

Primary and Secondary Salt effect

Salt effect

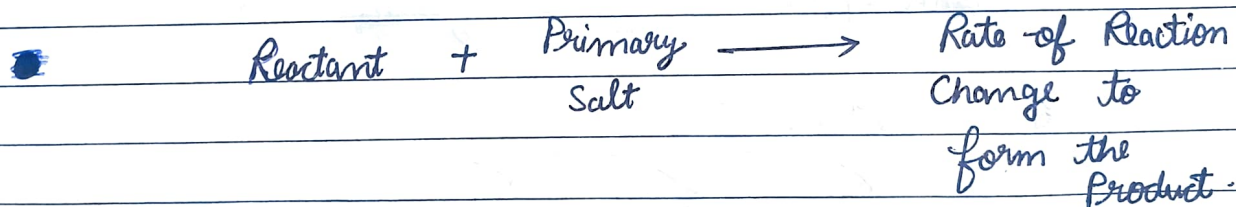
When salt add with chemical reactant the rate of the reaction change may be the rate of reaction increase or the rate of reaction decrease.

Salt effect is divided into ^{two} types :-

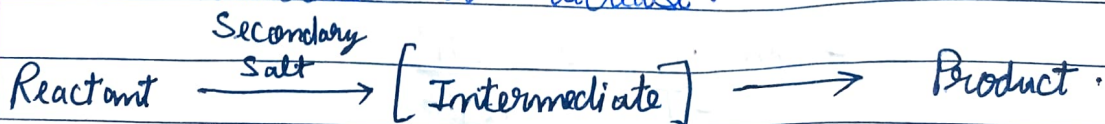
Primary Salt and Secondary Salt.

● Primary Salt :-

In Primary Salt effect. When salt add in a chemical reaction. the ions of the salt react with reactants of the reaction. and the rate of the reaction change.

● Secondary Salt :-

In Secondary Salt. When salt add in a chemical reaction. the ions of salt interact with reactant ~~or~~ or intermediate steps. to change speed of the reaction. the reaction may be increase or decrease.



Factors affect the Primary and Secondary salt:-

- ⑤ * The Charge and Concentration of the added electrolyte ions
- * The Charge and Size of the Reactants of the Reaction.
- * The temperature is also responsible for the salt and reactant interaction.
- * Solvent ~~is~~ used in the Reaction.

Applications of Salt effects:-

- * Salt effects can be used to increase or decrease the speed of the reaction.
- * Salt effect play an important role in electrode reaction.
- * Salt effect used to increase the Accuracy and precision of analytical method.

~~* Salt effects~~

#

Vant Hoff's equation:-

The Van't Hoff equation is a relationship in chemical thermodynamics that relates the change in the equilibrium constant K , of a chemical reaction to the change in temperature T . the equation is:-

$$\frac{d \ln K}{dT} = \frac{\Delta H^\circ}{RT^2}$$

Where,

ΔH° = is the standard enthalpy change of the reaction.

R = Gas Constant

T = Temperature

* Factors affect the ~~Van't Hoff~~ ^{equilibrium} Rate Constant.

* The equilibrium constant K is ~~is~~ inversely proportional to the temperature.

* If the temperature increases the equilibrium constant and the value of ΔH is less than zero.

* If the temperature decreases the equilibrium constant increases and the value of $\Delta H > 0$ ~~may be~~ [positive value].

