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## Thermodynamic Data in the form of Diagrams

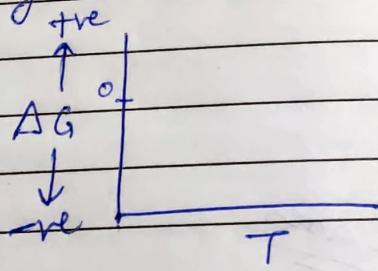
- (i) Ellingham Diagram
- (ii) Kelley Diagram
- (iii) Pourbaix Diagram

(i)  $\rightarrow \Delta G$  vs T  
Ellingham Diagram

Given by T. J. Ellingham in 1944

It allows rapid evaluation for the feasibility of any rxn. at different Temp.

The  $\Delta G$  values are plotted against Temp.



Helps know stability

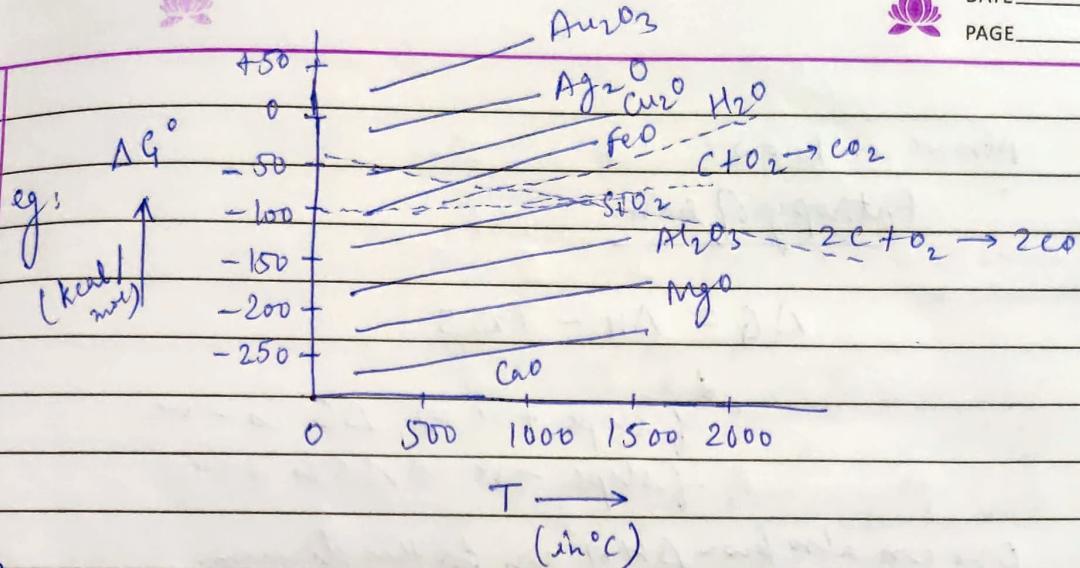
Helps know which metal can be reduced by a particular metal or not.

Used for: oxides, sulphides, halides, carbides

↓  
most commonly used for this

$\Delta H$  and  $\Delta S$

↓  
can also be evaluated from study of such diagrams

28] Uses:

(i) At any  $T$ , the  $\Delta G^\circ$  values of a metal oxide can be determined from the diagram (if it is drawn accurately)

(ii) The relative position of the different oxides is given, and we can assess which metal oxide is more stable.

(iii) We can see that some oxides (like  $\text{Au}_2\text{O}_3$ ,  $\text{Ag}_2\text{O}$ ,  $\text{Cu}_2\text{O}$ , etc.) are less stable. In fact some are so less stable (eg:  $\text{Au}$ ) that they are above the Zero line, and thus exist in native form (instead of oxides).

(iv) Some oxides (like  $\text{Fe}$  oxide,  $\text{Cu}$  oxide) are more stable than that of  $\text{Au}$ , say, but not v. stable. Thus, they can be reduced using reducing agents like C.

(v) Some oxides at lowest position (eg:  $\text{Al}$ ,  $\text{Mg}$ ,  $\text{Ti}$ , etc.) are v. stable, and it is difficult to reduce them. In fact the metals of these oxides can act as reductant for other oxides.

(eg: reduction of  $\text{Fe}_2\text{O}_3$  with  $\text{Al}$  → called Aluminothermy rxn.)

(used for Thermite welding) highly exothermic rxn. OR Thermite process)

(vi) Also we can know:

Entropy of rxn.

$$\Delta G = \Delta H - T\Delta S$$

$\therefore$  if slope +ve  $\Rightarrow \Delta S$  is -ve  
& if slope -ve  $\Rightarrow \Delta S$  is +ve

(vii) One can also know  $\Delta H$  of rxn. for this diagram.

29)

### Rates of Metallurgical Reaction

Thermodynamics  $\rightarrow$  tells us about feasibility of rxn.

But does not give any information about rate of rxn.

When rxn. occurs from Initial  $\rightarrow$  Final  
it goes through multiple steps

These are called the Mechanism of rxn.

30)

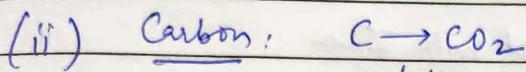
### Importance of Chemical Kinetics

(i) Fe, Cu, Zn, Pb, Al  $\rightarrow$  By Thermodynamics

Oxides of these are stable at room temp.

