

Chemical Equilibria

General representation



Where uppercase letters are chemical species and lowercase letters are coefficients (i.e. # of atoms or moles)

Equilibrium Constant

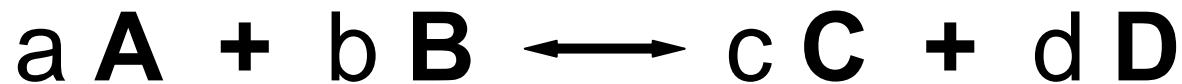
$$K = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

where [] = concentration, usually molar

True Thermodynamic Equilibrium Constant

$$K^{\circ} = \frac{(a_C)^c (a_D)^d}{(a_A)^a (a_B)^b}$$

For



K° Defined for standard conditions of 25 °C,
1 atm pressure and $I = 0$ (infinite dilution)

Many types of K's (equilibrium constants)

K_a for acid dissociation

K_b for base hydrolysis

K_w for water auto ionization

K_{sp} for solubility product

K_f for a formation constant

$K_1, K_2, K_3,$ etc. for stepwise formation constants

$\beta_1, \beta_2, \beta_3,$ etc. for overall formation constants

Solubility Calculated

Solubility (S) is the concentration of individual ions generated from an insoluble compound



$$S = [\text{Ba}^{2+}] = [\text{SO}_4^{2-}]$$

Activity Correction

$$K_{SP} = \frac{a_{Ba} a_{SO_4}}{1} = a_{Ba} a_{SO_4}$$

Since

$$a_{Ba} = \gamma_{Ba} [Ba^{2+}] \quad \& \quad a_{SO_4} = \gamma_{SO_4} [SO_4^{2-}]$$

Substituting

$$K_{SP} = a_{Ba} a_{SO_4} = \gamma_{Ba} [Ba^{2+}] \gamma_{SO_4} [SO_4^{2-}]$$

Solubility Calculation (completed)

Since

$$K_{SP} = [\text{Ba}^{2+}][\text{SO}_4^{2-}] \quad \& \quad \gamma_{\text{Ba}} = \gamma_{\text{SO}_4}$$

Then

$$\mathbf{S} = \sqrt{\frac{K_{SP}}{\gamma^2}}$$

To determine the solubility of BaSO_4 in a solution containing other ions (like SW), you must calculate the activity coefficient (γ)

Two ways to correct for activity

1) Correct each ion as discussed

$$K_{SP} = a_{Ba} a_{SO_4} = \gamma_{Ba} [Ba^{2+}] \gamma_{SO_4} [SO_4^{2-}]$$

2) Correct the equilibrium constant K

$$K' = \frac{K_{SP}}{\gamma^2} = [Ba^{2+}] [SO_4^{2-}]$$

Water Hydrolysis (very important)



Applying same rules for K expressions

$$K_w = \frac{a_{\text{H}^+} a_{\text{OH}^-}}{1} = a_{\text{H}^+} a_{\text{OH}^-}$$

Where H_2O (the solvent) is assigned activity $\underline{= 1}$

Remember pH

pH is defined as the negative logarithm of the hydrogen ion activity

$$\text{pH} = -\log a_{\text{H}^+}$$

Given the numerical value $K_w = 1 \times 10^{-14}$ & $K_w = a_{\text{H}^+} a_{\text{OH}^-}$ then we can always calculate OH^- from the pH

pH Examples

At neutral pH $\mathbf{a_{H^+} = a_{OH^-}}$ and

$$\mathbf{a_{H^+} = \sqrt{K_w} = 1 \times 10^{-7} = \text{pH } 7.00}$$

At seawater pH (e.g., 8.2)

$$\mathbf{a_{H^+} = 1 \times 10^{-8.2} = 6.3 \times 10^{-9}}$$

$$\mathbf{a_{OH^-} = \frac{K_w}{a_{H^+}} = \frac{1 \times 10^{-14}}{6.3 \times 10^{-9}} = 1.58 \times 10^{-6}}$$

Hydronium Ion

Water actually hydrolyses to form a hydronium ion (H_3O^+) rather than the lone proton (H^+)

(Once again an ion-water interaction akin to those discussed previously)

For the sake of simplicity, we will refer to this species as H^+ which is common practice

A Note on Strong & Weak Electrolytes

- Salts, Acids & Bases are all ionic compounds that dissociate (i.e., form ions) in water either partially or completely

- Complete dissociation = a strong electrolyte



- Partial dissociation = a weak electrolyte



Two step equilibrium = forward & back reactions

Acid-Base Equilibria

Fictitious Weak Acid (HA)



$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \quad \text{or} \quad \frac{\mathbf{a}_{\text{H}^+} \mathbf{a}_{\text{A}^-}}{\mathbf{a}_{\text{HA}}}$$

