

PRINCIPLES OF METAL EXTRACTION [MLL262]

Prof. T. R. Mankhand (Visiting Professor)

Prof. Nitya Nand Gosvami

LECTURE-1 (03/01/2023)

1] Metallurgy: The science and technology of the making, shaping of metals

Main steps of Mining of Ore

Mineral Beneficiation

Extraction

Refining

Alloying

Fabrication

Processing

Application

{ nowadays not followed } This is the old classification

2] Metallurgy (Classification)

(i) Extractive metallurgy

→ Process metallurgy

Ferrous
Extractive
metallurgy

(ii) Material Processing

Non-Ferrous
Extr. metallurgy

(iii) Physical Metallurgy

Chemical Metallurgy { Physical Chemistry
Inorganic Chemistry }

Mechanical Metallurgy → Fabrication
of metals

Physical Metallurgy

3] Occurrence of Metals in Nature

Earth's Crust
Sea Water } Natural

Sea Nodules

Metal Scrap → Man-made source

3] Earth's Crust

+
It is taken to be
15 km deep from surface

<u>Elements</u>	<u>w.%</u>	
O	46.7	V - 0.014
Si	27.7	Cr - 0.01
Al	8.1	Cu - 0.01
Fe	5.0	Ni - 0.008
Cu	3.6	Zn - 0.004
Na	2.8	Pb - 0.002
K	2.6	Co - 0.001
Mg	2.1	Sn - 0.0001
Ti	0.44	Hg - 0.00001
Mn	0.1	Ag - 0.000001
Zr	0.017	Au - 0.0000001

Observations : (i) O, Si - Make 75% of crust
(Not. v. useful)

(ii) First 8 elements > 98%.

only 2
useful metals

LECTURE-2 (05/01/2023)

Fe, Al

4] In water on Earth's surface

(NOTE: Crust → 70% water)

<u>Element</u>	<u>Constitution (g/ton)</u>
Na	10500
Mg	1270
Ca	400
K	380
Al	0.2
Li	0.10
Fe	0.02
Zn	0.014
Cu	0.012
Mn	0.01
Pb	0.005
Sn	0.003
Ni	0.0001
Au	0.000005

5] Sea Bed Nodules
 (or Ocean nodules)

these are about
 4 cm size diameter
 ("potato size")

several hundred
 billion tonnes

(these are also
 continuously forming at
 the rate of 10 million
 tons/year)

Composition \rightarrow (Mn); Fe, Ni, Co & Siliceous
 silt

Since Mn
 is mainly present

called \rightarrow Manganese Nodules
 (also called Polymetallic
 Nodules)

Element	Wt. in Nodules	Estimated reserves ($\times 10^9$ tons)	Ratio of Nodule Reserve to Land (Ore) Reserve
Mn	23.86	358	4000
Fe	13.80	207	4
Al	2.86	43	200
Ni	0.98	14.7	1500
Cu	0.52	7.9	130
Co	0.35	5.2	5000

If present below > 300 m

↓
v. difficult to extract

(Not economical)

When < 300 m \Rightarrow It is economical

only if present
in density 1,50,000 tons/sq. km

6] Primary metals \Rightarrow Metals obtained from ore directly

Secondary metals \Rightarrow Primary metals are

used to make some
application

↓
when they are dumped &
become scrap

↓
then they can be
recycled

↓
and are called

Secondary metals

By-product metals \Rightarrow When extracting
a main metal (e.g.: Zn from Zn ore)
from ore

↓
small amounts

of other metals (like Ag, Au, etc.)
may be segregated out separately
as impurities

these
are called
By-product metals

Zn production → Ag, Au

Cu production → Ag, Au

In India

Production of Gold is only
about 2 tons/year (Earlier
from Kolhar Gold Fields (KGF)
in Karnataka
But had to be
closed in 2002)

Birla Cu plant → in Dahej, Gujarat
capacity → 15 tons/yr
6 ton/yr

7] Advantages of Secondary metals:

(i) Since these metals are
non-renewable natural resources

we need to focus
on recycling

(ii) Disposal of waste (Wastes can be
utilised for production
of secondary metals)

(iii) Environmentally more acceptable

(iv) Energy : Al — Primary }
Secondary } 20 tons , Mg — 30 tons

8] Minerals and Ores:

