Equilibrium Calculations

Systematic Approach to Calculate Concentrations of Chemical Species

Systematic Equilibrium Calculations

Often, the species in an aqueous solution sets up multiple equilibria among themselves.

The species involved come from on or more of the following;

(a) dissolution of molecules
(b) dissociation/association of dissolved species
(c) hydrolysis of ions
(d) the ionization of the solvent.
(e) complex ion formation

Calculation of concentration of *all* species in solution:

Following the identification of *all* the species (say, *n, number of species*) present in the solution, identify *every* chemical equilibrium system in the chemical system.

To solve for the concentrations of *n* types of chemical species, it requires *n* independent equations.

Such a set of equations can be formulated from considering the following;

a. equilibrium constant expressions
b. charge balance equation – Conservation of charge
c. mass balance equations – Conservation of mass
d. system conditions *measurements* such as pH, pX etc. if available.

Charge balanced equation:

The solution being electrically neutral, sum total of all positive charges must be equal to that of all the negative charges.

$$\sum_i z_{+n}[A^{+n}] + \sum_j z_{-m}[B^{-m}] = 0$$

z_k charge on species with the sign.

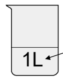
Mass balanced equation:

Components although present in various combined forms (species) originate from well defined 'sources'.

Relate concentrations of such components to their initiation. (Hint: look for conjugate bases and like)

Other info: pH of the solution

Example:



Dissolve 0.0100 moles H_3PO_4, add 0.0025 moles KOH

0.0100 M H_3PO_4 + 0.0025M KOH; starting concentrations
$[H_3PO_4]_0$ $[K^+]_0 = [OH^-]_0$:just before reaction

Each chemical equilibrium generates one equation (include solvent auto-protolysis).

H_3PO_4	+ KOH	$\rightarrow H_2O + KH_2PO_4$	
0.0100 M	0.0025M		
0.0075 M	0		0.0025M

a. Equilibria:

$$H_3PO_4(aq) \rightleftharpoons H^+(aq) + H_2PO_4^{-1}(aq) \qquad K_{1a} = \frac{[H^+][H_2PO_4^{-1}]}{[H_3PO_4]}$$

$$H_2PO_4^{-1}(aq) \rightleftharpoons H^+(aq) + HPO_4^{-2}(aq) \qquad K_{2a} = \frac{[H^+][HPO_4^{-2}]}{[H_2PO_4^{-1}]}$$

$$HPO_4^{-2}(aq) \rightleftharpoons H^+(aq) + PO_4^{-3}(aq) \qquad K_{3a} = \frac{[H^+][PO_4^{-3}]}{[HPO_4^{-2}]}$$

$$H_2O \rightleftharpoons H^+(aq) + OH^-(aq) \qquad K_w = [H^+][OH^-]$$

$$[K^+] = [K^+]_0$$

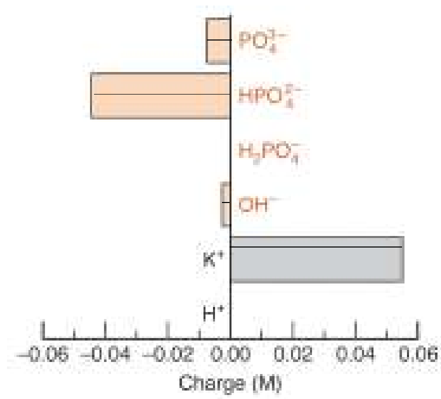
CBE: $\sum_i z_{+n}[A^{+n}] + \sum_j z_{-m}[B^{-m}] = 0$

$$[K^+] + [H^+] - [OH^-] - [H_2PO_4^{-1}] - 2[HPO_4^{-2}] - 3[PO_4^{-3}] = 0$$

MBE:

$$[H_3PO_4] + [H_2PO_4^{-1}] + [HPO_4^{-2}] + [PO_4^{-3}] = [H_3PO_4]_0$$

Select a chemical moiety present in ***more than one*** chemical species (form) that originated from a preferably a single compound if feasible.



CHEAQS

CHEAQS Next - is a free Windows program for calculating CHemical Equilibria in AQuatic Systems

http://www.cheaqs.eu/

Examples:

Study of the pH dependence of solubility (CaF_2).

