Chapter 12
part 1

Acids, bases and equilibrium

Theories of Acids and Bases

A- The Arrhenius Theory of acids and bases

- Acids are substances that produce hydrogen ions in aqueous solution as HCl.

$$HCl_{(aq)} \rightarrow H^{+}_{(aq)} + Cl^{-}_{(aq)}$$

- Bases are substances that produce hydroxide ions in aqueous solution as NaOH.

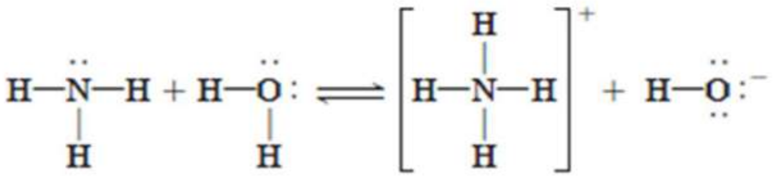
$$\mathrm{NaOH}(s) \xrightarrow{\mathrm{H_2O}} \mathrm{Na}^{+}(aq) + \mathrm{OH}^{-}(aq)$$

- **Limitation of the Arrhenius Definition of Acids and Bases**
- The Arrhenius definition can only describe acids and bases in an aqueous environment

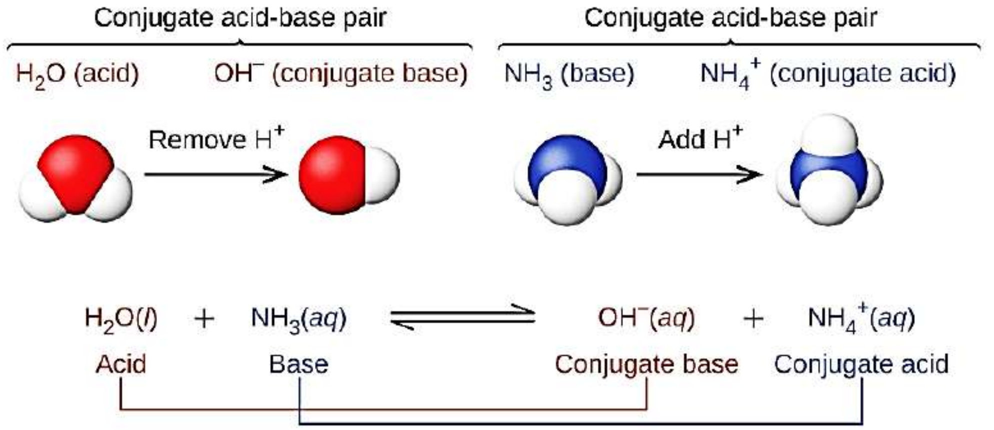
B- The Brønsted-Lowry Theory of acids and bases

- An acid is a proton (hydrogen ion) donor. We call the product that remains after an acid donates a proton the conjugate base of the acid (This species is a base because it can accept a proton to re-form the acid).
- A base is a proton (hydrogen ion) acceptor. We call the product that results when a base accepts a proton the conjugate acid of the base (This species is an acid because it can give up a proton and thus re-form the base)

Conjugate Acid-Base Pairs



$$\underset{\text{base}_1}{NH_3(aq)} + \underset{\text{acid}_2}{H_2O(l)} \rightleftharpoons \underset{\text{acid}_1}{NH_4^+(aq)} + \underset{\text{base}_2}{OH^-(aq)}$$



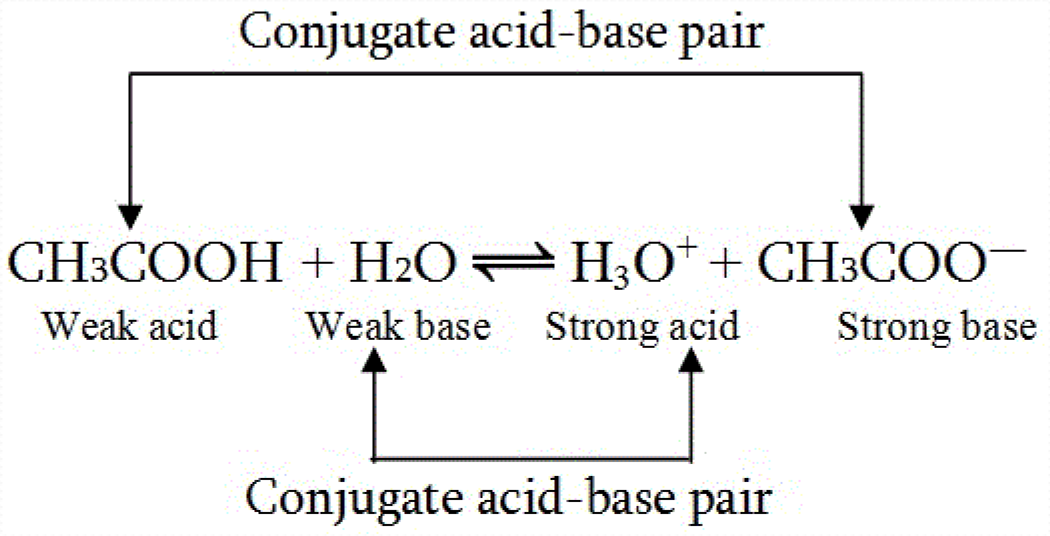
Conjugate acid-base pair

H_2O (acid) OH^- (conjugate base)

Conjugate acid-base pair

NH_3 (base) NH_4^+ (conjugate acid)

$$\underset{\text{Acid}}{H_2O(l)} + \underset{\text{Base}}{NH_3(aq)} \rightleftharpoons \underset{\text{Conjugate base}}{OH^-(aq)} + \underset{\text{Conjugate acid}}{NH_4^+(aq)}$$

