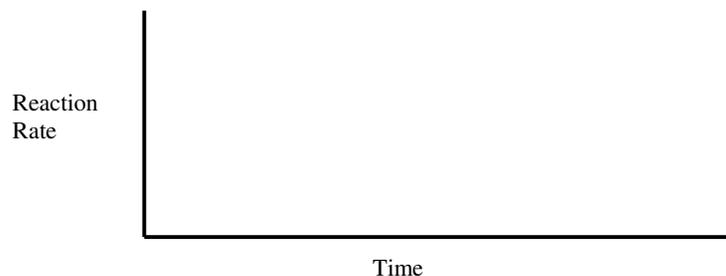


# Chemical Equilibrium

Many reactions are \_\_\_\_\_, i.e. they can occur in either direction.



The point reached in a reversible reaction where the rate of the forward reaction (product formation, or reactant loss) is \_\_\_\_\_ to the rate of the reverse reaction (reactant formation or product loss) is called \_\_\_\_\_. e.g.  $A + B \rightleftharpoons AB$   
(rate forward reaction = rate reverse reaction)



- Observations of some chemical systems in a closed system (where no matter is able to escape to the surroundings) will appear as though \_\_\_\_\_ change is occurring, i.e. an \_\_\_\_\_ has been achieved
- This does not mean that there is \_\_\_\_\_ activity at the molecular level, in fact chemical systems in equilibrium will have a \_\_\_\_\_ of "reactants moving forward towards "products" and the "products" moving in the reverse direction towards 'reactants"
- Equilibrium is maintained unless the system is \_\_\_\_\_ by a temperature change or by adding excess reactant or product molecules.
- A chemical system is said to be in a state of equilibrium if it meets the following criteria:

- 1.
- 2.
- 3.
- 4.

# Examples of chemical systems in equilibrium:

## 1. Solubility Equilibrium

- in solubility equilibrium the \_\_\_\_\_ solute particles continuously dissolve into solution, while an equal number of dissolved solute particles in solution crystallize or \_\_\_\_\_ out of solution

## 2. Phase Equilibrium

- in phase equilibrium particles in both phases are gaining or losing kinetic energy, such that they are \_\_\_\_\_ from one phase to another, while an equal number are moving in the reverse direction  
e.g.  $H_2O_{(l)} \rightarrow H_2O_{(g)}$

## 3. Chemical Reaction Equilibrium

- Quantitative reactions are those reactions where \_\_\_\_\_ of the limiting reagent is \_\_\_\_\_ in the reaction  
e.g.  $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$   
where the  $CO_2$  (in an open system, like this, escapes so that the reverse reaction \_\_\_\_\_ take place)

- If this reaction takes place in a closed container, both reactants and products can be found

- This is not considered to be a quantitative reaction

- can be explained by considering the reverse reaction:



- The equilibrium equation is  $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

- Using this knowledge leads to two types of manufacturing processes:

- 1) \_\_\_\_\_ where as in the limestone example - as limestone is used up, it is replaced with more to keep the reaction going
- 2) \_\_\_\_\_ where the reaction is done in a closed container and the products are taken out when the reaction is complete. i.e. microwave popcorn

- Another example is  $\text{N}_2\text{O}_4(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$

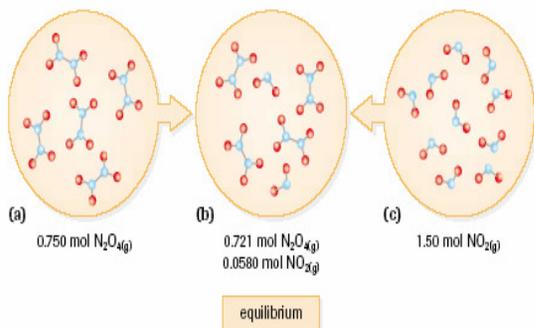
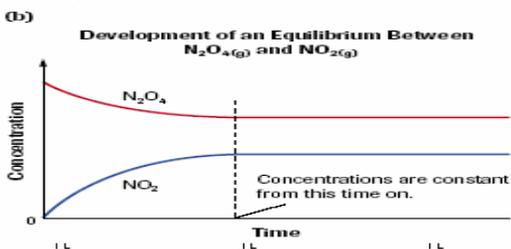
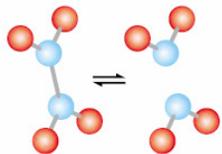


Figure 7

The same dynamic equilibrium composition is reached whether we start from pure  $\text{N}_2\text{O}_4(\text{g})$ , pure  $\text{NO}_2(\text{g})$ , or a mixture of the two, provided that environment, system and total mass remain the same.

➤ reactions such as these have led to this generalization for \_\_\_\_\_ in closed systems:

For a given overall system composition, the same equilibrium concentrations are reached whether equilibrium is approached in the forward or the reverse direction.

## Equilibrium Law in Chemical Reactions

- when considering chemical reactions that reach an equilibrium point \_\_\_\_\_ reactants and products will be in the mixture
- repetitive testing of various chemical reactions that reach equilibrium while beginning with different initial concentrations of reactants show that the concentrations of the reactants and products at equilibrium can be related through the equilibrium law:

Consider the reaction:  $aA + bB \rightarrow cC + dD$

The Equilibrium Law can be expressed as:

$$K =$$

$$r_f = k[A]^a[B]^b$$

$$r_r = k[C]^c[D]^d$$

$$K =$$

where: A, B, C and D are chemical entities in gas or aqueous phases  
a, b, c and d are the coefficients of the balanced equation  
K is the equilibrium \_\_\_\_\_

- The equilibrium law describes the behaviour of almost all \_\_\_\_\_ and \_\_\_\_\_ chemical equilibria the concentrations of the chemical entities are expressed in moles per litre (mol/L)
- Considering that the equilibrium constant is a \_\_\_\_\_ of the rate constant for the forward reaction to the rate constant for the reverse reaction, the magnitude of the equilibrium constant will allow us to determine whether products or reactants are \_\_\_\_\_ in an equilibrium reaction

