

RATE OF REACTION

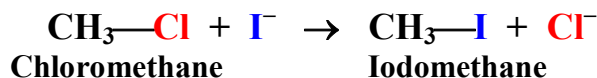
- The **speed** at which a chemical reaction occurs is called the **rate of reaction**. The study of reaction rates is called **chemical kinetics**.
- The **rate of a reaction** is measured by the amount of **reactant used up**, or the amount of **product formed**, in a certain period of **time**.

$$\text{Rate} = \frac{\text{change in concentration of reactant}}{\text{change in time}} = \frac{\Delta C_{\text{reactant}}}{\Delta t}$$

$$\text{Rate} = \frac{\text{change in concentration of product}}{\text{change in time}} = \frac{\Delta C_{\text{product}}}{\Delta t}$$

Example:

The reaction shown below was studied to determine its rate:



The concentration of iodomethane was initially found to be 0, and after 30 minutes it was found to be 0.12 M. Determine the rate of this reaction.

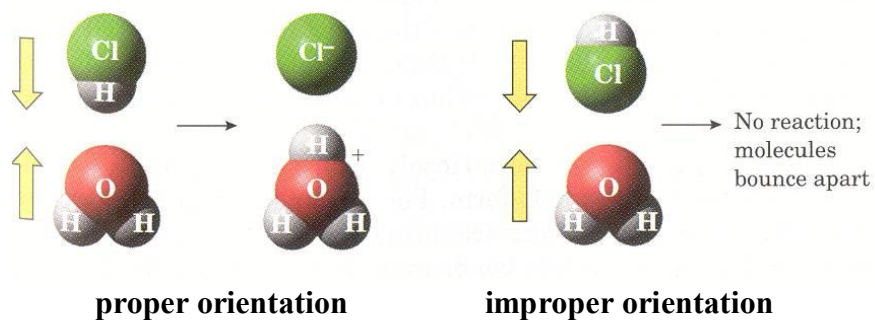
$$\text{Rate} = \frac{\Delta C_{\text{product}}}{\Delta t} = \frac{0.12 \text{ M} - 0 \text{ M}}{30 \text{ min}} = 0.004 \text{ M/min}$$

RATE OF REACTION

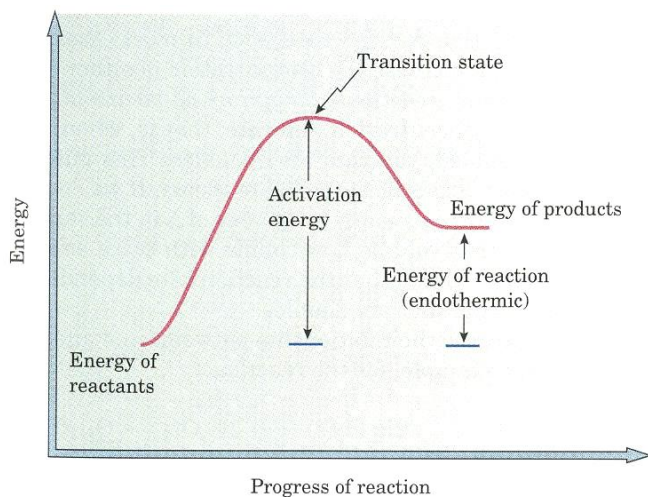
- To understand what causes the enormous variety in reactions rates, we must consider several factors.

Molecular Collisions

- For two **molecules or ions to react** with each other, they must first **collide**. Many collisions, however, do not lead to a reaction.
- Those collisions that do **lead to a reaction** are called **effective collisions**. For collisions to be **effective**, they must have sufficient **energy**, and the correct **orientation**.



- The **minimum energy** required to collisions to be effective is called **activation energy**.



Energy diagram for an endothermic reaction

FACTORS AFFECTING RATES OF REACTION

- The **rate** of a reaction can be **affected** by the nature of the reactants, changes in **temperature**, the **amounts of reactants** present, and the addition of **catalyst**.

Nature of Reactants

- In general, reactions between **ions** in aqueous solutions occur **very rapidly**, compared to reactions between **molecules**. This is due to the fact that with ions no covalent bonds need to be broken before reaction occurs.