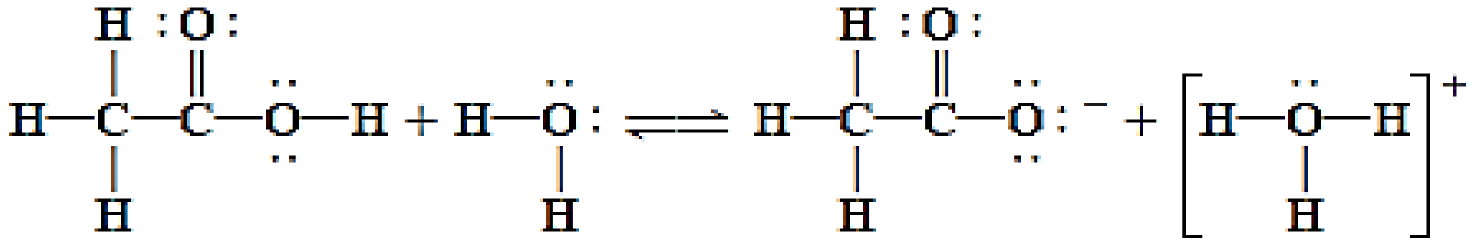


Conjugate acid-base pair

$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$

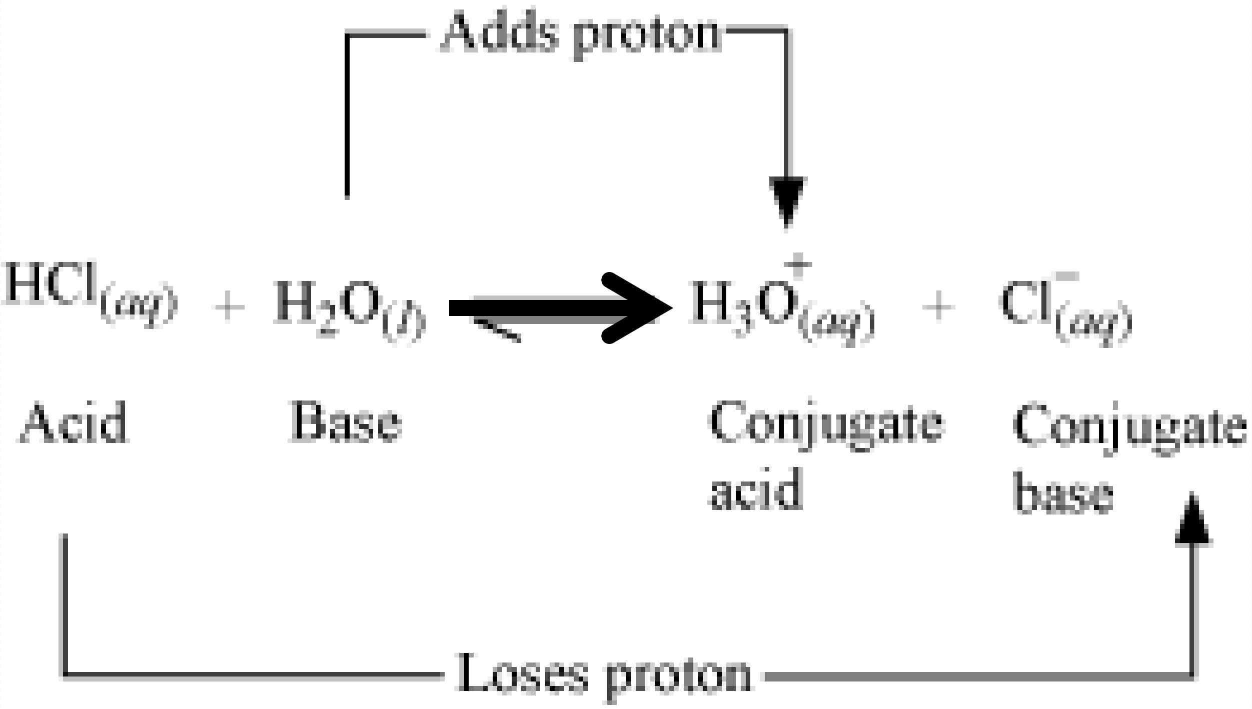
Weak acid Weak base Strong acid Strong base

Conjugate acid-base pair



$$H-\underset{H}{\overset{H}{C}}-\overset{:O:}{\overset{\|}{C}}-\ddot{\underset{\cdot\cdot}{O}}-H + H-\underset{H}{\ddot{O}}: \rightleftharpoons H-\underset{H}{\overset{H}{C}}-\overset{:O:}{\overset{\|}{C}}-\ddot{\underset{\cdot\cdot}{O}}:^- + \left[H-\underset{H}{\ddot{O}}-H\right]^+$$

$$\underset{acid_1}{CH_3COOH(aq)} + \underset{base_2}{H_2O(l)} \rightleftharpoons \underset{base_1}{CH_3COO^-(aq)} + \underset{acid_2}{H_3O^+(aq)}$$



Adds proton

$$HCl_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + Cl^-_{(aq)}$$

Acid

Base

Conjugate acid

Conjugate base

Loses proton

Bronsted acids

- **Monoprotic acids**; that is, each unit of the acid yields one hydrogen ion upon ionization:

$$
\begin{aligned}
\mathrm{HCl}(aq) &\longrightarrow \mathrm{H}^{+}(aq) + \mathrm{Cl}^{-}(aq)\\
\mathrm{HNO_3}(aq) &\longrightarrow \mathrm{H}^{+}(aq) + \mathrm{NO_3^{-}}(aq)\\
\mathrm{CH_3COOH}(aq) &\rightleftharpoons \mathrm{CH_3COO^{-}}(aq) + \mathrm{H}^{+}(aq)
\end{aligned}
$$

- The ionization of acetic acid is incomplete (note the double arrows), it is a weak electrolyte. For this reason it is called a weak acid
- On the other hand, HCl and HNO3 are strong acids because they are strong electrolytes, so they are completely ionized in solution (note the use of single arrows).

