CHAPTER 16. ACID-BASE EQUILIBRIA

16.2 COMMON ION EFFECT

common ion effect: The shift in equilibrium caused by the addition of a substance having an ion in common with the equilibrium mixture. Addition of the common ion causes the equilibrium to shift left; this suppresses the ionization of a weak acid or a weak base.

- The source of the common ion is typically provided by adding a strong acid, a strong base or a soluble salt to the equilibrium reaction mixture.

E.g. Given this reaction: $HC_2H_3O_2 \rightleftharpoons H^+ + C_2H_3O_2^-$. What happens to the pH of the acetic acid solution if we add (a) HCl? (b) $NaC_2H_3O_2$?

Common Ion Problems:
1) Include the <u>initial</u> concentration of the common ion in the ICE table.
2) Use the approximation method to solve the equilibrium constant expression.

16.3 BUFFER SOLUTIONS

Buffer: A solution that resists changes in pH when a small amount of acid or base is added.

The best buffer systems consist of either
   a) a weak acid and a salt containing its conjugate base (e.g. $HC_2H_3O_2$ and $NaC_2H_3O_2$);
   b) a weak base and a salt containing its conjugate acid (e.g. NH_3 and NH_4Cl).

For these buffer systems:
   1) The acid component of the buffer can neutralize added base and the base component of the buffer can neutralize added acid.
   2) Since they are a conjugate acid-base pair, the acid and base in the buffer don't react with one another.

Buffer capacity is the amount of acid or base the buffer can neutralize before there is a significant change in pH. The buffer capacity is a measure of the effectiveness of a buffer.
$\Rightarrow$ Buffer capacity is greater when larger amounts of HA and A^- are present.
$\Rightarrow$ pH will stay relatively constant as long as [HA] and [A^-] are greater than the amount of acid or base added.
$\Rightarrow$ Buffers work best when [HA] and [A^-] are approximately equal. For buffers to be effective, the ratio of Base:Acid should be between 1:10 to 10:1.

Consider the following weak acid buffer reaction: $\quad HA_{(aq)} \rightleftharpoons H^+_{(aq)} + A^-_{(aq)}$

The ionization constant, K_a, is given by $\quad K_a = \dfrac{[H^+][A^-]}{[HA]}$

$\qquad$ Rearrange: $\qquad [H^+] = K_a \dfrac{[HA]}{[A^-]}$

$\qquad$ Taking - log both sides: $- \log [H^+] = -\log K_a - \log \dfrac{[HA]}{[A^-]}$

$\quad$ **pH = pK$_a$ + log $\dfrac{[A^-]}{[HA]}$** $\qquad$ **Henderson-Hasselbalch equation**

$\Rightarrow$ In solving common ion and buffer problems, assume $[HA]_{eq}$ and $[A^-]_{eq}$ are equal to their initial concentrations. (That is, the approximation method is valid for these problems.)

$\Rightarrow$ A special situation occurs when $[HA] = [A^-]$:

By substitution, the K_a expression becomes: $[H^+] = K_a$.

Thus, $pH = pK_a$.

We can use the Henderson-Hasselbalch relationship to prepare a buffer solution with a certain pH - select an acid with a pK_a close to the pH you want ($pK_a \pm 1$), and adjust the [base]/[acid] ratio to obtain the desired pH.

Buffer Problems Involving Addition of Acid or Base

1) Stoichiometric calculation for the acid-base neutralization reaction; assume the neutralization reaction goes to completion:

If a strong acid is added, H^+ reacts with the conjugate base: $A^- + H^+ \rightarrow HA$

If a strong base is added, OH^- reacts with the weak acid: $HA + OH^- \rightarrow A^- + H_2O$

2) Equilibrium calculation – plug $[HA]$ and $[A^-]$ into the K_a expression for the acid ionization:

solve for x, where $x = [H^+]$: $\qquad [H^+] = K_a \dfrac{[HA]}{[A^-]}$

$\Rightarrow$ Since buffers contain a weak acid/base pair, you can set up the problem using either a weak acid ionization reaction and K_a or a weak base ionization reaction and K_b.