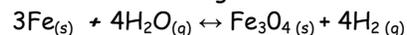
K	Description	Example
	Reaction proceeds to completion Products $\gg$ Reactants	$2\text{O}_3(\text{g}) \leftrightarrow 3\text{O}_2(\text{g})$ $K = 2.0 \times 10^{57}$
	Products = Reactants	$\text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g}) \leftrightarrow \text{CO}_2(\text{g}) + \text{H}_2(\text{g})$ at $700^\circ\text{C}$ $K = 5.09$
	Products $\ll$ Reactants	$\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \leftrightarrow 2\text{NO}_2(\text{g})$ $K = 1.0 \times 10^{-25}$

## Homogeneous and Heterogeneous Equilibria

- \_\_\_\_\_ equilibrium involves reactants and products in a \_\_\_\_\_, eg. all aqueous or all gas

- \_\_\_\_\_ equilibrium involves reactants and products in \_\_\_\_\_ than one phase, eg. liquid and gas

• Consider the following reaction with solid and gas phases:



the equilibrium law expression is:

**K =**

- But, the concentration of the \_\_\_\_\_  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}$  do \_\_\_\_\_ change during the reaction as their \_\_\_\_\_ are fixed; they \_\_\_\_\_ equilibrium

- As such the quantities  $[\text{Fe}_3\text{O}_4]$  and  $[\text{Fe}]$  are constant and could be incorporated in the equilibrium constant

$$K \frac{[\text{Fe}]^3}{[\text{Fe}_3\text{O}_4]} = \frac{[\text{Fe}_3\text{O}_4][\text{H}_2]^4}{[\text{Fe}]^3[\text{H}_2\text{O}]^4}$$

Or  $K' = \frac{[\text{H}_2]^4}{[\text{H}_2\text{O}]^4}$  where  $K'$  is the new equilibrium constant

- Similarly, in heterogeneous reactions that involve pure liquids and another phase, the concentration of the pure \_\_\_\_\_ is \_\_\_\_\_ (fixed density) and can also be incorporated into the equilibrium constant.

- The equilibrium constant reported in reference tables for heterogeneous equilibria will already incorporate the densities of pure solids or liquids.

- In the case where a heterogeneous reaction involves \_\_\_\_\_ and a pure solid, pure liquid, or gas, then a \_\_\_\_\_ equation is developed to eliminate \_\_\_\_\_ and show only those ions altered or involved in the chemical reaction.

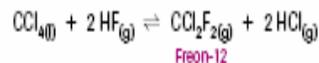
## Qualitative Changes In Equilibrium Systems

➤ Le Chatelier's Principle:

"When a chemical system at equilibrium is disturbed by a change in a property, the system adjusts in a way that \_\_\_\_\_ the change"

Le Chatelier's Principle & Concentration Changes

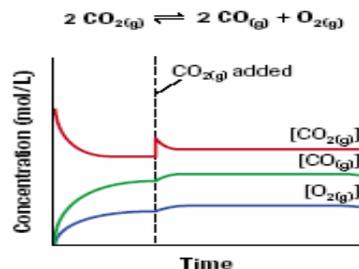
- this principle predicts if more reactant is added to a system at equilibrium, then the system will have a change in the equilibrium called an equilibrium \_\_\_\_\_



- E.g.

- to improve the \_\_\_\_\_ more  $\text{HF}_{(g)}$  can be added to the system, the added reactant "disturbs" the system and the system shifts to the \_\_\_\_\_ using up more of the  $\text{CCl}_4$  and producing more Freon-12 and making a new equilibrium state

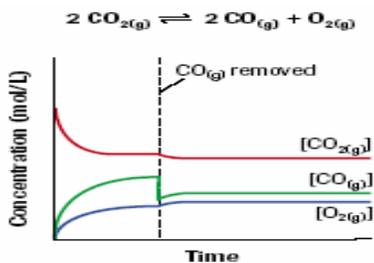
- in chemical equilibrium shifts, the imposed change in concentration is usually only partly counteracted and the concentrations are usually different than the original concentrations (see Fig. 2 below) - adding  $\text{CO}_2$



**Figure 2**

The reaction establishes an equilibrium that is then disturbed (at the time indicated by the vertical dotted line) by the addition of  $\text{CO}_{2(g)}$ . Some of the added  $\text{CO}_{2(g)}$  reacts, decreasing its concentration, while the concentration of both products increases until a new equilibrium is established. The concentrations eventually become constant again, at a new level. However, the initial  $K$  value and the final  $K$  value are the same.

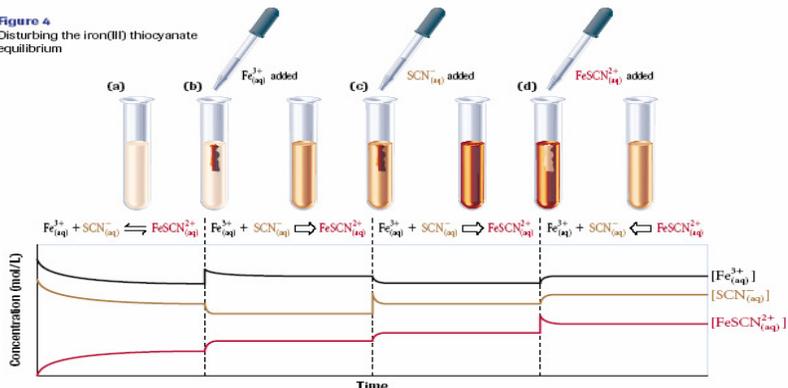
- by removing a product (decreasing concentration) will also shift an equilibrium forward, to the \_\_\_\_\_ (see Fig. 3)



**Figure 3**  
The reaction establishes an equilibrium that is disturbed (at the time indicated by the vertical dotted line) by the removal of  $\text{CO}(\text{g})$ . The equilibrium shifts forward; the concentration of  $\text{O}_2(\text{g})$  increases while the concentration of  $\text{CO}_2(\text{g})$  decreases, until a new equilibrium is established. The initial  $K$  value and the final  $K$  value are the same.