Concentration of Reactants

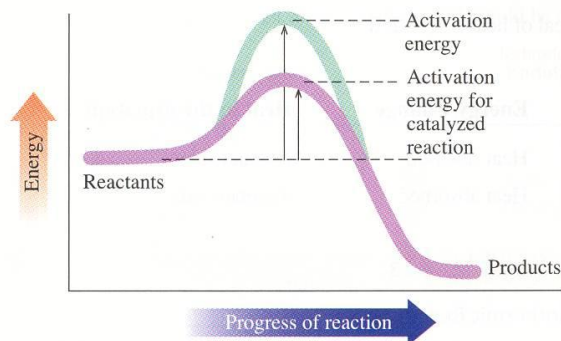
- The **increased amount of reactants** increases the **number of collisions** and therefore **increases the rate** of a reaction.

Temperature

- At **higher temperature**, the **increase in kinetic energy** of molecules allows them to **collide more often** and with **more energy**, creating **more effective collisions**.
- In general, **raising the temperature** of a reaction by **10°C** **doubles the rate** of the reaction.

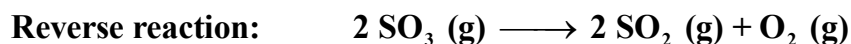
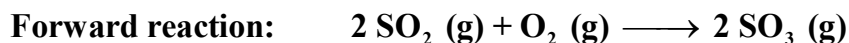
Addition of a Catalyst

- Addition of a **catalyst increases the rate** of the reaction by **decreasing the activation energy** for the reaction. As a result, more collisions **possess the required energy** and form product successfully.

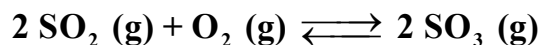


CHEMICAL EQUILIBRIUM

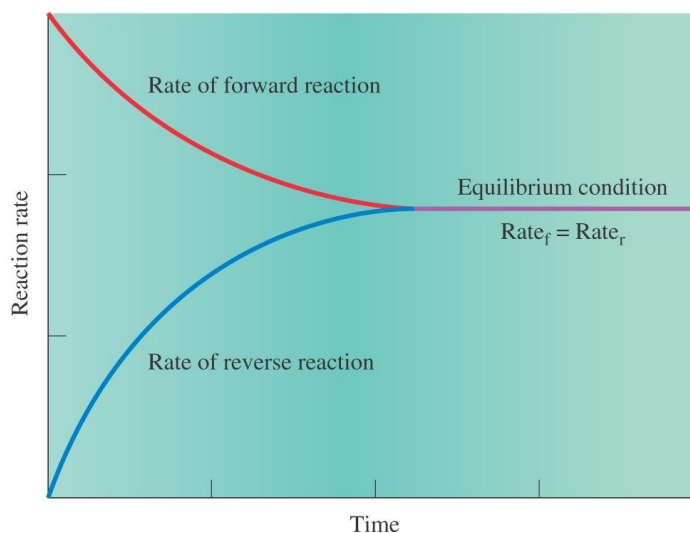
- In many reactions the products can combine and revert back to reactants. When a reaction occurs both in forward and reverse directions it is called a **reversible reaction**. For example:



- The forward and reverse reactions are usually shown in one equation by using a double arrow.

