

Simulating Aqueous Processes

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Simulation that includes aqueous modeling can also account for full vapor/liquid/solid equilibria modeling, including redox chemistry.

FOR YEARS, PROCESS SIMULATION WAS limited to the petrochemical industry and other related chemistries. Today, several simulation packages include aqueous thermodynamic capabilities that open process simulation up to a wide range of additional applications. This article will look at the theory of aqueous chemical equilibrium, its application to process simulators, and the application of simulation to aqueous chemical processes.

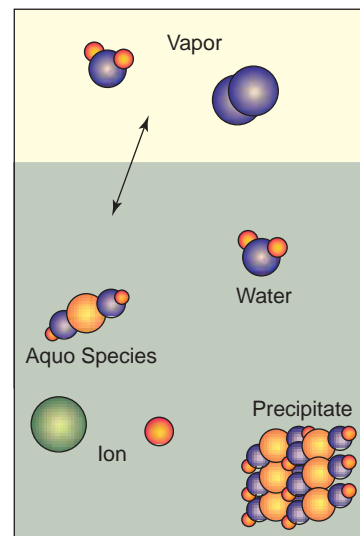
Aqueous chemistry

“Aqueous chemistry” refers to any chemical system that involves water and dissolved salts. This can also be called solution chemistry, aquatic chemistry, water chemistry, or electrolyte chemistry. Accounting for the ionization of water and other system components adds an incredible level of complexity to otherwise simple natural and chemical process systems.

While many chemical engineering processes are dependent on kinetics, solution chemistry is mainly a function of equilibrium thermodynamics. This actually makes simulation of electrolyte systems simpler, since equilibrium can be calculated for completely untried systems. What makes electrolyte simulation more complicated is the large number of possible species — a simple electrolyte simulation may consider the formation of over 1,000 species and require iterative calculations to solve the mass balance, charge balance, and all the governing equilibrium equations.

By understanding how aqueous systems work, you will be able to simulate them more accurately. Unfortunately, most chemical engineers are only exposed to the basic concepts of electrolyte simulation in Chemistry 101, which have been long-since forgotten. (You may want to pull out your old text to review.) Here’s a quick refresher.

Many inorganic species are formed in aqueous solutions (Figure 1). These include ions, hydrates, precipitates, complexes, amphoteric hydroxides, neutral species, gases dissolved in solution, and gases in the vapor space above the liquid. These must all be accounted for to obtain an accurate model of the process. Other dimensions of the physical state include temperature, pressure, concentration of each species (C_i), pH and oxidation/reduction potential.



■ Figure 1. Species in an electrolyte system.

Any given aqueous system includes the solution, vapor in the headspace, and solids present (the container plus any precipitates), as well as possibly one or more immiscible organic phases. Dissolved species may be non-polar aquo (*i.e.*, containing one or more water molecule) species, dissolved ions, and dissolved complexes. These species can transform from one to another depending on the compositions in the gas, liquid and solid phases in the system and on the composition, temperature and pressure.

The relationships commonly used to characterize aqueous systems are:

- Solubility product constant, K_{sp} :
dissolved species \leftrightarrow precipitated species
- Acidity constant, K_A :
dissolved acid species \leftrightarrow conjugate base species
- Stability constant, $K_{1 \dots n}$ or $\beta_{1 \dots n}$:
dissolved species \leftrightarrow dissolved complexes
- Henry's law constant, K_H :
gas phase over solution \leftrightarrow dissolved species

Consider the following examples.

1. *Dissolve salt (NaCl) in water.* Na and Cl completely ionize to form Na^+ and Cl^- in water. If you re-crystallized the salt, upon precipitation it would re-form to NaCl(s) , a crystalline solid. There is no mathematical equilibrium relationship for this process because the salt is fully ionized.

2. *Dissolve ammonia (NH_3) in water.* NH_3 is a weak base, and it would partially protonate to form a mixture of NH_4^+ and NH_3 , with OH^- forming from the protonation. The formal relationship is the acidity constant, or $\text{p}K_A$. For NH_4^+ to NH_3 , the $\text{p}K_A$ is 9.3.

3. *Dissolve ethylenediaminetetraacetic acid (EDTA) in an iron solution to complex the iron.* EDTA is a soluble complexing agent, so dissolved iron attaches to the EDTA molecule to form an aqueous complex. The formal relationship is the stability constant, or $\text{p}K_{1 \dots n}$. For H_4 (EDTA), $\text{p}K_1$ is 10.26, $\text{p}K_2$ is 16.42, $\text{p}K_3$ is 19.09, and $\text{p}K_4$ is 21.08.