- A **diprotic acid**, each unit of the acid gives up two H^+ ions, in two separate steps

$$H_2SO_4(aq) \longrightarrow H^+(aq) + HSO_4^-(aq)$$
$$HSO_4^-(aq) \rightleftharpoons H^+(aq) + SO_4^{2-}(aq)$$

- **Triprotic acids**, which yield three H^+ ions

$$H_3PO_4(aq) \rightleftharpoons H^+(aq) + H_2PO_4^-(aq)$$
$$H_2PO_4^-(aq) \rightleftharpoons H^+(aq) + HPO_4^{2-}(aq)$$
$$HPO_4^{2-}(aq) \rightleftharpoons H^+(aq) + PO_4^{3-}(aq)$$

Bronsted bases

- Sodium hydroxide (NaOH) and barium hydroxide Ba(OH)2 are strong electrolytes. This means that they are completely ionized in solution:

$$\mathrm{NaOH}(s) \xrightarrow{\mathrm{H_2O}} \mathrm{Na}^+(aq) + \mathrm{OH}^-(aq)$$
$$\mathrm{Ba(OH)_2}(s) \xrightarrow{\mathrm{H_2O}} \mathrm{Ba}^{2+}(aq) + 2\mathrm{OH}^-(aq)$$

- The OH^- ion can accept a proton as follows:

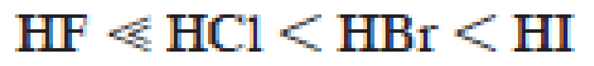
$$\mathrm{H}^+(aq) + \mathrm{OH}^-(aq) \longrightarrow \mathrm{H_2O}(l)$$

- Thus, OH^- is a Brønsted base.
- Ammonia (NH3) is classified as a Brønsted base because it can accept a H^+ ion

$$\mathrm{NH_3}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{NH_4^+}(aq) + \mathrm{OH}^-(aq)$$

Molecular Structure and the Strength of Acids

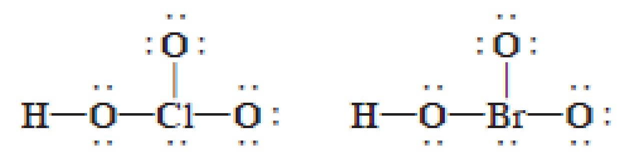
- In this series of **binary acids** (through a group, the atomic size increases), the weaker the bond (H—X), the stronger the acid. So that the strength of the acids increases as follows:



$HF \ll HCl < HBr < HI$

- In this series of binary acids (through a period, the electronegativity increases), the greater attraction of the bonding electron pairs (H—X), so easier to dissociate the H^{+}, the stronger the acid. So that the strength of the acids increases as follows:
  - $PH_3 < SH_2 < HCl$

- **Oxoacids** contain hydrogen, oxygen, and one other element Z, which occupies a central position.



- **Oxoacids having the same central atom** but different numbers of oxygen. Within this group, acid strength increases as the number of oxygen atoms increases.

$$HClO_4 > HClO_3 > HClO_2 > HClO$$

- **Oxoacids having different central atoms** but have the same number of oxygen. Within this group, acid strength increases with increasing electronegativity of the central atom.

$$HClO_3 > HBrO_3$$

C- Lewis acids and bases

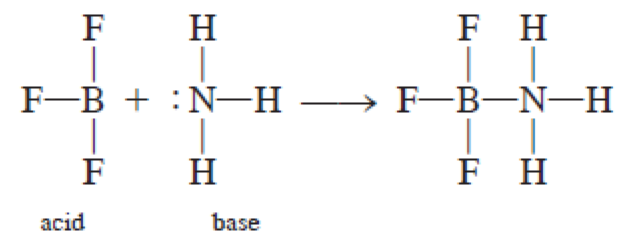
- According to Lewis's definition, a base is a substance that can donate a pair of electrons, and an acid is a substance that can accept a pair of electrons.
- The significance of the Lewis concept is that it is much more general than other definitions; it includes as acid-base reactions many reactions that do not involve Brønsted acids.

Bronsted acid

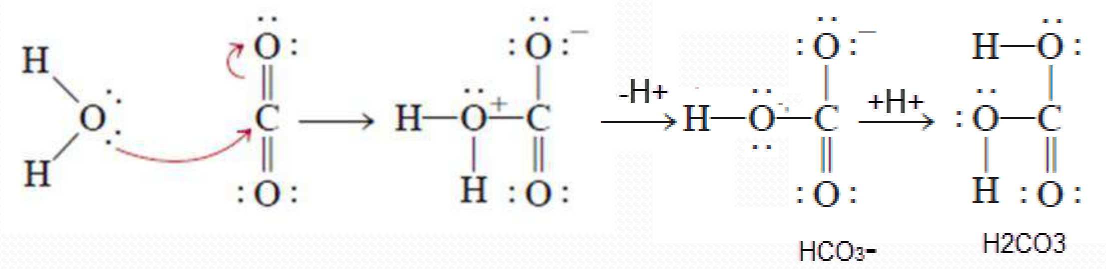
- **Bronsted acid** have an empty orbital capable of receiving electron pair from the base.
- **Chemical species that can function as lewis acid are:**

1. Molecules or atoms with incomplete octet as: $AlCl_3$, BF_3
2. Many simple cation as: Fe^{+3}, Cu^{+2}
3. Molecules in which the central atom with expanded octet as: $SnCl_4$, PF_5
4. Some molecules with acidic site because of one or more multiple bonds as: SO_2, CO_2

- Consider, for example, the reaction between boron trifluoride (BF3) and ammonia. The B atom in BF3 is sp2-hybridized. The vacant, unhybridized 2p orbital accepts the pair of electrons from NH3.
- Note that a coordinate covalent bond is formed between the B and N atoms.

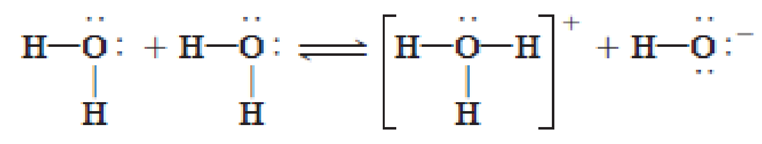


- The hydration of carbon dioxide to produce carbonic acid can be understood in the Lewis framework



The Ion Product of Water

- Water is a very weak electrolyte, but it does undergo ionization to a small extent:



$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

- This reaction is sometimes called the autoionization of water. At equilibrium: $K_w = [H_3O^+][OH^-] = [H^+][OH^-]$

  where Kw is called the ion-product constant.