Mineral: A mineral is a naturally
occurring inorganic ore

e.g. CaCO_3 (limestone)

FeS_2 (pyrite)

CuFeS_2 (chalcopyrite) (like O, Si, S, etc.) & a mineral has a fixed

Fe_2O_3 (Hematite)

of one or more metals
in association with
non-metals

composition, & well defined physical
& chemical properties

Rock: A combination of minerals naturally occurring in solid form

Ore: Naturally occurring aggregate of minerals (like rock)

↓
but from which one or more metals can be extracted economically

PbS → this will always
(Galena) be in a mineralized

↓
rock
But this rock may or may not be an ore of Pb

(depending on the conc. of Pb in the rock)

eg: (Some ores, like Magnetite
 (Fe_3O_4)) → high Fe conc.
(80-85%)

But Cu ore → 1% is also ore

Ag → 0.1% is also ore)

{ Iron ore with < 60% is generally not treated as ore in many countries }

PbS (Galena) } these are in
 ZnS (Sphalerite) } form of ore minerals

{ FeS_2 (pyrite) } gangue minerals

FeCO_3 (Siderite)

{ SiO_2 (Quartz) } gangue mineral

NOTE!

Ore has 2 parts

Ore mineral

Gangue mineral

These are not ores of Fe (as it is not economical)

(Valuable mineral)

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9] Factors influencing the economics of metal extraction from an ore

1. % of metal value in the ore

2. Fe oxide

Fe silicate

3. % of impurities present, and the nature of impurities

(e.g.: Bauxite $\rightarrow > 40\% \text{ Al}_2\text{O}_3$)

is considered economical

But also SiO_2 should be $< 5\%$

(otherwise it's difficult to extract)

4. Physical conditions of the ore

(whether in ground form → preferable as or sand or as massive rocks)

grinding is one of the most expensive steps

5. Location and magnitude of ore

And also whether it is underground or on the surface

(e.g.: Gold is now v. deep in the ground)

6. Physical & chemical properties of metal to be recovered

(if v. reactive, then cost increases)

e.g.: Titanium hard to extract b/c of this reason



7. Market value of the metal

10] Extraction of metals.

Three categories

I
Pyrometallurgy
Usually Temp. $> 500^{\circ}\text{C}$
then called pyrometallurgy

Hydrometallurgy

where metal
is separately (selectively)
dissolved & thus
separated from
rest of the substances

(using appropriate solvent)

& then the recovery
from the solution

Electrometallurgy
extraction & refining
of metals
using
electrical
energy

Factors deciding the choice of the process

- 1) Nature & stability of ore minerals
- 2) Properties of metal concerned
- 3) Degree of purity required of metal
- 4) Local facilities available
- 5) Concentration of ore

Pyromet \leftarrow Cu ore - H. Cu sulphide

Hydromet \leftarrow Cu ore - ly. Cu oxide

Pyromet - Fe

Pyromet-Electromet - Cu

Hydro-Electro - Al

Pyro - Distillation - Zn



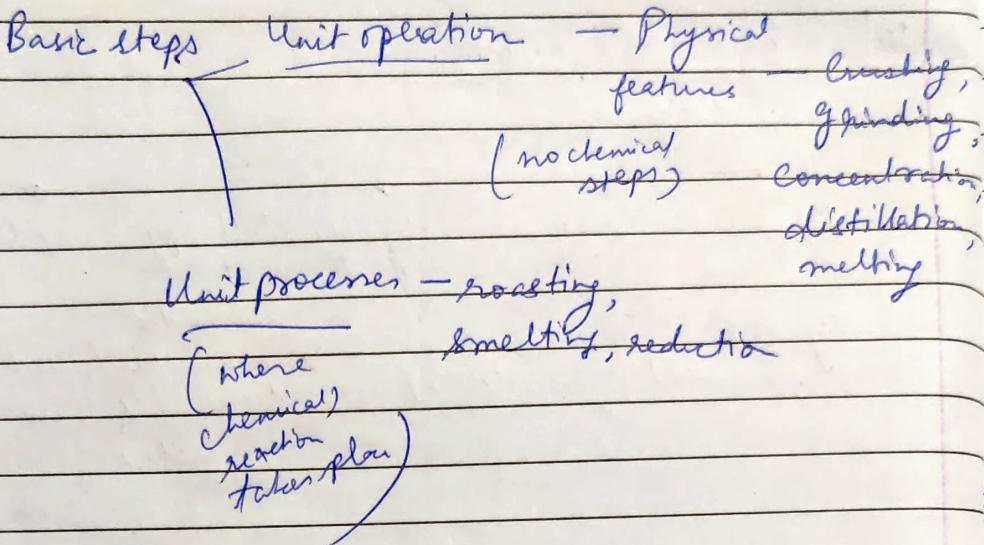
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Unit Processes