Basis for equilibrium

These equilibrium constants (K) can be calculated by:

$$\Delta G^\circ = -R T \ln K \quad (1)$$

where ΔG° is the free energy contributions of the system components, R is the universal gas constant and T is the absolute temperature.

The Gibb's free energy can be minimized either by using the equilibrium constants or by using free energy data for each species and performing a minimization calculation. The latter is simpler when non-standard conditions are used.

Understanding the vocabulary

The following terms and concepts are important to understanding aqueous chemistry.

Amphoteric behavior: Water complexes with many dissolved species to form a stepwise spectrum of hydrated species that vary with pH. Copper, for example, forms pH-dependent amounts of CuOH^+ , Cu^{2+} , Cu(OH)_2 , Cu(OH)_3^+ and Cu(OH)_4^{2-} when dissolved in water.

Carbon cycle: The earth's natural carbon cycle plays a big part in water chemistry. The seemingly insignificant $10^{-3.5}$ atm of CO_2 in the normal atmosphere becomes vital

Nomenclature

C_i	= concentration of ion i
$C_p(T)$	= heat capacity
C_T	= total carbon species in solution
E_H	= standard potential (in volts) relative to the standard hydrogen electrode reaction
F	= Faraday's constant = 1 mole of electrons
G	= Gibb's free energy; ΔG° = free energy contributions of the system components
G_f	= Gibb's free energy of formation
H_f	= enthalpy of formation
K	= equilibrium constant (subscripts define the specific equilibrium constant)
K_A	= acidity constant
K_H	= Henry's law constant
K_{sp}	= solubility product constant
$K_{1 \dots n}$	= stability constant (also $\beta_{1 \dots n}$)
M	= number of species
N	= number of components
P	= partial pressure of a component
R	= universal gas constant
S	= entropy
T	= absolute temperature
V	= partial molar volume
X	= initial guess of component concentrations for Newton-Raphson method
X'	= new guess of component concentrations for Newton-Raphson method
Z_i	= charge of ion i .

Symbols and Greek Letters

[]	= square brackets, <i>e.g.</i> , $[\text{Na}^+]$, denote concentrations
{ }	= braces, or curly brackets, <i>e.g.</i> , $\{\text{Na}^+\}$, denote activity
$\beta_{1 \dots n}$	= stability constant (also $K_{1 \dots n}$)
γ	= activity coefficient
μ	= ionic strength

Matrices and Vectors

i	= component
j	= chemical species
k	= component in current trial (used for convergence)
$A[i,j]$	= stoichiometric coefficient of component i in species j
$C[j]$	= concentration of species j
$E[i]$	= error in mass balance for component i
$E[k]$	= error in mass balance for component i in next iteration
$J[i,k]$	= the Jacobian, an $N \times N$ matrix derivative showing the effect of changing $X[i]$ on the quantity $E[k]$
$K[j]$	= log formation constant of species j
$T[i]$	= total concentration of component i
$X[i]$	= log free concentration of component i

Reactions and Separations

when you realize that CO_2 is very soluble in water above pH 5 and forms bicarbonate and carbonate buffers just from exposure to the atmosphere. If the copper solution is exposed to the atmosphere, add CuCO_3 and $\text{Cu}(\text{CO}_3)_2^{2-}$ to the list of copper species present, along with atmospheric CO_2 , dissolved CO_2 , carbonic acid (H_2CO_2), bicarbonate ion (HCO_3^-), and carbonate ion (CO_3^{2-}). Argon-purged pure water has a pH of 7, but when exposed to air, the pH drops to 5.65 due to the dissolved CO_2 .

Concentration vs. activity: Concentrations are shown in square brackets and are normally expressed in moles per liter, e.g., $[\text{Na}^+] = 1.1 \text{ mol/L}$. To correct for the apparent concentration and account for the crowding of ions in solution, the activity coefficient, γ , is used to convert concentration to activity, which is denoted in braces (curly brackets):

$$\gamma[\text{Na}^+] = \{\text{Na}^+\} \quad (2)$$

For dilute solutions, $[\text{Na}^+] \approx \{\text{Na}^+\}$.

Several relationships are used to calculate the activity coefficient for a system based on the ionic strength (μ), which is a measure of the total charge concentration in the solution:

$$\mu = 1/2 \sum C_i Z_i^2 \quad (3)$$

where C_i is the concentration and Z_i is the charge of ion i .