- An example of the effects of both forward and reverse shifts

**Figure 4**  
Disturbing the iron(III) thiocyanate equilibrium



When solutions containing  $\text{Fe}^{3+}(\text{aq})$  (colourless) and  $\text{SCN}^{-}(\text{aq})$  (brown) are mixed, an equilibrium is reached with the product  $\text{FeSCN}^{2+}(\text{aq})$  (deep red), as shown by the constant, uniform light brown colour of the equilibrium solution. On the graph, notice that the concentrations of  $\text{Fe}^{3+}(\text{aq})$  and  $\text{SCN}^{-}(\text{aq})$  drop after mixing as they react to form  $\text{FeSCN}^{2+}(\text{aq})$ . All three concentrations become constant when equilibrium is reached (flat lines).

$\text{Fe}^{3+}(\text{aq})$  is added. In response the system shifts to the right, producing more red  $\text{FeSCN}^{2+}(\text{aq})$ . Notice the spike in the graph of  $\text{Fe}^{3+}(\text{aq})$  when more is added, and that the concentration of  $\text{Fe}^{3+}(\text{aq})$  subsequently drops. The concentration of  $\text{FeSCN}^{2+}(\text{aq})$  rises as more is produced. As  $\text{SCN}^{-}(\text{aq})$  ions are used up, the concentration drops. Equilibrium is reestablished at a new level (flat lines).

The addition of more solution containing  $\text{SCN}^{-}(\text{aq})$  shifts the equilibrium to the right, producing more of the dark red  $\text{FeSCN}^{2+}(\text{aq})$  ions. Note the corresponding changes in the graph.

Adding  $\text{FeSCN}^{2+}(\text{aq})$  ions to the mixture forces the equilibrium to shift toward the reactants, giving the solution a paler colour. Note the corresponding changes in the graph.

- other examples of how Le Chatelier's Principle is used are:



as more  $\text{NO}(\text{g})$  is \_\_\_\_\_ by reacting it with  $\text{O}_2(\text{g})$  the system shifts to the \_\_\_\_\_ and more \_\_\_\_\_ is produced.



- as blood circulates to the \_\_\_\_\_, the high concentration of  $\text{O}_2(\text{g})$  shifts the equilibrium to the \_\_\_\_\_ and the haemoglobin gets \_\_\_\_\_.

- as the oxygenated blood travels through the body the reverse happens, the equilibrium shifts to the \_\_\_\_\_ and more oxygen is \_\_\_\_\_.

## Le Châtelier's Principle

- Note: 1) A catalyst speeds \_\_\_\_\_ the forward and reverse reaction to the \_\_\_\_\_ degree. A catalyst allows a reaction to obtain equilibrium \_\_\_\_\_.
- 2) An \_\_\_\_\_ gas added with \_\_\_\_\_ change in volume will not affect equilibrium.

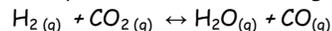
For example;  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g}) + 125 \text{ kJ}$

change	response	result [HI]
$\uparrow [\text{H}_2]$	shift right	$\uparrow [\text{HI}]$
$\downarrow [\text{I}_2]$	shift left	$\downarrow [\text{HI}]$
$\uparrow [\text{HI}]$	shift left	$\downarrow [\text{HI}]$
$\downarrow$ pressure	no shift	no change
$\downarrow$ temp.	shift right	$\uparrow [\text{HI}]$
catalyst	no shift	no change

## Determining Equilibrium Concentrations

- Simple calculations involving the equilibrium constant,  $K_c$ , requires knowledge of a combination of the concentrations of the reactants and products and the equilibrium constant

- An example involves the following reaction:



Where the concentrations at equilibrium are given as:

$$[\text{H}_2] = 0.24 \text{ mol/L} \quad [\text{H}_2\text{O}] = 0.88 \text{ mol/L}$$

$$[\text{CO}_2] = 1.80 \text{ mol/L} \quad [\text{CO}] = 0.88 \text{ mol/L}$$

the equilibrium law expression is:

$$K_{\text{eq}} = \frac{[\text{H}_2\text{O}][\text{CO}]}{[\text{H}_2][\text{CO}_2]}$$

$$K =$$

$$K =$$

You could also be asked to solve for the equilibrium constant,  $K_p$ , using partial pressures of gasses.

For example:

Chloromethane,  $\text{CH}_3\text{Cl}(\text{g})$ , is used in industry to produce silicones, which are often used as sealants. It is synthesized in the following reaction:



At 1500K, the mixture contains the following:  $P_{\text{CH}_4} = 0.13 \text{ atm}$ ;  $P_{\text{Cl}_2} = 0.035$ ;  $P_{\text{CH}_3\text{Cl}} = 0.24 \text{ atm}$ ;  $P_{\text{HCl}} = 0.47 \text{ atm}$ . Calculate  $K_p$ .

$$K_p = \frac{P_{\text{CH}_3\text{Cl}} P_{\text{HCl}}}{P_{\text{CH}_4} P_{\text{Cl}_2}}$$

## Measuring Equilibrium Concentrations

- We often need to find the concentration of each chemical in an equilibrium mixture. Equilibrium concentrations can be obtained in \_\_\_\_\_ steps:

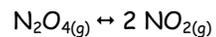
- Find the \_\_\_\_\_ concentration of each species.
- Use the balanced chemical equation to find the \_\_\_\_\_ in each concentration as the system comes to equilibrium.
- Find the \_\_\_\_\_ concentration of each species by \_\_\_\_\_ the results of steps 1 and 2.

For example:

- When 2.00 mol of phosgene,  $\text{COCl}_2$ , is put into an empty 1.00 L flask at  $395^\circ\text{C}$  and allowed to come to equilibrium, the final mixture contains 0.0398 mol of chlorine. Find  $K_c$ .

Equation	$\text{COCl}_2(\text{g})$	$\leftrightarrow$	$\text{CO}(\text{g})$	+	$\text{Cl}_2(\text{g})$
[initial]					
Change					
[equilibrium]					

- 2) The value of  $K_c$  for the reaction below is  $4.63 \times 10^{-3}$  at  $25^\circ\text{C}$ . What will the concentration of each gas be if 0.100 mol of  $\text{N}_2\text{O}_4$  comes to equilibrium in a 5.00 L flask at  $25^\circ\text{C}$ ?