But actually they are present in metallic form

This is  $\Rightarrow$  the conversion to oxides is v. slow at room temp.



oxidation  
at room temp. is feasible

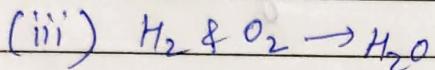
(i.e. C should burn  
at room temp.)

||

But in reality it requires

a certain activation  
energy

thus, needs  
to be heated  
to burn



Also feasible at room temp.

(But actually occurs at  $> 800^\circ C$ )

### 31] Two Types of Reactions

(i) Homogeneous: Occurs in single phase only  
(e.g.: gas or liquid)

Not v.  
common  
exn'd  
(so they  
are of  
less interest)

↓

much

easier to  
follow their  
kinetics

[If any solid is present in it  
it will not be considered  
homogeneous]

(ii) Heterogeneous:

eg: Solid-Solid

Solid-Liquid

Solid-Gas

Here it is confined  
to a sing

The heterogeneous rxn takes  
place at the interface  
of the two phases

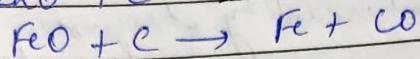
(In Homogeneous  $\rightarrow$  rxn. in entire  
volume  $\rightarrow$  thus it is  
much faster  
than heterogeneous)

Metallurgical  
processes  $\rightarrow$  generally  
heterogeneous.



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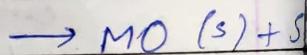
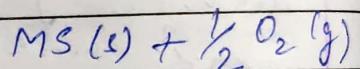
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(i) Two solidseg: Carbon in contact with Iron  
+  
Case Hardening / case Carburization(ii) Two liquids → <sup>eg:</sup> slag metal, slag-matte rxn., solvent extraction  
(organic solvents)(iii) Fluid-Solid: (a) Gas-Solid

(most common)

eg: Red<sup>n</sup> of  $\text{Fe}_2\text{O}_3$   
→ with CO

→ Roasting of metal sulphide.

(b) Liquid-Solid

eg: Leaching, Aqueous corrosion

(c) Gas-Liquid:eg: O<sub>2</sub> leaching in steel  
(O<sub>2</sub> is injected in steel)H<sub>2</sub> red<sup>n</sup> of Cu<sup>2+</sup> ion.

### 32] Factors affecting the rate of a rxn.

(i) Nature of reactants & products  
 ↓  
 eg: in oxidn of metals

(ii) ...

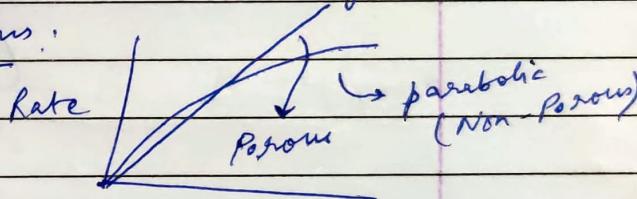
(iii) ...

(iv) ...

oxide film forms on the surface of metal & prevents further oxidn.

But if this film is porous  
 ↓  
 allows further diffusion of reactant through pores allowing further rxn.

If Non-Porous:

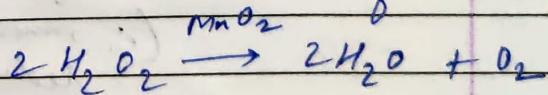


oxide formation

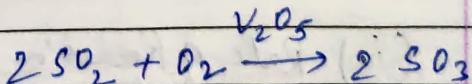
### (ii) Presence of catalyst:

Catalysis usually enhance/increase the rate of chemical rxn.

(eg:  $MnO_2$  catalyst increases rate of decomposition of  $H_2O_2$ )



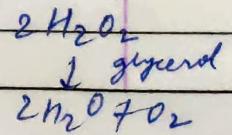
$MnO_2$   
 &  
 $V_2O_5$  etc.



called Positive catalysts)

eg: Glycerol:

If decrease → called negative catalyst or Inhibitors



### (iii) Surface Area

e.g. Particle size can be decreased  
leaching  $\downarrow$  in S.A.

Thus,  $\uparrow$  rate  
(such as in Leaching process  
by grinding the material thoroughly  
we can make  
smaller particles  
with  $\uparrow$  S.A.)

e.g. In Blast furnace

Sinter vs Lumps of Iron Ore

(The particles  
are put together  
in a bed, along with coke  
& then entered)

e.g. Coke vs Coal

this is  
much more  
porous than coal

thus Rate is  
much higher  
for Coke

(i.e. much better  
reducing agent)

### (iv) Rate of Reaction (Kinetics)

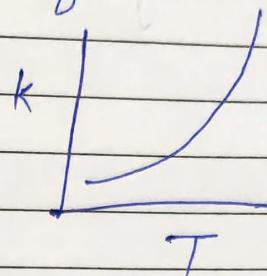
Rate  $\propto$  conc. of reactants

$$= k c_n$$



(v) Effect of Temperature on Rate of rxn.

$$\text{Rate} = k c_A$$



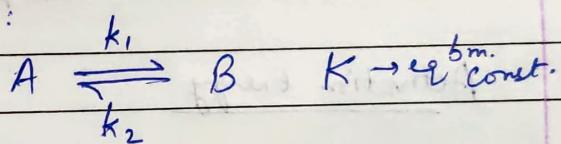
33] Arrhenius Equation:

(1889, S. Arrhenius)

$$\text{Van't Hoff Isochore}, \frac{d \ln k}{dT} = \frac{\Delta H}{RT^2}$$

Using this & with equilibrium dynamics  
Arrhenius came up with his eqn.

