**Multicomponent Ionic Equilibria**

K. Dorma

April 8, 2017

File: ionic\_equilibria\_rev\_5.xlsm

**Description**

Multiple component equilibrium involves competing reactions where each species is in chemical equilibrium according to all reactions. This requires the iterative solution of the material balance equations for each reaction, and the non-linear equilibrium expressions.

The following parts of the iterative algorithm are described in this paper.

1. Derivation of the iterative solution to the non-linear competing equilibrium problem.
2. Development of the matrix equations in partitioned form.
3. Estimation of the solubility of a gas species, and the correction for the specified temperature.
4. Correction for the equilibrium constants (K values) at the specified temperature.

**Description**

Let the number of equilibrium reactions be m, and the number of equilibrium reactions be n. The following chemical equations are considered, with each equation having an equilibrium constant Ki and an extent of reaction ri. The current reactions and species j used are for CO2 and H2S dissolved in NaOH.

H2S + OH- = HS- + H2O (K1, r1)

CO2 + OH- = HCO3- (K2, r2)

HCO3- + OH- = CO3-2 + H2O (K3, r3)

H+ + OH- = H2O (K4, r4)

HS- + OH- = S-2 + H2O (K5, r5)

The reaction stoichimetry is expressed as a matix S(m,n).

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Equations** | **OH-** | **H2S** | **HS-** | **CO2** | **HCO3-** | **CO32-** | **H+** | **S2-** | **H2O** |
| H2S + NaOH = NaHS + H2O | 1 | 1 | -1 |  |  |  |  |  | -1 |
| CO2 + NaOH = NaHCO3 | 1 |  |  | 1 | -1 |  |  |  |  |
| NaHCO3 + NaOH = Na2CO3 + H20 | 1 |  |  |  | 1 | -1 |  |  | -1 |
| H+ + OH- = H2O | 1 |  |  |  |  |  | 1 |  | -1 |
| NaHS + NaOH = Na2S + H2O | 1 |  | 1 |  |  |  |  | -1 | -1 |

Each species has an initial concentration. The species balance for each ionic species (except for Na+) is given by equations 1 – 8, where each reaction has an extent of reaction r.

[OH-] = [OH-]ic – r1 – r2 –r3 –r4–r5 (1)

[H2S] = [H2S]ic –r1 (2)

[HS-] = [HS-]ic + r1- r5 (3)

[CO2] = [CO2]ic –r2 (4)

[HCO3-] = [HCO3-]ic +r2- r3 (5)

[CO3-2] = [CO3-2]ic + r3 (6)

[H+] = [H+]ic – r4 (7)

[S-2] = [S-2]ic + r5 (8)

The reaction extents ri are related to the species material balance through the reaction stoichiometry matrix S.

Each of the five equilibrium products are

K1 = [HS-] / [H2S] [OH-]

K2 = [HCO3-] / [CO2] [OH-]

K3 = [CO3-2] / [HCO3-] [OH-]

K4 = 1 / [H+] [OH-]

K5 = [S-2] / [OH-] [HS-]

These non-linear equations are expressed in a linear form by taking the logarithm.

ln K1 = ln [HS-] – ln [H2S] – ln [OH-] (9)

ln K2 = ln [HCO3-] - ln [CO2] – ln [OH-] (10)

ln K3 = ln [CO3-2] – ln [HCO3-] – ln [OH-] (11)

ln K4 = 0 – ln [H+] – ln [OH-] (12)

ln K5 = ln [S-2] – ln [OH-] – ln [HS-] (13)

There now exists two variables for the concentration of a species: the actual concentration, and the logarithm of the concentration. These two variables are related by the nonlinear identity

x = exp(ln x)

We seek a linear approximation to relate the actual concentration and the logarithm of the concentration.

Note that the derivative is

dx / d(ln x) = exp(ln x)

If we assume that we have known values of x and ln x at the n iteration level, we can use a Taylor series to write a linear equation for the value of x and ln x at the n+1 iteration level

is equation couples the value of the concentration to the logarithm of concentration. This relationship is important because it ensures that we only use real values for concentrations. A negative value for a concentration does not impact the solution to the linear system.

The Taylor series expansion for each unknown concentration is

[OH-]n+1 = [OH-] + (ln [OH-]n+1 – ln [OH-]) [OH-] (14)

[H2S] …

[HS-] …

[CO2] …

[HCO3-] …

[CO3-2] …

[H+] …

[S-2] … (21)

Note that the Taylor series equations are linear, but include coefficients that are related to the past guess for ln[x].