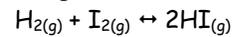
Equation	$\text{N}_2\text{O}_{4(g)}$	$\leftrightarrow$	$2\text{NO}_{2(g)}$
[initial]			
Change			
[equilibrium]			

### ICE Tables and the QUADRATIC FORMULA ... YIKES!

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

$$ax^2 + bx + c = 0$$

- 3) The following reaction has a  $K_{eq}$  of 25.



If 2.00 mol of  $\text{H}_{2(g)}$  and 3.00 mol of  $\text{I}_{2(g)}$  are placed in a 1.0 L container at 1100K, what is the equilibrium concentration of each gas?

	$\text{H}_{2(g)}$	+	$\text{I}_{2(g)}$	$\leftrightarrow$	$2\text{HI}_{(g)}$
Initial [mol/L]					
Change [mol/L]					
Eq'm [mol/L]					

## Approximating Concentrations in $K_c$ Calculations

When  $K_c$  is really \_\_\_\_\_, (e.g.  $5.0 \times 10^{-10}$ ) the reaction favors the reactants:

$$[\text{initial}] - [\text{change}] = \text{approximately } [\text{initial}]$$

To determine if an approximation can be used follow the steps below:

i) If  $[\text{initial}] / K_c > \text{_____}$ , use the approximation.

Let the  $[\text{initial}]$  represent the  $[\text{equilibrium}]$

ii) If  $[\text{initial}] / K_c < 500$ , do \_\_\_\_\_ use the approximation. [Most likely QUADRATIC!]

Let the  $[\text{initial}] - [\text{change}]$  represent the  $[\text{equilibrium}]$

For example;

The value of  $K_c$  for the reaction below is  $4.2 \times 10^{-8}$  at  $211^\circ\text{C}$ . What will the concentration of each gas be if 0.085 mol of  $\text{N}_{2(g)}$ , 0.038 mol of  $\text{O}_{2(g)}$  comes to equilibrium in a 1.00 L flask.

Equation	$\text{N}_{2(g)}$	+	$\text{O}_{2(g)}$	$\leftrightarrow$	$2\text{NO}_{(g)}$
[initial]					
Change					
[equilibrium]					

## Calculating the Reaction Quotient ( $Q_c$ )

The reaction quotient is an expression that is identical to the equilibrium constant expression ( $K_c$ ), but its value is calculated using concentrations \_\_\_\_\_ necessarily at equilibrium.

Comparisons of  $K_c$  and  $Q_c$  can provide the following information about the state of equilibrium.

i)  $Q_c = K_c$       The system is at \_\_\_\_\_

ii)  $Q_c > K_c$       "favors \_\_\_\_\_ formation"

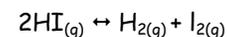
- The system must shift towards the \_\_\_\_\_ to reach equilibrium, because the product to reactant ratio is too \_\_\_\_\_.

iii)  $Q_c < K_c$       "favors \_\_\_\_\_ formation"

- The system must shift towards the \_\_\_\_\_ to reach equilibrium, because the product to reactant ratio is too \_\_\_\_\_.

For example:

1. The following reaction occurs in a closed container at  $445^\circ\text{C}$ . The equilibrium constant is 0.020.



Is the system at equilibrium in each of the following cases? If not, predict the direction in which the reaction will proceed to reach equilibrium.

a)  $[\text{HI}] = 0.14 \text{ mol/L}$ ,  $[\text{H}_2] = 0.04 \text{ mol/L}$ ,  $[\text{I}_2] = 0.01 \text{ mol/L}$

b)  $[\text{HI}] = 0.20 \text{ mol/L}$ ,  $[\text{H}_2] = 0.15 \text{ mol/L}$ ,  $[\text{I}_2] = 0.09 \text{ mol/L}$

# Ion product constant for water, $K_w$

$$\frac{[H^+_{(aq)}][OH^-_{(aq)}]}{[H_2O_{(l)}} = K$$

$$\frac{[H^+_{(aq)}][OH^-_{(aq)}]}{[H_2O_{(l)}} = \underbrace{K[H_2O_{(l)}}_{\text{constant}}$$

$$[H^+_{(aq)}][OH^-_{(aq)}] = K_w$$

- in \_\_\_\_\_ water the concentrations of hydrogen & hydroxide ions are \_\_\_\_\_ and measurements have shown that the conc. is \_\_\_\_\_.
- at SATP, therefore,

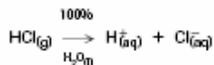
In neutral solutions	$[H^+_{(aq)}] = [OH^-_{(aq)}]$
In acidic solutions	$[H^+_{(aq)}] > [OH^-_{(aq)}]$
In basic solutions	$[H^+_{(aq)}] < [OH^-_{(aq)}]$

- the numerical value for  $K_w$  is valid at \_\_\_\_\_ but \_\_\_\_\_ at temperatures that are much higher or lower
- for higher temperatures  $K_w$  is greater so products are favoured
- we can use  $K_w$  to calculate either the \_\_\_\_\_ or \_\_\_\_\_ if the concentrations are \_\_\_\_\_

Since  $K_w = [H^+_{(aq)}][OH^-_{(aq)}]$   
 then  $[H^+_{(aq)}] = \frac{K_w}{[OH^-_{(aq)}]}$   
 and  $[OH^-_{(aq)}] = \frac{K_w}{[H^+_{(aq)}]}$

## STRONG ACIDS

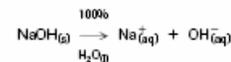
- strong acids \_\_\_\_\_ greater than \_\_\_\_\_ but assuming 100% we would see



