which cause changes in solute concentrations.

Limitations of Thermodynamic Data

Models require thermodynamic data such as equilibrium constants, solubility product constants, and enthalpy values, in their calculations, but not all thermodynamic data are of equal accuracy and precision. If a model's developer chose inaccurate thermodynamic data for the database, then the modeling results will also be inaccurate.

If experimentally determined thermodynamic data are not available for each solute of interest, then estimated or indirectly calculated values must be used. However, an equilibrium constant can be calculated for the reaction only when the free energy of formation is known for each desired component in a reaction. Enthalpy data are required in the model to correct equilibrium constants if the modeled solution's temperature differs from the standard state, usually 25°C.

Required User Input

The user of a model must supply chemical information specific to the problem to be modeled. The data required usually include temperature, pH, Eh, and the concentration of each cationic and anionic component in the system to be modeled. Depending on the model, the data must be written to a file with specific formatting requirements or into a preprocessor which writes the properly formatted input file.

Models require that the concentration of some form of inorganic carbon, such as the partial pressure of CO*, dissolved inorganic carbon, or the inorganic carbon portion of alkalinity be supplied. None of these is completely straightforward While the atmospheric partial pressure of carbon dioxide is approximately 0.0003 atm at the earth's surface, the partial pressure of CO_2 in soils can range up to about 0.01 atm (Hassett and Banwart, 1992), due to microbial respiration. Knowledge of the specific soil CO_2 content is needed. Dissolved inorganic carbon is the total of all inorganic carbon species in solution, which includes all dissolved species of carbon dioxide plus ion pairs that include carbonate or

bicarbonate. Total dissolved inorganic carbon can be determined by the acidic evolution of CO_2.

Generally, the pH and Eh can be fixed in the model or allowed to vary as solution conditions change during the calculation.

If the user wishes to include minerals in the calculation, then data for the concentration of each mineral must be entered in the model. The database will usually include data for end-member compositions only. This is not a problem for minerals such as calcite ($CaCO_3$) or hematite (Fe_2O_3) which generally do not enter into solid solution or ionic substitution, but can become a significant source of error for clay minerals, such as smectites and mixed layer clays with variable composition. For example, the smectite mineral beidellite has an ideal composition of $Ca_{0.25}Al_2(Si_{3.5}Al_{0.5})O_{10}(OH)_2 \times nH_2O$. However, in nature, the chemical composition generally will be somewhat more complicated and unpredictable due to polymorphic substitution and inclusion of impurities. A more representative, but less exact chemical formula for beidellite might be $(Na,K,Ca)_{0.25}(Al,Mg,Fe^{3+},Fe^{2+})_2$ $(Si_{4-x}Al_x)O_{10}(OH)_2 \times nH_2O$. It is not possible to determine a general equilibrium constant for real smectites because of the large range of possible compositions.

Information Available From Models

The information returned by models typically includes the input data set, the charge balance for the initial solution, the distribution of species in solution, the distribution of components in various species, minerals dissolved or precipitated, the mass of each solid phase remaining at equilibrium, the concentrations of solutes at equilibrium, and the saturation indices of all possible solids.

Available Models

Several models are available free on the Internet or for a fee from the authors. Among the more widely used are MINTEQA2 and its preprocessor, PRODEFA2; ALCHEMI; PHREEQC; and PHRQPITZ. Other available models are C SALT, EQ3/6, GEOCHEM-PC, HYDROGEOCHEM, LEACHM, REACT, SOlLCHEM, and SOLMINEQ.

MINTEQA2 (Allison et al., 1991) is a chemical equilibrium model for dilute solutions with ionic strengths up to about 0.5m. The program was originally developed by Battelle Pacific Northwest Laboratory (Felmy et al., 1984) in the mid-80s as MJNTEQ. MINTEQA2 was derived from MINTEQ. MJNTEQA2 has 6 1 inorganic and 28 organic components available to describe the chemical system. The components are used as reactants in over 900 dissolved species, over 500 solid species, 2 1 gas species, 42 surface complexation species relevant to adsorption on au amorphous iron oxide surface, and 13 species of complexes of trace elements with dissolved organic matter (Allison and Brown, 1995). MINTEQA2 includes seven options for modeling adsorption-desorption. It also has the ability to conduct "sweeps," or titrations, in which the output data from one execution are used as input for the next execution of the program.