One relationship that can be used to calculate the activity coefficient is the Güntelberg approximation of the Debye-Hückel equation (which applies to monovalent ions at 15°C):

$$-\log \gamma_i = (0.5 Z_i^2 \mu^{1/2}) / (1 + \mu^{1/2}) \quad (4)$$

Solution pH: Many of us learned in high school chemistry that pH is defined as the negative log of the hydrogen ion concentration ($\text{pH} = -\log[\text{H}^+]$). The International Union of Pure and Applied Chemistry (IUPAC) defines the pH of a solution as the negative log of the hydrogen ion activity:

$$\text{pH} = -\log\{\text{H}^+\} = -\log(\gamma[\text{H}^+]) \quad (5)$$

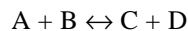
This corresponds to pH values that can be measured with a pH meter.

Solution pC: Just like pH, pC is a negative log quantity, in this case of concentration ($\text{pC} = -\log C_i$). It is often used in aqueous chemistry because it simplifies working over wide ranges of concentrations. Aqueous phase diagrams are often in pC vs. pH format.

Chemical equilibria

The calculation of solution chemistry is normally done based on the equilibrium states. Since most aqueous reactions take place nearly instantly, the equilibrium calculation is normally a good assumption. In the case of specia-

tion, concentrations can be calculated more accurately than they can be measured. The calculation uses equilibrium constants, which represent the lowest free energy state. The use of equilibrium constants follows from LeChatlier's Principle, where:



The equilibrium constant is:

$$K = [\text{C}][\text{D}] / [\text{A}][\text{B}] \quad (6)$$

This relationship predicts reversible reactions, common ion effects, limiting reagent effects, and the effect of concentration on reaction progress.

Chemical equilibria calculations may use an equilibrium constant, K , or alternatively may use the Gibb's free energy, G . The equilibrium constant is based on the point where the Gibb's free energy is minimized. The equilibrium point is described by:

$$K_w = [\text{H}^+][\text{OH}^-] = 10^{-14} \quad (7)$$

where the subscript w denotes water.

For vapor-liquid equilibria, Henry's law applies since the systems are dilute. This simplifies the calculation. However, droplets and mist must be treated as liquid and not vapor. For example, for CO_2 , the aqueous CO_2 would be represented by:

$$[\text{H}_2\text{CO}_{3(\text{aq})}] \approx [\text{CO}_{2(\text{aq})}] = K_H P_{\text{CO}_2} = (10^{-1.5})(10^{-3.5}) = 10^{-5} \text{ M} \quad (8)$$

where P_{CO_2} is the partial pressure of CO_2 .

Mass must be conserved — the mass of each component in a system must sum to the total mass in the system. In manual calculations, each element is totaled separately, such as in this molar balance for carbon:

$$C_T = [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \quad (9)$$

To preserve electroneutrality, the charge must also be conserved — the positive charge must equal the negative charge. For example:

$$[\text{H}^+] = [\text{OH}^-] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]^2 \quad (10)$$

Complexes form from aqueous species coordinating with each other to form new dissolved species. They include one or more central atoms and bond with other molecules or parts called ligands, which may be water, ammonia, phosphate, chloride or other species. Complexes form to reduce the solution free energy, and equilibrium constants can be developed for each of these reactions, as well.

In precipitation and dissolution, K_{sp} is a measure of sol-

ability. It is based on the minimized free energy of a mineral or salt in equilibrium with an aqueous solution. For example, for the reaction $\text{Ni}(\text{OH})_2(s) \leftrightarrow \text{Ni}^{2+} + 2\text{OH}^-$,

$$K_{sp} = [\text{Ni}^{2+}][\text{OH}^-]^2 / [\text{Ni}(\text{OH})_2(s)] = 10^{-15.26} \quad (11)$$

Precipitation is a weak area in process simulation, since the K_{sp} is based on ideal conditions. The actual mechanism of precipitation is based on the surface energy of the solid forming, and not on the overall bulk energy of the solid. While this has been known for about 40 years, it is very difficult to measure the critical parameters and apply them to general situations.

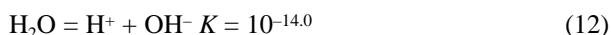
A system involving more than two or three of these individual relationships becomes very cumbersome to evaluate and characterize mathematically. Using linear algebra, solving the problem becomes a series of linearized equations, which can be solved using conventional matrix techniques. This is illustrated later in the article.

Dissociation of water and redox potential

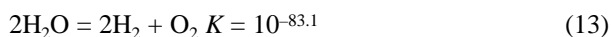
Water molecules can undergo two key reactions: the loss of protons and the loss of electrons. These reactions are characterized by pH and pE.

Water can exist in a range of oxidation-reduction (redox) conditions; beyond that range, an aqueous solution begins to generate oxygen or hydrogen. The solution pH and pE can be used to calculate the concentrations of oxygen and hydrogen in solution, as well as the "pull" on other ions to oxidize or reduce.