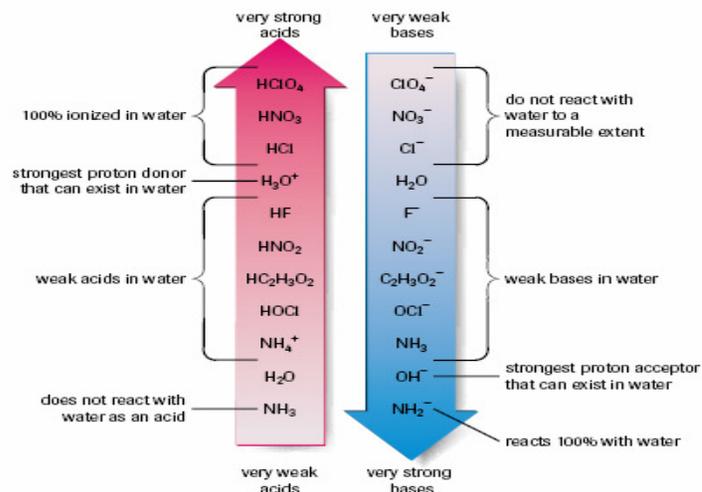
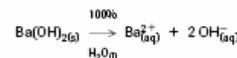
- so in looking at a bottle of  $HCl_{(aq)}$  that has a molar concentration 1.0 mol/L, we would assume that the bottle contained 1.0 mol/L of  $H^+_{(aq)}$  and 1.0 mol/L of  $Cl^-_{(aq)}$
- there are only a few strong acids e.g.  $HCl_{(aq)}$ ,  $HBr_{(aq)}$ ,  $H_2SO_{4(aq)}$ ,  $HNO_{3(aq)}$  and  $H_3PO_{4(aq)}$  to name some familiar ones
- \_\_\_\_\_ contain only 1 "ionizable" H atom

## STRONG BASES

- according to Arrhenius, a base is a substance that \_\_\_\_\_ to produce  $[OH^-]$  and increase the hydroxide concentration of a solution
- ionic hydroxides are all \_\_\_\_\_ bases as are all of the hydroxides of \_\_\_\_\_ elements i.e.  $LiOH$ ,  $NaOH$ , etc.



- Group \_\_\_\_\_ elements also form \_\_\_\_\_ bases, which dissociate to produce \_\_\_\_\_ moles of  $OH^-$  for every mole of metal hydroxide.



1. The conjugate base of a strong acid is a very weak base.
2. The conjugate base of a weak acid is a weak base.
3. The conjugate base of a very weak acid is a strong base.
4. The conjugate acid of a very weak base is a strong acid.
5. The conjugate acid of a weak base is a weak acid.
6. The conjugate acid of a strong base is a very weak acid.

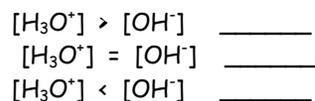
## Calculations Involving Acids and Bases

### 1. Calculations involving pH

The pH of a substance reflects the degree of acidity of that substance.

Note: a pH unit represents a factor of \_\_\_\_.

The relative concentrations of  $[H_3O^+]$  and  $[OH^-]$  ions are as follows:



pH can be calculated using the following formula(s):

$$\begin{aligned} \text{pH} &= -\log [H_3O^+] & \text{or} & & [H_3O^+] &= 10^{-\text{pH}} \\ \text{pOH} &= -\log [OH^-] & \text{or} & & [OH^-] &= 10^{-\text{pOH}} \\ \text{pH} + \text{pOH} &= 14 \end{aligned}$$

For example:

1) What is the pH of a solution with a  $[H_3O^+]$  of  $1 \times 10^{-2} \text{ M}$  ?

2) Gastric juice has a pH of 1.5. What is the  $[H_3O^+]$  ?

## Calculations involving the Acid and Base Dissociation Constants ( $K_a, K_b$ )

- The homogeneous equilibrium of a weak monoprotic acid in aqueous solution can be expressed as:

- The Acid Dissociation Constant (\_\_\_\_) represents the equilibrium value for the dissociation of a weak acid.

- The homogeneous equilibrium of a weak base in aqueous solution can be expressed as:

- The Base Dissociation Constant (\_\_\_\_) represents the equilibrium value for the dissociation of a weak base.

- The \_\_\_\_\_ of  $K_a$  or  $K_b$  provides a measure of the \_\_\_\_\_ of acidity or basicity.

- The \_\_\_\_\_ of an acid or base can be determined by expressing the fraction of molecules that dissociate out of 100.

The equation is:  $\frac{[H_3O^+]}{[\text{acid}_{\text{initial}}]} \times 100$  or  $\frac{[OH^-]}{[\text{base}_{\text{initial}}]} \times 100$

For example:

1. The pH of a 0.10 mol/L methanoic acid solution is 2.38. Calculate the percent ionization of methanoic acid.

Equation	$HCOOH$	+	$H_2O(l)$	$\leftrightarrow$	$H_3O^+(aq)$	+	$COOH^-(aq)$
[initial]							
Change							
[equilibrium]							

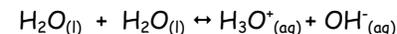
2. One of the uses for aniline,  $C_6H_5NH_2(l)$ , is in the manufacturing of dyes. Aniline is soluble in water and acts as a weak base. When a solution containing 5.0 g/L of aniline was prepared, the pH was determined to be 8.68. Calculate the  $K_b$  for aniline.