$\Rightarrow$ If you start with the weak base reaction, set up the K_b expression and solve for x, where $x = [OH^-]$.

16.4 ACID-BASE TITRATIONS

Acid–base titration curve: plot of pH vs. volume added during a titration; 4 important regions.

Equivalence point: the point at which the acid and base are present in equal stoichiometric amounts.

Titration of a Strong Acid by a Strong Base

Titration Curve for SA/SB
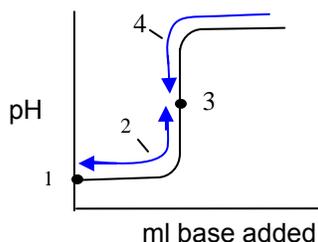
Calculations for finding pH during Strong Acid – Strong Base Titration

Net-ionic neutralization reaction for SA/SB titration: $H^+ + OH^- \rightarrow H_2O$

1) **Initial pH**: depends on the concentration of the strong acid.

A strong acid is 100 % ionized: $HA_{(aq)} \rightarrow H^+_{(aq)} + A^-_{(aq)}$

The reaction is complete; thus, $[H^+] = [HA]$.

2) **pH after initial but before equivalence point**: depends on the amount of excess acid remaining after neutralization.

$$[H^+] = \frac{\text{moles acid initial} - \text{moles base added}}{\text{volume solution}}$$

where moles acid = $L_{acid} \times M_{acid}$ and moles base = $L_{base} \times M_{base}$

volume solution = volume (acid + base)

3) **pH at equivalence point**: pH = 7 only for SA/SB (or SB/SA) titrations because a neutral salt water solution is present.

   $\Rightarrow$ The acid has been completely neutralized by the base, leaving a neutral salt solution. Recall that the cation of a strong base (e.g. Na^+) and the anion of a strong acid (e.g. Cl^-) are neutral ions, so they do not react with water.

4) **pH after equivalence pt**: depends on the amount of excess base remaining after the neutralization reaction.

$$[OH^-] = \frac{\text{moles base added} - \text{moles acid initial}}{\text{volume solution}}$$

   pOH = - log $[OH^-]$; pH = 14.00 – pOH

Titration of a Weak Acid by a Strong Base

Titration curve for WA/SB
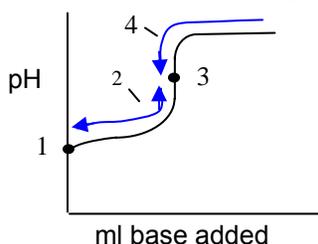
Calculations for finding pH during Weak Acid-Strong Base Titration

1) **Initial pH**: A weak acid does not completely ionize; so $[H^+] \neq [HA]$.

   To find $[H^+]$ for a weak acid, set up the ICE table and K_a expression, then solve for x.

   RXN (1) $HA_{(aq)} \rightleftharpoons H^+_{(aq)} + A^-_{(aq)}$
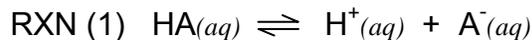
   $K_a = \dfrac{[H^+][A^-]}{[HA]} = \dfrac{x^2}{[HA]}$ $\Rightarrow$ x = $[H^+]$ = $\sqrt{K_a[HA]}$

2) **pH after initial but before equivalence point**: a buffer solution (HA/A^-) is present.

   A. Calculate the amount of A^- formed & HA remaining after the neutralization reaction:

   RXN (2)   Neutralization Reaction: HA + OH^- → A^- + H_2O
      moles HA remaining = initial moles acid - moles base added
      moles A^- formed = moles base added

   B. Convert moles to M, then plug [HA] and $[A^-]$ into the K_a expression for RXN (1).

   solve K_a for $[H^+]$: $[H^+]$ = $K_a \dfrac{[HA]}{[A^-]}$

3) **pH at equivalence point:** pH **DOES NOT** = 7 due to hydrolysis of the conjugate base, A^-.