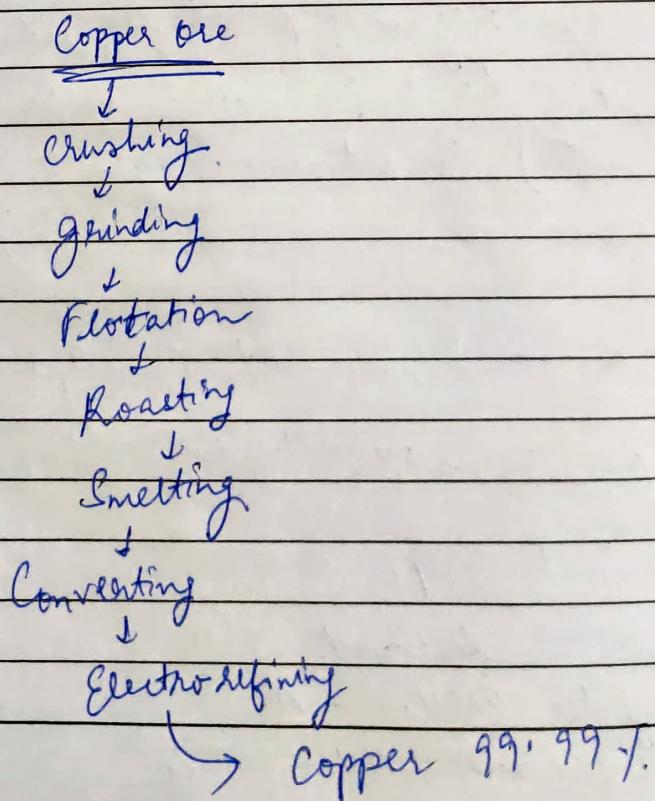
Basic steps



12]

Flow sheet: A combination of various unit processes and operations leading to formation of flow sheet for a particular metal

e.g.: Copper Extraction Flow sheet by pyrometallurgy



LECTURE - 4 (MLL262)

Chemical thermodynamics

There are 3 forms which are considered in the study of chemical thermodynamics:

1. Heat Energy (Enthalpy H)
2. Degree of disorder (Entropy S)
3. Energy for driving force of chemical reaction known as free energy, represented by G

Thermodynamics is based on 3 empirical laws, based on some well established results:

1. First law of thermodynamics
2. Second law of thermodynamics
3. Third law of thermodynamics

These laws are independent of any assumption. They are concerned with Macro-system. Not involved with individual molecules.

Main objectives of Chemical Thermodynamics

1. Feasibility of a process.
Eg: $\text{Fe}_2\text{O}_3 + 3\text{C} \rightarrow 2\text{Fe} + 3\text{CO}_2$
Occurs at 1200°C
 $\text{Al}_2\text{O}_3 + 3\text{C} \rightarrow 2\text{Al} + 3\text{CO}_2$
This is not feasible at 1200 degrees, which is why it cannot be performed in normal conditions, and is a more expensive process
2. Quantity of heat change.
(Endo or Exo)
3. To determine the extent of reaction

Most of the laws of physical chemistry are derived from thermodynamics.

Metallurgical (Material) Thermodynamics is chemical thermodynamics applied to a metallurgical process.

Eg: $\text{Fe}_2\text{O}_3 + 3\text{C} \rightarrow 2\text{Fe} + 3\text{CO}_2$

This reaction occurs in a blast furnace.

Air blows from the bottom, reacts with coke and makes CO.

This goes above and reacts to form CO₂. But if some CO remains, that is not good as it means coke isn't completely reacted.

Limitations of thermodynamics:

1. Thermodynamics applicable only to Macro-system (i.e. bulk) and not to Microsystems.
Thus it ignores the molecular level and the internal structure.