Equation	$C_6H_5NH_2(aq)$	+ $H_2O(l)$	$\leftrightarrow$	$C_6H_5NH_3^+(aq)$	+ $OH^-(aq)$
[initial]					
Change					
[equilibrium]					

## Calculations involving the Ion Product Constant for Water

### $K_w$

Experiments have revealed that some water molecules react with each other to produce  $H_3O^+(aq)$  and  $OH^-(aq)$  ions according to the following equation:



- The production of ions occurs as the result of an ionization process in which a \_\_\_\_\_ is transferred from one molecule to another. The heterogeneous water equilibrium obeys the equilibrium law.

$$K_w = [H_3O^+(aq)][OH^-(aq)]$$

- In \_\_\_\_\_ solutions:  $[H_3O^+(aq)]$  and  $[OH^-(aq)] =$  \_\_\_\_\_

- The Ion Product Constant (\_\_\_\_) represents the equilibrium value for the ionization of water:

$$K_w = [1.0 \times 10^{-7} \text{ mol/L}] [1.0 \times 10^{-7} \text{ mol/L}]$$

$$K_w = 1.0 \times 10^{-14} \text{ mol/L} @ \text{ SATP}$$

- We can use the ion product constant for water to calculate the  $[H^+(aq)]$  or  $[OH^-(aq)]$  in an aqueous solution of a \_\_\_\_\_ acid or base at SATP if the other concentrations are known.

$$\text{Since: } K_w = [H_3O^+(aq)][OH^-(aq)]$$

$$\text{then: } [H_3O^+(aq)] = \frac{K_w}{[OH^-(aq)]}$$

$$\text{then: } [OH^-(aq)] = \frac{K_w}{[H_3O^+(aq)]}$$

For example:

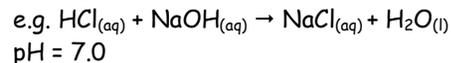
1. A 0.15 mol/L solution of hydrochloric acid at SATP is found to have a hydrogen ion concentration of 0.15 mol/L. Calculate the concentration of the hydroxide ions.

2. Calculate the hydroxide concentration in a 0.25 mol/L  $HBr(aq)$  solution.

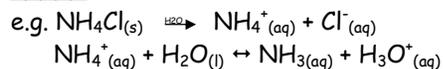
## SALT SOLUTIONS: Acidic, Basic, Neutral

What do I have to do in order to determine if the salt solution I make will be acidic, basic, or neutral?

NEUTRAL = \_\_\_\_\_ of a \_\_\_\_\_ is reacted with an \_\_\_\_\_ of a \_\_\_\_\_

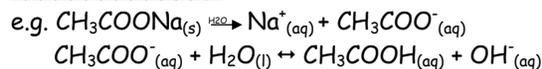


ACIDIC = A \_\_\_\_\_ consisting of an \_\_\_\_\_ of a \_\_\_\_\_ and the \_\_\_\_\_ of a \_\_\_\_\_ ionizes in water.



Because \_\_\_\_\_(aq) are produced, the salt solution is \_\_\_\_\_!  
 pH < 7.0

BASIC = A \_\_\_\_\_ consisting of the \_\_\_\_\_ of a \_\_\_\_\_ and the \_\_\_\_\_ of a \_\_\_\_\_ ionizes in water.



Because \_\_\_\_\_(aq) are produced, the salt solution is \_\_\_\_\_!  
 pH > 7.0

## Buffers

- A solution that contains a weak acid/conjugate base mixture or a weak base/conjugate acid mixture is called a \_\_\_\_\_ solution. Buffer solutions \_\_\_\_\_ changes in \_\_\_\_\_ when \_\_\_\_\_ amounts of an acid or base is \_\_\_\_\_ to it.



The buffer \_\_\_\_\_ is the quantity of acid or base that can be added without \_\_\_\_\_ change in \_\_\_\_\_.

For example;

1. A buffer solution was made by mixing equal volumes of 0.20 mol/L solutions of acetic acid and sodium acetate at 25°C. What is the pH of this buffer solution?

Equation	$\text{CH}_3\text{COOH}_{(aq)}$	+	$\text{H}_2\text{O}_{(l)}$	$\leftrightarrow$	$\text{H}_3\text{O}^+_{(aq)}$	+	$\text{CH}_3\text{COO}^-_{(aq)}$
[initial]							
Change							
[equilibrium]							

## Henderson-Hasselbalch Equation

- You can calculate the      of a      solution or the concentration of the acid and base using the Henderson-Hasselbalch equation.

For weak acids/conjugate bases

For weak bases/conjugate acids

$$pK_a = -\log K_a$$

[A<sup>-</sup>] = molar concentration of conjugate base

[HA] = molar concentration of weak acid

$$pK_b = -\log K_b$$

[HB<sup>+</sup>] = molar concentration of conjugate acid

[B] = molar concentration of weak base

Limitations:

- can't use with relatively      acids or bases (pKa more than a couple units away from 7),      or very      solutions (less than 1 mM or greater than 1M)

For example:

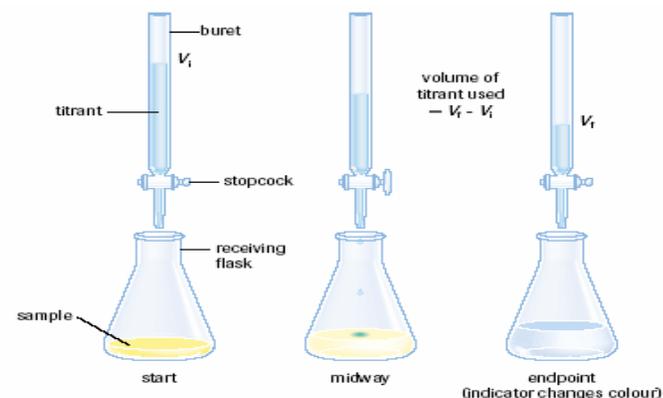
1. A buffer is prepared containing 1.00 M ammonia and 1.00 M ammonium chloride.