The pH behavior of water is described by:



The pE behavior of water is described by:



pH is defined as $-\log\{\text{H}^+\}$. pE and E_H are equivalent measures of the redox potential of a system. E_H is a measured voltage, and pE is the electron analog of pH, defined as $-\log_{10}\{e^-\}$. Many published redox potentials use E_H rather than pE.

E_H can be converted to pE by:

$$\text{pE} = FE_H / 2.3RT \quad (14)$$

where F is the Faraday, the charge per mole of electrons. At 25°C:

$$\text{pE} = 16.9E_H \quad (15)$$

The pE behavior involves a redox reaction transferring four electrons.

The equilibrium expression for water can be simplified to:

$$\log P_{\text{O}_2} - 4\text{pH} - 4\text{pE} = -83.1 \quad (16)$$

and

$$\text{pE} = -14 - 1/2 \log P_{\text{H}_2} + \text{pOH} \quad (17)$$

When $P_{\text{H}_2} = 1$ atm, $\text{pE} = -14 + \text{pOH}$. Also, when P_{O_2} is 0.21 atm, $\text{pE} = 20.6 - \text{pH}$.

This equation is used to construct the pH/pE diagram for water (Figure 2). This type of figure is often overlaid

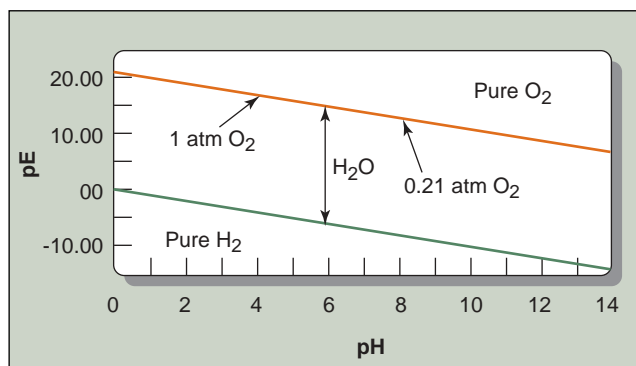


Figure 2. pH/pE diagram for water.

with phase diagram information and called a Pourbaix diagram. If the solution pH and pE reach the upper line, oxygen gas will bubble out. If the solution pH and pE reach the lower line, hydrogen gas will bubble out. During electrolysis of water, one electrode is in the H_2 space, the other is in the O_2 space, and the distance between them is the voltage difference between the electrodes.

Solution chemistry prediction

For simple systems, the equilibrium constant is solved for the species in question from the known concentrations. In more complex systems, a conditional equilibrium constant is calculated based on the known conditions.

The prediction of equilibrium of a large system of chemicals calls for specialized computational methods, such as linear algebra, to solve the system of equations for the unknowns. It can be performed on a personal computer and can be integrated into a spreadsheet, but more often a commercial process simulation package is used.

Equilibrium constants are published for a wide variety of systems. These constants are converted to stepwise formation constants (which are the reciprocal of the normal form of equilibrium constants, Eq. 11):

$$\beta_n = [\text{Complex Formed}][\text{Central Ion}]^{-1}[\text{Ligand}]^{-n} \quad (17)$$

For example, $\beta_1 = [\text{NiOH}^+] / [\text{Ni}^{2+}][\text{OH}^-]^1$. For hydrolysis products, the H^+ form is used and the constant is designated β^* .

Potential pitfalls

Several aspects of aqueous simulations require special consideration.

1. The equilibrium point for solids may require geologic time. Many solid species require very long times, often on the order of geologic time scales, to convert from one crystal structure to another. An example of this is the transformation of aragonite to calcite (both forms of CaCO_3). This requires screening for species that may be considered metastable by the software but appear stable in experiments.

2. The interface between the adsorption surface and the solution is not accounted for. This can be a problem in specialized systems. For general process screening, it can be ignored, but for more detailed work, such as troubleshooting a process crystallizer, this becomes the key variable.

3. The surface/solution charge is also not accounted for. Because of this, colloidal chemistry is not accounted for either. If colloids form in the process (intentionally or unintentionally), then they will not be simulated correctly.

4. Surface tension affects precipitation. The actual mechanism of precipitation is based on the surface tension of the liquid interface around the newly formed particle or around an insoluble impurity. This is why seeding is often used for crystallization. The K_{sp} equilibrium constant represents an idealized thermodynamic case. Precipitation may not be accurately modeled due to surface tension.

5. At high ionic strengths (>30), the solution thermodynamics are not known. However, activity coefficients at high ionic strengths are the subject of current research, so this may not be a problem in the future.