   $\Rightarrow$ At the equivalence point all of the strong base and weak acid have been consumed in RXN (2), leaving the conjugate base, A^- , in solution. A^- is a weak base – it reacts with H_2O to produce OH^- ions:

   RXN (3) A^- + H_2O $\rightleftharpoons$ HA + OH^-

$$K_b = \frac{[HA][OH^-]}{[A^-]}$$

where $K_b = \frac{K_w}{K_a}$ and $[A^-] = \frac{\text{initial moles acid}}{\text{total volume of solution}}$

From the ICE table: $K_b = \frac{x^2}{[A^-]}$

Thus, the $[OH^-]$ is found by solving for x: $\qquad x = \sqrt{K_b[A^-]}$

4) **pH after equivalence pt**: depends on the amount of excess base present (same as SA/SB). Excess strong base is the primary source of OH^-. Hydrolysis of the conjugate base, A^-, also produces OH^-, but this amount is much smaller than the OH^- obtained from the strong base, so we can neglect the OH^- formed by the conjugate base hydrolysis.

Shape of Strong Acid – Strong Base Curve vs. Weak Acid – Strong Base Curve

- The initial pH of a strong acid is lower than that of a weak acid of similar concentration due to the complete ionization of the strong acid; thus, the initial $[H^+]$ is higher for a strong acid.
- Region 2 for the weak acid curve: initially, the pH rises abruptly as base is added due to suppression of the acid ionization, but then the pH levels off as the HA/A^- buffer mixture is formed.
- At the half-neutralization point of the weak acid, the moles of acid remaining = moles of conjugate base formed, so $[HA] = [A^-]$. Thus, pH = pK_a at the half equivalence point.
- At the equivalence point: pH = 7 for a SA/SB titration since a neutral salt water solution is present; pH > 7 for a WA/SB titration because the salt contains the conjugate base, A^-, which reacts with water to produce OH^- ions.
- Near the equivalence pt: pH rises very sharply for the strong acid titration from about pH 3 to pH 11; whereas, the pH rises less for a weak acid titration from about pH 7 to pH 11.
- After the equivalence point: the shape of the curves is the same because pH is determined by the excess OH^- ions provided by the strong base.

Titration of a Strong Base by a Strong Acid

Titration Curve for SB/SA

pH

ml acid added
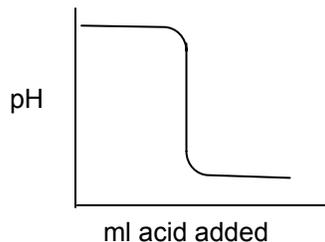
Titration of a Weak Base by a Strong Acid

Titration Curve for WB/SA

pH

ml acid added
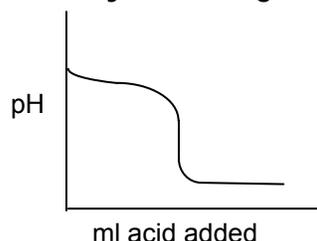
16.5 ACID-BASE INDICATORS

End point- an experimentally observed point at which the indicator changes color.

Indicator - substance that changes color over a specific pH range; an indicator can exist in either its acid or base form and it changes color when proton gain/loss occurs.

$$HIn \quad + \quad H_2O \rightleftharpoons H_3O^+ \quad + \quad In^-$$
Acid form   Base form
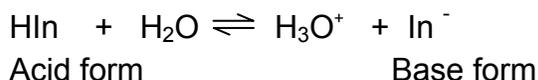
- When $[HIn]/[In^-] \geq 10$, mostly HIn exists and the acid color prevails.
- When $[HIn]/[In^-] \leq 0.1$, mostly In^- exists and the base color prevails.
- When $0.1 < [HIn]/[In^-] < 10$, the color is a mixture of acid and base colors.

  e.g. methyl red: pH range is 4.2-6 (red in acid form, yellow in base form)
  phenolphthalein: pH range 8.2-10 (clear in acid form, pink in base form)

For a given acid-base titration, a suitable indicator changes color over a pH range that coincides with the portion of the curve where the pH rises sharply.