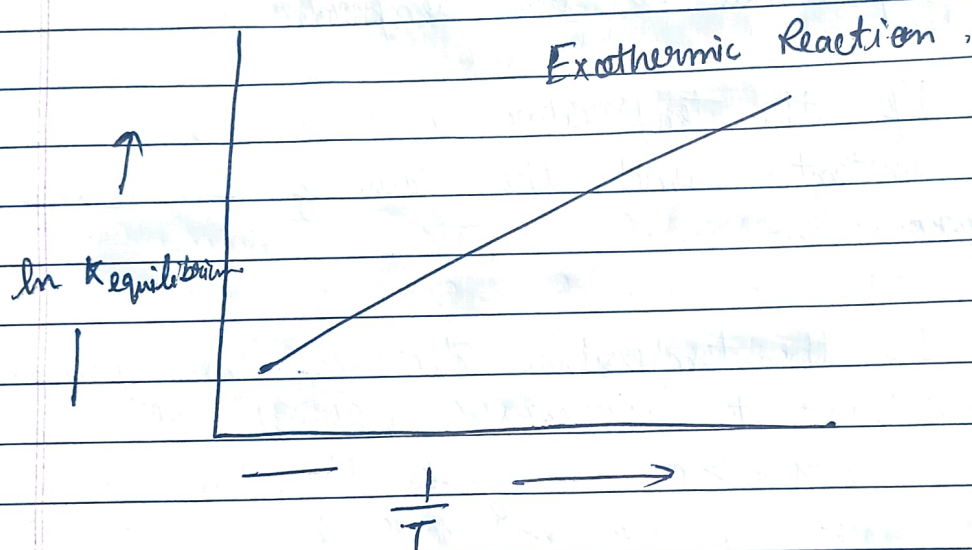
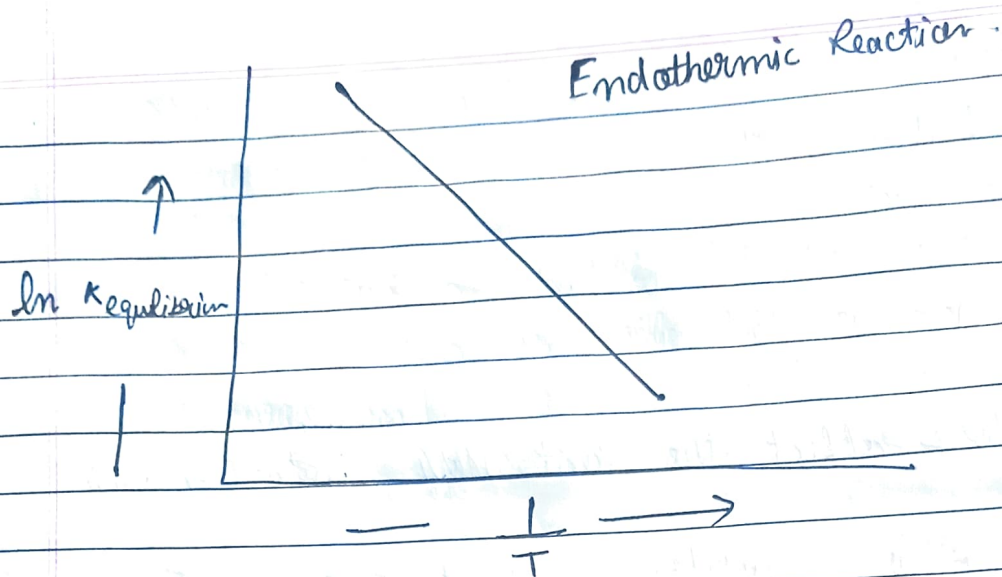
ΔH Enthalpy in this equation.

* Exothermic Reaction :- when heat energy is evolved in the reaction. then the heat enthalpy is ~~post~~ negative.

$$\Delta H < 0 \quad [\Delta H = -ve]$$

* Endothermic Reaction:- when heat energy is absorbed in the reaction. then the heat enthalpy is positive.

$$\Delta H > 0 \quad [\Delta H = +ve].$$



[Van't Hoff equation is used to determine the enthalpy change of a reaction.]

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Volume of Activation

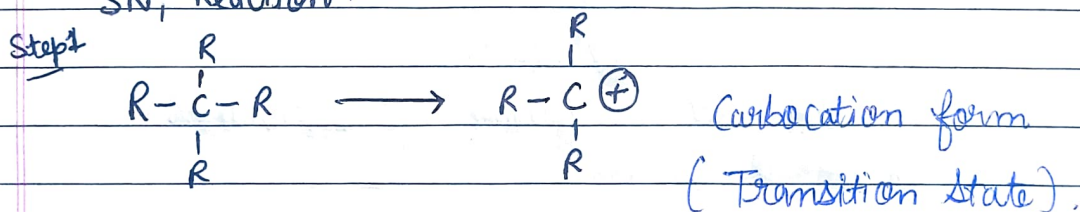
- * It is difference in molar Volume between the transition state and the Reactants.
- * The Symbol of Volume of Activation is $(\Delta V^\ddagger)$.
- * It is used to measure the change in volume when the reactants are transformed into transition state.