6. Even though it is possible to simulate redox reactions, in practice they are very difficult to simulate accurately. Calculation engines are based on H^+ as the master variable, and optimizing both e^- and H^+ may go beyond the manner in which the engine code is written without a work-around.

7. Oxidation with air is a very complex process, and is one area where improvement is needed both in the understanding of the basic mechanisms of chemical oxidation and in simulator design.

Any one of these concerns can affect the quality of the simulation. Beyond these issues, the actual process chemistry can be very accurately modeled, often more accurately than sampling and analysis techniques can determine. In fact, many of the methods described in this article were developed by analytical chemists in an effort to properly characterize aqueous solutions.

Calculation procedure

Consider a system with three components and six species made of those components, where N = number of components, M = number of species, $X[i]$ = log free concentration of component i , $T[i]$ = total concentration of component i , $E[i]$ =

error in mass balance for component i , $C[j]$ = concentration of species j , $K[j]$ = log formation constant of species j , and $A[i,j]$ = stoichiometric coefficient of component i in species j .

The equilibrium data are a combination of a stoichiometric matrix, or tableau, and a vector of associated equilibrium constants. The example that follows will illustrate their use.

Two basic sets of equations must be solved, the mass balance and the equilibrium equations. The mass balance becomes the T (total) matrix, while X denotes the vector of component concentrations.

The equilibrium equation for formation is linearized to the form:

$$(A \times \log X) + K = \log C \quad (19a)$$

$$\log C[j] = K[j] + A[i,j] \times X[i] \quad (19b)$$

Note that taking the log of C and X linearizes Eqs. 19a and 19b. Also, the matrix A acts as the logic table to show whether a component/species interaction exists.

The mass balance relationship to be satisfied is that the weighted sum of all species containing component i be equal to the total concentration of component i , that is:

$$T_{calc}[i] = A[i,j] \times C[j] \quad (20)$$

$$E[i] = |T_{calc}[i] - T[i]| \quad (21)$$

The solution to the system occurs where, for a vector X , the error (all $E[i]$) = 0. The iterative procedure used to solve a particular system of components and species is the multidimensional Newton-Raphson method. The algorithm is given a guess, X , at the component concentrations, and must find a new guess, X' , which will result in a lower error vector, E . The one-dimensional (non-matrix) Newton-Raphson method is used to find a new converging guess, X' , using the new error matrix, $E[k]$, from X' as a comparison:

$$X' = X - Y/(dy/dx) \quad (22)$$

$J[i,k]$ is the Jacobian, an $N \times N$ matrix derivative showing the effect of changing $X[i]$ on the quantity $E[k]$.

Example. Let's set up the solution of this simple example: Add 10^{-3} mol/L of CaCO_3 to water. The components to consider are: Ca^{2+} , CO_3^{2-} , and H^+ . Note that OH^- is considered $\text{H}_2\text{O} - \text{H}^+$. Water is always included implicitly. In this respect, any four components can be used that allow each species to be defined. The species to consider are: CaCO_3 , HCO_3^- , H_2CO_3 , CaHCO_3 , CaOH^- , OH^- , Ca^{2+} , CO_3^{2-} , and H^+ . The initial variables are $N = 3$ and $M = 9$. The components added (in mol/L) are entered in the T matrix, Eq. 23, and the error tolerance (required to test for convergence) is given by Eq. 24. Then an initial guess, Eq.

25, is required to seed the calculation. If a solution is not reached, the guess was too far off and another iteration is required.

$K[j]$, Eq. 26, is the vector of equilibrium constants that describe the formation of species from the components. Note that the K matrix is made of formation constants, not stability constants, and must be constructed stepwise from the components. Thus, β s are used rather than K s.

$A[i,j]$, Eq. 27, is a matrix of the stoichiometric coefficients of component i in species j , and it is constructed using the data in Table 1.

Calculations produce the final matrix of concentrations given in Eq. 28.

From this simple example, it is clear that a system with 20 or more species would involve very complex calculations. A computer simulation will allow calculations that were never made previously. This enables us to consider more complex interactions than were possible previously.

While this procedure uses equilibrium constants, these calculations can also be done with the underlying thermodynamic parameters, Gibb's free energy of formation (G_f) and enthalpy of formation (H_f) at standard states. The entropy (S), heat capacity ($C_p(T)$), and partial molar volume (V) can also be used for a more accurate solution. These values are published for a wide variety of species. For unpublished solid precipitates, the group contribution method of Mostafa *et al.* (2) may be used. (For example, when applied to ammonium paratungstate (APT), $(\text{NH}_4)_6\text{W}_7\text{O}_{24}\cdot 6\text{H}_2\text{O}$, the method found that $\Delta H_f^{298} \approx -14,620$ kJ/mol and $\Delta G_f^{298} \approx -12,714$ kJ/mol.)