Equilibrium dynamics:



$$K = \frac{k_1}{k_2}$$

By putting this in van't Hoff isochore:

$$\frac{d \ln k_1}{dT} - \frac{d \ln k_2}{dT} = \frac{\Delta H}{RT^2}$$

$$\text{Let's say: } \Delta H = E_1 - E_2$$

$E_1$  = for forward rxn  
 $E_2$  = for backward rxn

∴ We can say:

$$\frac{d \ln k_1}{dT} = \frac{E_1}{RT^2} + C_1$$

$$\frac{d \ln k_2}{dT} = \frac{E_2}{RT^2} + C_2$$

In Integral form:

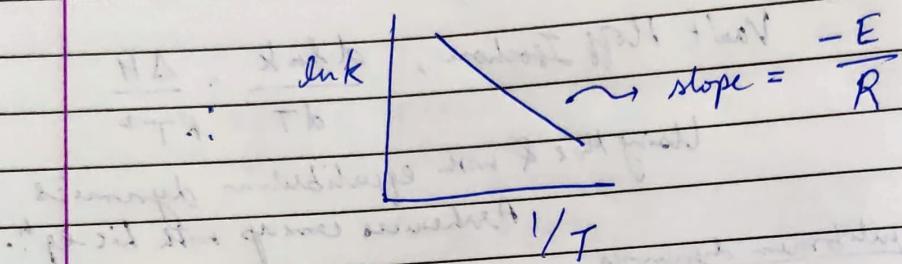
$$\ln k = -\frac{E}{RT} + \ln A$$

$$\text{or } K = A e^{-E/RT}$$

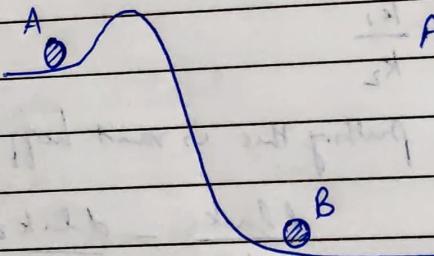
$A \rightarrow$  frequency factor

$k \rightarrow$  rate constant

$E \rightarrow$  activation energy

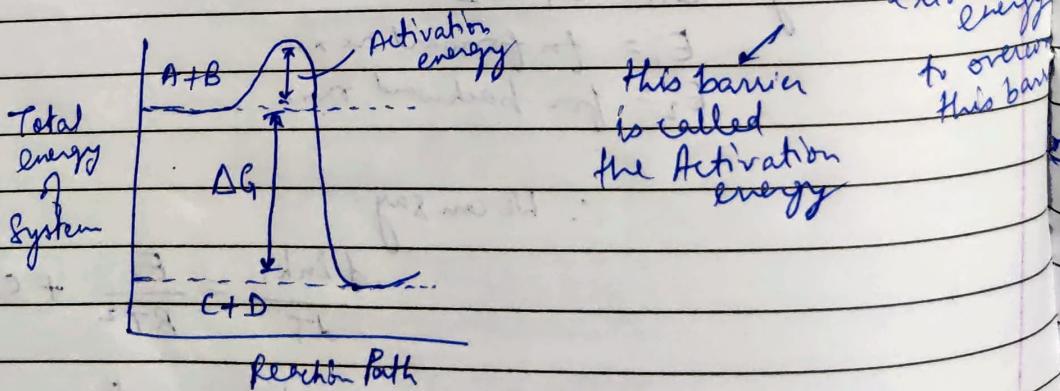


### 34] Activation Energy:



A wants to go to B  
But there is a barrier  
which needs to  
be crossed  
first

(i.e. we need  
to give ~~more~~  
extra energy  
to overcome  
this barrier)





## 35] Importance of Activation Energy

Tells that even if rxn. is feasible by  $\Delta G$  (thermodynamically) i.e.

may not be feasible due to high Activation energy

e.g.: metals — Al, Cu, Fe, Zn

$$\Delta G < 0$$

But remain in native form  
in nature

e.g.: Coal,  $C + O_2 \rightarrow CO_2$  (should happen  
on its own, theoretically  
by  $\Delta G$ )

But doesn't happen unless  
provided energy (by heat)