What is its pH?  $K_b$  for ammonia is  $1.77 \times 10^{-5}$

Equation	NH <sub>3(aq)</sub>	+	H <sub>2</sub> O(l)	↔	NH <sub>4</sub> <sup>+</sup> (aq)	+	OH <sup>-</sup> (aq)
[initial]							
Change							
[equilibrium]							

## ACID-BASE TITRATION

- a chemical analysis used to determine the concentration of an acid or base (sample) by adding an acid or base (    ) of a      concentration until a point of neutralization is found and a calculation is done to find out the concentration of the     



- the titrants commonly used are referred to as      and are available in a pure & stable form, which can be used to prepare an accurate concentration of titrant

- acid-base titration involves a reaction between an acid and a base and the addition of titrant continues until one reactant is consumed by the other--> this is called the      point

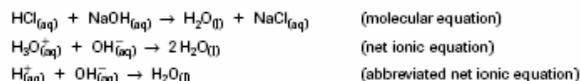
- an      is used to indicate the change in the sample and is called the     

- this method is not very precise as one is using      to pinpoint a change
- common indicators include bromothymol blue &

Indicator	Acid Color	Range	Base Color
Methyl violet	yellow	0.0-1.6	blue
Cresol red	red	1.0-2.0	yellow
Orange IV	red	1.4-2.6	yellow
Phloxine B	colorless	2.1-4.1	pink
2,4-Dinitrophenol	colorless	2.8-4.0	yellow
Methyl orange	red	3.2-4.4	yellow
$\alpha$ -Naphthyl red	red	4.0-5.6	yellow
Methyl red	red	4.8-6.0	yellow
4-Nitrophenol	colorless	5.4-6.6	yellow
Bromothymol blue	yellow	6.0-7.6	blue
Brilliant yellow	yellow	6.6-7.9	orange
Cresol red	yellow	7.0-8.8	red
2,6-Dianilylidene-cyclohexanone	yellow	7.8-9.4	red
Ethyl bis(2,4-dinitrophenyl) acetate	colorless	8.4-9.6	blue
Thymolphthalein	colorless	9.4-10.6	blue
Aizarin yellow R	yellow	10.0-12.0	red
Malachite green hydrochloride	green-blue	10.2-12.5	colorless
Methyl blue	blue	10.6-13.4	pale violet
Orange G	yellow	11.5-14.0	pink
2,4,6-Trinitrotoluene	colorless	11.7-12.8	orange

## Titrating a Strong Acid with a Strong Base

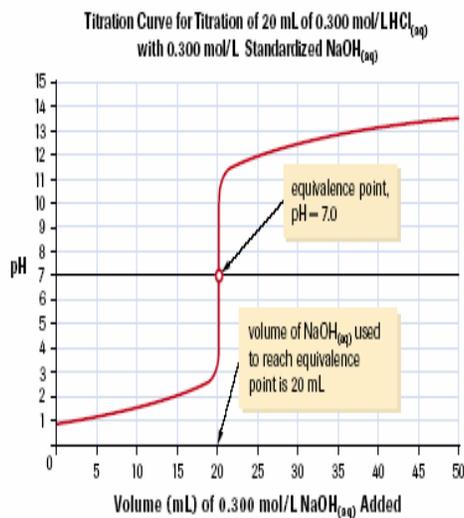
- consider the reaction between  $\text{HCl}_{(aq)}$  and  $\text{NaOH}_{(aq)}$ :



- calculations after a titration usually include a minimum of \_\_\_ trials and must be: stoichiometric, spontaneous, fast and quantitative

- if we plotted the pH of the solution flask in a titration of a strong acid with a strong base it would look like:

Section 8.4



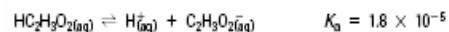
**Figure 2**

This curve is typical of curves depicting the titration of a strong acid with a strong base. Notice that the curve sweeps up and to the right as  $\text{NaOH}_{(aq)}$  is added, beginning at a pH below 7 and ending at a pH above 7. The equivalence point is reached at pH 7.

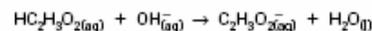
- remember that the conjugates of a strong acid and base are a weak conjugate base and a weak conjugate acid which cannot hydrolyze, therefore the pH is \_\_\_\_\_

## Titrating a Weak Acid with a Strong Base

- titrating acetic acid with  $\text{NaOH}$  is an example of this as acetic acid ionizes very little

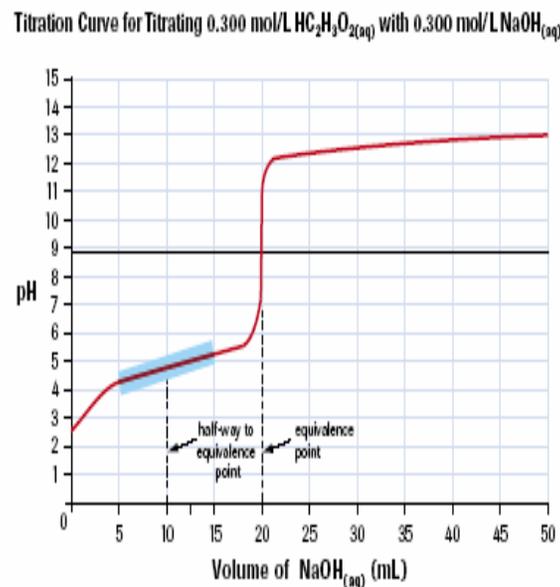


- the \_\_\_  $K_a$  indicates that the acetic acid exists as acetic acid particles in solution and as  $\text{NaOH}$  is added, the  $\text{OH}^-$  ions react with the acetic acid as,



- as more  $\text{OH}^-$  ions are added more acetic acid molecules are consumed \*remember even though acetic acid is weak, it will still react quantitatively with the  $\text{OH}^-$  ions until all the molecules are used up (consumed)

- if we plotted the pH of the solution flask in a titration of a weak acid with a strong base it would look like:

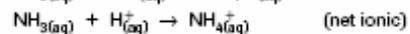
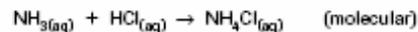


**Figure 4**

This curve is typical of curves depicting the titration of a weak acid with a strong base. Notice that the curve sweeps up and to the right as  $\text{NaOH}_{(aq)}$  is added, beginning at a pH below 7 and ending at a pH above 7. The equivalence point is reached at a pH greater than 7.