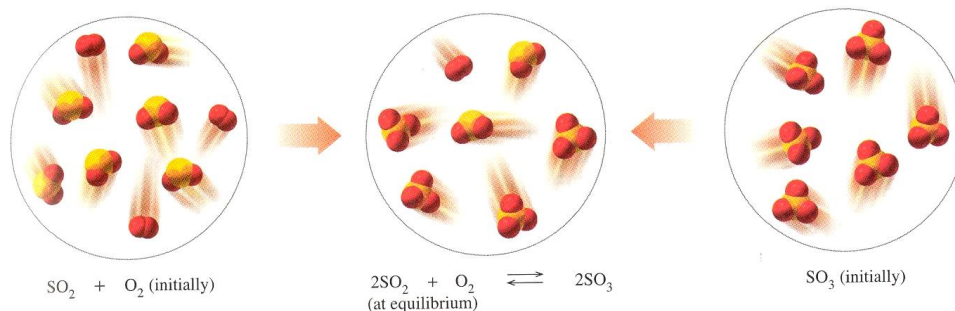


- In a reversible reaction, the **rate of the forward reaction is great** at the **start** of the reaction. As the reaction proceeds, the **rate of the forward reaction decreases**, due to a **decrease in the concentration of the reactants**.
- On the other hand, the **rate of the reverse reaction is very small** at the **start**. As the reaction proceeds, the **rate of the reverse reaction increases**, due to an **increase in the concentration of the products**.
- Eventually the **rate of the forward reaction equals** the **rate of the reverse reaction**. At this point, the reaction is said to have reached **chemical equilibrium**.
- At **equilibrium**, there are **no further changes in the concentration of reactants or products**.

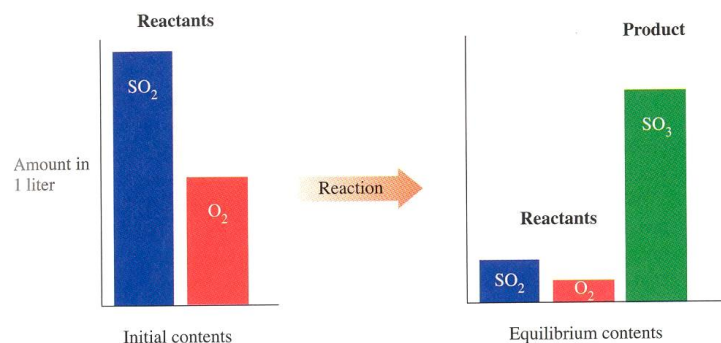


CHEMICAL EQUILIBRIUM

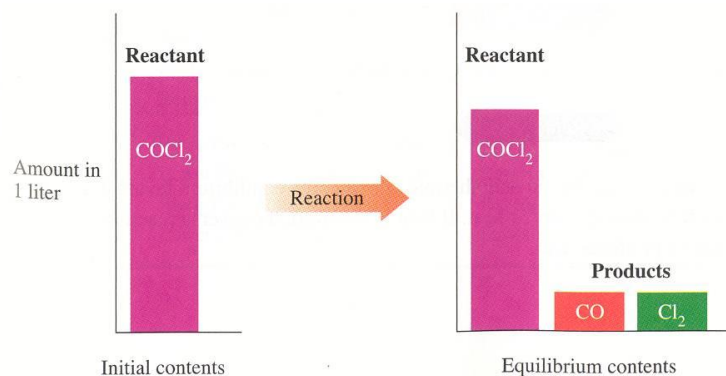
- 1) The same **equilibrium** mixture is obtained whether the reaction starts with reactants or products. However, this **does not mean** that the **amount of reactant** becomes **equal** to the **amount of product**.



- 2) In some reversible reactions **equilibrium** is reached when **most reactants** have combined to form products. In these reactions, we say the **equilibrium favors the formation of products**.



- 3) In other reversible reactions **equilibrium** is reached when **few reactants** have combined to form products. In these reactions, we say the **equilibrium favors the formation of reactants**.

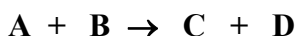


CHANGES IN EQUILIBRIUM

- 4) When a reaction reaches **equilibrium**, the **rate of the forward and reverse reactions are equal**, and the **concentration** of all the components **do not change**, if the system is left **undisturbed**.
- 5) If we **disturb** a system at equilibrium, by changing the **ratio of the reactants to products** or by adding or removing **heat**, we say there is a **stress on the equilibrium**.
- 6) When a **stress is applied** to an equilibrium, then according to **Le Chatelier's principle**, the **equilibrium will shift** to relieve the stress.

Effect of Concentration

- For most reactions the **rate of reaction increases** as **reactant concentrations increase**.
- An **equilibrium is disturbed** when the concentration of one or more of its components is changed.
- As a result, the concentration of all species will change and a **new equilibrium** mixture will be established.
- Consider the reversible reaction at equilibrium, shown below:



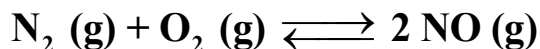
Stress: Increase the concentration of B

Shift: Increases the rate of forward reaction

New Equilibrium: Concentration of A decreases; concentrations of B, C and D increase.