ALCHEMI (Schecher and Driscoll, 1995) is a specialized program that was designed to evaluate the chemistry of Al as it reacts with OK, F, H_4SiO_4, and SO_4^{2-} in natural waters. It can be used to calculate the speciation of Al in water affected by acidic deposition and thereby assess the potential toxicity of Al in the water. ALCHEMI can also be used to calculate the saturation indices of well-defined mineral phases so that the solubility of Al can be evaluated, but is limited in its array of chemical reactions in acidic, low ionic strength waters.

PHREEQC (Parkhurst, 1995) is a program distributed by the U.S. Geological Survey. This program provides for the aqueous speciation of elements, dissolution and precipitation of solid phases, reaction path modeling (in which the progress of a reaction is followed), advective-transport calculations, and so-called inverse modeling. In inverse modeling, the amounts of solids and gases that must be removed from or added to a system to account for specified differences between beginning and final

compositions of a system are calculated. PHREEQC is appropriate for solutions of low ionic strength, but the results must be interpreted with care. The thermodynamic data in the database are not internally consistent because they were taken from various sources and the author did not attempt to determine whether the data were obtained in similar aqueous solutions (Parkhurst, 1995).

PHRQPITZ (Plummer et al., 1988) incorporates the Pitzer virial-coefficient equation to adapt the model PHREEQE, the predecessor of PHREEQC, to use for high ionic strength aqueous solutions. PHRQPITZ is capable of calculating aqueous speciations, mineral saturation indices, mineral solubilities, mixing and titration of aqueous solutions, irreversible reactions, and reaction paths, but PHRQPITZ does not calculate oxidation-reduction reactions.

The capabilities of other generally available geochemical models are listed in Table 1. All can calculate aqueous speciation and dissolution and precipitation of solid phases. Beyond that, the models differ in their other capabilities. REACT (Bethke, 1996) appears to be unique in its ability to integrate simple kinetic rate laws.

Application of Thermodynamic Chemical Equilibrium Models

Chemical equilibrium models can be used to aid our understanding or predict the behavior of a chemical system. For example, Schwab (1995) used the model MINTEQA2 to help in understanding which minerals were responsible for controlling aqueous elemental concentrations in leachates from coal combustion residues. Schwab (1995) used analytical data for leachates as input to the model. In initial executions of the program, solids were not allowed to precipitate. In this mode, the speciation of components and the saturation index of each potential solid phase were calculated. In a subsequent execution of the program, solids were allowed to precipitate in order to calculate changes in solution composition upon precipitation of the solids.

The potential solids suggested by the model and the solution analytical data were plotted in activity diagrams (Figure 3) to indicate visually the degree of saturation of the solutions with respect to certain minerals.

The effects of changing parameters in a chemical system can be predicted by using chemical equilibrium modeling. For example, one might wish to know the effect on leachate chemistry when gob is amended with limestone. The user would input leachate chemistry and gob mineralogy to the model. An initial execution would be made to establish equilibrium conditions, then the desired amount of calcium carbonate would be included in the input data, either as the solid or as equivalent amounts of dissolved species. Several executions of the model could be made with varying amounts of calcium carbonate. Other parameters, such as Eh or temperature, can be changed to determine their influence on chemistry and mineralogy.

If one of the models designed for use with solutions of high ionic strength is used, the user can simulate the evaporation of water in a reaction path model. The model will indicate the precipitation of various solids as water is removed from the system.

Another important ability of some models, such as EQ3/6, is that volume changes can be calculated as changes occur in the mineralogy of a deposit. This function could be applied to calculate the potential volume change in an area used for the storage of fluidized-bed combustion (**FBC**) ash as calcium oxide is hydrated to calcium hydroxide, then as it reacts with carbon dioxide to form calcium carbonate. Other mineralogical changes can occur as the FBC ash weathers. If the overall effect is that the ash will swell on weathering, will it damage a confining structure? A user might want to know whether a material to be disposed of in an impoundment is expected to cause adverse reactions in a liner material. A chemical equilibrium model could serve this purpose. In this type of application, the user could model the reaction of leachate from the disposed material with different minerals in the liner material and check for mineralogical and volumetric changes that could weaken the liner or induce

fractures, that would allow leakage of the leachate.