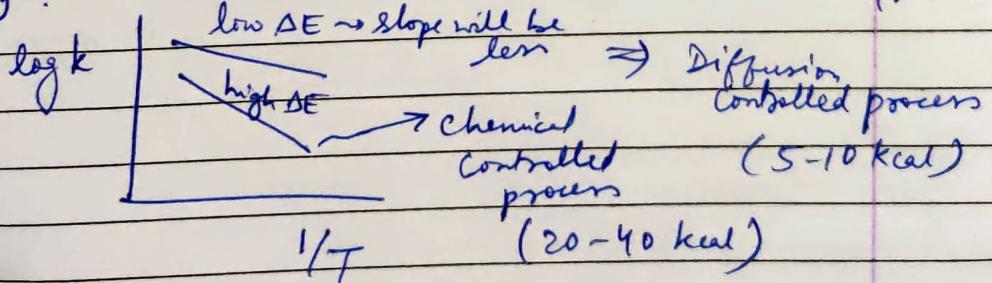
This is the reason why all  $\rightarrow$  fossil fuels  
remain in their form  
for millions of years under the  
Earth without changing

But as soon as  
energy (e.g. heat)  
provided  
 $\downarrow$   
they burn

NOTE: Higher the Activation energy  $\rightarrow$  more the energy is reqd. to be supplied

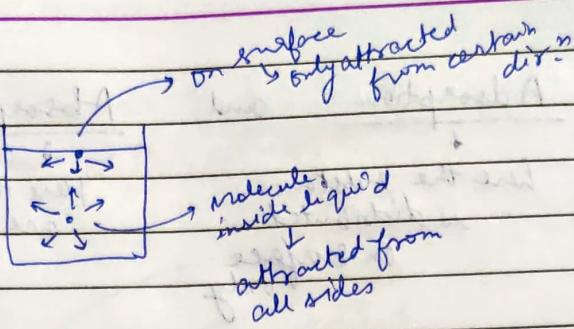
thus even more difficult is the rxn. to occur

How to determine Activation Energy? :



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## Adsorption



Liquid surface is unbalanced

Residual forces lead to Surface Tension.

Similarly in solids also

$\downarrow$   
surface molecules  
attract gas particles

Ans - Conc. of gas particles on surface is much more than inside the solid

37] Adsorption : The existence of higher conc. of any molecular gasses / compound on the surface, compared to the bulk of the solid.

When solids are ~~mixed~~ divided (iii)

Surface area  $\uparrow$  considerably

thus this force of attraction is more significant in solids.

Solids which adsorb gas particles  
↓ on surface

called Adsorbant  $\rightarrow$  e.g.: charcoal, silica gel, clay

and the gas particles which get adsorbed on  
the surface of adsorbent  
are called adsorbate



38]

Adsorption

and

Absorption

↓  
here the substance  
is distributed  
on surface  
only

↓  
here the substances  
are uniformly distributed  
throughout the body  
of the solid or liquid

eg: Water vapour  
(H<sub>2</sub>O)

absorbed by Calcium chlor  
adsored by Silica gel

Dissicator: ...

Getter : Reactive materials which are kept  
in chambers to remove traces  
of gases by adsorption.

39]

Factors affecting adsorption

- (i) Temperature
- (ii) Pressure
- (iii) Nature of gas
- (iv) Nature of adsorbant

Note: Fleet of adsorption

As a result of adsorption  
there is decrease in  
residual forces acting  
along surface  
of adsorbant

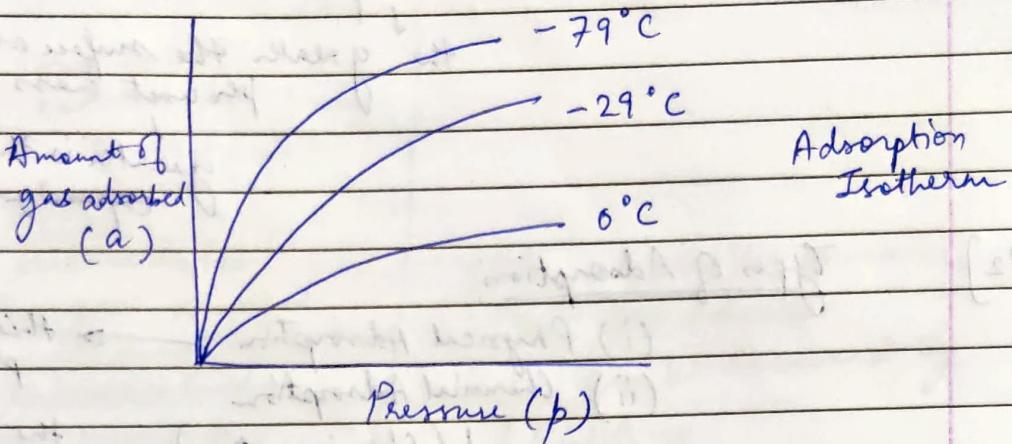
leading to release of  
heat

By Le Chatelier's principle:

Magnitude of adsorption  
decreases with increase in  
temp.

(and vice versa)

And with  $P$  in Pressure,  
there is  $P$  in adsorption



This relationship can be given by :

$$a = kp^n \quad (k = \text{rate constant}, n = \text{some constant which usually is } < 1)$$

$$\log a = \log k + n \log p$$

(thus,  $\log a$  vs  $\log p$  will be a straight line graph)

#### 40] Nature of Gas and Adsorbent

more readily soluble & easily liquefiable gases

like  $\text{NH}_3$ ,  $\text{HCl}$ ,  $\text{Cl}_2$ ,  $\text{SO}_2$

are adsorbed more

as compared to  
so called "Permanent Gases"

like  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{H}_2$  etc.