Example:

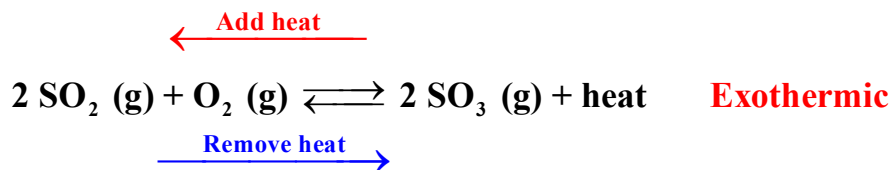
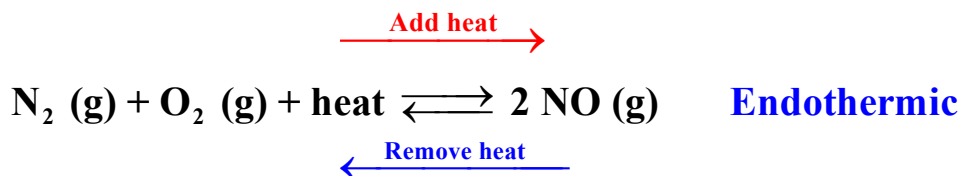
Complete the table for the equilibrium shown below:



Stress	Shift	[N ₂]	[O ₂]	[NO]
increase O ₂				
decrease O ₂				
increase NO				
decrease NO				

CHANGES IN EQUILIBRIUM
Effect of Temperature

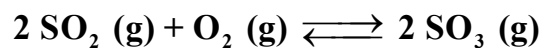
- To predict the effect of temperature on equilibrium, **heat** can be treated as a **reactant in endothermic** reactions and a **product in exothermic** reactions.


Effect of Volume & Pressure

- Changes in volume only affect reactions when one or more reactants or products are in the gas phase. In these cases, reducing the volume has the effect of increasing the pressure.
- Increasing the pressure shifts the equilibrium to the side with the least number of gas molecules (moles). Decreasing the pressure shifts the equilibrium to the side with the largest number of gas molecules (moles).

Example:

Consider the equilibrium shown below:

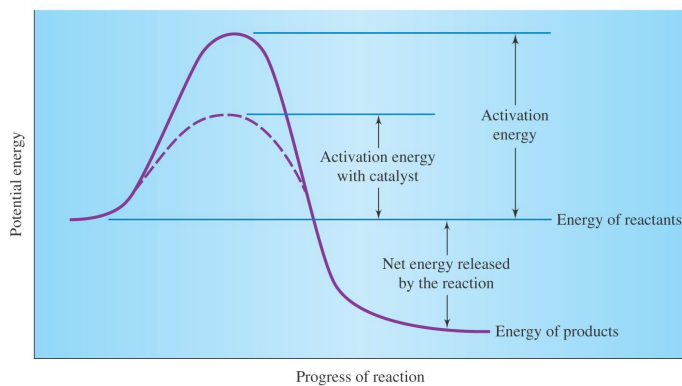


Stress	Shift	[SO ₂]	[O ₂]	[SO ₃]
increase temperature				
decrease temperature				
increase pressure				
decrease pressure				

CHANGES IN EQUILIBRIUM

Effect of Catalyst

- A catalyst speeds up a reaction by lowering the activation energy while not changing the energy of the reactants or products.
- Since a catalyst affects both the rate of the forward and reverse reactions equally, it does not affect the equilibrium.