Let the solubility be; S_{CaF2} mol/L

Pertinent Reactions (equilibria):

$$CaF_2(s) = \underline{Ca^{+2}}(aq) + 2\underline{F^-}(aq) \qquad K_{sp,CaF2} = [Ca^{+2}][F^-]^2$$

$$F^-(aq) + H_2O = \underline{HF}(aq) + \underline{OH^-}(aq) \qquad K_{b,F^-} = \frac{[HF][OH^-]}{[F^-]}$$

$$H_2O = \underline{H^+}(aq) + OH^-(aq) \qquad K_w = [H^+][OH^-]$$

CBE:

$$[H^+] + 2[Ca^{+2}] = [OH^-] + [F^-] \qquad \sum_i z_{+n}[A^{+n}] + \sum_j z_{-m}[B^{-m}] = 0$$

MBE:

$$[HF] + [F^-] = 2[Ca^{+2}]$$

Solubility, S, of CaF_2; $S = [Ca^{+2}]$

Solving the five equations 'analytically' is a formidable task.

One strategy would be to calculate the concentrations of the species *assuming* a value for a pH, i.e. for an assumed [H+], and continue the procedure for a series of different pH values. Or,

$$K_{b,F} = \frac{[HF][OH^-]}{[F^-]} \qquad \Rightarrow [HF] = \frac{K_b[F^-]}{[OH^-]}$$

$$[HF] + [F^-] = 2[Ca^{+2}]$$

$$\frac{K_b[F^-]}{[OH^-]} + [F^-] = 2[Ca^{+2}] \qquad \Rightarrow [F^-] = \frac{2[Ca^{+2}]}{1 + \frac{K_b}{[OH^-]}}$$

$$[Ca^{+2}][F^-]^2 = [Ca^{+2}]\left(\frac{2[Ca^{+2}]}{1 + \frac{K_b}{[OH^-]}}\right)^2 = K_{sp,CaF2}$$

$$4[Ca^{+2}]^3\left(\frac{1}{1 + \frac{K_b}{[OH^-]}}\right)^2 = K_{sp,CaF2}$$

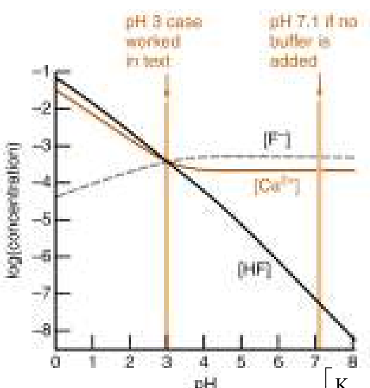
$$4[Ca^{+2}]^3 = K_{sp,CaF2}\left(1 + \frac{K_b}{[OH^-]}\right)^2$$

$$[Ca^{+2}] = \left(\frac{K_{sp,CaF2}}{4}\left(1 + \frac{K_b}{[OH^-]}\right)^2\right)^{1/3}$$

$$[Ca^{+2}] = \left[\frac{K_{sp,CaF2}}{4}\left(1 + \frac{K_{b,F}}{[OH^-]}\right)^2\right]^{1/3}$$

$$[Ca^{+2}] = \left[\frac{K_{sp,CaF2}}{4}\left(1 + \frac{K_{b,F}[H^+]}{K_w}\right)^2\right]^{1/3}$$

$$S = [Ca^{+2}] = \left[\frac{K_{sp,CaF2}}{4}\left(1 + \frac{K_{b,F}10^{-pH}}{K_w}\right)^2\right]^{1/3}$$



$$[F^-] = \frac{2[Ca^{+2}]}{1 + \frac{K_b 10^{-pH}}{K_w}}$$

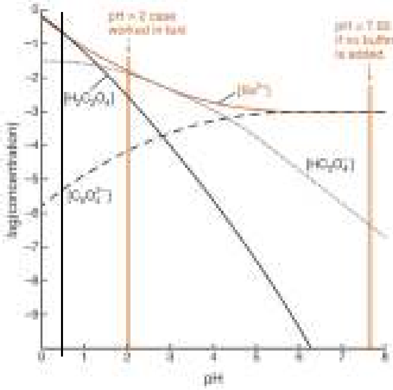
$$[HF] = \frac{K_b[F^-]10^{-pH}}{K_w}$$

$$[Ca^{+2}] = \left[\frac{K_{sp,CaF2}}{4}\left(1 + \frac{K_{b,F}10^{-pH}}{K_w}\right)^2\right]^{1/3}$$

Examples:

Study of the pH dependence of solubility (BaC_2O_4).

Let the solubility be; S_{BaC2O4} mol/L


pH = 2 case
worked in text
$[Sr^{2+}]$
$[H_2C_2O_4]$
$[HC_2O_4^-]$
$[C_2O_4^{2-}]$
log(concentration)
pH