~~Negative volume~~

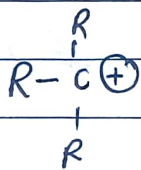
Positive volume of Activation:-

The Positive Volume of Activation take place in SN_1 Reaction.

SN_1 Reaction.



Step 2

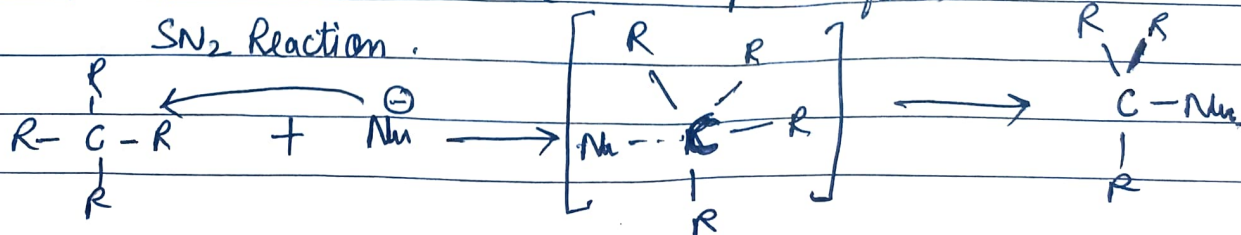


This Carbocation has more repulsion force.

The Positive Volume of activation indicates that the transition state is unable to overcome this repulsive pressure and form a bond.

Negative volume of Activation:-

The Negative Volume of Activation take place in SN_2 reaction. (Low Repulsive force)



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Nucleophile directly remove the leaving group from the substrate.

The Negative Volume of Activation indicates that transition state is able to overcome Repulsive Pressure and form a bond.

Volume of Activation Can be used to estimate the activation energy:-

$$\Delta E_a = -RT \Delta V^\ddagger$$

Where,

- ΔE_a = Activation energy
- R = Gas Constant
- T = Temperature
- $\Delta V^\ddagger$ = Volume of Activation.

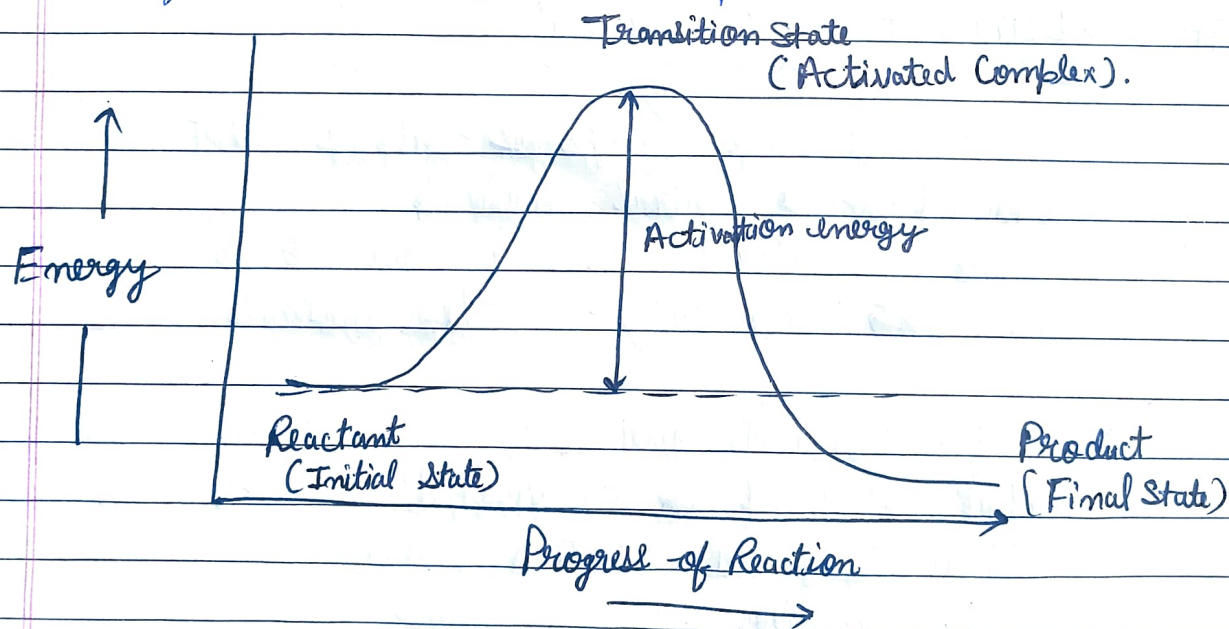
* ΔE_a (Activation energy) is directly proportional to the volume of activation ($\Delta V^\ddagger$).

