

(A) Corrosion

Corrosion may be defined as the gradual deterioration of a metal by chemical or electrochemical reaction with its environment. Corrosion is either chemical or electrochemical in nature --

Some examples of corrosion are

- (i) Rusting of iron
- (ii) Formation of green layer of basic carbonate
- (iii) Reaction of chlorine with tin.

Causes of Corrosion

In nature, most metals (except noble metals) exist in combined state as their compounds i.e. oxides, hydroxides, carbonates etc. The metals are extracted from these compounds after expending lot of energy. The metal will have a natural tendency to convert back to its natural thermodynamically stable state i.e. combined state. This is the basic reason for metallic corrosion.

Types of Corrosion

- (1) Galvanic Corrosion - This is the most common form of corrosion. When two different metals are electrically connected and exposed to an electrolyte, the metal higher in electrochemical series undergoes corrosion. Such type of corrosion is called galvanic corrosion.

(2) Erosion Corrosion - It is caused by the combined effect of the abrading action of turbulent flow of gases, vapours and liquids and the metal mechanical rubbing action of solids over a metal surface. The major cause for its corrosion is the removal of protective surface film.

(3) Crevice Corrosion - It is a local corrosion and is usually created by dirt deposits, corrosion products, cracks in paint coatings etc.

(4) Pitting corrosion - It is usually due to the breakdown, or cracking of the protective film on a metal. It is a localized accelerated attack, resulting in the formation of cavities around which the metal is relatively unsaturated and this corrosion results in the formation of pinholes, pits and cavities in the metal.

(5) Soil Corrosion - Corrosion by soils is very imp. in case of water mains, electric cables and other underground etc. are embedded in the soil. The various factors that are responsible for the soil corrosion are as follows:

- (i) Acidity of soil.
- (ii) Moisture content
- (iii) Micro-organisms present
- (iv) Content of organic matter

(v) Physical properties of the soil

(6) Microbiological Corrosion - Corrosion caused by the metabolic activity of various micro organisms, is called microbiological corrosion.

Bacteria, fungi, algae etc are capable of forming microbiological film on the surface of metal.

(7) Stray Current Corrosion - Metal str. such as water pipes, gas pipes and cable sheaths adjacent to DC circuit may get corroded due to leakage from the main circuit.

✓ Electrochemical Theory of Corrosion

This theory is based on Nernst's theory according to which all metals have tendency to pass into solution. The electrochemical theory states that corrosion occurs due to the existence of separate anodic and cathodic areas b/w which current flows through the conducting solⁿ. At anodic area, oxidation takes place, so anodic metal is destroyed by either dissolving or obtaining it in combined state. Therefore, corrosion always occurs at anodic area.

At cathodic areas, reduction takes place.

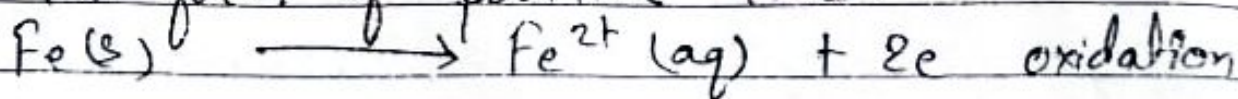
The corrosion of iron is called rusting. According to electrochemical theory rusting

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of iron is explained as follows.

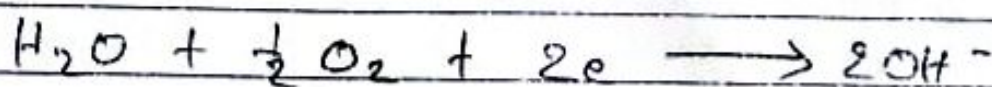
Anodic reaction

At the anode, iron loses electrons to the environment and pass into solution in the form of positive ions.