Equations 1 – 21 produce a matrix equation with the following structure

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | OH- | H2S | HS- | CO2 | HCO3- | CO32- | H+ | S2- | r1 | r2 | r3 | r4 | r5 | OH- | H2S | HS- | CO2 | HCO3- | CO32- | H+ | S2- |
| OH- balance | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 1 | 1 | 1 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| H2S balance | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| HS- balance | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | -1 | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| CO2 balance | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| HCO3 balance | 0 | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | -1 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| CO32- balance | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | -1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| H+ balance | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| S2- balance | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | -1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Linearized eqm r1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | -1 | -1 | 1 | 0 | 0 | 0 | 0 | 0 |
| Linearized eqm r2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | -1 | 0 | 0 | -1 | 1 | 0 | 0 | 0 |
| Linearized eqm r3 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | -1 | 0 | 0 | 0 | -1 | 1 | 0 | 0 |
| Linearized eqm r4 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | -1 | 0 | 0 | 0 | 0 | 0 | -1 | 0 |
| Linearized eqm r5 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | -1 | 0 | -1 | 0 | 0 | 0 | 0 | 1 |
| linearization of OH- | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | -6.24E-12 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| linearization of H2S | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | -0.003163 | 0 | 0 | 0 | 0 | 0 | 0 |
| linearization of HS- | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | -6.22E-06 | 0 | 0 | 0 | 0 | 0 |
| linearization of CO2 | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | -0.002064 | 0 | 0 | 0 | 0 |
| linearization of HCO3- | 0 | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | -4.13E-05 | 0 | 0 | 0 |
| linearization of CO32- | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | -1.6E-11 | 0 | 0 |
| linearization of H+ | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | -4.75125E-05 | 0 |
| Linearization of S2- | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | -5.3E-17 |

The shaded pink blocks are obtained from the stoichiometry matrix S.

Given the known values for the right hand side vector b, these 21 equations and unknowns form a matrix equation of the form

*A xn+1 = b*

Where

The next guess for each of the 21 unknowns is obtained by

*xn+1 = A-1 b*

The values of the next guess for each of the 21 unknowns is then substituted into the Taylor series portion of the matrix equation, and solved again.

A suitable initial guess for each unknown is zero. Convergence is slow, but reliable, and requires approximately 25 iterations to converge all of the concentrations and logarithms to sufficient significant digits.

**Gas Solubility**

The solubility of CO2 and H2S in water is determined by Henry’s law

Ptot yCO2 = HCO2 [CO2]

Ptot yH2S = HH2S [H2S]

The Henry law constant for CO2 and H2S were obtained from the NIST Webprop database at the standard temperature of 298 K. The Henry law constant is a function of temperature, and the accepted functional form is

Where the constant a is determined by experiment, and is tabulated in the NIST Webprop database. This equation allows us to extrapolate the value of the Henry constant from the standard temperature of 298 K to the specified temperature.

**Equilibrium Constant and Temperature Effects**

The equilibrium constant Ki is tabulated at standard conditions (298 K) for each reaction. This equilibrium constant is related to temperature through the Clausius Clapeyron equation.

The heat of reaction DHRXN at standard conditions (298 K) is obtained from the standard heat of formation, and the stoichiometry coefficients in the matrix S. The standard heat of formation are the vector hf

|  |  |
| --- | --- |
| [OH-] | -230 J/gmol |
| [H2S] | -20.6 |
| [HS-] | -18 |
| [CO2] | -393 |
| [HCO3-1] | -692 |
| [CO3-2] | -677 |
| [H+] | 0 |
| [S-2] | 33 |
| H2O | -286 |

The heat of reaction vector hr is

hr = S hf

And I should add the difference in heat capacity for the second order correction to the DH reaction at higher temperatures. That will come.

**Calculation Methodology**

The key inputs are the pressure, temperature and mole fraction of CO2 and H2S in the vapour phase.

The concentration of dissolved CO2 and H2S is obtained by Henry`s law. It is assumed that the equilibrium processes do not consume a significant amount of CO2 or H2S.

Initial guesses for the concentrations and log concentrations are set to zero.

The next guesses for the concentrations and log concentrations are determined with the solution to the large matrix equation.

These updated guesses are then used as the initial guesses for the next iteration.

Typically 25 – 30 iterations are needed to converge all unknowns.

Algorithm for Scilab

Ionic only, no gas phase yet

Define ionic species formula vector ie, formula = [HCO-3, HSO4-1…]

Define standard heat of formation for each species

Define molar heat capacity for each ionic species

Define stoichiometry for each reaction

Define standard heat of reaction for each reaction