Table 1. Values for constructing $A[i,j]$ for the example calculation.

	Ca ²⁺	CO ₃ ²⁻	H ⁺
CaCO ₃	1	1	0
HCO ₃ ⁻	0	1	1
H ₂ CO ₃	0	1	2
CaHCO	1	1	1
CaOH ⁻	1	0	-1
OH ⁻	0	0	-1
Ca ²⁺	1	0	0
CO ₃ ²⁻	0	1	0
H ⁺	0	0	1

Commercial process simulators

Several commercially available process simulators that are intended to model continuous, steady-state processes include aqueous solution calculations. To model batch processes, one can use a one-hour basis as one batch, and can represent each step in one tank as a separate tank even though they are actually performed in the same tank. Non-steady-state processes can be broken down into a series of steps and treated as separate steps in the process.

To describe the process to the simulator, process flowsheets are drawn on a screen with lines for the streams and

icons for the unit operations. When the flowsheet definition is complete and the stream and unit operation conditions specified, the simulation can be run, which initiates the calculation sequence:

1. calculate equilibria of feed streams
2. calculate sequence of unit operations
3. calculate unit operations in sequence
4. create output report with mass balance and heat balance.

Example: Tungsten hydrometallurgy

Tungsten ore is refined by hydrometallurgical methods. Ore is commonly dissolved (digested) in an NaOH solution to form soluble tungstate ion, then purified in a sequence of process steps (Figure 3). For the process simulation, the dissolution (digestion) step is represented as a reactor and a solids separator (Figure 4).

First, the thermodynamic database for this system is built. This particular database is named m58. We start with a list of incoming chemicals (Table 2a), which define the entire chemical space. The databank is assembled consid-

$$T[i] = \begin{bmatrix} 0.001 \\ 0.001 \\ 0 \end{bmatrix} \quad (23)$$

$$E = \begin{bmatrix} 0.0001 \\ 0.0001 \\ 0.0001 \end{bmatrix} \quad (24)$$

$$T_{\text{guess}} = \begin{bmatrix} 0.001 \\ 0.0001 \\ 10^{-10} \end{bmatrix} \quad (25)$$

$$K[j] = \begin{bmatrix} 1,000 \\ 1.58 \times 10^{10} \\ 3.16 \times 10^{16} \\ 3.98 \times 10^{11} \\ 6.31 \times 10^{-13} \\ 1 \times 10^{-14} \\ 1 \\ 1 \\ 1 \end{bmatrix} \quad (26)$$

$$A = \begin{bmatrix} 1 & 1 & 0 \\ 0 & 1 & 1 \\ 0 & 1 & 2 \\ 1 & 1 & 1 \\ 1 & 0 & -1 \\ 0 & 0 & -1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad (27)$$

$$X[i] = \begin{bmatrix} 2.94 \times 10^{-4} \\ 2.29 \times 10^{-4} \\ 1.52 \times 10^{-8} \\ 3.90 \times 10^{-6} \\ 1.28 \times 10^5 \\ 3.00 \times 10^{-4} \\ 6.79 \times 10^{-4} \\ 4.33 \times 10^{-4} \\ 3.33 \times 10^{-11} \end{bmatrix} \quad (28)$$

Reactions and Separations

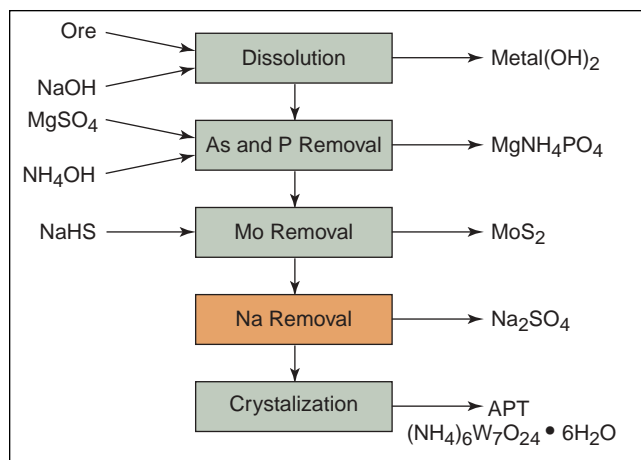


Figure 3. Hydrometallurgical process for refining tungsten ore.