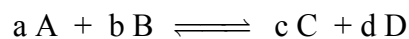


EFFECT of CHANGES on EQUILIBRIUM

Factor	Change (stress)	Shift in Equilibrium
Concentration	Add reactant Remove reactant Add product Remove product	Forward → Reverse ← Reverse ← Forward →
Temperature	Raise T for endothermic reaction Lower T for endothermic reaction Raise T for exothermic reaction Lower T for exothermic reaction	Forward → Reverse ← Reverse ← Forward →
Pressure	Increase pressure Decrease pressure	Shifts towards less moles Shifts towards more moles
Volume	Increase volume Decrease volume	Shifts towards more moles Shifts towards less moles
Catalyst	Add catalyst	No effect

EQUILIBRIUM CONSTANTS

- At equilibrium the rates of the forward and reverse reactions are equal, and the concentrations of the reactants and products are constant.
- The equilibrium constant (K_{eq}) is a value representing the unchanging concentrations of the reactants and the products in a chemical reaction at equilibrium.
- For the general reaction

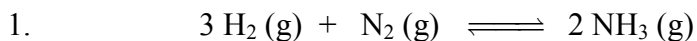


at a given temperature,

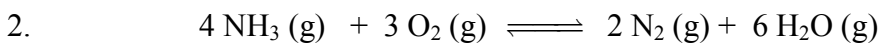
$$K_{eq} = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Examples:

Write equilibrium constant expression (K_{eq}) for each reaction shown below:



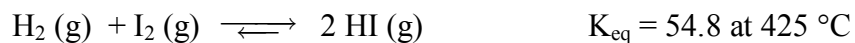
$$K_{eq} =$$



$$K_{eq} =$$

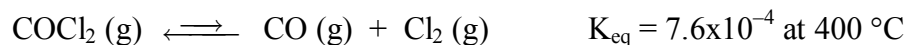
EQUILIBRIUM CONSTANTS

- The magnitude of an equilibrium constant indicates the extent to which the forward and reverse reactions take place.
- When K_{eq} is large, it indicates more product than reactant is present at equilibrium.



More product than
reactant is present at
equilibrium

- When K_{eq} is small, it indicates more reactant than product is present at equilibrium.



More reactant than
product is present at
equilibrium

- The K_{eq} for a reaction can be calculated from the equilibrium concentrations of reactants and products.

Examples:

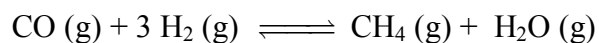
- Calculate the K_{eq} for the following reaction based on concentrations of $\text{PCl}_5 = 0.030 \text{ M}$, $\text{PCl}_3 = 0.97 \text{ M}$ and $\text{Cl}_2 = 0.97 \text{ M}$ at $300 \text{ }^\circ\text{C}$.



$$K_{eq} =$$

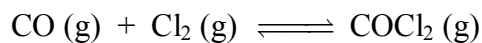
Examples:

2. What is the K_{eq} for the following equilibrium at 1000 °C

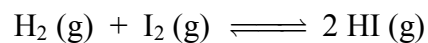


if $[\text{H}_2] = 0.30 \text{ M}$, $[\text{CO}] = 0.51 \text{ M}$, $[\text{CH}_4] = 1.8 \text{ M}$, and $[\text{H}_2\text{O}] = 2.0 \text{ M}$

3. The equilibrium shown below has a constant $K_{\text{eq}} = 5.0$. If at equilibrium the concentration of Cl_2 is 0.25 M and COCl_2 is 0.80 M, what is the equilibrium concentration of CO?

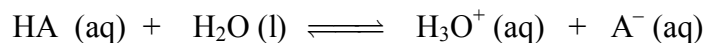


4. The equilibrium constant, K_{eq} , for the reaction shown below is 54 at 425 °C. If the equilibrium mixture contains 0.030 M HI and 0.015 M I_2 , what is the equilibrium concentration of H_2 ?



IONIZATION CONSTANTS

- Weak acids ionize partially in solutions to reach the following equilibrium:



or simply,



- The equilibrium constant for these reactions is called **acid ionization constant** (K_a) and has the following form:

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

Examples:

- At 25 °C, a 0.100 M solution of $\text{HC}_2\text{H}_3\text{O}_2$ is 1.34% ionized and has an $[\text{H}^+]$ of 1.34×10^{-3} M. Calculate K_a for acetic acid.