Other applications might include modeling the solubility of fertilizer components, such as phosphates, under different conditions of mine soil amendment, or calculating the concentration of a particular chemical form in an isolated location.

A Note of Caution

There is a tendency to give more credence than is warranted to almost anything that comes from a computer. Chemical equilibrium models are meant to help our understanding of the chemical processes that occur in a system, not to define them. Each system will define its own chemical processes. The model serves to help us recognize and understand those processes. Models do not predict, future behavior, they merely suggest the reaction paths that are expected for a specified system. Lastly, the results of modeling must be verified by field or laboratory experiments and by observations.

Conclusions

Thermodynamic chemical equilibtium models can be very beneficial for understanding rock-water interactions and "predicting" the effects of on a reaction system of changing chemical parameters. The limitations of models must be recognized. To be accepted as valid, the results of modeling must be verified by laboratory or field observations.

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Table 1. Capabilities of some available thermodynamic chemical equilibrium models

Model name	Low ionic strength	High ionic strength	Aqueous speciation	Dissolution/precipitation	Oxidation-reduction	Surface adsorption	Ion exchange	Titration	Reaction path	Simple kinetics	Saturation index	Solute transport	Inverse modeling	Temperature correction	Gas phase
ALCHEMI	✓		✓	✓		✓					✓				
C SALT	✓	✓	✓	✓										✓	✓
EQ3/6	✓		✓	✓	✓				✓		✓			✓	✓
GEOCHEM-PC	✓		✓	✓	✓										
HYDROGEOCHEM	✓		✓	✓	✓	✓	✓					✓		✓	
MINTEQA2	✓		✓	✓	✓	✓		✓			✓			✓	✓
PHREEQC	✓		✓	✓	✓	✓	✓		✓		✓	✓	✓		✓
PHRQPITZ		✓	✓	✓				✓	✓		✓			✓	
REACT	✓		✓	✓	✓	✓		✓	✓	✓	✓			✓	✓
SOILCHEM	✓		✓	✓		✓									
SOLMINEQ		✓	✓	✓	✓	✓	✓	✓			✓			✓	✓

Figure 1. Carbonate species in aqueous solutions as a function of pH
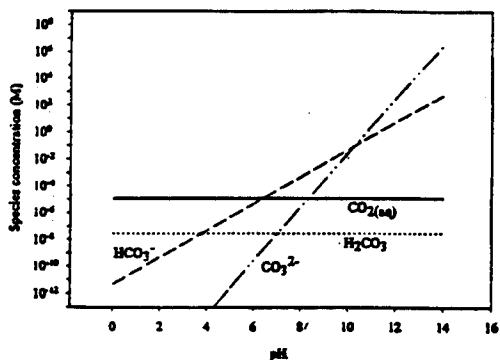
Figure 2. Comparison of emperical activity coefficient expressions with experimental data for HCL, HNO₃, NACLO₄, and KCL. (From Butler, 1964. Used with permission from author.)
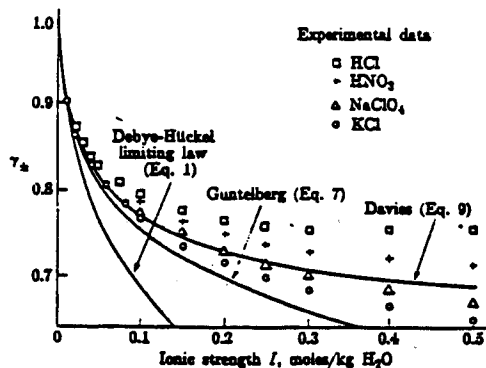

Figure 3. Activites of Ca^{2+} and SO_4^{2-} in (A) field and (B) laboratory samples. (From Schwab, 1995. Used with permission from author.)