

Chapter 6 cont'd

For R_x: **a A + b B = c C + d D**

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

Gibbs Free Energy combines Enthalpy and Entropy.

$$\Delta G = \Delta H - T \Delta S$$

If ΔG is negative, then reaction is favored.

Relationship of free energy and equilibrium constant:

$$K = e^{-(\Delta G^\circ/RT)} \quad \text{where } R \text{ is gas constant}$$

T is temperature (K)

What does K_{sp} tell us??



- if $K_{sp} < [A]^a[B]^b$ then precipitation!!!!
- $K_{sp} > [A]^a[B]^b$ then no precipitation (soluble)!!!!
- $K_{sp} = [A]^a[B]^b$ solution is **saturated** - contains all the dissolved A and B it can **under equilibrium** conditions

Complex Formation

Lewis acids and bases react with each by sharing electrons.

Example: Positive charged metals and negative charged ions



- Typically, negative ion is called the ligand and said to “attach” to the metal.
- The ligands can attach is various arrangements to make both neutral molecule or molecular ions that are stabilized in water.
- These molecular ions are referred to as complex ion (because the metal is “complexed” to the ligand.
- There are formation constants associated with the formation of the complex ions. They are denoted by β values.



From Ionic Equilibria in Analytical Chemistry, by Freiser and Fernando

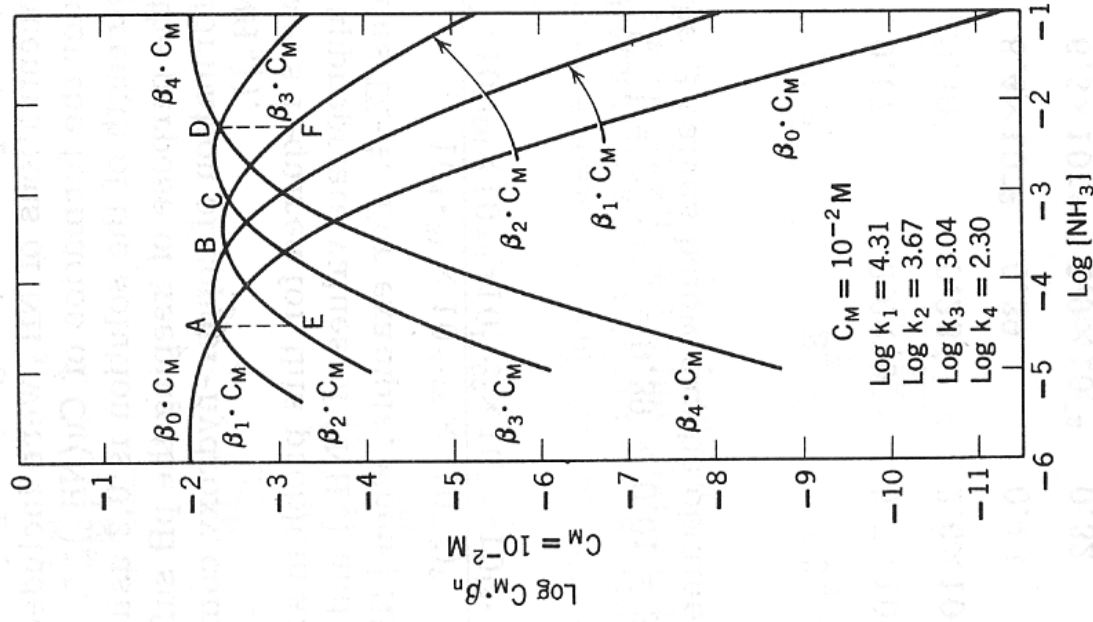


Fig. IX-1 — Logarithmic Diagram of the Copper-Ammonia System

ACID – BASE CHEMISTRY:

Protic Acids and Bases (Bronsted-Lowry)

- Acid \Rightarrow increases $[\text{H}_3\text{O}^+]$ or $[\text{H}^+]$
- Base \Rightarrow increases $[\text{OH}^-]$
- Protic \Rightarrow transfer of H^+
- Bronsted acid \Rightarrow proton donor (like HCl)
- Bronsted base \Rightarrow proton acceptor (like NaOH)
- Salt \Rightarrow ionic solid made from reaction of acid and base
(like $\text{CaCl}_2 - \text{R}_x$ of $2\text{HCl} + \text{Ca}(\text{OH})_2 = \text{CaCl}_2 + 2\text{HOH}$)
- Conjugate \Rightarrow acid-base pair
(like acetic acid $\text{H}_3\text{C}-\text{C}(=\text{O})-\text{OH}$ and acetate ion $\text{H}_3\text{C}-\text{C}(=\text{O})-\text{O}^-$)

Equilibrium of Water



- K_w allows you to calculate $[\text{H}^+]$ and $[\text{OH}^-]$
- $[\text{H}^+]$ and $[\text{OH}^-]$ describes the acid/base content of solution
- Since K_w is small, $[\text{H}^+] [\text{OH}^-]$ will also be small.
- $-\log [\text{H}^+]$, or pH, OR $-\log [\text{OH}^-]$, or pOH, is a useful way to report $[\text{H}^+]$ or $[\text{OH}^-]$
- $K_w = [\text{H}^+] [\text{OH}^-] = 1.0 \times 10^{-14}$ So....

$$pK_w = \text{pH} + \text{pOH} = 14$$

Example: What is the $[\text{OH}^-]$ of a solution at pH 4.3?

