→ Countometry

Countometry is a measurement of electrolytic conductivity to monitor a progress a chemical reaction. Countometry has a application in analytical chemistry where countometry titration is a standard techinique. In usually analytically chemistry pratice the term of countometry is used as a synonmous of countometric titration.

Application of Countometry titration.

- The solubility of purily solution (salt) is express as the solubility products. It is the products of the concentration ion in the solution which are in equilibrium with the solid ion. These concentration can be determination by a conductivity measurement.

$$\underset{(\text{solid})}{PbSO_4} \rightleftharpoons \underset{(\text{liquid})}{Pb^{2+}} + \underset{(\text{liquid})}{SO_4^{2-}}$$

Pb^{2+} concentration = SO_4^{2-} concentration = C

$$K_{sp} = [Pb^{2+}][SO_4^{2-}]$$
$$= [C][C]$$
$$\boxed{K_{sp} = C^2}$$

Date / /

The measurement of specific conductivity K of the saturated solution. Let to a volume of the constant

$$K_{sp} = \left(\frac{K}{\Lambda_0}\right)^2 \qquad \left\{ C = \frac{K}{\Lambda_0} \right\}$$

Date
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⇒ Ionic Product of water:

Pure water is a very weak electrolyte for electro system and ionic (ionization) according to this equations.

$$H_2O \longleftrightarrow H^+ + OH^-$$

apply law of mass action at equillibrium the value of dissociation of constant 'K'

$$K = \frac{[H^+][OH^-]}{H_2O}$$

Since, dissociation takes place to a very small ~~above~~ amount the concentration of in dissociate water molecule H_2O.

Thus the products H_2O gives another constant $\boxed{K_w = [H^+][OH^-]}$

The constant is turns as ionic products of water, the product of conc. of H & OH^- H_2O at a particular temperature is known as ionic product of water.

In Neutral Soln

$[H^+] = [OH^-] = 1 \times 10^{-7} m$ $[H^+] > 1 \times 10^{-7} M$

$[OH^-] < 1 \times 10^{-7} M$

in Acid soln, $[H^+] > [\bar{O}H]$

The value of ionic product of water increase of temp. the conc. of H^+ & OH^-

Temperature (0°C)	value of Kw
0	0.11×10^{-14}
10	0.31×10^{-14}
25	1.00×10^{-14}
100	7.58×10^{-14}

Note

Acid ⇒ $[H^+] > [OH]$

Base ⇒ $[OH^-] > [H^+]$

Similarly when a base is add the $\bar{O}H$, increase the concentration.

In alkaline, $[\bar{O}H] > [H^-]$

$[OH] > 1 \times 10^{-7} M$

$[H^+] < 1 \times 10^{-7} M$

$[\bar{O}H^+] \Rightarrow 10^0, 10^{-1}, 10^{-2}, 10^{-3}, 10^{-4}, 10^{-5}, 10^{-6}$ (Acid)

$[\bar{O}H^+] \Rightarrow 10^{-7}$ (Neutral)

$[OH] \Rightarrow 10^{-14}, 10^{-13}, 10^{-12}, 10^{-11}, 10^{-10}, 10^{-9}, 10^{-8}$

~~Alkaline~~.

we shall have the following table.

⇒ Complex rea^{n} ⇒ Those rea^{n} which occur in two or more step are term as complex rea^{n} From the point of view of chemical kinetics each step of it is a simple rea^{n} and elementary rea^{n} has it's on molecularity depending upon the no. of molecules of the reactant or reactant taking part in that single reaction.