- In pure water at 25C, the concentrations of both ions are equal and found to be 1.0 x 10^{-7} M. Thus,

$$K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$$

- In practice, we can change the concentration of either H^+ or OH^- ions in solution, but we cannot vary both of them independently. This mean increase the H^+ conc. accompanied by decrease in OH^- conc. and vice versa.

pH—A Measure of Acidity

- The concentrations of H^+ ions in aqueous solutions are frequently very small numbers and therefore inconvenient to work with. A more practical measure called pH:

$$\mathrm{pH} = -\log[\mathrm{H_3O^+}] \quad \text{or} \quad \mathrm{pH} = -\log[\mathrm{H^+}]$$

Acidic solutions:	$[\mathrm{H^+}] > 1.0 \times 10^{-7}\,M$, $\mathrm{pH} < 7.00$
Basic solutions:	$[\mathrm{H^+}] < 1.0 \times 10^{-7}\,M$, $\mathrm{pH} > 7.00$
Neutral solutions:	$[\mathrm{H^+}] = 1.0 \times 10^{-7}\,M$, $\mathrm{pH} = 7.00$

- Notice that pH increases as $[H^+]$ decreases.
- Similarly, we define pOH as:

$$\mathrm{pOH} = -\log[\mathrm{OH^-}]$$

- The relationship between pH and pOH is

$$\mathrm{pH} + \mathrm{pOH} = 14.00$$

Weak Acids and Acid Ionization Constants

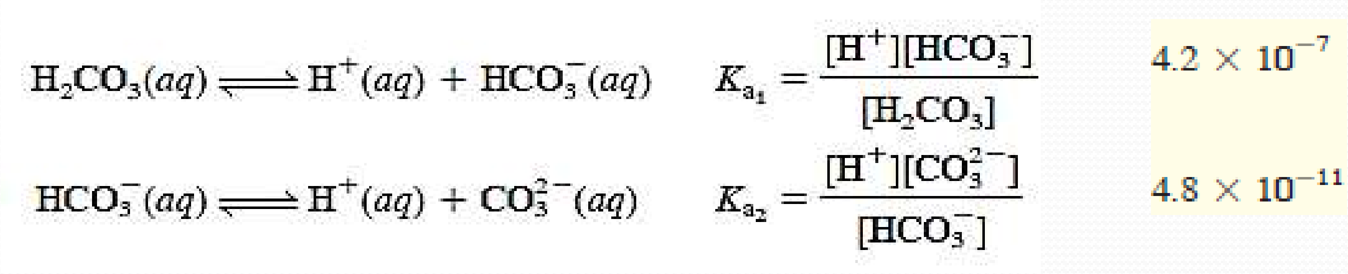
- Consider a **weak monoprotic acid**, HA. Its ionization in water is represented by:

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq) \qquad HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$$

- The equilibrium expression for this ionization is

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \quad \text{or} \quad K_a = \frac{[H^+][A^-]}{[HA]}$$

- where Ka, the acid ionization constant, is the equilibrium constant for the ionization of an acid at a given temperature. The strength of the acid HA is measured quantitatively by the magnitude of Ka. The larger Ka, the stronger the acid.
- Only weak acids have Ka values associated with them.

- Diprotic and polyprotic acids ionize in a stepwise manner, that is, they lose one proton at a time. An ionization constant expression can be written for each ionization stage.
- 

$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq) \qquad K_{a_1} = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} \qquad 4.2 \times 10^{-7}$$

$$HCO_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^{2-}(aq) \qquad K_{a_2} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} \qquad 4.8 \times 10^{-11}$$

- For a given acid, the first ionization constant is much larger than the second ionization constant, and so on.
- This trend is reasonable because it is easier to remove an H^+ ion from a neutral molecule than to remove another H^+ from a negatively charged ion derived from the molecule.

Weak Bases and Base Ionization Constants

- The ionization of weak bases is treated in the same way as the ionization of weak acids.
- When ammonia dissolves in water, it undergoes the reaction

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

- The base ionization constant (Kb), is the equilibrium constant for the ionization reaction,

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

- The larger Kb, the stronger the base. Only weak bases have Kb values associated with them.

The Relationship Between Conjugate Acid-Base Ionization Constants

$$CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$$

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$$

$$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$$

write the base ionization constant as

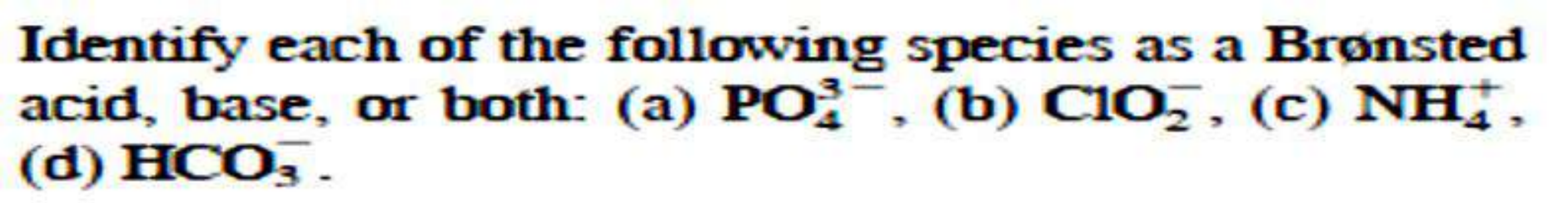
$$K_b = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]}$$

The product of these two ionization constants is given by

$$\begin{aligned} K_aK_b &= \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} \times \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]} \\ &= [H^+][OH^-] \\ &= K_w \end{aligned}$$

$$K_aK_b = K_w$$

$$pK_a + pK_b = 14.00$$

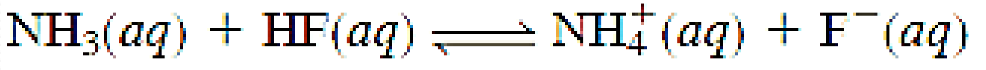


Identify each of the following species as a Brønsted acid, base, or both: (a) PO_4^{3-}, (b) ClO_2^-, (c) NH_4^+, (d) HCO_3^-.

Answer: a) Brønsted base. (b) Brønsted base.(c) Brønsted acid. (d) Brønsted base and Brønsted acid (amphoteric).

- Identify the conjugate acid-base pairs in the reaction between ammonia and hydrofluoric acid in aqueous solution.