Reason is that the

Van-der-Waals forces are more predominant in the former case

41]

## Nature of Adsorption

Usually, since it's a surface phenomenon

the greater the surface area per unit mass

greater is the adsorption capacity

42)

## Types of Adsorption

(i) Physical Adsorption → this is a physical phenomenon

(ii) Chemical Adsorption

↓ (Chemisorption)

the gas molecules are weakly retained on the surface

Type of adsorption  
when some  
chemical bond  
is formed

↓ forces involved a  
van-der-wa  
forces

between the gas molecules &  
the solid surface

e.g.: O<sub>2</sub> - chemisorbed on W (Tungsten)

CO & H<sub>2</sub> - chemisorbed on Ni

The chemisorbed gas cannot be removed from  
surface by changing T & P

whereas physisorbed gases can be removed  
by decreasing P & increasing T

43)

## Difference b/w Chemisorption and Physical Adsorption

### Chemisorption

- It ↑ with ↑ T  
in the same way as any  
chemical rxn. ↑ with ↑ in T.

### Physical Adsorption

- ↓ with ↑ in T.  
Thus, it usually occurs at lower T



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PAGE \_\_\_\_\_

- 2) The heat evolved is of higher order ( $10-100 \text{ kcal/mol}$ )  
↓  
Some as heat evolved during chemical rxn.
- Heat evolved usually quite low  
(around  $1-10 \text{ kcal/mol}$ )
- 3) It is irreversible as the gas adsorbed cannot be recovered back by  $\downarrow P$  or  $\uparrow T$   
(Here gas has chemically reacted with solid substrate)
- It is reversible process, as gas adsorbed can be recovered by  $\downarrow P$  and  $\uparrow T$
- 4) It forms a monolayer of molecule as chemical forces fall out (weaken) with increase in no. of layers  
Gas adsorbed is of multi-layer  
As van-der-waal forces can extend from one layer of molecule to another -
- 5) It is associated with some activation energy ( $\approx 20 \text{ kcal/mol}$ ) and is relatively slow process at low  $T$   
It is not associated with any activation energy & predominantly is favoured at low  $T$
- 6) For chemisorption, it has no correlation with ease of liquefaction of gases  
Here the extent of adsorption is approximately related with ease of liquefaction of gas.  
For more easily liquefiable gas, adsorption is more.

44) Adsorption Isotherm

If for a given system  
one keep  $T$  const. &  
studies amount of  
adsorption as a function of  $P$   
that relation is known  
as Adsorption isotherm.

Many have been studied, but  
simplest is Langmuir isotherm.

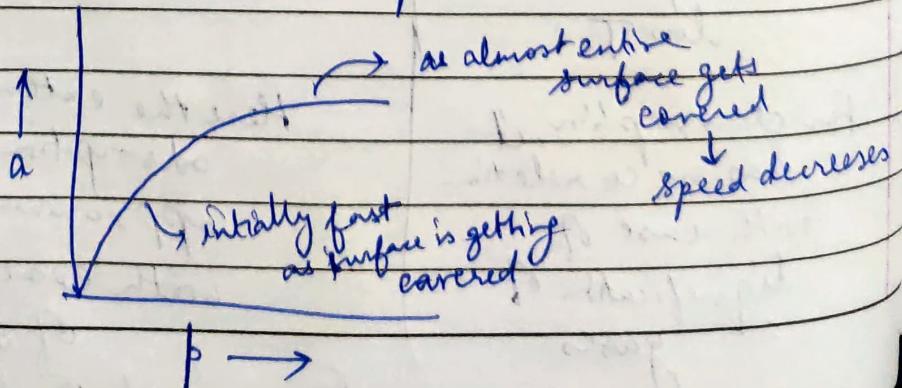
1916, Irving Langmuir  
suggested the relation b/w  
surface area of solid  
& adsorption to gas

He suggested that  
the gases adsorbed on solid  
surface cannot be  
more than 1 molecule  
in thickness

thus, the magnitude of  
adsorption goes on increasing  
until entire surface is  
covered by uniform  
layer, if exposed  
to gas

This adsorption is known as

adsorption isotherm.



45] Assumptions:

(i) Only unimolecular layer is formed, and  
~~(ii)~~ Adsorption is chemisorption in nature

(iii) There are fixed no. of adsorption sites on surface, and each site can hold only 1 atom or molecule.

(iv) There is no interaction b/w adsorbed molecules (Ideal adsorption).

(v) Gas molecules occupy single site on surface & they are not dissociated.

(vi) The enthalpy change is same for all sites.

Langmuir visualised that the adsorption site is dominated by two opposing forces.