$$3A + 2B \longrightarrow P + Q \longrightarrow ①$$

step envolved → ⓐ $A + B \longrightarrow C + D$

ⓑ $A + C \longrightarrow E$

ⓒ $A + D \longrightarrow F$

ⓓ $E + F + B \longrightarrow P + Q$

overall rea^{n} $3A + 2B \longrightarrow P + Q$

⇒ Oppose reaction ⇒ Reaction may be proceed to state a equillibrium which differ appriceable from complexion. The simplest case of the occur when both both forward and reverse reaction are of the Ist order. So,

$$A \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} X$$

⇒ Parallel rea^{n} :- These rea^{n} are those in which the reacting molecule convert through more than one chemical yield different set of product the reaction resulting in the product is known as the main or as the major rea^{n} & the other rea^{n}

are ~~after~~ refered as side or parallel rea^n. The calculate the overall rate, the rate of the side rea^n taken into same yield

The rate two these reaction are,

$$\frac{d[B]}{dt} = k_1[A]$$

$$\frac{d[C]}{dt} = k_1'[B]$$

the overall reaction rate

$$-\frac{d[A]}{dt} = [k_1[A]] + [k'[A]]$$

$$\boxed{-\frac{d[A]}{dt} \Rightarrow [k+k'][A]}$$

ex:- $C_6H_5OH + HNO_3 \rightarrow C_6H_4(OH)NO_2 + H_2O$

$C_6H_5OH + HNO_3 \rightarrow C_6H_4(OH)NO_2 + H_2O$

⇒ Steady State Approxiamation Rea^n

In a case when a rea^n are invuestigation under such condition that the slowest rate determining step does not exist. when assume the steady state Approximate for the transition ~~state~~, ~~from the~~ for the intermediate in such a short mechanism.

$$R \xrightarrow{k_0} I_1 \xrightarrow{k_1} I_2 \cdots \xrightarrow{k_n} I_n \cdots \xrightarrow{k_\infty} I_\infty$$

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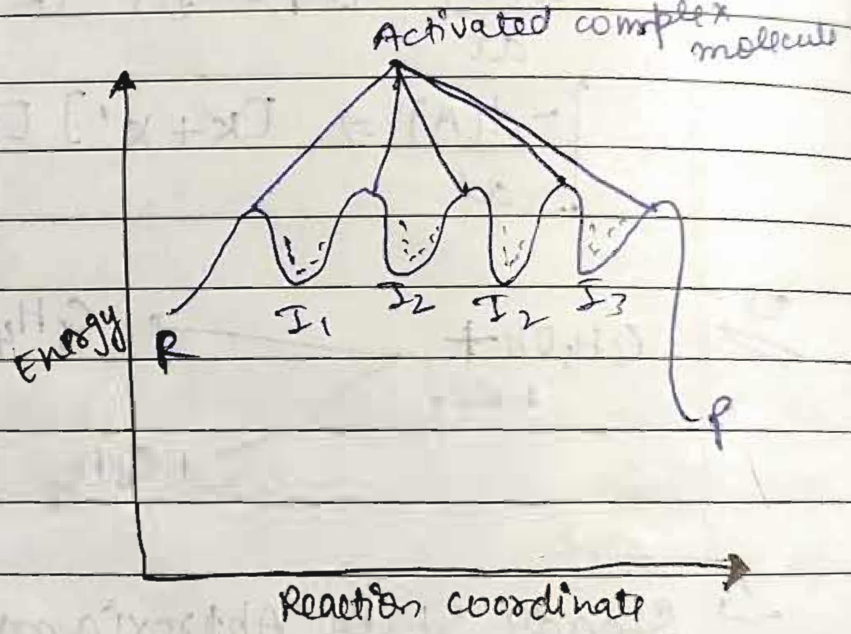
⇒ Equilibrium approximation rea^n :-

Consider a rea^n in which a reactant are gives rise to product 'P' through the formation of series a of constructive intermediate like $I_1, I_2, I_3 --- I_n --- I_\infty$

$$R \xrightarrow{k_0} I_1 \xrightarrow{k_1} I_2 \xrightarrow{k_2} I_3 ------ \overset{k_{n-1}}{I_n} ---- \overset{k_n}{P}$$

The whole reaction ~~simples~~ sequences may be decribe in term of a single rea^n coordinate of the individual step



In order to derive the rate of rea^n for the simple rea^n.