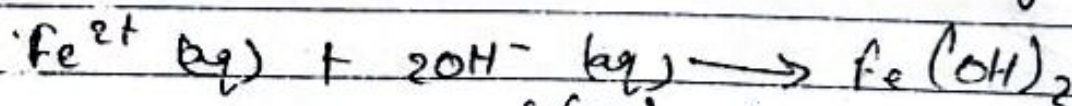


Cathodic reaction

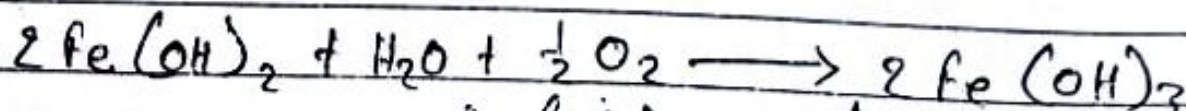
The moisture in presence of air gains electron to form hydroxide



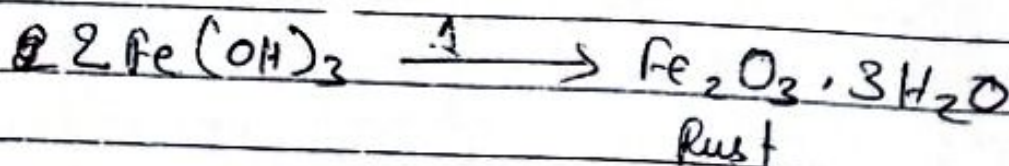
Fe^{2+} ions react with OH^- ions to form $\text{Fe}(\text{OH})_2$



$\text{Fe}(\text{OH})_2$ in presence of air and water gets $\text{Fe}(\text{OH})_3$



$\text{Fe}(\text{OH})_3$ when heated gives rust



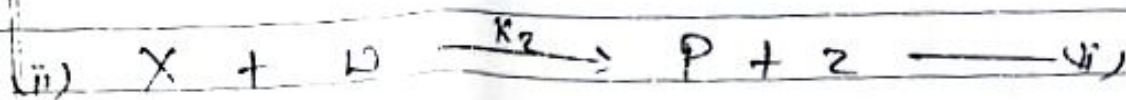
Catalysis and Oscillatory Behaviour

General Mechanism and Kinetics of Catalytic reactions:

In the simplest type of catalysed reaction involving only one substrate, the substrate and catalyst form a complex which subsequently decomposes to the product with regeneration of catalyst.

In other cases, the complex involves the catalyst and two substrate molecules. In more complicated type of catalysis, the catalyst may act in different ways by giving rise to free radicals which initiates chain process.

A kinetic study for the phenomenon associated with one substrate was put forward by Herzfeld. Consider the rxn as



Here C represents the catalyst, S is the substrate, X is the intermediate complex, Y is the same substance which is formed in addition to complex, W is a molecule which reacts with the complex to give product P with the elimination of a molecule.

Consider the reaction — (i)

- Rate of the forward reaction = $k_1 [C][S]$
Rate of backward reaction = $k_{-1} [X][Y]$
At equilibrium $k_1 [C][S] = k_{-1} [X][Y]$

or, $\frac{k_1}{k_{-1}} = \frac{[C][S]}{[X]}$

- $\frac{k_1}{k_{-1}} = \frac{[X][Y]}{[C][S]} = K$ (eq^m constant) — (ii)

This expression allows the concⁿ of X to be calculated in terms of concⁿ Y, [C] & [S] but [C] & [S] don't correspond to the initial concⁿ. Since, by hypothesis, appreciable amount of C & S have become combined to form the intermediate complex [X]. If [C]₀ & [S]₀ are initial concⁿ of C & S it follows that

- $[C] = [C]_0 - [X]$ — (iv)

$$[S] = [S]_0 - [X] \quad \text{--- (v)}$$

- Therefore eq^m — (iii) becomes

$$K = \frac{[X][Y]}{([C]_0 - [X])([S]_0 - [X])} \quad \text{--- (vi)}$$

It is more convenient to consider two cases.