(i) Tendency of gas molecules to adsorb on the surface (condense)

(ii) Tendency of gas molecules to evaporate (desorb)

At equilibrium, rate of adsorption = rate of desorption

Let at any instant,  
fraction of surface covered is  $\theta$   
then fraction net covered is  $(1-\theta)$

Thus, as per Kinetic Theory of gases, we can say the rate of adsorption:

$$\text{Rate of adsorption} \propto \rho(1-\theta)$$

$$= k_1 \rho(1-\theta)$$



Similarly, Rate of desorption =  $k_2 \theta$

At equilibrium, Rate of adsorption = Rate of desorption  
 $\Rightarrow k_1 p (1-\theta) = k_2 \theta$

$$\text{or } \frac{\theta}{1-\theta} = \frac{k_1}{k_2} p = K_p$$

where  $K$  is the equilibrium const.  
for Adsorption-D reaction

Solving this, we get:

$$\boxed{\theta = \frac{K_p}{1 + K_p}}$$

## LECTURE 11

24/01/2023

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### Kinetics of Gas-Solid Reaction

Heterogeneous Reaction : Here the rxn. takes place b/w 2 phases (the reactants are in different phases at the interface/boundary of no.

e.g.: (i) Gas-Solid Reaction

(ii) Gas-Liquid Reaction — e.g.:  $BDF$ ,  $\xrightarrow{\text{above}} \text{gas oxygen furnace}$

(iii) Liquid-Liquid Rxn. —

Hydrogen reduction of metal oxides

(iv) Liquid-Solid Rxn. — aqueous leaching of ores

e.g.: Matte smelting,  
slag-metal reaction  
Solvent extraction

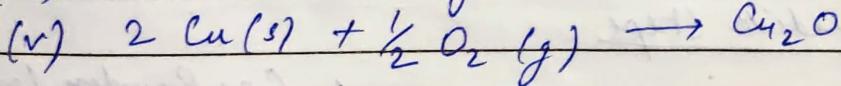
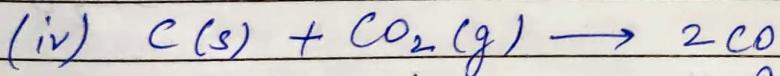
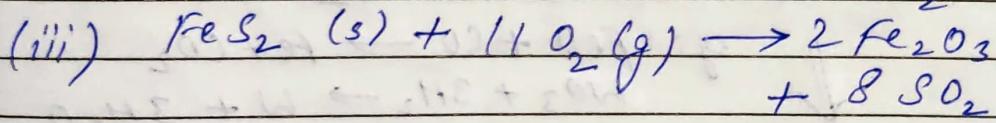
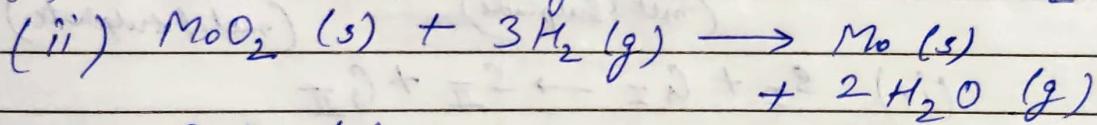
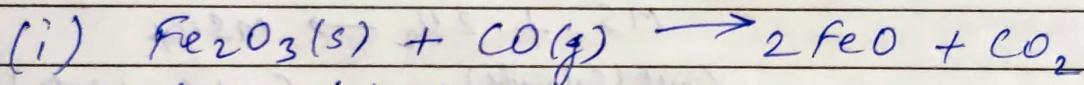
(v) Solid-Solid rxn. — e.g.: Sintering of iron ore,  
Carburization of iron etc.

We will only talk about  
Gas-Solid reactions here.

{ They are the most  
important heterogeneous  
reactions }

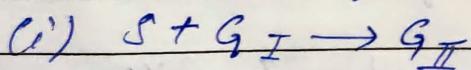
e.g.: Iron oxide reduction,  
roasting of sulphides,  
Combustion of solid fuel — coal,  
coke

### Oxidation of metals

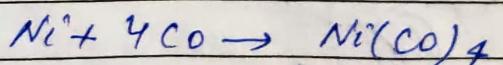
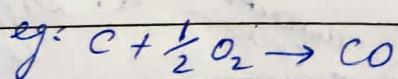


### 47] Elementary steps in Gas-Solid Reaction

may be of different types

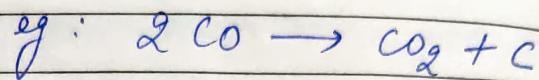
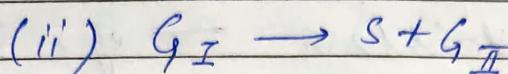


{ S: solid  
G: gas }



Ni-carbonyl (it is volatile)

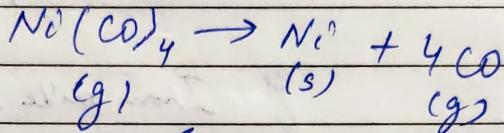
↓  
this is used for  
purification of Ni metal



called Carbon Deposit Reaction

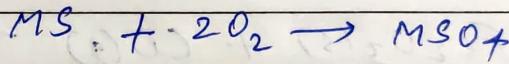
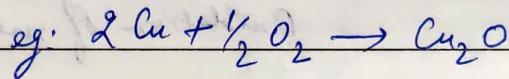
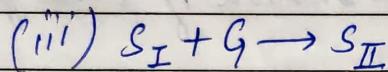
OR