⇒ Activation Energy :- It proposed the following emperical equation for calculating the energy of activation of a rea^n having rate constant 'k' and temperature 't'.

$$\boxed{K = Ae^{-Ea/RT}}$$

where, Ea is the Arrhenius Activation energy
A is Arrhenius experimental factor

$$\log k = \log A - \frac{Ea}{RT}$$

$$\boxed{\ln K = \ln A - \frac{Ea}{RT}} \leftarrow ①$$

y

It is evident that a plot of log k, the reciprocal of absolute temp. 1/T give the straight line curve and slope is Ea/RT and intercept is log A.

Differentiate this eqn ~~with res~~ w.r.t temp.

$$\cancel{d\ln K} = \cancel{d\ln A} - \cancel{\frac{Ea}{RT^2}}$$

$$\boxed{\frac{d\ln K}{dt} = \frac{Ea}{RT^2}}$$

then, integrated b/w temperature T_1, T_2 when the corresponding rate constant K_1 & K_2 & Ea → constant

$$\ln \frac{K_2}{K_1} = \frac{Ea}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

OR

$$✓\ \boxed{\ln \frac{K_2}{K_1} = \frac{Ea}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]} \rightarrow \text{Arrhenius eqn}$$

CONDUCTANCE

Transport No. :→ The fraction of total current carried by each ion called ——.

Acc. to Faraday Ist law

$$t_+ = \frac{u_+}{u_+ + u_-}$$

→ mobility of cation

T. No. of cation.

→ mobility of anion

$$t_- = \frac{u_-}{u_+ + u_-}$$

and $t_+ + t_- \Rightarrow 1$

Two Methods

or Hittorf theoritical device

ⓐ **Hittorf's Method :-** based on conc. change observed vicinity of the electrode.

"we know"

$$\frac{\text{Mobility of cation } (u_+)}{\text{Mobility of anion } (u_-)} = \frac{\text{Fall of conc. round anode}}{\text{Fall of conc. round cathode}}$$

and, we know ~~Acc~~ transport no. of cation,

$$t_+ = \frac{u_+}{u_+ + u_-}$$

∴

$$t_+ = \frac{\text{Fall of conc. round anode}}{\text{Fall of conc. round anode} + \text{Fall of conc. round cathode}}$$

$$t_+ \Rightarrow \frac{\text{Fall of conc. round anode}}{\text{Total fall of conc.}}$$

If conc. are measured in term of gram equivalent, then,

$$t_+ = \frac{\text{No. of gram equivalent lost from anodic compartment}}{\text{Total no. of gram equivalent lost from both compartment}}$$

or

$$t_+ = \frac{\text{No. of gram equivalents lost from anodic comp.}}{\text{No. of gram equivalents deposited on each electrode.}}$$

Acc. to farraday IInd. law,

$$t_+ = \frac{\text{No. of gram equivalent lost from the anodic comp.}}{\text{No. of gram equivalent of copper deposited in the coulometer.}}$$