CASE - I: If the initial concⁿ of the substrate is much greater than that of the intermediate

$$\therefore [S]_0 - [X] \approx [S]$$

Now eqⁿ (vi) becomes

$$k = \frac{[X][Y]}{\{[C]_0 - [X]\} [S]}$$

$$\text{or } [X][Y] = k \{ [C]_0 - [X] \} [S]$$

$$\text{or } [X][Y] = k [C]_0 [S] - k [X][S]$$

$$\text{or } [X] \{ [Y] + k [S] \} = k [C]_0 [S]$$

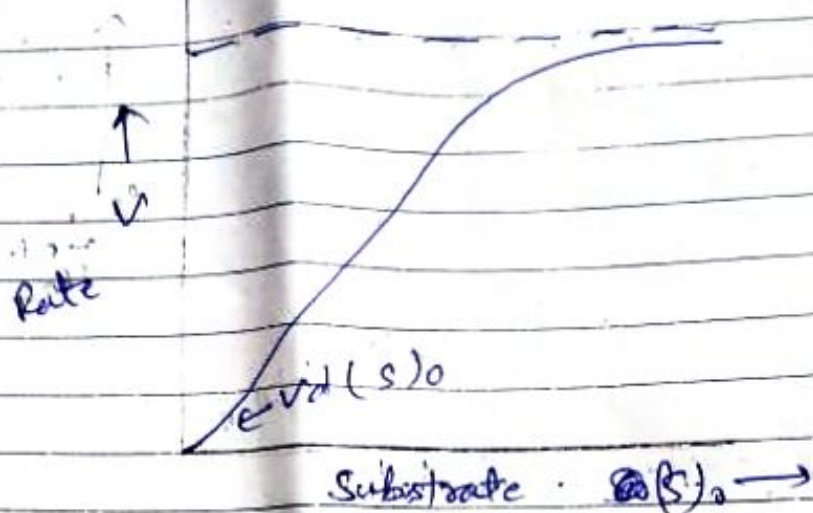
$$\text{or } [X] = \frac{k [C]_0 [S]}{[Y] + k [S]}$$

The rate of reacⁿ = $k_2 [X][W]$

$$-\frac{dS}{dt} = \frac{k_2 k [C]_0 [S]_0 [W]}{[Y] + k [S]} \quad \text{--- (vi)}$$

When a graph is plotted b/w rate and substrate concⁿ the nature of the graph is as beside

Both graphs are given for consider.



Thus, when $k[S]_0 \ll [Y]$, then the rate vary linearly with initial rate conc^m, whereas at high substrate, conc^m $k[S]_0 \gg [Y]$.

The rate is independent of $[S]$.

CASE - II: If the initial conc^m of the catalyst is much greater than that of intermediate (X).
 $[C]_0 \gg [X]$.

then eq^m (vi) becomes
 $[C]_0 - X \approx [C]$.