Titration Type	Equivalence Point	pH Range Near Equivalence Point	Suitable Indicator
SA by SB	7	3-11	phenolphthalein, methyl red
SB by SA	7	3-11	phenolphthalein, methyl red
WA by SB	> 7	7-11	phenolphthalein
WB by SA	< 7	3-7	methyl red

16.6 SOLUBILITY EQUILIBRIA

Important biological examples:
- tooth decay - tooth enamel dissolves in acidic solutions
- formation of kidney stones - salts precipitate in kidney

Many salts are only slightly soluble in water and form solid precipitates in aqueous solutions. (Recall solubility rules from Section 4.2.)

These "insoluble" salts dissolve to a small extent and form a saturated solution.

The undissolved solid and the dissociated ions in solution establish an equilibrium system.

An example of this is the dissolution of AgBr: $AgBr_{(s)} \rightleftharpoons Ag^+_{(aq)} + Br^-_{(aq)}$

$$K_{sp} = [Ag^+][Br^-]$$

K_{sp} is called the solubility product constant; it is the equilibrium constant for insoluble salts.

It is a measure of how soluble a salt is in water - the smaller the K_{sp}, the less soluble the salt.

- Values for K_{sp} are found in Table 16.2 (p 702).

E.g. Write the solubility equilbrium reaction and the K_{sp} expression for MgF_2.

E.g. Which salt is less soluble?

(A) CdS, $K_{sp} = 8.0 \times 10^{-28}$ (B) PbS, $K_{sp} = 3.4 \times 10^{-28}$ (C) CoS, $K_{sp} = 4.0 \times 10^{-21}$ (D) FeS, $K_{sp} = 6.0 \times 10^{-19}$

Relationship between K_{sp} & salt solubility:

Solubility - the maximum amount of salt that will dissolve in a given quantity of solvent; units can be or g/L or mol/L. (For molar solubility, the units are mol/L.)

- Molar Solubility = concentration of the dissolved salt; ion concentrations are related to the solubility of the salt by their coefficients.

$\Rightarrow$ For MgS , $MgS_{(s)} \rightleftharpoons Mg^{2+}_{(aq)} + S^{2-}_{(aq)}$
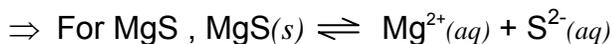
Solubility of MgS = [MgS] $\Leftarrow$ This is the concentration of the salt that dissolved in solution.

From the balanced equation, for each mole of MgS that dissolves, one mole of magnesium ions and one mole of sulfide ions form.

Thus, [MgS] = $[Mg^{2+}]$ = $[S^{2-}]$

E.g. (a) Calculate K_{sp} for Ag_2S if $[Ag^+]$ = 5.8 x 10^{-17} M. (b) What is the solubility of Ag_2S?

Predicting Precipitation Reactions– Does a precipitate form?

We can modify the solubility of salts to dissolve minerals and ores, to precipitate ions from solution, and to separate and purify ions.

From calculating the reaction quotient, we can determine if dissolution or precipitation will occur. For solubility problems, Q is called the ion product.

3 Possibilities

1) If Q < K_{sp}, an unsaturated solution is present $\Rightarrow$ precipitation does not occur. The ion concentrations are not high enough to form a solid.
2) If Q = K_{sp}, the system is at equilibrium so dissolution and precipitation occur at equal rates; a saturated solution exists in which the ion [ ]'s are just high enough for precipitation to occur.
3) If Q > K_{sp}, precipitation occurs as the reaction shifts left. There are excess ions in solution that will precipitate out to form a solid.

Types of problems

$\Rightarrow$ Calculate Q based on the [ ]'s of the ions in the salt and compare to K_{sp} to determine whether or not the salt will precipitate.

$\Rightarrow$ Predict whether or not a precipitate will form when two solutions are mixed.

16.7 SEPARATION OF IONS BY FRACTIONAL PRECIPITATION

Often we have a mixture of ions present in solution; we can separate the ions by the method of fractional precipitation.