Carbon Loss reaction



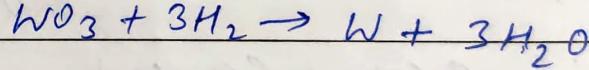
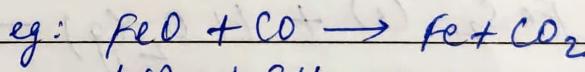
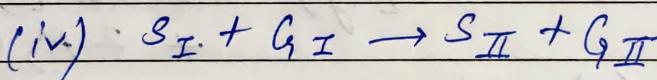
(g) (s) (g)

{after getting condensed}



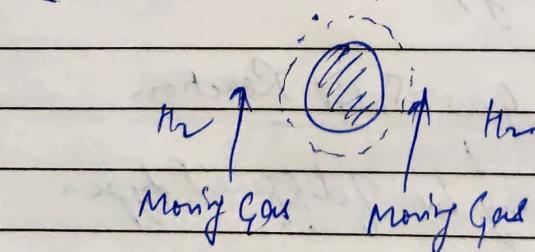
(metal sulphide)

(metal sulphate)



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### Intermediate steps

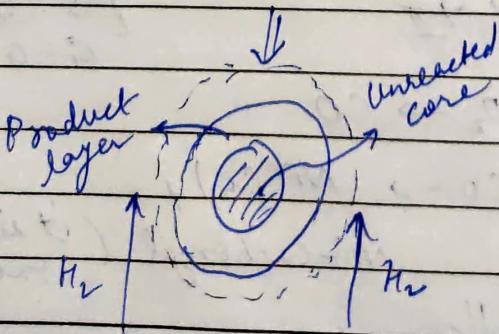


1. Gas Boundary Layer / Diffusion

{ diffusion through boundary layer & comes

to the surface }

2. Diffusion of gaseous reactant through solid product layers to reaction interface

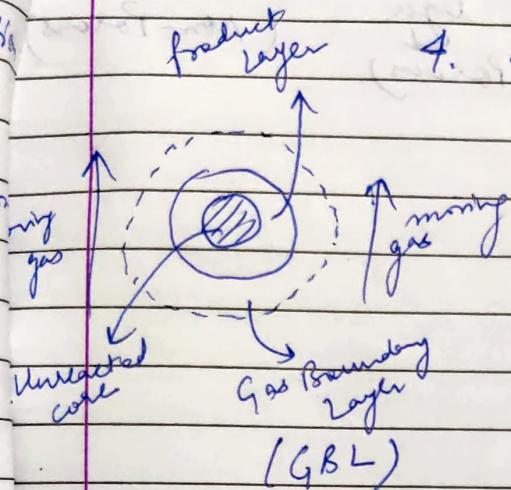




### 3. Chemical reaction at the interface (including adsorption - desorption)

product layer

### 4. Diffusion of the product gas through the solid product layer



### 5. Gas boundary layer diffusion of the product gas to bulk of gas stream

Other things that can influence the kinetics of the rxn. :

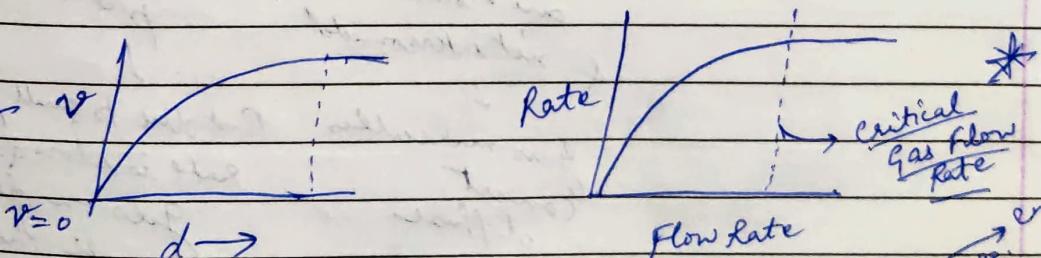
(i) Heat Transfer

(ii) Structural changes {eg: Sintering, change in pore structure}

\* NOTE: The effects

of all points above  
(1 to 5)  
are additive to the rate

#### (i) Gas Boundary Layer Diffusion



#### (ii) Diffusion through the product layer

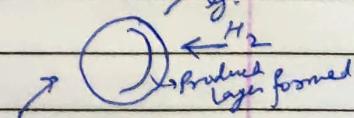
Two possibilities: (a) Rxn. with a porous particle

(b) Rxn. with a non-porous particle

OR

Topochemical reach ← Topochemical  
Rxn. model

OR Shaking core model



here

entire can't  
get reduced

(as product layer  
acts as protection)

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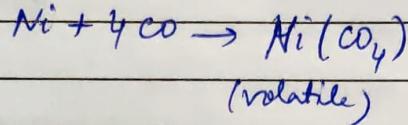
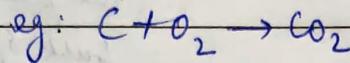
Three possibilities for Non-porous particle:

Product layer  
may not form  
(Volatile)

Product layer  
(Porous)

Product layer  
(Non-Porous)