	$\text{HC}_2\text{H}_3\text{O}_2 \rightleftharpoons \text{H}^+ \text{ (aq)} + \text{C}_2\text{H}_3\text{O}_2^- \text{ (aq)}$		
Initial	0.100 M	0	0
Δ	$-x$	$+x$	$+x$
Equilibrium	0.100 -x	x	x

$$K_a = \frac{[\text{H}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = \frac{x^2}{0.100 - x}$$

$$x = [\text{H}^+] = [\text{C}_2\text{H}_3\text{O}_2^-] = 1.34 \times 10^{-3} \text{ M}$$

2. What is the $[H^+]$ in a 0.50 M $HC_2H_3O_2$ solution? The ionization constant, K_a , for $HC_2H_3O_2$ is 1.8×10^{-5} .

	$HC_2H_3O_2 \rightleftharpoons$		
Initial			
Δ			
Equilibrium			

$K_a =$

3. Calculate the percent ionization for the solution in Problem 2.

$$\% \text{ ionization} = \frac{[H^+] \text{ or } [A^-]}{[HA]} \times 100$$

PERCENT YIELD

- Percent yield of a reaction can be calculated from the following equation:

$$\% \text{ yield} = \frac{\text{amount of product formed at equilibrium}}{\text{amount of product formed in absence of equilibrium}} \times 100$$

Examples:

1.0 mol each of H₂ and I₂ are placed in a flask and allowed to come to equilibrium at a particular temperature, as shown below. At equilibrium 1.58 mol of HI are present. Calculate K_{eq} and the percent yield of this reaction.

$$\text{H}_2 + \text{I}_2 \rightleftharpoons 2 \text{HI}$$

Initial			
Δ			
Equilibrium			
No equilibrium			

$$K_{\text{eq}} =$$

$$\% \text{ yield} =$$

1.0 mol of H₂ and 1.2 mol I₂ are placed in a flask and allowed to come to equilibrium at the same temperature, as shown above. At equilibrium 1.70 mol of HI are present. Calculate K_{eq} and the percent yield of this reaction.

$$\text{H}_2 + \text{I}_2 \rightleftharpoons 2 \text{HI}$$

Initial			
Δ			
Equilibrium			
No equilibrium			

$$K_{\text{eq}} =$$

$$\% \text{ yield} =$$

SOLUBILITY PRODUCT CONSTANT

- Slightly soluble salts (commonly called insoluble) dissolve to a very small amount and produce the following equilibrium:



$$K_{\text{eq}} = \frac{[\text{Ag}^+][\text{Cl}^-]}{[\text{AgCl}]}$$

- Due to slight solubility of these salts $[\text{AgCl}]$ remains constant the equilibrium expression can be summarized as shown below:

**Solubility
product constant**

$$K_{\text{eq}} [\text{AgCl}] = [\text{Ag}^+][\text{Cl}^-]$$

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

Examples:

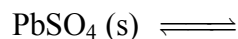
- The solubility of silver chloride in water is 1.3×10^{-5} M. Calculate the K_{sp} value for AgCl.

When 1 mol of AgCl dissolves it produces 1 mol of Ag^+ and 1 mol of Cl^- .

Therefore, $[\text{Ag}^+] = [\text{Cl}^-] = 1.3 \times 10^{-5}$ M

$$K_{\text{sp}} = [\text{Ag}^+][\text{Cl}^-] = (1.3 \times 10^{-5})(1.3 \times 10^{-5}) = 1.7 \times 10^{-10}$$

- The K_{sp} value for PbSO_4 is 1.3×10^{-8} . Calculate the solubility of PbSO_4 in M.



$$K_{\text{sp}} =$$

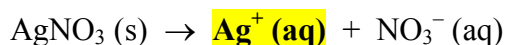
- The solubility of silver chromate, Ag_2CrO_4 , is 7.8×10^{-5} M. Calculate the K_{sp} value for this salt.

THE COMMON ION EFFECT

- A shift in the equilibrium position upon addition of an ion already contained in the solution is known as the *common ion* effect.
- As an example, silver chloride forms the following equilibrium:



- When solid silver nitrate (as soluble salt) is added to this solution, it dissociates as follows:



- Silver ions (Ag^+) are common in both equations and must therefore be considered in the calculations.