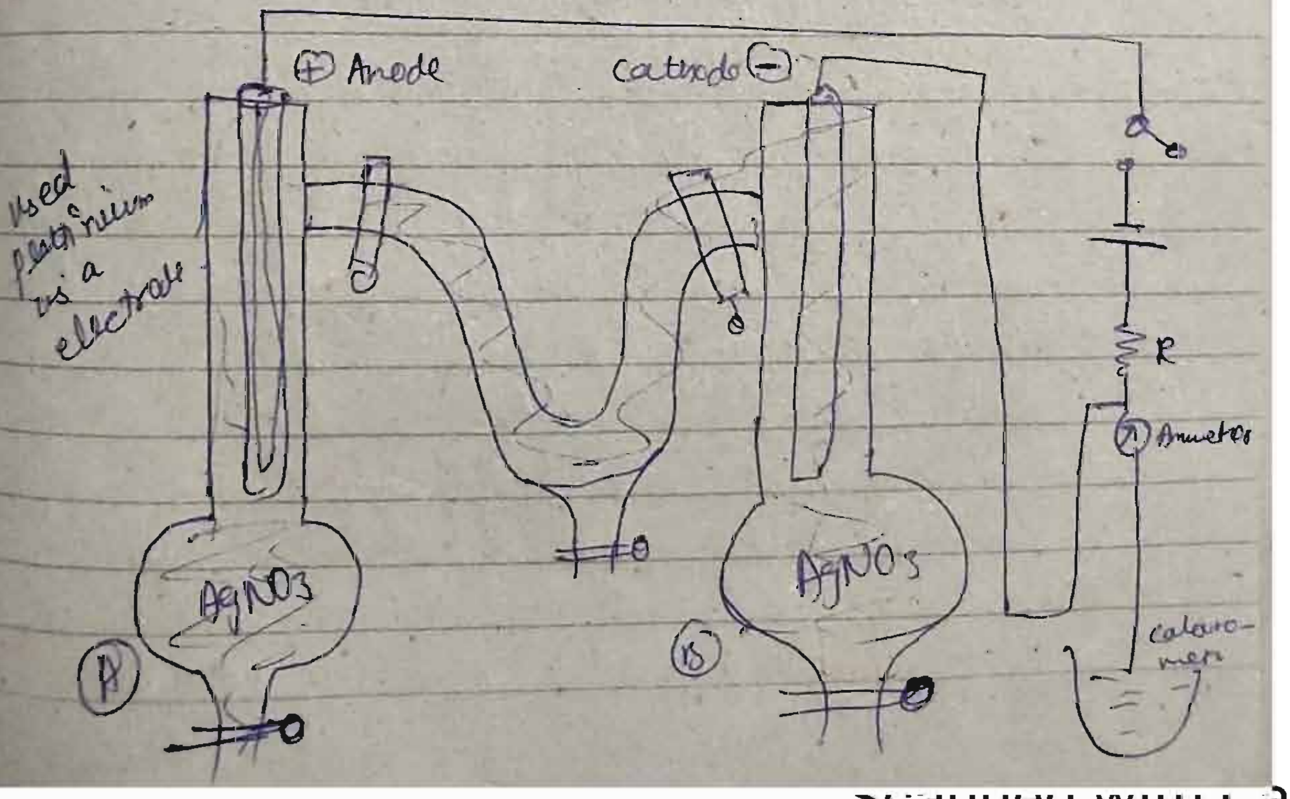
also,

$t_+ + t_- \Rightarrow 1$

$t_- = 1 - t_+$,

$t_{Ag^+} = \frac{\overset{\text{before (AgI)}}{x} - \overset{\text{after electrolysis}}{y}}{z}$

$t_{NO_3^-} \Rightarrow 1 - \frac{x-y}{\underset{\uparrow \text{Total}}{z}}$



✱ Kahlrausch's law

$$\Lambda^\circ_m = \lambda^\circ_+ + \lambda^\circ_-$$

of anion

molar conductance

Molar ionic conductance of cation

⇒ Calculation of Molar Ionic conductance.

$$t_+ = \frac{u^\circ_+}{u^\circ_+ + u^\circ_-}$$

$$\lambda \propto u \quad , \quad t^\circ_+ = \frac{\lambda^\circ_+}{\lambda^\circ_+ + \lambda^\circ_-} \Rightarrow \boxed{t_+ = \frac{\lambda_+}{\Lambda^\circ_m}}$$

⇒ Relation Ionic molar conduct. & Ionic mobility

$$\boxed{u^\circ = \frac{\lambda^\circ}{F}}$$

→ Applications

① Calculation of molar conductance at Infinite dillution for weak electrolyte.

molar conductance at infinite dillutia of HCl, sodium acetate & NaCl.