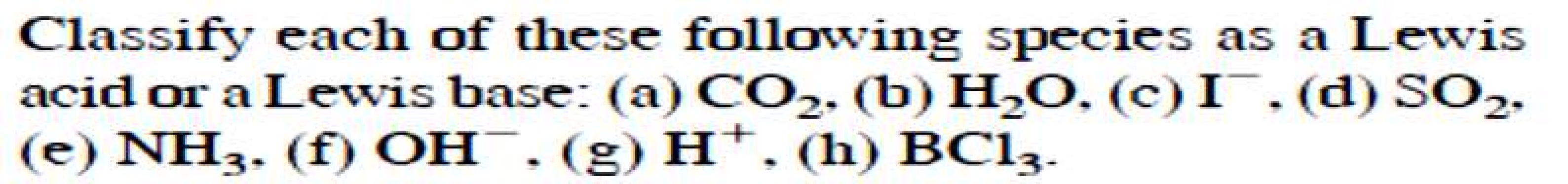
Answer



$$NH_3(aq) + HF(aq) \rightleftharpoons NH_4^+(aq) + F^-(aq)$$

HF and F^- are acid 1 with conjugated base 1

NH3 and $NH4^+$ are base2 with conjugated acid2



Classify each of these following species as a Lewis acid or a Lewis base: (a) CO_2, (b) H_2O, (c) I^-, (d) SO_2, (e) NH_3, (f) OH^-, (g) H^+, (h) BCl_3.

a- acid - b- base -c- base -d- acid -e- base -f- base -g- acid h- acid

- A solution of carbon dioxide in water has a hydronium ion concentration of 2.0×10^{-6}M. What is the concentration of hydroxide ion at 25 °C?

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0\times10^{-14}}{2.0\times10^{-6}} = 5.0\times10^{-9}$$

- What is the hydronium ion concentration in an aqueous solution with a hydroxide ion concentration of 0.001 M at 25°C?

$$K_w = [H^+][OH^-] = 1.0\times10^{-14}$$

$$\frac{K_w}{[OH^-]} = \frac{1.0\times10^{-14}}{0.001}$$

$$[H_3O^+] = 1\times10^{-11}\,M$$

In a NaOH solution $[OH^-]$ is 2.9×10^{-4} *M*. Calculate the pH of the solution.

$$\begin{aligned} pOH &= -\log[OH^-] \\ &= -\log(2.9 \times 10^{-4}) \\ &= 3.54 \end{aligned}$$

$$\begin{aligned} pH + pOH &= 14.00 \\ pH &= 14.00 - pOH \\ &= 14.00 - 3.54 = 10.46 \end{aligned}$$

If the concentration of $NaOH$ in a solution is 2.5×10^{-4} M, what is the concentration of H_3O^+?

$$NaOH(s) \xrightarrow{H_2O} Na^+(aq) + OH^-(aq)$$

$$K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$$

$$\frac{1.0 \times 10^{-14}}{[OH^-]} = [H_3O^+]$$

$$\frac{1.0 \times 10^{-14}}{2.5 \times 10^{-4}} = [H_3O^+] = 4.0 \times 10^{-11}\ M$$

Calculate the pH of the above solution?

$$pH = -\log\ 4.0 \times 10^{-11}$$

pH= 10.4

Find the pH of a solution of 0.002 M of HCl.

$$\mathrm{HCl}(aq) \longrightarrow \mathrm{H}^{+}(aq) + \mathrm{Cl}^{-}(aq)$$

$$[H^{+}] = 2.0 \times 10^{-3}\ M$$

$$pH = -\log[2.0 \times 10^{-3}] = 2.70$$

Calculate the pH of a 0.020 *M* $\mathrm{Ba(OH)_2}$ solution.

$\mathrm{Ba(OH)_2}$ is a strong base; each $\mathrm{Ba(OH)_2}$ unit produces two $\mathrm{OH^-}$ ions:

1 mole of $\mathrm{Ba(OH)_2}$ equivalent to 2 mole of $\mathrm{OH^-}$
So 0.02 mole of $\mathrm{Ba(OH)_2}$ equivalent to 0.04 mole of $\mathrm{OH^-}$

$$[\mathrm{OH^-}] = 0.040\ M$$

$$\mathrm{pOH} = -\log 0.040 = 1.40$$

$$\begin{aligned} \mathrm{pH} &= 14.00 - \mathrm{pOH} \\ &= 14.00 - 1.40 \\ &= 12.60 \end{aligned}$$

The pH of rainwater collected in a certain region of the northeastern United States on a particular day was 4.82. Calculate the H^+ ion concentration of the rainwater.

$$\text{pH} = -\log[\text{H}^+] = 4.82$$

$$\log[\text{H}^+] = -4.82 \qquad [\text{H}^+] = 10^{-4.82} = 1.5 \times 10^{-5}\,M$$

If moist soil has a pH of 7.84, what is the H^+ concentration of the soil solution?

$$pH = -\log[H^+]$$

$$7.84 = -\log[H^+]$$

$$[H^+] = 1.45 \times 10^{-8}\,M$$

The pH of a 0.10 *M* solution of formic acid (HCOOH) is 2.39. What is the K_a of the acid?

$$HCOOH \rightleftharpoons H^+ + HCOO^-$$

$$pH = -\log[H^+]$$

$$[H^+] = 4.1 \times 10^{-3}\ M$$

	$HCOOH(aq)$	$\rightleftharpoons$	$H^+(aq)$	+	$HCOO^-(aq)$
Initial (*M*):	0.10		0.00		0.00
Change (*M*):	-4.1×10^{-3}		$+4.1 \times 10^{-3}$		$+4.1 \times 10^{-3}$
Equilibrium (*M*):	$(0.10 - 4.1 \times 10^{-3})$		4.1×10^{-3}		4.1×10^{-3}

$$K_a = \frac{[H^+][HCOO^-]}{[HCOOH]} = \frac{(4.1 \times 10^{-3})(4.1 \times 10^{-3})}{(0.10 - 4.1 \times 10^{-3})} = 1.8 \times 10^{-4}$$

What is the Kb of the base?

$$K_b = \frac{K_w}{K_a}$$

$K_b = 1 \times 10^{-14}/1.8 \times 10^{-4} = 5.56 \times 10^{-11}$

What is the concentration of hydronium ion and the pH in a 0.534-*M* solution of formic acid?

$$HCO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_2^-(aq) \quad K_a = 1.8 \times 10^{-4}$$