Fractional precipitation: add a reagent that enables you to separate the ions according to differences in their solubility.

16.8 THE COMMON ION EFFECT AND SOLUBILITY

Common ion effect: solubility is decreased when a common ion is added.

e.g. $AgCl_{(s)} \rightleftharpoons Ag^+_{(aq)} + Cl^-_{(aq)}$

If we add NaCl, $[Cl^-] \uparrow$, which causes the reaction to shift left. Some AgCl precipitates out of solution; thus, adding the common ion (Cl^-) decreases the solubility of $AgCl_{(s)}$.

Calculations for Common Ion problems

a) Include concentration of the common ion in the ICE table.
b) Use the approximation method ([common ion] >> x).
c) Solve K_{sp} for x, where x = solubility of salt.

16.9 pH AND SOLUBILITY

Addition of an acid can increase the solubility of an insoluble salt if the salt contains a basic anion.

E.g. $CaF_{2(s)} \rightleftharpoons Ca^{2+}_{(aq)} + 2F^-_{(aq)}$

Adding a strong acid (e.g. HCl) provides H^+ ions: $H^+ + F^- \rightleftharpoons HF$

Overall: $2H^+ + CaF_{2(s)} \rightleftharpoons Ca^{2+}_{(aq)} + 2HF_{(aq)}$
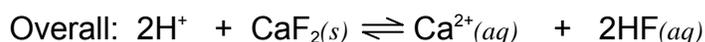
$\Rightarrow$ Addition of H^+ causes $[F^-]$ to decrease (i.e. F^- is removed); so the equilibrium shifts right to form more F^-, thus the solubility of the salt increases as the salt dissolves.

E.g. For the following salts, predict whether the salt will dissolve in an acidic solution.

A. AgBr _____   B. $CdCO_3$ _____

C. $PbCl_2$ _____   D. BaS _____

16.10 COMPLEX ION EQUILIBRIA AND SOLUBILITY (p 713-715 only)

$\Rightarrow$ Formation of complex ions can increase the solubility of an insoluble salt.

Complex ion: ion containing a central metal cation bonded to one or more molecules or ions. The molecules or ions act as Lewis bases (E.g. NH_3, H_2O, OH^-).

Complex ion formation is another type of equilibrium process.

E.g. $Ag^+_{(aq)} + 2NH_{3(aq)} \rightleftharpoons Ag(NH_3)_2^+$ $K_{formation} = 1.5 \times 10^7$
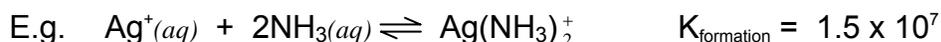
The equilibrium constant for the formation of a complex ion is called $K_{formation}$ or K_f.

E.g. Addition of NH_3 to AgCl solution increases the solubility of AgCl:

(1) $AgCl_{(s)} \rightleftharpoons Ag^+_{(aq)} + Cl^-_{(aq)}$ $K_1 = 1.6 \times 10^{-10}$

(2) $Ag^+_{(aq)} + 2NH_{3(aq)} \rightleftharpoons Ag(NH_3)_2^+_{(aq)}$ $K_2 = 1.5 \times 10^7$

Overall: (3) $AgCl_{(s)} + 2NH_{3(aq)} \rightleftharpoons Ag(NH_3)_2^+_{(aq)} + Cl^-_{(aq)}$ $K_{net} = K_1 \times K_2 = 2.4 \times 10^{-3}$
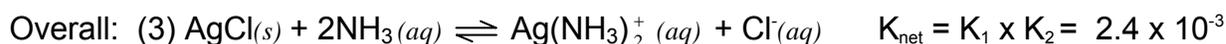
- Forming a complex ion with NH_3 removes Ag^+ from solution, causing reaction (1) to shift right.
- Application: can use ammonia to dissolve a AgCl precipitate.

Example. Which of the following solutions could dissolve a AgCl precipitate?
A. NH_3 B. KCl   C. HNO_3 D. $AgNO_3$ E. all of these