### (a) Volatile Product layer



Routing of Hgs

Oxidation of Mo ( $900^\circ\text{C}$ )  $\text{MoO}_3$

### (b) Formation of Porous Prod. Layer

### (c) Formation of NonPorous Prod. layer

eg:  $\text{Fe}_2\text{O}_3$  by  $\text{H}_2$  oxidn. by  $\text{Cu}$

Pores are small but interconnected  
so molecular diffusion takes place through them

If pores are very small & not interconnected

gas molecules cannot diffuse

But due to small pores rate is slow & it goes on decreasing with thickness of prod. layer

↓

Ion diffusion

that takes place

(also called Solid-state diffusion)

→ such processes are called

Diffusion control processes

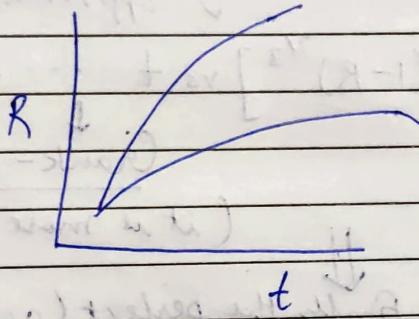
{ Slowest amongst all diffusion processes }

## 50] Determination of Rate controlling steps

Needs to find Activation Energy

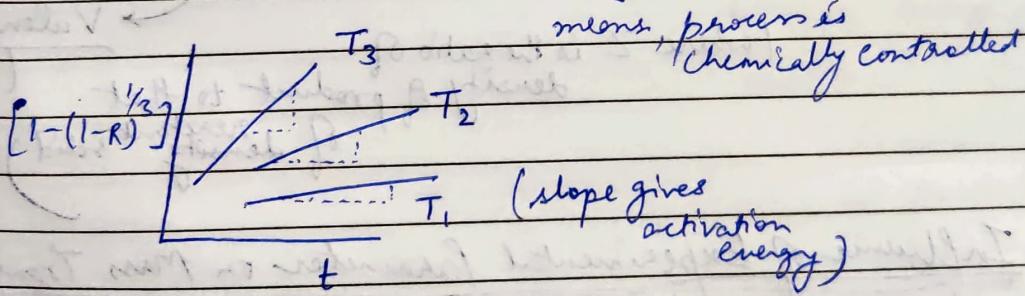
found using  
Experimental Data

obtained by  
studying rate of rxn.

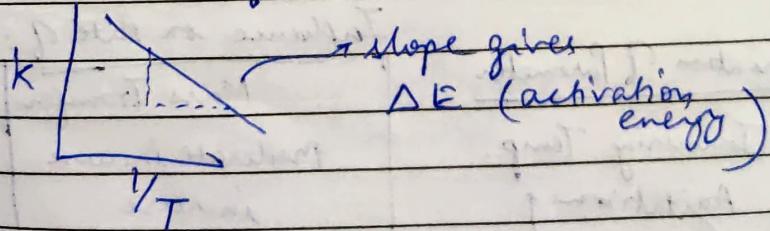


% Reduction  $\rightarrow$  Fraction reacted  
(R) converted to means  
(e.g.: if 50%  $\rightarrow$  0.5 reduction is fraction reacted)  
\* (i.e. they are equivalent)

e.g.:  $[1 - (1-R)^{1/3}]$  vs t gives straight line



In the Arrhenius Eq<sup>n</sup>: if we plot k vs  $1/T$ :





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$y: [1 - (1-R)^{1/3}]^2$  vs  $t$  gives st. line  
 ↓  
 means,

diffusion controlled

(but this eq: is  
 also an approximation)

called Tander's Equation of Approximation

↓ later a  
 mathematician  
 gave a better  
 approximation

$[1 - \frac{2}{3}R - (1-R)^{2/3}]$  vs  $t$  ...

↓ Crank-Gibeling equation

(it is more correct)

↓ finally the perfect (accurate)  
 eq: was given later:

$[1 - (z-1)R]^{2/3} + [(z-1)(1-R)^{2/3}]$  vs  $t$  ...

→ Valensis  
 (where  $z$  is the ratio of density of product to that of reactant solid)  
 (Acc.)

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## Influence of Experimental Parameter on Mass Transfer and Chemical Reaction

### Variation of Parameter

Increasing Temp.

Agitation ↑

Interfacial area ↑

Porosity of solid ↑

### Influence on Rate of:

#### Mass Transfer

Moderate increase

Increase

Moderate increase

Moderate ↑

#### Chemical Reaction

Large increase

No effect

Large increase

Large ↑



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PAGE \_\_\_\_\_

Presence of catalyst

No increase  
(No influence)

Increase

Activation Energy (AE)  
is 1-5 kcal/mol $\rightarrow$  GBL diffusionAE is 5-15 kcal/mol  $\rightarrow$  Diffusion controlAE is 15-60 kcal/mol  $\rightarrow$  Chemical control

## 52] Material and Heat Balance Processes

The product output of process  
depends upon amt. of material consumed

& the chemical reactions taking place

That will decide output

Similarly energy requirement  
is related to heat required  
to raise temp. of raw  
material to temp. where

Chemical reaction can  
be sustained

& material can be  
transferred to desired  
state of products.

So the calculation of material & energy/heat balance  
are amounted

main aim is to  
estimate inflow &  
outflow

These are  
plant records

of materials & heat

& routine calculations for  
plant operation