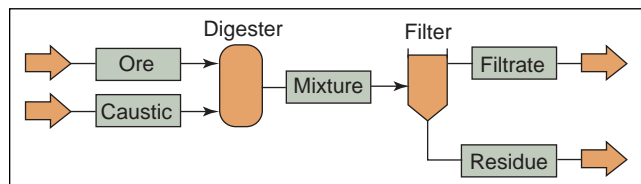


Figure 4. Tungsten digestion step.

ering the ionic species in Table 2b and then the non-ionic species (gases, aquo species and precipitates) in Table 2c. Notice that CO_2 was not included, greatly simplifying the system. Even though this process is a closed system, in reality CO_2 exposure is inevitable, and more-detailed process models must include the accumulation of atmospheric CO_2 , especially in high-pH systems like caustic digesters and caustic scrubbers.

Next, the feed conditions and process conditions are defined: one 50-kg bag of ore (35% MnWO_4 , 35% FeWO_4 , 10% CaO , 10% MnO , 10% FeO); 100 gal (380 L) of NaOH (13 N); 100 psig (545 kPa); temperature varies from 200°F to 270°F (38°C to 132°C); time — to equilibrium point.

The time of an equilibrium reaction is not specified. If the reaction is not nearly instantaneous, reaction kinetic parameters should be determined to properly model the process or, at a minimum, compare a model to an experiment for verification.

Run the process model. The simulator runs the process simulation and executes a series of FORTRAN modules to calculate the sequence, stream data and unit operations. In this case, the temperature of dissolution was not known, so a series of temperatures was used to determine the conversion at each temperature (Figure 5).

At temperatures below 250°F (121°C), this ore will not fully dissolve. This agrees with published data (2) as well as actual practice. Keep in mind that the plot of conver-

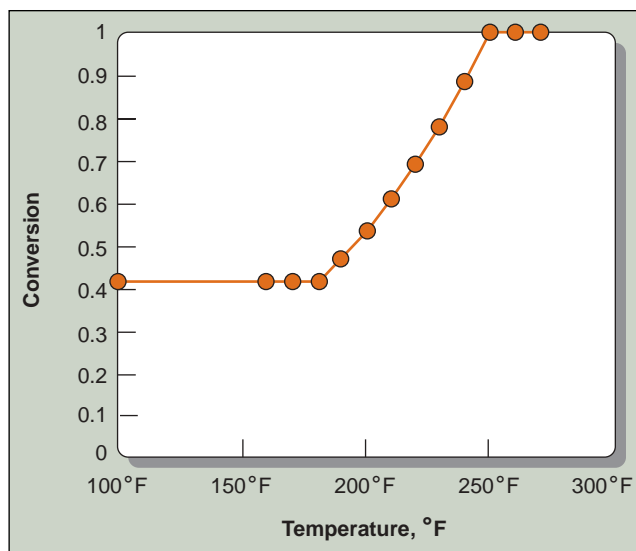


Figure 5. Conversion of ore as a function of temperature.

sions in Figure 5 is completely theoretical — there are no actual data other than the basic thermodynamic parameters of ΔH_f^{298} and ΔG_f^{298} for each species. This type of predictive power can be applied with or without additional experimental data to provide extremely accurate and powerful models of a step, process, or an entire chemical plant.

Simulation procedure. The software used allows graphical entry of streams and unit operations via menus and command toolbars. In this case, a vent line was added to the flowsheet to vent the reactor. After the simulation ran, no flow was indicated, which shows that there was no vapor leaving in the simulation. This type of extra stream can be used to identify environmental problems in any stage of process work. Note that to accurately model tank vents, the incoming air must be included in the unit's feed streams. To account for CO_2 problems, the air stream should include the atmospheric concentration of CO_2 .

This example was done with Pro/II with ProVision, with Electrolytes, which is published by Simulation Sciences, Inc. (www.simsci.com).

Example: Sour gas stripper

Ammonia-bearing wastewater is stripped and the ammonia is recovered using reactive distillation with lime in a tower that uses 17 theoretical trays and approximates a 51-ft packed bed.

In this process, lime slurry is injected into waste ammonium chloride to form calcium chloride and ammonium hydroxide. At pH above 10.3, the ammonium hydroxide is converted to ammonia and can be removed in the stripping section of the column and recovered as pure 28% ammonium hydroxide. As ammonia is stripped, base is lost and the pH drops. At the same time, lime slurry is slowly releasing calcium and hydroxide ions into the solution to re-

Table 2. Building the databank for the tungsten process example.