2. It can only tell the initial and final stages of the reaction. It cannot tell about the rate (i.e. we don't know how much time it will take to complete the reaction). This is why study of Kinetics is needed to determine rate.

References:

1. Darken and Gurry - Physical chemistry of Metals
2. Parker - Introduction to chemical metallurgy
3. Gaskell - Introduction to Metallurgical Thermodynamics
4. Kubaschewski and Evan - Metallurgical Thermochemistry

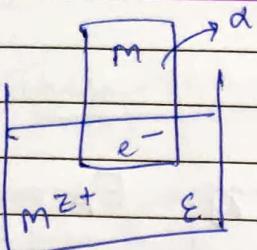
Terms in Thermodynamics:

1. Matter - Anything which occupies space in the universe, and whose behavior is concerned or under study in thermodynamics.
2. System
3. Surrounding - Rest of the matter other than the system which might be in position to exchange energy or matter with the system.
4. Isolated system - Cannot exchange anything.
5. Closed system - Can exchange energy but not matter
6. Open system - Can exchange energy as well as matter
7. Homogeneous system - Complete uniformity in composition of system. It is a one phase system. It is a physically distinct and not mechanically separable portion.
8. Heterogeneous system
9. Extensive properties - depend upon the amount of the system present (eg: mass, volume, etc.)
10. Intensive - doesn't depend upon mass of the system. Independent of amount. Eg: Pressure, density, etc.



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$$dU_\alpha = T_\alpha dS_\alpha - P_\alpha dV_\alpha + \sum \phi_\alpha dq_\alpha + \sum \mu_\alpha dn_\alpha$$

Can be written as:

$$dU_\alpha = T_\alpha dS_\alpha - P_\alpha dV_\alpha + \phi_\alpha^M dq_\alpha^M + \phi_\alpha^e dq_\alpha^e + \mu_\alpha^M dn_\alpha^M + \mu_\alpha^e dn_\alpha^e$$

LECTURE 5

01/01/2023

MLL 262

13] First Law of Thermodynamics

It states that Energy can neither be created nor destroyed in a system of constant mass

Although it can be converted from one form to another

↓
This is called the Law of conservation of energy.

The energy of a system

2 categories :

(i) By the Position of the system :- P.E., K.E. etc.

But this is not concerned with Thermodynamics

(ii) Internal energy :- consists of vibrations of atoms + chemical bonding +

+ structural energy

Initially we can have intrinsic I.E.

It is

also depends on amount

depends on:

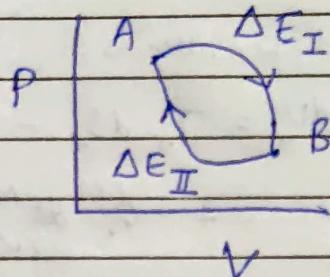
chemical nature

Temp, pressure & volume of system

The exact value of I.E. can't be measured, but we can find change in I.E.

14]

Internal energy & first law



Energy: E_A and E_B
System only undergoes change in pressure & vol.

$$|\Delta E_I| = |\Delta E_{II}| \quad \therefore \Delta E = E_B - E_A$$

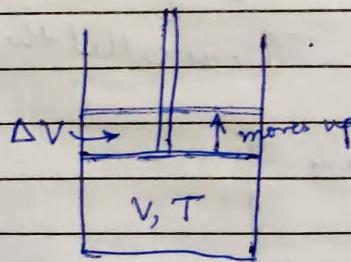
Work can be done from surroundings on the system as well

if work done on the surroundings by the system $\rightarrow W$ is +ve

15]

Pressure & work

Here we have only PV work



$$\therefore W = P \Delta V$$

Taking heat = q
We get:

$$q = \Delta E + W$$

$$\text{or } \Delta E = q - W = q + P\Delta V$$

Enthalpy of system

$$\Delta E = q - P\Delta V \Rightarrow q = \Delta E + P\Delta V$$

We define, $H = E + PV$

Total energy = I.E. of system + Energy used in doing work $P\Delta V$

16] Thermochemistry

Chemical rxn :- combustion, roasting, reduction, formation of compound, neutralization of acids or alkalis, dissolution, dissolution of solute

Heat of reaction :

Exothermic — Heat evolved from system ; ΔH is -ve

Endothermic — Heat is absorbed ; ΔH is +ve

17] How energy is stored?