Examples:

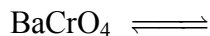
1. Silver nitrate is added to a saturated AgCl solution until the $[\text{Ag}^+] = 0.10 \text{ M}$. What will be the $[\text{Cl}^-]$ remaining in solution? ($K_{\text{sp}} \text{ AgCl} = 1.7 \times 10^{-10}$)

$$K_{\text{sp}} =$$

After AgNO_3 has been added $[\text{Ag}^+] =$

$$[\text{Cl}^-] =$$

2. 0.010 mol of Na_2CrO_4 is added to 1.0 L of saturated BaCrO_4 solution. What is the $[\text{Ba}^{2+}]$? ($K_{\text{sp}} \text{ BaCrO}_4 = 8.5 \times 10^{-11}$)



$$K_{\text{sp}} =$$



What is the common ion? _____ Concentration: _____

$$[\text{Ba}^{2+}] =$$

HYDROLYSIS OF SALTS

- When soluble ionic salts dissolve in water they form ions.



- Some of the ions formed can react with water to form the parent weak acid or weak base.



- The reaction of salts with water is called *hydrolysis*.

Salts of Weak Acid and Strong Base

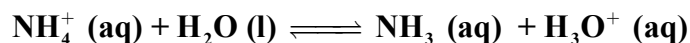
- Salts formed from the reaction of weak acids and strong bases hydrolyze to form basic solutions.



- Sodium ion (Na^+) does not hydrolyze because its parent base (NaOH) is a strong base.

Salts of Strong Acid and Weak Base

- Salts formed from the reaction of strong acids and weak bases hydrolyze to form acidic solutions.



- Chloride ion (Cl^-) does not hydrolyze because its parent acid (HCl) is a strong acid.

Salts of Strong Acid and Strong Base

- Salts formed from the reaction of strong acids and strong bases do not hydrolyze and form neutral solutions



- Neither ion hydrolyzes because their parent acid (HCl) and base (NaOH) are strong.

HYDROLYSIS OF SALTS

Summary of Hydrolysis:

Type of Salt	Nature of Solution	Examples
Weak acid Strong base	Basic	$\text{NaC}_2\text{H}_3\text{O}_2$ K_2CO_3
Strong acid Weak base	Acidic	NH_4Cl NH_4NO_3
Strong acid Strong base	Neutral	NaCl KBr

Examples:

For each salt shown below, identify the parent acid and base and determine whether the solution would be acidic, basic or neutral.

Salt	Parent Acid	Parent Base	Acidic, Basic or Neutral
NaCN			
NH_4NO_3			
NaF			
K_2SO_4			

BUFFER SOLUTIONS

- Many biological systems require a very narrow control of the pH in order to operate properly. For example blood must be maintained between pH of 7.35 and 7.45 for efficient transport of oxygen from lungs to the cells.
- **Buffer** solutions are solutions of weak acids and bases with their conjugate salts that resist changes in pH upon addition of acid or base.
- Two types of buffer solutions are:

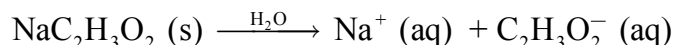
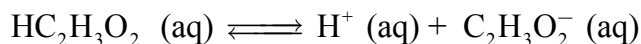
1. Solution of a weak acid and its conjugate base



2. Solution of a weak base and its conjugate acid



- In each of these buffer solutions the weak acid or base forms an equilibrium with its conjugate base or acid. For example, in the first case



- The acetate ion formed from the ionization of sodium acetate acts as a common ion and suppresses the ionization of acetic acid in the equilibrium above. As a result the pH of a 0.1 M buffer solution is higher (4.74) compared to the pH of 0.1 M acid solution (2.87).