a. Feed Species		b. Ionic Species	
(NH ₄) ₆ W ₇ O ₂₄ •6H ₂ O (APT)	OH ⁻	CaOH ⁺	Fe(II) ²⁺
FeWO ₄	Fe(II)OH ⁺	H ₂ P ₂ O ₇ ²⁻	H ₂ PO ₄ ⁻
Mg ₃ (PO ₄) ₂	H ₃ P ₂ O ₇ ⁻	H ⁺	HP ₂ O ₇ ³⁻
CaSO ₄	HPO ₄ ²⁻	HSO ₄ ⁻	Mg ²⁺
MnWO ₄	MgOH ⁺	Mn ²⁺	Mn(OH) ₃ ⁻
NaOH	Mn(OH) ₄ ²⁻	MnOH ⁺	Na ⁺
N ₂	NaSO ₄ ⁻	NH ₄ ⁺	NH ₄ SO ₄ ⁻
	Ca ²⁺	P ₂ O ₇ ⁴⁻	PO ₄ ³⁻
	SO ₄ ²⁻	WO ₄ ²⁻	
c. Nonionic Species			
H ₂ O	H ₂ SO ₄	N ₂	NH ₃
CaSO ₄	MnWO ₄	NaOH	Ca(HSO ₄) ₂
CaWO ₄	FeWO ₄	H ₃ PO ₄	Mg(HSO ₄) ₂
MgNH ₄ PO ₄	Mn(HSO ₄) ₂	Na ₂ WO ₄	Mg ₃ (PO ₄) ₂
NH ₄ OH	FeII(OH) ₂	MgSO ₄	Mn(OH) ₂
MnSO ₄	Ca(OH) ₂	FeII SO ₄	H ₂ WO ₄
Mg(OH) ₂	MgWO ₄	Na ₂ HPO ₄	Na ₂ SO ₄
Na ₃ PO ₄	NaH ₂ PO ₄	NaHSO ₄	(NH ₄) ₂ HPO ₄
(NH ₄) ₂ SO ₄	(NH ₄) ₂ WO ₄	(NH ₄) ₃ PO ₄	NH ₄ H ₂ PO ₄
APT•5H ₂ O	CaSO ₄ •2H ₂ O	FeII SO ₄ •1H ₂ O	FeII SO ₄ •4H ₂ O
FeII SO ₄ •7H ₂ O	MgNH ₄ PO ₄ •6H ₂ O	MgSO ₄ •1H ₂ O	MgSO ₄ •6H ₂ O
MgSO ₄ •7H ₂ O	MnSO ₄ •1H ₂ O	MnSO ₄ •5H ₂ O	MnSO ₄ •7H ₂ O
Na ₂ HPO ₄ •12H ₂ O	Na ₂ HPO ₄ •2H ₂ O	Na ₂ HPO ₄ •7H ₂ O	Na ₂ SO ₄ •10H ₂ O
NaH ₂ PO ₄ •1H ₂ O	NaH ₂ PO ₄ •2H ₂ O	NaOH•1H ₂ O	(NH ₄) ₂ HPO ₄ •2H ₂ O
(NH ₄) ₃ PO ₄ •3H ₂ O			

place the missing base. Also reacting are metals and ions in the waste solution that may be dissolving or precipitating based on equilibrium conditions.

Table 3. Component list for the sour-gas stripper example.


H ₂ O	NH ₃	Ca(OH) ₂ (Lime)
NH ₄ Cl	NH ₄ OH	CaCl ₂
Ca ²⁺	CaOH ⁺	NH ₄ ⁺
H ⁺	HCl	CaCl _{2(s)}
Ca(OH) ₂	NH ₄ Cl _(s)	CaCl _{2(s)}
Cl ⁻	OH ⁻	SALT1 = CaCl ₂ •4W
SALT2 = CaCl ₂ •6W	SALT3 = CaCl ₂ •W	SALT4 = CaCl ₂

Gases and Ions

H ₂ O	NH ₃	NH ₄ OH	Ca ²⁺	CaOH ⁺
NH ₄ ⁺	H ⁺	HCl	Cl ⁻	OH ⁻

The feeds for this process are: steam (H₂O), 12,000 lb/h; lime slurry (Ca(OH)_{2(aq)}), 20% slurry; waste ammonia (NH₄Cl_(aq)), 2%, 120 gal/min. The simulator uses the component list shown in Table 3. Then the software picks other ions and reactions. It's a good idea to check the generated list for species that may form and are not on the list.

For the stripping to be effective, the pH of the still bottoms must be greater than 10.3. Modeling showed that the excess lime required to keep the bottoms pH over 10.3 required an excess of lime slurry beyond the practical slurry velocities in the tower, causing plugging that required regular cleaning. By using simulation, a method was devised to provide a stepwise addition of lime slurry, allowing a soluble reaction throughout. Further simulations were used to optimize the energy consumption using pinch technology. With the use of an aqueous process model, conditions throughout the process can be determined and then verified with a minimum of sampling and chemical analysis.

The simulation work for this example was done with Aspen Plus, which is published by Aspen Technology, Inc. (www.aspentech.com). 

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