	HCO_2H +	H_2O $\rightleftharpoons$	H_3O^+
Initial concentration (*M*)	0.534	~0	0
Change (*M*)	$-x$	x	x
Equilibrium concentration (*M*)	$0.534 + (-x)$	$0 + x = x$	$0 + x = x$

$$K_a = 1.8 \times 10^{-4} = \frac{[H_3O^+][HCO_2^-]}{[HCO_2H]}$$

$$= \frac{(x)(x)}{0.534 - x} = 1.8 \times 10^{-4}$$

$$K_a = 1.8 \times 10^{-4} = \frac{x^2}{0.534}$$

$$x^2 = 0.534 \times (1.8 \times 10^{-4})$$

$$= 9.6 \times 10^{-5}$$

$$x = \sqrt{9.6 \times 10^{-5}}$$

$$= 9.8 \times 10^{-3}$$

$\longrightarrow$

$$[H_3O^+] = 0 + x = 0 + 9.8 \times 10^{-3}\ M$$

$$= 9.8 \times 10^{-3}\ M$$

$$pH = -\log(9.8 \times 10^{-3}) = 2.01$$

What is the pH of a 0.40 *M* ammonia solution? K_b 1.8×10^{-5}

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

	NH_3	NH_4^+	OH^-
Initial (*M*):	0.40	0.00	0.00
Change (*M*):	$-x$	$+x$	$+x$
Equilibrium (*M*):	$0.40 - x$	x	x

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

$$1.8 \times 10^{-5} = \frac{x^2}{0.40 - x}$$

$$x = 2.7 \times 10^{-3}\ M$$

At equilibrium, $[OH^-] = 2.7 \times 10^{-3}\ M$. Thus,

$$\begin{aligned} pOH &= -\log(2.7 \times 10^{-3}) \\ &= 2.57 \end{aligned}$$

$$\begin{aligned} pH &= 14.00 - 2.57 \\ &= 11.43 \end{aligned}$$

. Calculate K_b and pK_b of the butyrate ion ($CH_3CH_2CH_2CO_2^-$). The pK_a of butyric acid at 25°C is 4.83. Butyric acid is responsible for the foul smell of rancid butter.

$$pK_a + pK_b = 14.00$$

$$4.83 + pK_b = 14.00$$

$$pK_b = 14.00 - 4.83 = 9.17$$

Because $pK_b = -\log K_b$, K_b is $10^{-9.17} = 6.8 \times 10^{-10}$.

Calculate K_a and pK_a of the dimethylammonium ion ($(CH_3)_2NH_2^+$). The base ionization constant K_b of dimethylamine ($(CH_3)_2NH$) is 5.4×10^{-4} at 25°C.

$$K_a K_b = K_w$$

$$K_a(5.4 \times 10^{-4}) = 1.01 \times 10^{-14}$$

$$K_a = 1.9 \times 10^{-11}$$

$$pK_a = -\log(1.9 \times 10^{-11}) = 10.72.$$

Chapter 12
part 2

Solubility equilibrium

Solubility Equilibrium

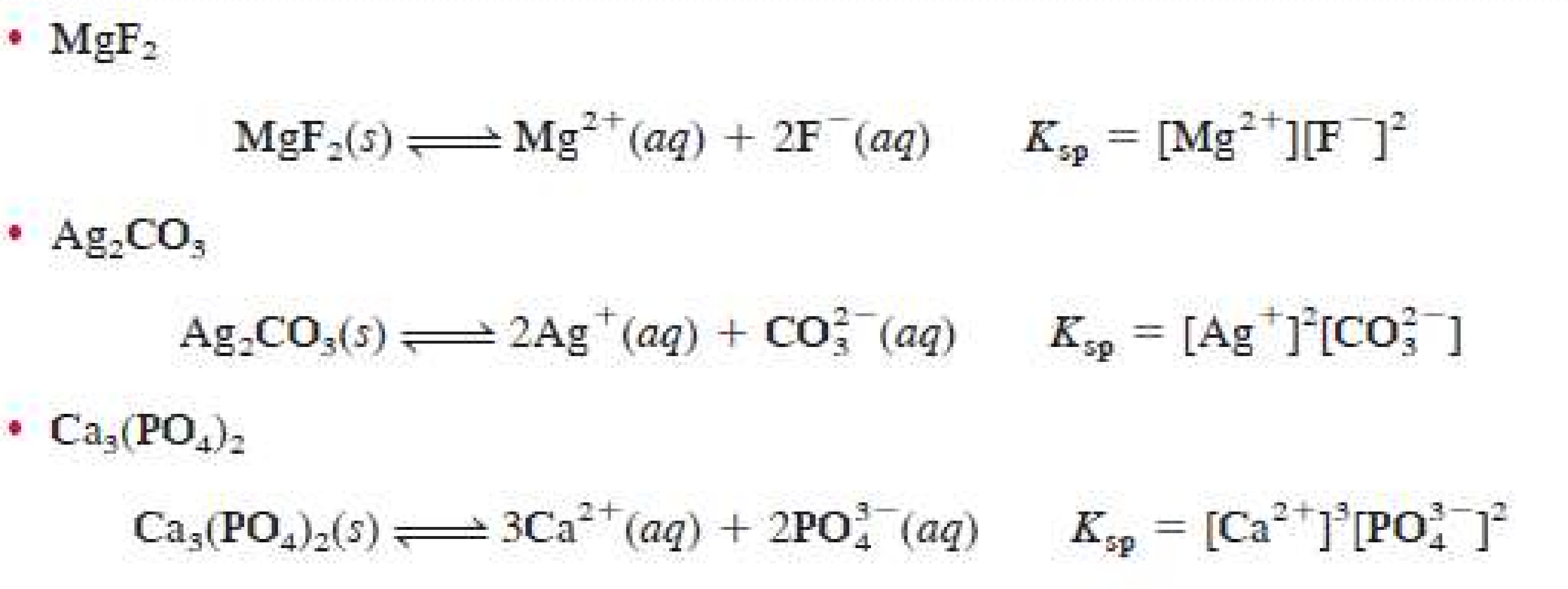
- **Solubility equilibrium** is a type of dynamic heterogenous equilibrium that exists when a chemical compound in the solid state is in chemical equilibrium with a solution of that compound.

$$AgCl(s) \rightleftharpoons Ag^{+}(aq) + Cl^{-}(aq)$$

- The solubility product constant, Ksp , is the equilibrium constant for a solid substance dissolving in an aqueous solution. It represents the level at which a solute (ionic compound) dissolves in water. The more soluble a substance is, the higher the Ksp value it has.