$$\lambda^\circ_{CH_3COO^-} + \lambda^\circ_{H^+} \Rightarrow \lambda^\circ_{H^+} + \lambda^\circ_{Cl^-} + \lambda^\circ_{CH_3COO^-} + \lambda^\circ_{Na^+} - (\lambda^\circ_{Na^+} + \lambda^\circ_{Cl^-})$$

i.e $\Lambda^\circ_{CH_3COOH} = \Lambda^\circ_{m\,HCl} + \Lambda^\circ_{m\,CH_3COONa} - \Lambda^\circ_{m\,NaCl}$

similarly,

$$\Lambda^\circ_{m\,NH_4OH} = \Lambda^\circ_{m\,NH_4Cl} + \Lambda^\circ_{m\,NaOH} - \Lambda^\circ_{m\,NaCl}$$

② Determination of Transport no

$$t^\circ_\pm = \frac{\lambda^\circ_\pm}{\Lambda^\circ_m} \Rightarrow \frac{\lambda^\circ_\pm}{\lambda^\circ_+ + \lambda^\circ_-}$$

&

$$\lambda^\circ_\pm = F u^\circ_\pm$$

So,

$$t^\circ_\pm = \frac{u^\circ_\pm}{u^\circ_+ + u^\circ_-}$$

Note

⇒ Ostward dillution law

acc. to arrehenius theory of electrolytic dissociation
↳ law of chemical equillibrium,
consider electrolyte AB,

$$AB \rightleftharpoons A^+ + B^-$$

Initial conc	c	0	0
Final conc	$c(1-\alpha)$	$c\alpha$	$c\alpha$

law of mass action

$$K = \frac{c\alpha \times c\alpha}{c(1-\alpha)} \Rightarrow \frac{c^2\alpha^2}{c(1-\alpha)}$$

$$K = \frac{c\alpha^2}{1-\alpha} \text{ —— ①}$$

$$\because \alpha = \frac{\Lambda_m}{\Lambda_m^\circ}$$

put in ① eqn

$$K = \left[\frac{\left(\frac{\Lambda_m}{\Lambda_m^\circ}\right)^2}{1-\left(\frac{\Lambda_m}{\Lambda_m^\circ}\right)}\right] c$$

$$1 - \frac{\Lambda_m}{\Lambda_m^\circ} = \frac{1}{K}\left[\left(\frac{\Lambda_m}{\Lambda_m^\circ}\right)^2 \cdot c\right]$$

devide by Λ_m

$$\frac{1}{\Lambda_m} - \frac{1}{\Lambda_m^\circ} = \frac{1}{K}\left[\frac{(\Lambda_m)}{(\Lambda_m^\circ)^2} \cdot c\right]$$

Ostw law dil {

$$\boxed{\frac{1}{\Lambda_m} = \frac{1}{\Lambda_m^\circ} + \frac{c\Lambda_m}{K(\Lambda_m^\circ)^2}}$$

Chemical Kinetics

$r_n \Rightarrow (dm^3) \; mol \; s^{-1}$
↳ unit of rate

* Integrated Rate Expression

① Ist Order reax.

differential rate exp. for Ist order, $A \rightarrow P$

$$r = -\frac{dC_A}{dt} = \frac{dC_P}{dt} = K_1 C_A$$

seperating variables →

$$-\frac{dC_A}{dt} \qquad -\frac{dC_A}{C_A} = k_1 t$$

On integrat

$$-\int_{C_0}^{C} \frac{dC_A}{C_A} = \int_0^t K_1 \, dt$$

$$\left[-\ln C_A\right]_{C_0}^{C} = \left[K_1 t\right]_0^t$$

$$-\ln (C/C_0) = k_1 t$$

$$\boxed{C = C_0 e^{k_1 t}}$$

or

$$\boxed{K_1 = \frac{1}{t} \ln\left(\frac{C_0}{C}\right)}$$

Or

$$K_1 = \frac{1}{t} \ln\left(\frac{a}{a-x}\right)$$

a & x are initial con of reacta

② II^{nd} order rea^n.

