Chemical Equilibria

General representation

$$a\,\mathbf{A} + b\,\mathbf{B} \rightleftarrows c\,\mathbf{C} + d\,\mathbf{D}$$

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

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

For

$$a\,\mathbf{A} + b\,\mathbf{B} \longleftrightarrow c\,\mathbf{C} + d\,\mathbf{D}$$

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

β_1, β_2, β_3, etc. for overall formation constants

Solubility Calculated

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

$$BaSO_{4(s)} \longleftrightarrow Ba^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)}$$

$$S = [Ba^{2+}] = [SO_4^{2-}]$$

Activity Correction

$$K_{SP} = \frac{a_{Ba}\, a_{SO4}}{1} = a_{Ba}\, a_{SO4}$$

Since

$a_{Ba} = \gamma_{Ba} [Ba^{2+}]$ & $a_{SO4} = \gamma_{SO4} [SO_4^{2-}]$

Substituting

$$K_{SP} = a_{Ba} a_{SO4} = \gamma_{Ba} [Ba^{2+}] \gamma_{SO4} [SO_4^{2-}]$$

Solubility Calculation (completed)

Since

$$K_{SP} = [Ba^{2+}][SO_4^{2-}] \quad \& \quad \gamma_{Ba} = \gamma_{SO4}$$

Then

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

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

$$K_{SP} = a_{Ba}a_{SO4} = \gamma_{Ba}[Ba^{2+}]\gamma_{SO4}[SO_4^{2-}]$$

2) Correct the equilibrium constant K

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

Water Hydrolysis (very important)

$$H_2O \longleftrightarrow H^+ + OH^-$$

Applying same rules for K expressions

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

Where H_2O (the solvent) is assigned activity = 1

Remember pH

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

$$\mathbf{pH = -log\ a_{H+}}$$

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

pH Examples

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

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

At seawater pH (e.g., 8.2)

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

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

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 $\mathbf{H^+}$ 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

  $NaCl \xrightarrow[H_2O]{} Na^+ + Cl^-$ no equilibrium
- Partial dissociation = a weak electrolyte

$H_2CO_3 \rightleftarrows H^+ + HCO_3^-$ K_{a1}

$HCO_3^- \rightleftarrows H^+ + CO_3^{2-}$ K_{a2}

Two step equilibrium = forward & back reactions

Acid-Base Equilibria

Fictitious Weak Acid (HA)

$$HA \longleftrightarrow H^+ + A^-$$

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

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^+)

$$B + H_2O \longleftrightarrow BH^+ + OH^-$$

$$K_b = \frac{[BH^+]\,[OH^-]}{[B]} \quad \text{or} \quad \frac{\mathbf{a}_{BH^+}\ \mathbf{a}_{OH^-}}{\mathbf{a}_{B}}$$

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

$$\mathrm{Mg^{2+}}_{(aq)} + \mathrm{SO_4^{2-}}_{(aq)} \longleftrightarrow \mathrm{MgSO}_{4(aq)}$$

$$K_f = \frac{a_{\mathrm{MgSO_4}}}{a_{\mathrm{Mg}}\, a_{\mathrm{SO4}}}$$

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 x 10^{-2}** mol/kg

and total SO_4 is **C_{SO4} = 2.82 x 10^{-2}** mol/kg

knowing that

$$Mg^{2+}_{(aq)} + SO_4{}^{2-}{}_{(aq)} \longleftrightarrow MgSO_{4(aq)}$$

and the value of the K_f or **K_{MgSO_4} = 2.29 x 10^2**

Steps in the Manual Solution of Simple Equilibrium Problems

1) Start with a recipe: **C_{Mg} = 5.28 x 10^{-2}** mol/kg

C_{SO4} = 2.82 x 10^{-2} mol/kg

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

3) List reaction(s): $Mg^{2+} + SO_4^{2-} \leftrightarrow MgSO_4$

4) Write Mass Balance equations:

$C_{Mg} = [Mg^{2+}] + [MgSO_4] = 5.28 \times 10^{-2}$ mol/kg

$C_{SO4} = [SO_4^{2-}] + [MgSO_4] = 2.82 \times 10^{-2}$ mol/kg

Steps in the Manual Solution of Simple Equilibrium Problems

5) Write a Charge Balance equation:

$$[Mg^{2+}] = [SO_4^{2-}]$$

6) Write equilibrium constant expression(s):

$$K_f = \frac{a_{MgSO_4}}{a_{Mg}\, a_{SO_4}} \quad \text{or} \quad \frac{[MgSO_4]}{[Mg^{2+}]\,[SO_4^{2-}]}$$

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:

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

to give **$[MgSO_4] = C_{Mg} - [Mg^{2+}]$**

$C_{SO4} = [SO_4^{2-}] + [MgSO_4]$ rearranges

giving **$[SO_4^{2-}] = C_{SO_4} - [MgSO_4]$**

We must also substitute the 1st into the 2nd

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

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

$C_{SO4} = [SO_4^{2-}] + [MgSO_4]$ rearranges

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

Substituting the 1st into the 2nd for $[MgSO_4]$

Gives $\mathbf{[SO_4^{2-}] = C_{SO_4} - (C_{Mg} - [Mg^{2+}])}$

Now we can

Substitute into K

$$\mathbf{K_f = \frac{[MgSO_4]}{[Mg^{2+}][SO_4^{2-}]}}$$

Our resulting equation looks like

$$K_{MgSO4} = \frac{C_{Mg} - [Mg^{2+}]}{[Mg^{2+}]\,(C_{SO_4} - (C_{Mg} - [Mg^{2+}]))}$$

Be careful of signs in denomenator

$$K_{MgSO4} = \frac{C_{Mg} - [Mg^{2+}]}{[Mg^{2+}]\,(C_{SO_4} - C_{Mg} + [Mg^{2+}])}$$

Cast in the form of a quadratic

$$K[Mg^{2+}]C_{SO_4} - K[Mg^{2+}]C_{Mg} + K[Mg^{2+}]^2 = C_{Mg} - [Mg^{2+}]$$

Set equal to zero and solve with the quadratic formula

Equation from previous slide

$$K[Mg^{2+}]C_{SO_4} - K[Mg^{2+}]C_{Mg} + K[Mg^{2+}]^2 = C_{Mg} - [Mg^{2+}]$$

Set equal to 0 & rearrange in form for quadratic formula

$$K[Mg^{2+}]^2 + K[Mg^{2+}]C_{SO_4} - K[Mg^{2+}]C_{Mg} + [Mg^{2+}] - C_{Mg} = 0$$

Gather terms

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

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

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

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

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

C_{Mg}

Solving this problem with the quadratic formula

And substituting in the known values for:

$\mathbf{K_f}'$ which equals $\mathbf{K_f}\ \gamma^2$

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

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

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

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

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

Activity Coefficient

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

From Davies Equation Mg^{2+} activity coefficient

$$\ln \gamma = - A Z^2 [I^{0.5}/(1 + I^{0.5}) - 0.2 I]$$

If Z = 2 & A = 1.17 then ln **γ** = - 1.47 & **γ = 0.23**

Calculate All Species

Given **C_{Mg} = 5.28 x 10^{-2}** mol/kg

and **C_{SO_4} = 2.82 x 10^{-2}** mol/kg

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

By difference **$[MgSO_4]$ = 9.30 x 10^{-3}** mol/kg or **18 %**

We can likewise calculate **$[SO_4^{2-}]$** concentration & %

C_{SO_4} - $[MgSO_4]$ = $[SO_4^{2-}]$ = **1.89 x 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., $MgSO_4$)