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

- The solubility product constant of a compound is the product of the molar concentrations of the constituent ions, each raised to the power of its stoichiometric coefficient in the equilibrium equation.
- Molar solubility is the number of *moles* of solute per liter of solution.
- Molar solubility, solubility, and solubility product all refer to a saturated solution.



- MgF_2

$$MgF_2(s) \rightleftharpoons Mg^{2+}(aq) + 2F^-(aq) \qquad K_{sp} = [Mg^{2+}][F^-]^2$$

- Ag_2CO_3

$$Ag_2CO_3(s) \rightleftharpoons 2Ag^+(aq) + CO_3^{2-}(aq) \qquad K_{sp} = [Ag^+]^2[CO_3^{2-}]$$

- $Ca_3(PO_4)_2$

$$Ca_3(PO_4)_2(s) \rightleftharpoons 3Ca^{2+}(aq) + 2PO_4^{3-}(aq) \qquad K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2$$

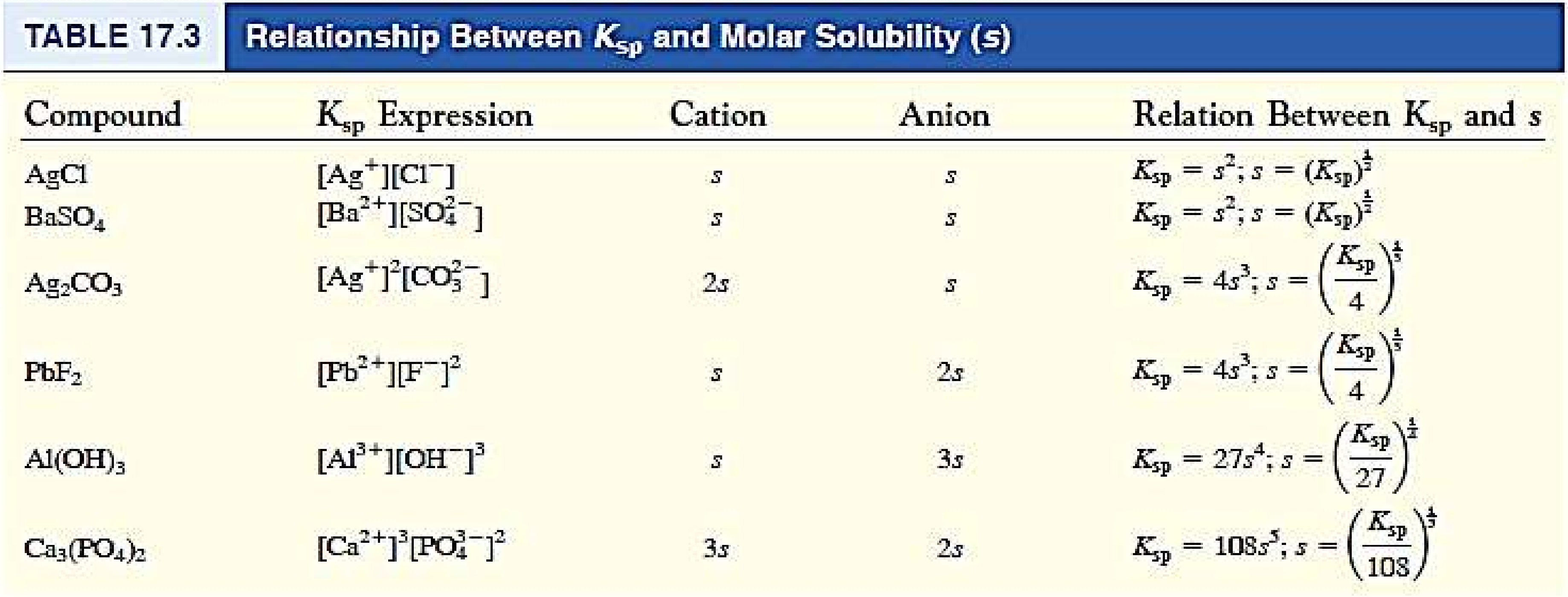


TABLE 17.3 Relationship Between K_{sp} and Molar Solubility (s)

Compound	K_{sp} Expression	Cation	Anion	Relation Between K_{sp} and s
AgCl	$[Ag^+][Cl^-]$	s	s	$K_{sp} = s^2;\ s = (K_{sp})^{\frac{1}{2}}$
$BaSO_4$	$[Ba^{2+}][SO_4^{2-}]$	s	s	$K_{sp} = s^2;\ s = (K_{sp})^{\frac{1}{2}}$
Ag_2CO_3	$[Ag^+]^2[CO_3^{2-}]$	$2s$	s	$K_{sp} = 4s^3;\ s = \left(\frac{K_{sp}}{4}\right)^{\frac{1}{3}}$
PbF_2	$[Pb^{2+}][F^-]^2$	s	$2s$	$K_{sp} = 4s^3;\ s = \left(\frac{K_{sp}}{4}\right)^{\frac{1}{3}}$
$Al(OH)_3$	$[Al^{3+}][OH^-]^3$	s	$3s$	$K_{sp} = 27s^4;\ s = \left(\frac{K_{sp}}{27}\right)^{\frac{1}{4}}$
$Ca_3(PO_4)_2$	$[Ca^{2+}]^3[PO_4^{3-}]^2$	$3s$	$2s$	$K_{sp} = 108s^5;\ s = \left(\frac{K_{sp}}{108}\right)^{\frac{1}{5}}$