Case-I) When a reactant are diff.

$$A + B \longrightarrow P$$

initial conc. a b 0

After time t (a-x) (b-x) x.

diff^n rate expression,

$$r = -\frac{d[A]}{dt} = -\frac{d[B]}{dt} = k_2[A][B]$$

$$r = -\frac{dC_A}{dt} = -\frac{dC_B}{dt} = K_2 C_A C_B$$

or $$r = \frac{dx}{dt} = k_2(a-x)(b-x)$$

$$\frac{dx}{(a-x)(b-x)} = K_2 t$$

On partial fraction. ($a>b$)

$$\frac{1}{(a-x)(b-x)} \Rightarrow \frac{1}{a-b}\left[\frac{1}{b-x} - \frac{1}{a-x}\right]$$

$$\int\frac{dx}{(a-x)(b-x)} = \frac{1}{a-x}\left[\int\frac{1}{b-x} - \int\frac{1}{a-x}\right] \Rightarrow K_2\int dt$$

$$\frac{1}{a-b}\left(-\ln(b-x) - \{-\ln(a-x)\}\right] = K_2 t + c$$

$$\frac{1}{a-b}\ln\left(\frac{a-x}{b-x}\right) = k_2 t + C$$

Let $t=0$, $x=0$ so,

$$c = \frac{1}{a-b}\ln\left(\frac{a}{b}\right)$$

$$\frac{1}{a-b}\ln\left(\frac{a-x}{b-x}\right) = k_2 t + \frac{1}{a-b}\ln\left(\frac{a}{b}\right)$$

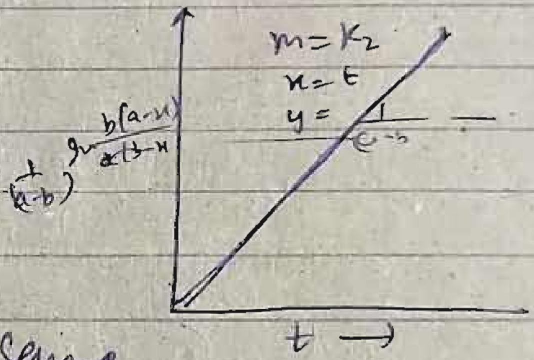
Rearranging

$$K_2 = \frac{1}{(a-b)t}\left[\ln\left(\frac{a-x}{b-x}\right) - \ln\left(\frac{a}{b}\right)\right]$$

$$K_2 \Rightarrow \frac{1}{(a-b)t}\ln\frac{b(a-x)}{a(b-x)} \quad (a>b)$$

or

$$K_2 = \frac{1}{(b-a)t}\ln\frac{a(b-x)}{b(a-x)} \quad (b>a)$$



Case II, when both reactant are same

$$2A \longrightarrow P$$

$$r = \frac{dx}{dt} = K_2(a-x)^2$$

$$\int\frac{dx}{(a-x)^2} = K_2\int dt$$

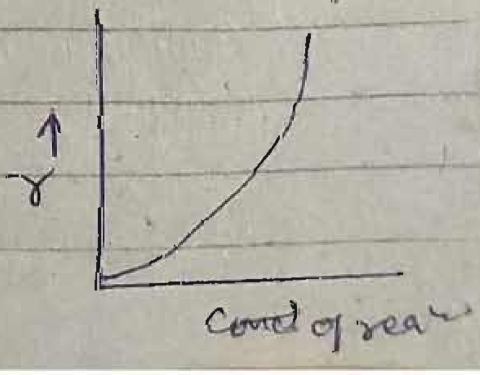
$$\left(\frac{-1}{a-x}\right)(-1) = K_2 t + c \quad \text{or} \quad \frac{1}{a-x} = K_2 t + c \quad \text{—①}$$