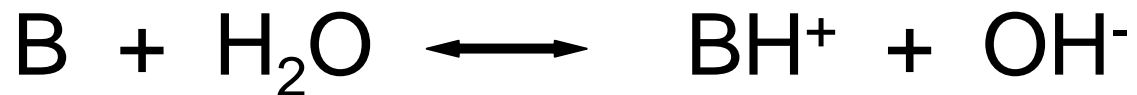
The smaller the K_a the weaker the acid

Strong acids have no K_a it approaches
infinity

Acid-Base Equilibria

Fictitious Weak Base (B)

Capable of accepting a proton (H⁺)



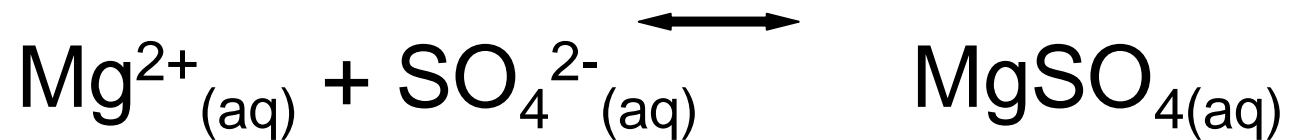
$$K_b = \frac{[BH^+][OH^-]}{[B]} \quad \text{or} \quad \frac{a_{BH^+} a_{OH^-}}{a_B}$$

The smaller the K_b the weaker the base

Strong bases have no K_b it approaches
infinity

Ion Pair or Complex Formation Equilibria

Dozens of Ion Pairs form in SW & even
more complexes – deal with them the same
way



$$K_f = \frac{a_{\text{MgSO}_4}}{a_{\text{Mg}} a_{\text{SO}_4}}$$

Larger K_f = stronger formation – reaction 

Typical Problem in SW

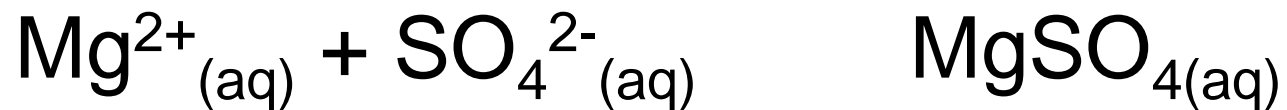
Find Various Forms or Species

Given total concentration data for certain constituents in SW, find % of species

Example: If total Mg is $C_{Mg} = 5.28 \times 10^{-2}$ mol/kg

and total SO_4 is $C_{SO_4} = 2.82 \times 10^{-2}$ mol/kg

knowing that



and the value of the K_f or $K_{MgSO_4} = 2.29 \times 10^{17}$ m^2

Steps in the Manual Solution of Simple Equilibrium Problems

1) Start with a recipe: $C_{\text{Mg}} = 5.28 \times 10^{-2}$
mol/kg

$C_{\text{SO}_4} = 2.82 \times 10^{-2}$
mol/kg

2) List the species: Mg^{2+} , SO_4^{2-} , MgSO_4

3) List reaction(s): $\text{Mg}^{2+} + \text{SO}_4^{2-} \rightleftharpoons \text{MgSO}_4$

4) Write Mass Balance equations:

$$C_{\text{Mg}} = [\text{Mg}^{2+}] + [\text{MgSO}_4] = 5.28 \times 10^{-2}$$

mol/kg

$$C_{\text{SO}_4} = [\text{SO}_4^{2-}] + [\text{MgSO}_4] = 2.82 \times 10^{-2}$$

Steps in the Manual Solution of Simple Equilibrium Problems

5) Write a Charge Balance equation:

$$[\text{Mg}^{2+}] = [\text{SO}_4^{2-}]$$

6) Write equilibrium constant expression(s):

$$K_f = \frac{a_{\text{MgSO}_4}}{a_{\text{Mg}} a_{\text{SO}_4}} \quad \text{or} \quad \frac{[\text{MgSO}_4]}{[\text{Mg}^{2+}] [\text{SO}_4^{2-}]}$$

There are 3 species or 3 unknown concentrations

There are also 3 equations (actually 4) to solve

We can solve the 3 equations simultaneously to get an answer

Solve for free Mg concentration first = $[Mg^{2+}]$

Rearrange the mass balance equations:

$$C_{Mg} = [Mg^{2+}] + [MgSO_4] \quad \text{rearranges}$$

$$\text{to give} \quad [MgSO_4] = C_{Mg} - [Mg^{2+}]$$

$$C_{SO_4} = [SO_4^{2-}] + [MgSO_4] \quad \text{rearranges}$$

$$\text{giving} \quad [SO_4^{2-}] = C_{SO_4} - [MgSO_4]$$

We must also substitute the 1st into the 2nd

$$C_{\text{Mg}} = [\text{Mg}^{2+}] + [\text{MgSO}_4] \quad \text{rearranges}$$

to give
$$[\text{MgSO}_4] = C_{\text{Mg}} - [\text{Mg}^{2+}]$$

$$C_{\text{SO}_4} = [\text{SO}_4^{2-}] + [\text{MgSO}_4] \quad \text{rearranges}$$

giving
$$[\text{SO}_4^{2-}] = C_{\text{SO}_4} - [\text{MgSO}_4]$$

Substituting the 1st into the 2nd for $[\text{MgSO}_4]$

Gives
$$[\text{SO}_4^{2-}] = C_{\text{SO}_4} - (C_{\text{Mg}} - [\text{Mg}^{2+}])$$