Examples

- **The solubility of calcium sulfate (CaSO4) is found to be 0.67 g/L. Calculate the value of *K*sp for calcium sulfate.**
- The molar solubility of CaSO4 [CaSO4]= **0.67/136** mole/L

$$= 4.9 \text{ x } 10^{-3} \text{ M}$$

[CaSO4] represent only the concentration of the dissolved solid

- As each 1 mole of (CaSO4) give 1 mole for each of the ions, So

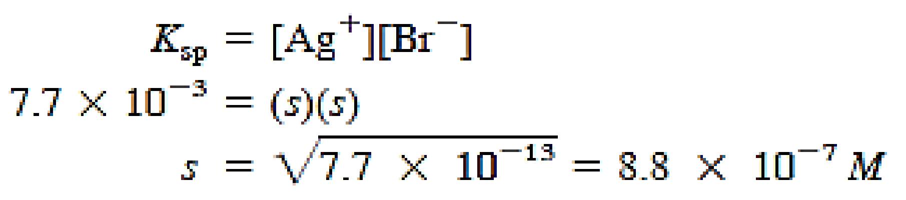
$$\underset{}{CaSO_{4\,(s)}} \rightleftharpoons \underset{S}{Ca^{2+}{}_{(aq)}} + \underset{S}{SO_4{}^{2-}{}_{(aq)}}$$

- [CaSO4]= $[Ca^{2+}] = [SO_4{}^{2-}] = 4.9x10^{-3}\,M$

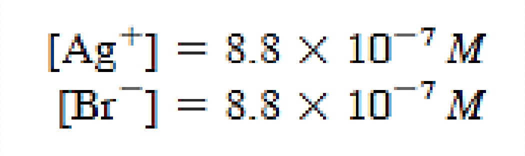
$$\begin{aligned} K_{sp} &= [Ca^{2+}][SO_4^{2-}] \\ &= (4.9 \times 10^{-3})(4.9 \times 10^{-3}) \\ &= 2.4 \times 10^{-5} \end{aligned}$$

Examples

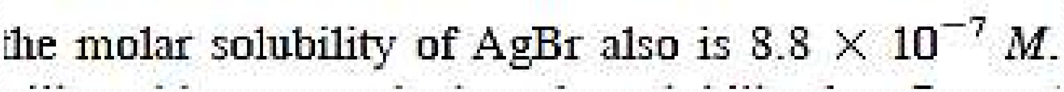
- **The Ksp of silver bromide (AgBr) is 7.7 x 10⁻¹³. Calculate its molar solubility and solubility (g/L).**



$$K_{sp} = [Ag^+][Br^-]$$
$$7.7 \times 10^{-3} = (s)(s)$$
$$s = \sqrt{7.7 \times 10^{-13}} = 8.8 \times 10^{-7}\,M$$



$$[Ag^+] = 8.8 \times 10^{-7}\,M$$
$$[Br^-] = 8.8 \times 10^{-7}\,M$$



the molar solubility of AgBr also is $8.8 \times 10^{-7}\,M$.

Calculate the solubility of copper(II) hydroxide, $Cu(OH)_2$ in g/L. Ksp of $Cu(OH)_2$ 2.2×10^{-20}

	$Cu(OH)_2(s) \rightleftharpoons$	$Cu^{2+}(aq)$	$+\ 2OH^-(aq)$
Initial (*M*):		0	0
Change (*M*):	$-s$	$+s$	$+2s$
Equilibrium (*M*):		s	$2s$

$$K_{sp} = [Cu^{2+}][OH^-]^2$$
$$= (s)(2s)^2 = 4s^3$$

$$2.2 \times 10^{-20} = 4s^3$$
$$s^3 = \frac{2.2 \times 10^{-20}}{4} = 5.5 \times 10^{-21}$$

Molar solubility(mol/L) ← $s = 1.8 \times 10^{-7}\ M$

solubility of $Cu(OH)_2$ $= 1.8 \times 10^{-7} \times 97.57$ g/l → Molar mass of $Cu(OH)_2$

$$= 1.8 \times 10^{-5}\ \text{g/L}$$

Predicting Precipitation Reactions

- We can predict whether a precipitate will form when we mix two solutions or add a soluble compound to a solution.
- We use Q, called the ion product, to represent the quantity obtained by substituting the initial concentrations of the ions into the Ksp expression.

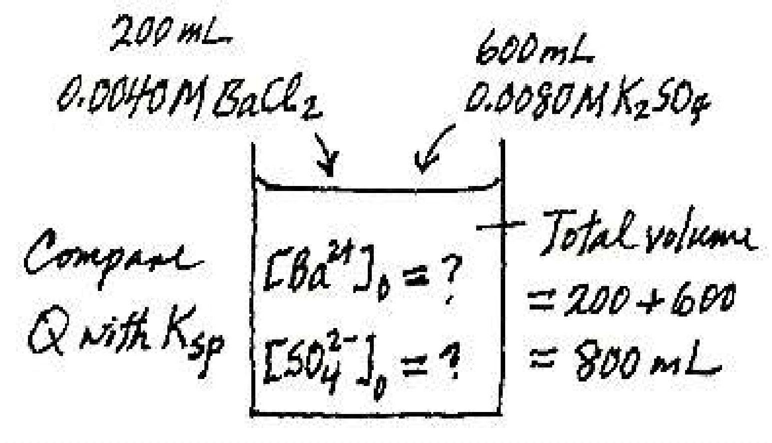
Q < Ksp Unsaturated solution, no precipitation.

Q = Ksp Saturated solution, no precipitation.

Q > Ksp Supersaturated solution; precipitation occur.

Example

- **If exactly 200 mL of 0.0040 M $BaCl_2$ are added to exactly 600 mL of 0.0080 M of potassium sulfate. Will a precipitate form? Given that:** $BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq) \qquad K_{sp} = 1.1 \times 10^{-10}$



$K_2SO_4(aq) + BaCl_2(aq) \rightarrow 2KCl(aq) + BaSO_4(s)$

$\therefore Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$

- For BaCl2, M1.V1 = M2.V2

200 x 0.004 = M2 x 800

M2 = 0.001 M = molar solubility of BaCl2= molar solubility of Ba^{+2}

- For K2SO4, M1.V1 = M2.V2

600 x 0.008 = M2 x 800

M2 = 0.006 M = molar solubility of K2SO4 = molar solubility of $SO4^{-2}$

$$Q = [\mathrm{Ba}^{2+}]_0[\mathrm{SO}_4^{2-}]_0 = (1.0 \times 10^{-3})(6.0 \times 10^{-3})$$
$$= 6.0 \times 10^{-6}$$

- Q > Ksp, The solution is supersaturated because the value of Q indicates that the concentrations of the ions are too large. Thus, some of the BaSO4 will precipitate out of solution.