$$\text{pOH} = 14 - \text{pH} = 14 - 4.3 = 9.7$$

$-\log[\text{OH}] = 9.7 \iff$ You know this number should be between 10^{-9} & 10^{-10}

$$\text{antilog}(-10) = 2 \times 10^{-10}$$

Acid/Base Strength

Strong acids and bases COMPLETELY dissociate



MEMORIZE TABLE 6-2: Know your strong acids and bases

Weak acids and bases: PARTIAL dissociation



Common Weak Acids

Carboxylic acid	K_a value
1 carbon – Formic acid	1.80×10^{-4}
2 carbon - Acetic acid (vinegar)	1.75×10^{-5}
3 carbon – Propanoic acid	1.34×10^{-5}
4 carbon – Butanoic acid	1.52×10^{-5}

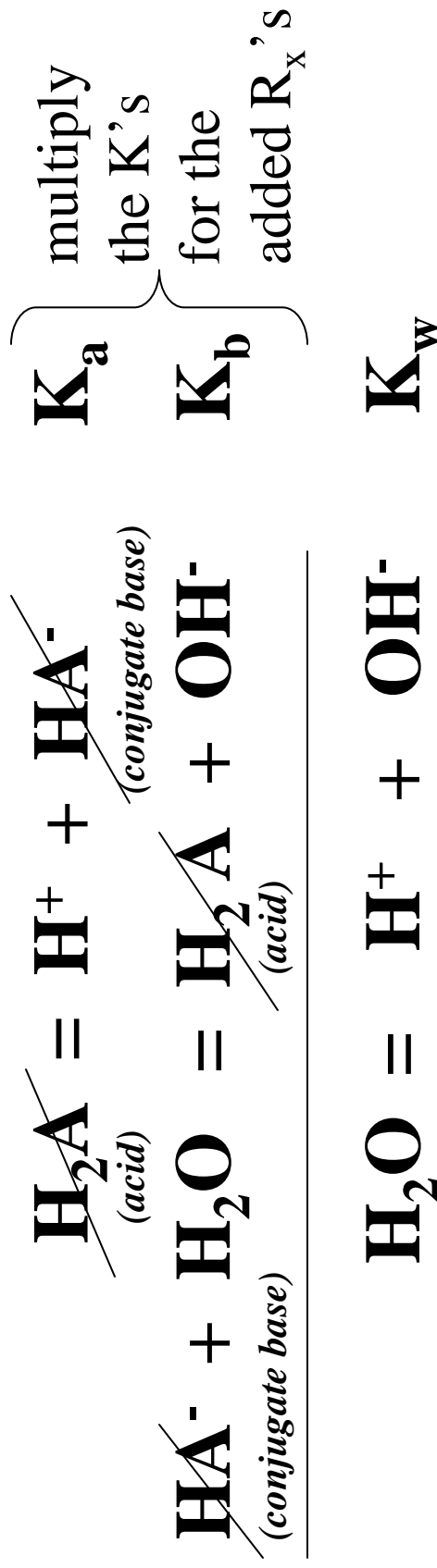
Common Weak Bases

Primary amines	
1 carbon – methylamine	2.3×10^{-11}
2 carbon – ethylamine	2.31×10^{-11}
Secondary amines	
1 carbon – dimethylamine	1.68×10^{-11}
2 carbon – diethylamine	1.17×10^{-11}
Tertiary amines	
1 carbon – trimethylamine	1.58×10^{-10}
2 carbon – triethylamine	1.93×10^{-11}

Relationship of K_a and K_b

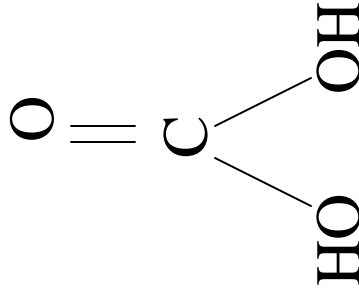
The relationship between K_a and K_b for a conjugate pair is:

$$K_a \times K_b = K_w = 1 \times 10^{-14}$$

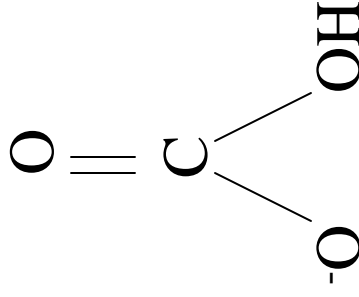


Polyprotic Acids and Bases

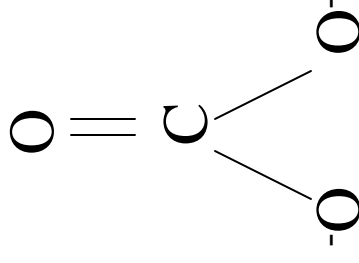
- These acids and bases can donate or accept more than one proton.
- These acids and bases have more than one K_a or K_b .



Carbonic acid



Bicarbonate



Carbonate

$$K_{a1} = 4.45 \times 10^{-7} \quad K_{a2} = 4.69 \times 10^{-11}$$

You are asked to dissolve CaF_2 in water. You are told to make a saturated solution using distilled, deionized water.
 K_{sp} for $\text{CaF}_2=3.9 \times 10^{-11}$.

The measured amount Ca^{+2} is incorrect; you learn that you used tap water instead of ddi water. The F^- content is 0.001 M F^- in the tap water. Recalculate the Ca^{+2} content based on the common ion effect.

What is the Ca^{+2} concentration in the tap water expressed as ppm?