$$K = \frac{[X][Y]}{[C]_0 \{ [S]_0 - [X] \}}$$

$$[X][Y] = K [C]_0 [S]_0 - K [X][C]_0$$

$$[X] \{ [Y] + K [C]_0 \} = K [C]_0 [S]_0$$

$$\text{or } [X] = \frac{K [C]_0 [S]_0}{[Y] + K [C]_0}$$

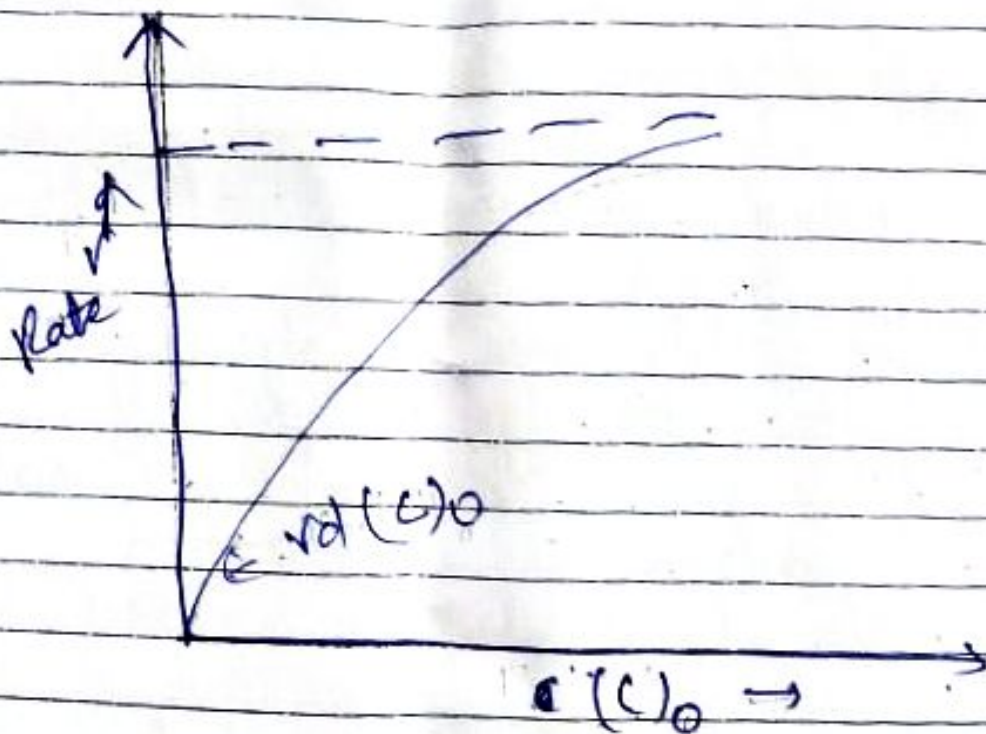
✓

(L) $\frac{Rate}{Rate} = \frac{1}{1}$

$$\text{Rate of reaction} = k_2 [X] [W]$$

$$-\frac{ds}{dt} = \frac{k_2 k [C]_0 [S]_0 [W]}{[Y] + k [C]_0} \quad \text{--- (vii)}$$

The rate law varies linearly with the concⁿ of substrate as long as $[C]_0 \gg [S]$.



The rate becomes independent of $[C]_0$.

Effect of Salt on Acid-Base Catalysis

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the

The effect of salt on acid-base catalysis is important because a salt may exert influence by changing the activity co-efficients of other species in solutions. The much of the early evidence regarding catalysis by species other than hydrogen and hydroxyl ion must be counted. The ~~apparent~~ catalytic action being in reality a salt effect.

In the study of acid-base catalysis, it is convenient to classify salt effect arise from the fact that the rate of bimolecular interaction in solution b/w A & B is given by a

$$\text{rate} = K_a [A][B] \frac{f_A \cdot f_B}{f^{\ddagger}}$$

where f's are activity co-efficients

The secondary salt effect are not considered with the direct influence of salt on the rate of reaction but with it's influence on the concⁿ of reactants. The eqⁿ constant for the dissociation of weak acid HA can be written as



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

where K_a is dissociation constant at given temp.

Since salts influence the activity co-efficients, also, the concⁿ of the H^+ , A^- & HA in this way indirectly influence the rate of reaction.

The activity co-efficients for neutral molecule is only slightly influenced by the ionic strength while f_{H^+} & f_{A^-} are decreased by increasing the ionic strength.

A/c to Debye-Huckel rule -

$$-\log f = -Q Z_i^2 \mu^{\frac{1}{2}}$$

$$\text{or, } [\log \gamma = 0.509 Z^2 \sqrt{\mu}]$$

μ = ionic strength

Z = charge

Q = const. = 0.509

Now, net result is

therefore an increase in the degree of dissociation of HA . The fundamental work on both primary and secondary salt-effects in chemical kinetics has been done by Bronsted and his co-workers.

Secondary salt-effects have been observed in acid catalysed reactions. Since salts inc. the degⁿ of dissociation & hence the hydrogen ion concⁿ of strong acids & base, the sec. salt effects are small, since the

inc. ionic strength
↓
relative molality
↓
result
degree of dissociation
inc.

✓ proton from substrate molecule to the base

species are almost completely dissociated under all conditions.

Bronsted - Catalysis Law

Since acid-base catalysis, the transfer of a proton from the acid catalyst or to the base catalyst, it is natural to seek a correlation between the effectiveness of the catalyst and its strength as an acid or base.

A connection b/w the catalytic const. K_a & acid const. K'_a was made by Bronsted

$$K_a = G_a \cdot K'_a \quad \alpha \quad (1)$$

where G_a and α are constants. The value of α is generally always less than unity. Likewise, for base, the eqⁿ will be

$$K_b = G_b \cdot K'_b \quad \beta \quad (2)$$

K_b the dissociation constant of the base. K'_b refers to rate const. of base catalysis where G_b & β are const.