(i) Potential energy — Bonding energy
(due to breaking & forming of chemical bonds)

(ii) Kinetic energy — Vibrational kinetic energy

Different Types of Heat of Reaction

(i) Heat of formation of compound

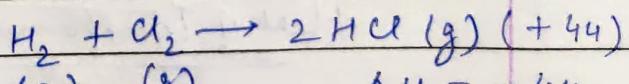
The heat released when 1 gram mole of that compound is formed from its elements

e.g.: formation of CO_2 from graphite & oxygen : $\text{C}(\text{s}) + \text{O}_2 \rightarrow \text{CO}_2 \text{ (+94)}$
 $\Delta H = -94 \text{ kcal}$

Formation of HCl(g)

from H_2 and Cl_2 :

↓
Exothermic rxn.



$$\Delta H = -\frac{44}{2}$$

$$= -22 \text{ kcal}$$

18]

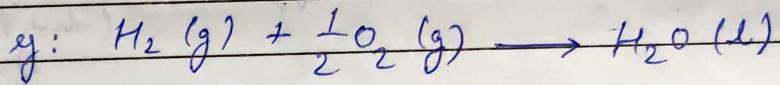
Standard Heat of formation, ΔH°
298 K

It is the heat of formation
at 298 K and 1 atm pressure

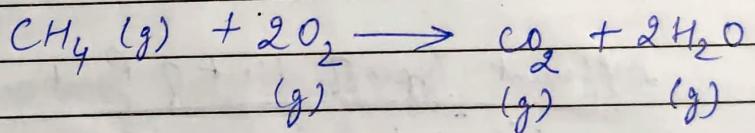
By convention, the heat of formation for standard states of pure elements at 298 K & 1 atm is taken as zero (0).

Heat of combustion

It is the heat change due to complete combustion of 1 mol of that substance



$$\Delta H = -68.4 \text{ kJ}$$



$$\Delta H = -212.8 \text{ kJ}$$

Heat of Neutralization

It is the heat change due to the neutralization of acid or base

Heat of Solution

When a solute is dissolved in water the heat change may occur (either released or absorbed) (or some solvent)

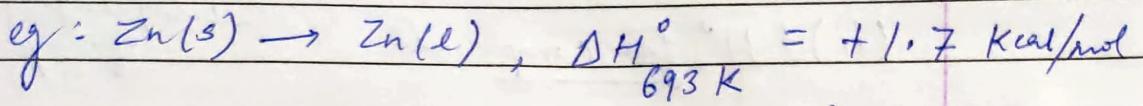
Heat of Transformation (also called Latent heat of transformation)

Occurs during change from one physical state to another

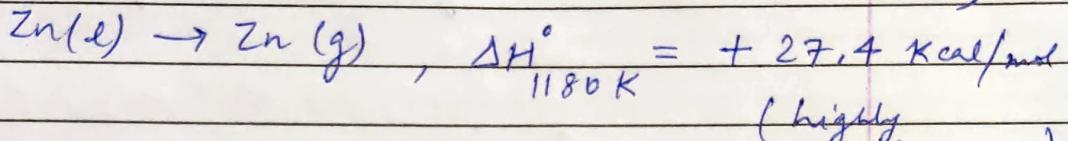


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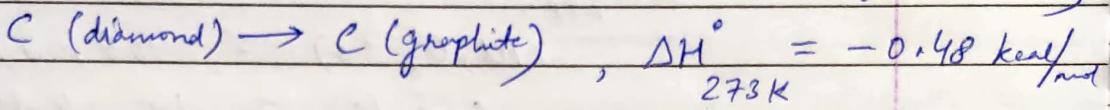
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(endothermic rxn.)



(highly endothermic)



(exothermic)

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Calculation of Enthalpy change of a particular rxn.

ΔH depends on:

(i) Temp.