for value of c, $x=0$, $a=0$,

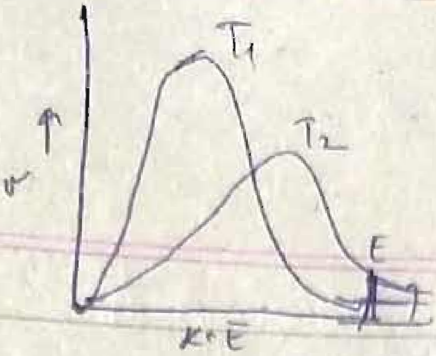
so, $c = 1/a$

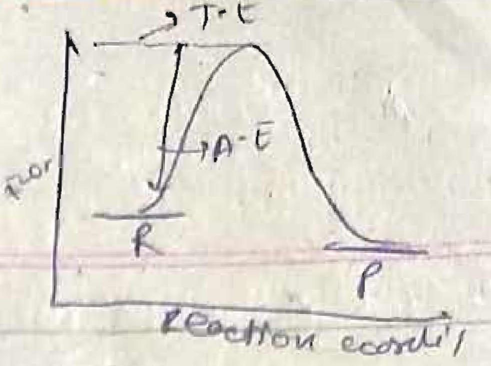
eqn ① is

$$\frac{1}{a-x} = K_2 t + \frac{1}{a}$$



$$\boxed{K_2 = \frac{1}{t}\left[\frac{x}{a(a-x)}\right]}$$

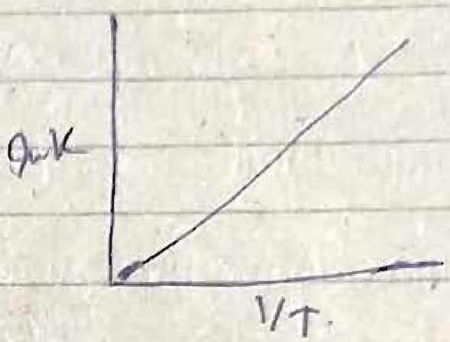




Arrehenius Eq^n

$K = Ae^{-Ea/RT}$

$\ln K = -\frac{Ea}{RT} + \ln A$



diff^n w.r.t T

$$\frac{d \ln k}{dt} = \frac{Ea}{RT^2}$$

Integrate

$$\ln \frac{K_2}{K_1} = \frac{Ea}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

★ Coolision Theory.

let E is the Energy per mol at T (temp.) is given by boltzman factor $e^{-Ea/RT}$, molecule must have energy $E = E_1 + E_2$. Energy of Activation than Probability

$$e^{-(E_1+E_2)RT} = e^{-E/RT}$$

If we conside a bimolecular reaⁿ

$$2HI(g) \rightleftharpoons H_2 + I_2 \quad -①$$

reaction velocity,

$$\frac{dx}{dt} = z' e^{-E/RT} \quad -②$$

$$\frac{dx}{dt} = k n^2 \quad -③$$

$z' \Rightarrow$ No. of molecule per millilitre of the gas
$E \Rightarrow$ energy of activation
$n \Rightarrow$ no. of molecu

so, $z' e^{-E/RT} = k n^2$

$$\boxed{k = \frac{z' e^{-E/RT}}{n^2}}$$

where $z' = 4n^2 \sigma^2 \left(\frac{\pi RT}{M}\right)^{1/2}$

$M =$ molecular weight
$\sigma \Rightarrow$ molecular collision diameter

$$k = 4\sigma^2 \left(\frac{\pi RT}{M}\right)^{1/2} e^{-E/RT}$$

or

$$k = z e^{-E/RT}$$

{z = collision no.}

Taking log

$$\log k = \log\left[4\sigma^2 \left(\frac{\pi RT}{M}\right)^{1/2}\right] - \frac{E}{RT}$$