Now we can

Substitute into K

$$K_f = \frac{[\text{MgSO}_4]}{[\text{Mg}^{2+}] [\text{SO}_4^{2-}]}$$

Our resulting equation looks like

$$K_{\text{MgSO}_4} = \frac{C_{\text{Mg}} - [\text{Mg}^{2+}]}{[\text{Mg}^{2+}] (C_{\text{SO}_4} - (C_{\text{Mg}} - [\text{Mg}^{2+}]))}$$

Be careful of signs in denominator

$$K_{\text{MgSO}_4} = \frac{C_{\text{Mg}} - [\text{Mg}^{2+}]}{[\text{Mg}^{2+}] (C_{\text{SO}_4} - C_{\text{Mg}} + [\text{Mg}^{2+}])}$$

Cast in the form of a quadratic

$$K[\text{Mg}^{2+}]C_{\text{SO}_4} - K[\text{Mg}^{2+}]C_{\text{Mg}} + K[\text{Mg}^{2+}]^2 = C_{\text{Mg}} -$$

Set equal to zero and solve with the quadratic formula

Equation from previous slide

$$K \frac{[\text{Mg}^{2+}]C_{\text{SO}_4}}{[\text{Mg}^{2+}]} - K[\text{Mg}^{2+}]C_{\text{Mg}} + K[\text{Mg}^{2+}]^2 = C_{\text{Mg}} -$$

Set equal to 0 & rearrange in form for quadratic formula

$$K[\text{Mg}^{2+}]^2 + K[\text{Mg}^{2+}]C_{\text{SO}_4} - K[\text{Mg}^{2+}]C_{\text{Mg}} + [\text{Mg}^{2+}] - C_{\text{Mg}} =$$

Gather terms

$$K[\text{Mg}^{2+}]^2 + (KC_{\text{SO}_4} - KC_{\text{Mg}} + 1)[\text{Mg}^{2+}] - C_{\text{Mg}} = 0$$

Remember the quadratic formula ?

Equation from previous slide

$$K[Mg^{2+}]^2 + (KC_{SO_4} - KC_{Mg} + 1)[Mg^{2+}] - C_{Mg} = 0$$

Quadratic formula

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

Solve for **x** which for us is $[Mg^{2+}]$ where

$$a = C_{Mg} K \quad b = (KC_{SO_4} - KC_{Mg} + 1) \quad c = -$$

Solving this problem with the quadratic formula

And substituting in the known values for:

K_f' which equals $K_f \gamma^2$

Where $K_f = K_{MgSO_4} = 2.29 \times 10^2$ and $\gamma = 0.23$

$C_{Mg} = 5.28 \times 10^{-2}$ mol/kg

$C_{SO_4} = 2.82 \times 10^{-2}$ mol/kg

The answer is: $x = [Mg^{2+}] = 4.35 \times 10^{-2}$ mol/kg

Since $C_{Mg} = 5.28 \times 10^{-2}$ mol/kg then $[Mg^{2+}] = 82 \%$

Activity Coefficient

At typical ionic strengths for SW $I = 0.5$ to **0.7**

From Davies Equation Mg^{2+} activity coefficient

$$\ln \gamma = -A Z^2 \left[\frac{I^{0.5}}{1 + I^{0.5}} - 0.2 I \right]$$

If $Z = 2$ & $A = 1.17$ then $\ln \gamma = -1.47$ & $\gamma =$
0.23

Calculate All Species

Given $C_{\text{Mg}} = 5.28 \times 10^{-2}$ mol/kg

and $C_{\text{SO}_4} = 2.82 \times 10^{-2}$ mol/kg

We calculated $[\text{Mg}^{2+}] = 4.35 \times 10^{-2}$ mol/kg or **82**
%

By difference $[\text{MgSO}_4] = 9.30 \times 10^{-3}$ mol/kg or **18**
%

We can likewise calculate $[\text{SO}_4^{2-}]$ concentration &
%

$C_{\text{SO}_4} - [\text{MgSO}_4] = [\text{SO}_4^{2-}] = 1.89 \times 10^{-2}$ mol/kg

Problems

- Went through a moderately difficult calculation & only calculated species for 1 reaction in SW
- If considered more complicated equilibria where several reactions were going on, the math would quickly get out of hand
- Didn't consider any other reactions involving Mg or SO_4 that might influence our results

Other Problems

- Equilibrium constants can vary as much as 5% depending on the source
- Concentration data vary as well
- Activity corrections can also vary depending on the method used
- We only considered activity corrections for charged species, while neutral species may also have γ 's that are non unity (e.g., MgSO_4)