(ii) Pressure

(iii) Physical states of reactants & products

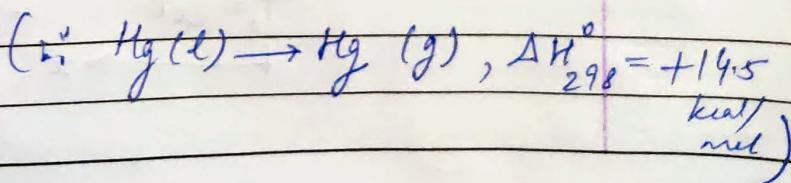
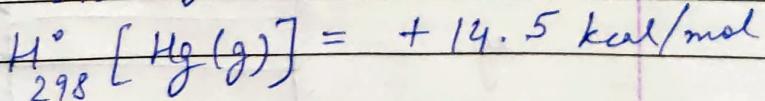
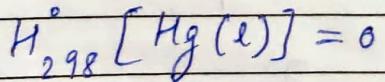
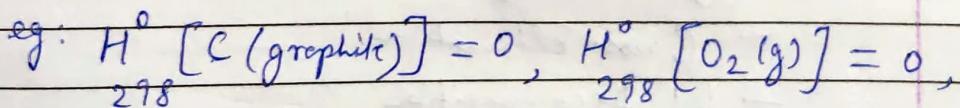
(iv) Amount of substance

Standard enthalpy: $\Delta H^\circ = \Delta H^\circ_{\text{product}} - \Delta H^\circ_{\text{reactants}}$

gases - 1 atm

solid - pure state

(i) H° for elements - zero at ref. temp. 298 K



MLL 26220] Second Law of Thermodynamics

1] The energy always transfers from higher to lower end on its own without doing any external work.

2] Similarly it is impossible to construct a machine operating in cycles with 100% efficiency (proved by Carnot)

3] An isolated system tends to take up a more (most imp.) disordered form & never on its own become more order. A spontaneous process is always accompanied by an increase in the entropy of the system and surroundings.

21] Spontaneous process : Is that which proceeds on its own without any help required

Entropy : Describes the randomness or disorder of a system.

e.g.: Melting of ice → occurs on its own
Water is more disordered than ice

Evaporation of water

A change that brings randomness is more likely to occur than a change that brings order



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Entropy $\rightarrow 'S'$ Change in entropy $\rightarrow \Delta S'$

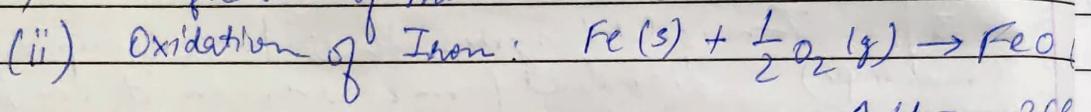
$$\Delta S = S_{\text{Final}} - S_{\text{Initial}}$$

When $S_f > S_i$, $\Delta S > 0$

$$\boxed{\Delta S_{\text{system}} + \Delta S_{\text{surrounding}} \geq 0}, \text{ always}$$

Q1:

(i) Solidification of molten metal



$$\Delta H = 266$$

Q2]

Quantitative expression of entropy

When an amount of heat q is supplied to a body at temp. T then the magnitude of entropy change is due to 2 factors -

$$(i) \Delta S \propto q$$

$$(ii) \Delta S \propto \frac{1}{T}$$

$$\therefore \boxed{\Delta S = \frac{q}{T}}$$

Q3]

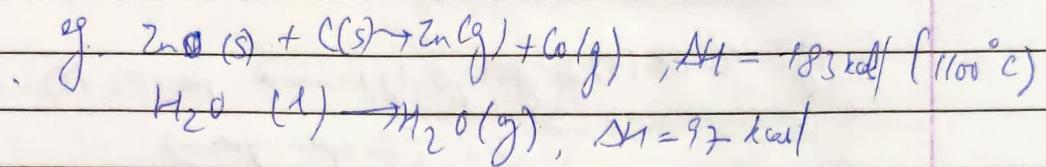
Third Law of Thermodynamics

At absolute zero, the entropy of pure crystals is also zero.

$$\text{i.e. } S=0 \text{ at } 0 \text{ K}$$



The sign of ΔH cannot be a sufficient criteria for feasibility of the reaction
Here we use Entropy



24] Driving force

(i) State of minimum energy attainment (Exothermic rxn.)

(ii) Tendency of system to attain maximum randomness

In Thermodynamics, the entropy is expressed by S
If entropy increases, ΔS is +ve.

$T\Delta S$ is quantitative measure of the randomness at the particular temp. T

Driving force is resultant of two factors:

(i) ΔH

(ii) $T\Delta S$

The fraction of energy which is not available for work is given as $T\Delta S$.