The relationship b/w the catalytic const. of a base and acid may be expressed as

$$K_b = G_b \left(\frac{1}{K'_a} \right)^\beta \quad (3)$$

It comes from the fact that for conjugate acid-base relationship,

$$K'a \cdot K'b = 1$$

$$\text{or, } K'b = \frac{1}{K'a}$$

The eqⁿ (1), (2) & (3) are commonly known as Bronsted - catalysis's relationship.

ACID - BASE CATALYSIS :

Acid - base catalysis include rxnⁿ in solⁿ which are catalysed by acids or bases or both.

A rxnⁿ which is catalysed by H^+ (or H_3O^+) is said to be proton catalysed rxnⁿ eg.

(1) Solvolysis of ester

(2) Inversion of cane - sugar

A rxnⁿ is catalysed by Bronsted acid is an example of general acid catalysis.

Similarly, a rxnⁿ catalysed by hydroxyl ion is said to be base catalysed rxnⁿ while a rxnⁿ catalysed by

Bronsted base is an example of general base catalysis.

There are also rxnⁿ such as the mutarotation of glucose which require the presence of both proton donor and proton acceptor. This is an example of

$$[SH^+] = \frac{k_1 [S] [AH^+]}{[k_{-1} + k_2] [A]}$$

The rate of formation of the product is given by

$$\checkmark \frac{dP}{dt} = k_2 [SH^+] [A]$$

$$\text{or } \frac{dP}{dt} = k_2 \frac{k_1 [S] [AH^+] [A]}{[k_{-1} + k_2] [A]}$$

$$= \frac{k_2 k_1 [S] [AH^+]}{[k_{-1} + k_2]} \checkmark$$

This is the expression of general acid catalysis.

Oscillatory Reactions or B-Z reactions

The chemical rxn based on auto-catalysis and oscillations are called oscillatory rxn.

One of the best known rxn is the so called B-Z reaction or Belousov-Zhabotinski rxn named after two Russian scientists.

Organic reactions in oxidation is carried out by bromide

Belousov-Zhabotinsky (BZ) reaction.

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and catalysed by inorganic ions are B-Z rxn.

Consider the rxn



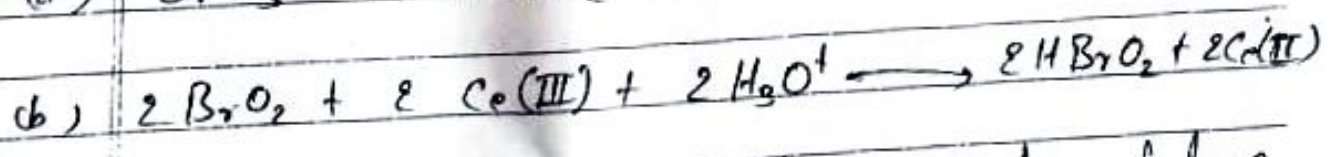
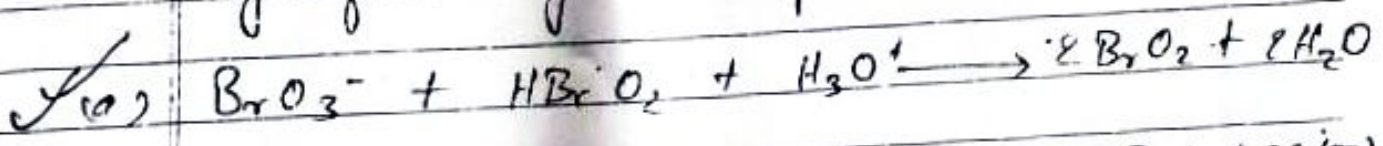
where P is the product

If the rate law is given by

$$r = k[A][P]$$

then the product is said to catalyse the rxn.

The B-Z rxn is described by following example



Both are the examples of auto catalysis. The product $HBrO_2$ is a reactant in step (a).

In autocatalysis, several intermediates cause oscillations which are not ordinary oscillations but a superposition of such oscillations leading to complexity in the reaction mechanism.