# Titrating a Weak Base with a Strong Acid

- titrating  $\text{NH}_3(\text{aq})$  with  $\text{HCl}(\text{aq})$  is an example

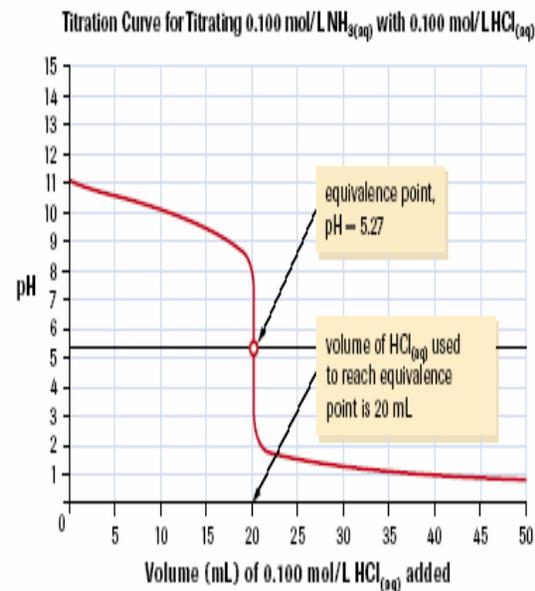


For example:

- 20 mL of 0.20 M  $\text{NH}_3(\text{aq})$  is titrated against 0.20 M  $\text{HCl}(\text{aq})$ . Calculate the pH at equivalence.  $K_b$  for  $\text{NH}_3$  is  $1.8 \times 10^{-5}$ .

Equation	$\text{NH}_4^+(\text{aq})$	+	$\text{H}_2\text{O}(\text{l})$	$\leftrightarrow$	$\text{NH}_3(\text{aq})$	+	$\text{H}_3\text{O}^+(\text{aq})$
[initial]							
Change							
[equilibrium]							

- if we plotted the pH of the solution flask in a titration of a strong acid with a weak base it would look like:



**Figure 5**

This curve is typical of curves depicting the titration of a weak base with a strong acid. Notice that the curve sweeps down and to the right as  $\text{HCl}(\text{aq})$  is added, beginning at a pH higher than 7 and ending at a pH lower than 7. The equivalence point is reached at a pH lower than 7.

## The Solubility Product Constant, $K_{sp}$

- special case of equilibrium involves cases where excess solute is in equilibrium with its aqueous solution
- can be done by either preparing a saturated solution with excess solute remaining or by mixing 2 solutions of salt that results with a product that precipitates out of solution

- Example:



The solubility equilibrium law equation is

$$K = \frac{[\text{Cu}^{2+}_{(aq)}][\text{Cl}^{-}_{(aq)}]^2}{[\text{CuCl}_{2(s)}]}$$

which simplifies to

$$K = [\text{Cu}^{2+}_{(aq)}][\text{Cl}^{-}_{(aq)}]^2$$

as the concentration (density) of the  $\text{CuCl}_{2(s)}$  is constant and so is incorporated into the value of the equilibrium constant. The value of this equilibrium constant is

$$K = 1.7 \times 10^{-7} \text{ at } 25^{\circ}\text{C}.$$

- for any solute that forms \_\_\_\_\_ in solution, the solubility equilibrium constant is found by \_\_\_\_\_ the concentrations of the ions in solution raised to the \_\_\_\_\_ equal to the \_\_\_\_\_ of each entity in the balanced equation
- this value of K is called the \_\_\_\_\_,  $K_{sp}$
- in the above example,  $K_{sp} = [\text{Cu}^{2+}_{(aq)}][\text{Cl}^{-}_{(aq)}]^2$   
 $K_{sp} = 1.7 \times 10^{-7} \text{ at } 25^{\circ}\text{C}$

2. Calculate the concentrations of iron ions and hydroxide ions in a solution of iron(II) hydroxide ( $K_{sp} = 1.8 \times 10^{-15}$ ).

Equation	$\text{Fe}(\text{OH})_{2(s)} \rightleftharpoons$	$\text{Fe}^{2+}_{(aq)}$	+	$2\text{OH}^{-}_{(aq)}$
[initial]				
Change				
[equilibrium]				

## Calculating the Ion Product Constant ( $Q_{sp}$ )

- This value is identical to the solubility product constant ( $K_{sp}$ ), but its value is calculated using concentrations that are \_\_\_\_\_ necessarily at equilibrium.
- Comparisons of  $K_{sp}$  and  $Q_{sp}$  can be used to predict the formation of a \_\_\_\_\_.

### SUMMARY

### Using Q to Predict Solubility

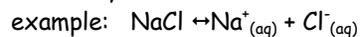
- Ion product,  $Q > K_{sp}$  (supersaturated solution) Precipitate will form.
- Ion product,  $Q = K_{sp}$  (saturated solution) Precipitate will not form.
- Ion product,  $Q < K_{sp}$  (unsaturated solution) Precipitate will not form.

For example:

1. If 25 mL of  $2.00 \times 10^{-2}$  mol/L sodium hydroxide is added to 80 mL of  $3.2 \times 10^{-2}$  mol/L magnesium chloride, will a precipitate form?  $K_{sp}$  for magnesium hydroxide is  $1.2 \times 10^{-11}$ .

## The Common Ion Effect

- when an equilibrium exists in a solution involving ions, the equilibrium can be shifted by \_\_\_\_\_ into the solution another compound that adds a \_\_\_\_\_, or reacts with one of the ions already in solution.



add a few drops of HCl and additional crystals of NaCl will form

- the explanation for this from Le Chatelier's Principle is that when we add HCl it releases large numbers of \_\_\_\_\_ ions into solution which will cause the reaction to shift to the \_\_\_\_\_...producing more \_\_\_\_\_to precipitate out
- the \_\_\_\_\_ of the solubility of an ionic compound (in this case the NaCl) by adding a common ion is called the \_\_\_\_\_

For example:

1. What is the molar solubility of calcium carbonate ( $K_{sp} = 9.0 \times 10^{-9}$ ) in 0.15 mol/L sodium carbonate?  $[\text{CO}_3^{2-}_{(aq)}]$  from sodium carbonate =  $[\text{Na}_2\text{CO}_3] = 0.15 \text{ mol/L}$ . This problem involves the common ion effect.

Equation	$\text{CaCO}_{3(s)} \leftrightarrow$	$\text{Ca}^{2+}_{(aq)}$	+	$\text{CO}_3^{2-}_{(aq)}$
[initial]				
Change				
[equilibrium]				