differen w.r.t T

$$\frac{d}{dT}(\log k) = \frac{1}{2T} + \frac{E}{RT^2}$$

$$\boxed{\frac{d \log k}{dt} = \frac{E}{RT}}$$

* Lindemann Theory

unimolecular rea^n $A \rightarrow P$

$$A + A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A^* + A$$

$$A^* \xrightarrow{k_2} P$$

s.s.a, for $[A]^*$

$$K_{-1}[A][A^*] + k_2[A^*]$$

Thus,

$$\frac{d[A^*]}{dt} = k_1[A]^2 - k_{-1}[A^*][A] - k_2[A^*] = 0$$

$$[A^*] = \frac{k_1[A]^2}{k_{-1}[A] + k_2}$$

rate of rea^n

$$r = -\frac{d[A]}{dt} = k_2[A^*]$$

$$r = \frac{k_1 k_2 [A]^2}{k_{-1}[A] + k_2}$$

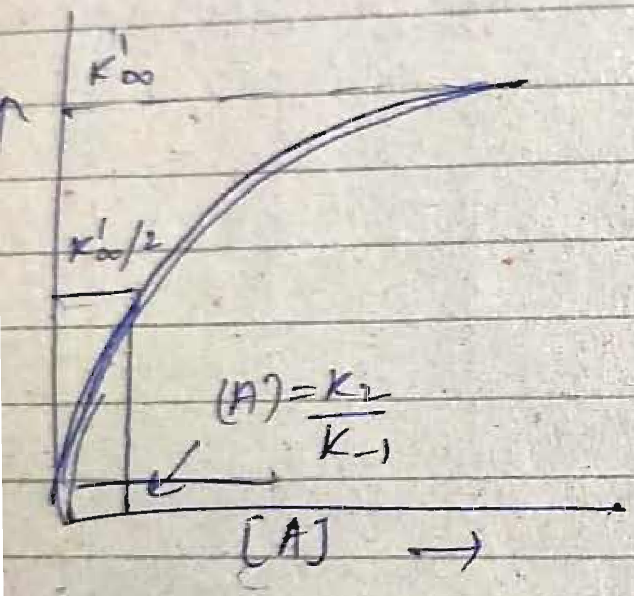
case-1) $k_1[A] >> k_2$ high pressu

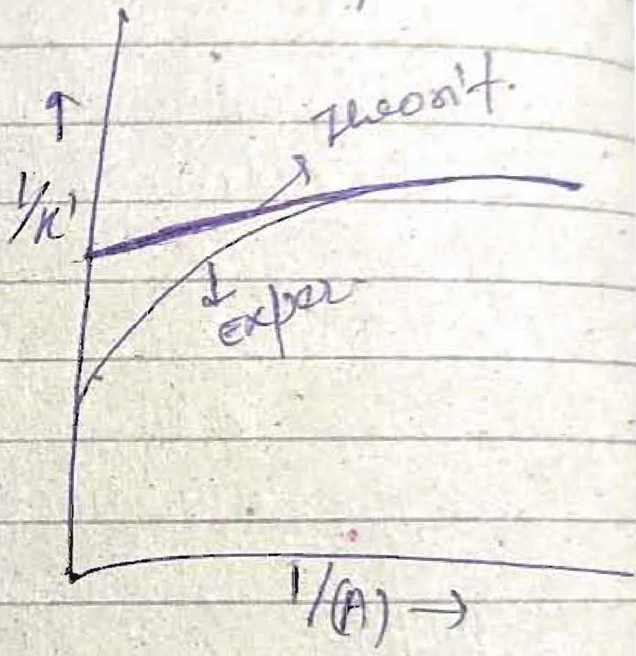
$$r = \frac{k_1 k_2 [A]}{k_{-1}}$$ (Ist order)

case-2) $k_2 >> k_1[A]$

$$r = k_1 [A]^2$$ Second orn

low pressur





$$\frac{k_2}{k_{-1}} = \frac{k'_\infty}{k_1}$$