Examples:

1. Indicate whether each of the following would make a buffer solution:

a) HCl and NaCl _____

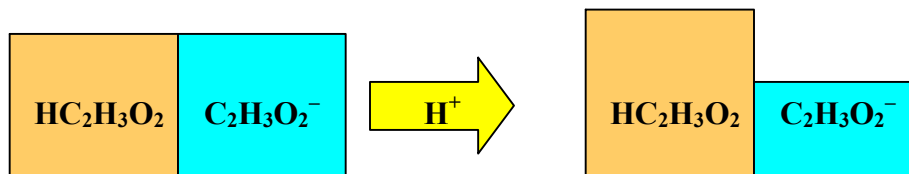
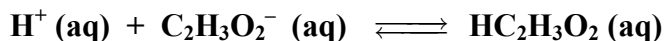
b) H₃PO₄ _____

c) HF and NaF _____

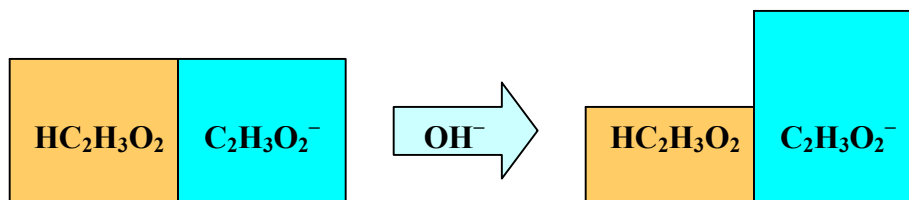
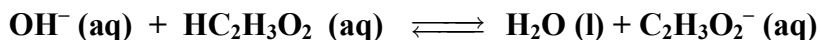
2. Will a mixture of NaCl and Na₂CO₃ make a buffer solution?

BUFFERING CAPACITY

- When small amounts of acid is added to this buffer, the H^+ from the acid reacts with the acetate ion to form unionized acetic acid (as shown) and maintain the pH of the solution.



- When small amounts of base is added to this buffer, the OH^- from the base reacts with acetic acid to neutralize the base (as shown) and maintain the pH of the solution.



- Buffering capacity** is the ability of a solution to resist large changes in pH when a strong acid or strong base is added.
- Buffering capacity of a buffer solution is determined by the **ratio** of the conjugate salt to the weak acid or base.

$$\text{Buffering Capacity} = \frac{[\text{Conjugate Salt}]}{[\text{Weak Acid or Base}]}$$

Type 1 Buffer:

$$\text{Buffering Capacity} = \frac{[\text{NaC}_2\text{H}_3\text{O}_2]}{[\text{HC}_2\text{H}_3\text{O}_2]}$$

Type 2 Buffer:

$$\text{Buffering Capacity} = \frac{[\text{NH}_4\text{Cl}]}{[\text{NH}_3]}$$

- The ideal buffering capacity is equal to 1.

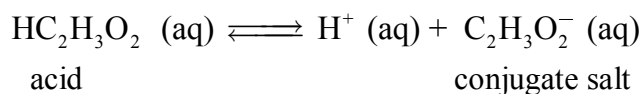
CALCULATING pH OF A BUFFER

- pH of a type I buffer can be calculated from the ratio of its buffering capacity as shown below:

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \qquad [\text{H}^+] = K_a \times \frac{[\text{HA}]}{[\text{A}^-]}$$

Examples:

- The K_a for acetic acid ($\text{HC}_2\text{H}_3\text{O}_2$) is 1.8×10^{-5} . What is the pH of a buffer prepared with 1.0 M acetic acid and 1.0 M sodium acetate?



$$[\text{H}^+] = K_a \times \frac{[\text{HC}_2\text{H}_3\text{O}_2]}{[\text{C}_2\text{H}_3\text{O}_2^-]} = 1.8 \times 10^{-5} \times \frac{1.0}{1.0} = 1.8 \times 10^{-5}$$

$$\text{pH} = -\log [\text{H}^+] = -\log(1.8 \times 10^{-5}) = 4.74$$

- One of the acid-base pairs that buffers the blood is $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ with a K_a of 6.2×10^{-8} . What is the pH of a buffer that is 0.50 M H_2PO_4^- and 0.40 M HPO_4^{2-} ?
- Two buffer solutions are prepared: the first contains 0.10 M H_2CO_3 and 0.10 M Na_2CO_3 , while the second contains 0.15 M H_2CO_3 and 0.050 M Na_2CO_3 .
 - Which solution has greater buffering capacity? Why?
 - Calculate and compare the pH of the 2 buffer solutions. K_a for H_2CO_3 is 4.3×10^{-7} .