The fraction of energy available for doing work is called free energy, G .

Free energy change, ΔG is measure of the useful work available from the rxn.

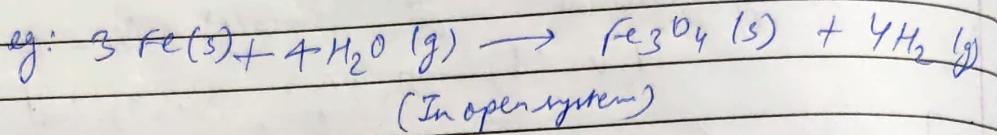
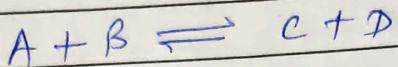
~~Nernst - Helmholtz equation~~

$$\therefore \Delta H = \Delta G + T\Delta S$$

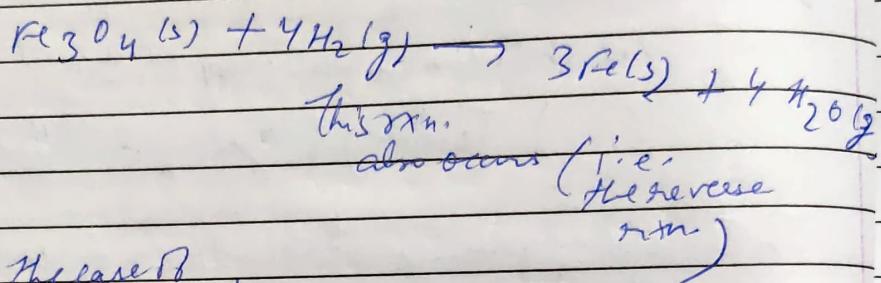
Total energy ↓ ↓
 Energy available to do work → Energy unavailable to do work → causes randomness

$$(\Delta G = \Delta H - T\Delta S) \Leftarrow$$

25]

Chemical Equilibrium

But in closed tube:



This is called
 Chemical eq/bm.

26]

Law of Mass Action

The rate at which a substance reacts is proportional to its active mass

Active mass: The conc of that substance in the reacting substance



(active masses
 represented
 in square
 brackets)

$$[A], [B] \\ [A] [B]$$

Forward rate $\propto [A][B]$

$$V_f = k_1 [A][B]$$

Similarly the backward/reverse rate will be:

$$V_r = k_2 [C][D]$$

where each k is the rate
 const.



$$\text{At eqm. : } k_1[A][B] = k_2[C][D]$$

$$\Rightarrow \frac{k_1}{k_2} = \frac{[C][D]}{[A][B]} \equiv K_c \quad \begin{matrix} \text{defined as:} \\ \text{equilibrium} \\ \text{constant} \end{matrix}$$

$$\text{For } aA + bB \rightleftharpoons cC + dD \Rightarrow K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b} \text{ or } \frac{C_C^c \times C_D^d}{C_A^a \times C_B^b}$$

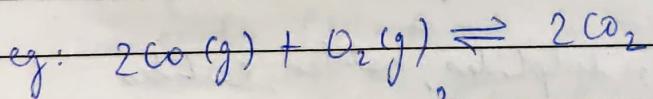
If $K_c > 1$, products will dominate
and rxn. has tendency to
move forward
(thus, rxn. is feasible)

If $K_c < 1$, backward tendency
(rxn. not feasible)

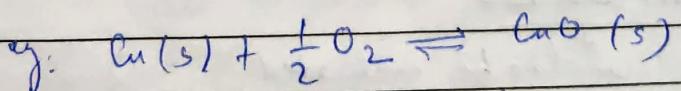
$$K_c = 1 \rightarrow \text{equilibrium}$$

for Gases

K_p used (eq^{bm} pressure const.)



$$K_p = \frac{p_{\text{CO}_2}^2}{p_{\text{CO}}^2 \times p_{\text{O}_2}}$$



$$\text{Mixed case} \Rightarrow K = \frac{[\text{CuO}]}{[\text{Cu}] p_{\text{O}_2}^{1/2}} = \frac{1}{p_{\text{O}_2}^{1/2}}$$

NOTE: If $\Delta G \leq 0$ and $K \geq 1$, then rxn. is feasible