* If ~~the~~ Volume of Activation ($\Delta V^\ddagger$) increases the ΔE_a (Activation energy) increases.

* If Volume of Activation ($\Delta V^\ddagger$) decreases the ΔE_a (Activation energy) decreases.

Transition State theory:-

- * It is used to explain the rates of chemical reactions.
- * In this the chemical reaction proceeds through a high energy intermediate called the activated complex.
- * The Activated complex is formed when the reactants collide with each other and they have enough energy to overcome the activation energy barrier.
- * When activated complex formed again the compound break into reactants and proceed forward to form the product.



- * The Rate of chemical reaction is determined by the concentration of the reactants and the activation energy barrier.
- * If the activation energy is high the reaction will get slow.

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TST (Transition State theory) is used to derive the Arrhenius equation.

$$k = A e^{(-E_a/RT)}$$

where k = Rate Constant

A = pre exponential factor

E_a = Activation energy

R = Gas Constant

T = Temperature

TST is normally used to understand the rates of chemical reaction.

#

Substituent and Correlation effects

* Substituent are groups of atoms that are attached to a central molecule.

* The Substituent can increase or decrease the ~~rate~~ reactivity of the molecule.

* : The Hammett equation is a quantitative tool that is used to measure the effect of substituents on reaction rates.

The equation is :-

$$\log \frac{k}{k^*} = \rho \sigma$$

Where

k = Rate Constant for Reaction with ^{Substituent} ~~sub~~

k^* = " " " " without "

ρ = Reaction Constant

σ = Substituent Constant.

σ (Substituent Constant)

* It measure the electron withdrawing or electron donating ability of the substituent.

Positive σ (Substituent Constant)

The Positive σ value measure the electron withdrawing ability of the substituent.

Negative σ (Substituent Constant)

The Negative σ value measure the electron donating ability of the substituent.

ρ (Reaction Constant)

It measure the electronic effect of the substituent.

~~Positive~~ ρ

Large ρ value :- it ~~measure~~ shows the high electronic effect of the substituent.

Low ρ value :- it shows the low electronic effect of the substituent.

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Hammett equation - LFER

- * LFER stands for Linear free energy relationship.
- * The Hammett equation is a type of linear free energy relationship [LFER].

* : The Hammett equation is a quantitative tool that is used to measure the effect of substituents on reaction rates.

The equation is :-

$$\log \frac{k}{k^*} = \rho \sigma$$

Where

k = Rate Constant for Reaction with ~~sub~~ Substituent

k^* = " " " " without " ^

ρ = Reaction Constant

σ = Substituent Constant.

σ (Substituent Constant)

* It measures the electron withdrawing or electron donating ability of the substituent.

σ Positive σ (Substituent Constant)

The Positive σ value measures the electron withdrawing ability of the substituent.

Negative σ (Substituent Constant)

The Negative σ value measures the electron donating ability of the substituent.

ρ (Reaction Constant)

It measures the electronic effect of the substituent.

Positivity

Large ρ value :- it ~~measures~~ shows the high electronic effect of the substituent.

Low ρ value :- it shows the low electronic effect of the substituent.

Taft equation

* The Taft equation is another linear free energy relationship.

* it is used to measure the effect of substituents on reaction rates.

The equation is :-

$$\log \frac{k}{k^*} = \rho^* \sigma^*$$

Where

k = Rate Constant for the Reaction with the substituent.

k^* = Rate Constant for the Reaction without the substituent.

ρ^* = Reaction Constant

σ^* = Taft Substituent Constant.

σ^* (Taft Substituent Constant):-

* It is used to measure the steric effect of the substituents.

* Large value of σ^* means the substituent is bulky.

* Small value of σ^* means the substituent is not bulky.

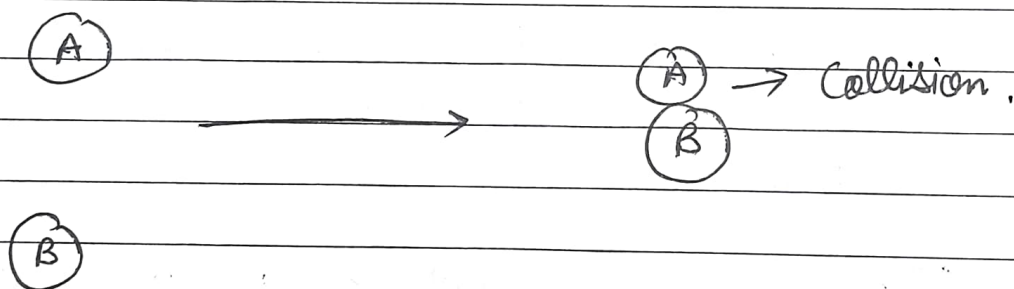
* Large value of σ^* indicate the high steric effects of the substituent.

* Small value of σ^* indicate the low steric effects of the substituent.

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Diffusion Controlled Reactions (full microscopic diffusion control):-

- * Diffusion controlled reactions also known as diffusion-limited reactions.
- * In this reaction the rate of reaction is determined by the rate at which the reactants can diffuse together.
- * The Rate of Diffusion is very fast because the reactants can collide with each other many times per second.



Reactant molecules

Full microscopic diffusion controlled reaction.

- * This is a special type of reaction in which the reactants must collide with each other in a specific orientation in order to react.
- * These reactions are faster than other diffusion controlled reactions.

Rate of diffusion-controlled reaction can be calculated by using the Smoluchowski equation:-

$$K_D = 4\pi N_A D_{(AB)} R$$

where K_D = Rate Constant for the Reaction.

N_A = Avogadro's Number.

D_{AB} = Diffusion Coefficient of the Reactants A and B.

R = Distance of closest Approach between the Reactants.

This is used to measure the Speed of molecule to react or [collide each other].

Factors affect the Rate of Diffusion-Controlled Reactions:-

(1) Concentration of the Reactants:-
at Higher Conc. the rate of reaction will be fast.

(2) Temperature
at High temperature the rate of reaction will be fast.

Single Sphere Activated Complex - - Influence of Ionic Strength [Bronsted - Bjerrum equation].

Single Sphere Activated Complex

* It is theoretical concept to understand the behavior of ~~understanding~~ ionic reactions in solution.

* The Single-Sphere Activated Complex model can be used to derive in Bronsted - Bjerrum equation.

* It is quantitative expression for the influence of ionic strength on the rate of an ionic reaction.

Statement of Bronsted - Bjerrum equation :-

It states that the rate constant k of an ionic reaction is ~~directly~~ ^{directly} proportional to the square root of the ionic strength (I) of the solution.

Mathematical Expression for Bronsted - Bjerrum equation :-

$$\cancel{k = k_0} \\ \frac{k}{k_0} = \sqrt{1 + 1.07 AZ \sqrt{I}}$$

Where k = Rate constant of the reaction.

k_0 = Rate constant of the reaction at infinite dilution

A = Constant

Z = Valence of the ions

I = Ionic Strength of the solution.

Factors affect Rate Constant.

$$k \propto \frac{1}{\sqrt{I}}$$

Rate constant is ~~inversely~~ ^{directly} proportional to the Ionic strength of the solution.

- * If the Ionic strength of the solution increases the rate constant increases.
- * If the Ionic strength of the solution decreases the rate constant decreases.