dt: 09-12-19.

Introduction

Metallurgy is that branch of engineering, which deals with the extraction of metals, their uses and service to mankind.

✓Metal.

Metal is that material, which posses lusture, strength, high hardness, high ductility and high thermal and electrical conductivities.

Ex: Aluminium, copper, iron, cobalt, nickel, etc.

Non-metal

Non-metal is that material, which has low value of lusture, strength, hardness and conductivity.

Ex: carbon, sulphur, Phosphorous, glass, etc

Metalloid

Metalloid posses the characteristics of both metals and non metals, such as antimony and arsenic.

✓Gangue

Gangues are the impurities or unwanted material present in the ore.

Ex: Magnesia, silica, etc.

✓Flux

Flux is used to react with the gangue materials and it also lowers down the operating temperature of the process.

Ex: Limestone, Dolomite

✓Slag

Slag contains the impurities of ore minerals or other feed materials of the furnace. slag is generally the product of flux and gangue materials present in the charge.

Flux + Impurities ---> Slag

✓Smelting

Smelting is a process of applying heat to ore in order to extract a base metal. It is a form of extractive metallurgy.

Melting or Fusion

It is a physical process that results in the phase transition of a substance from a solid to a liquid.

Ex: Ice Cube → Water
(solid) (liquid)

(Assignment No: 1.)

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Organic

The defination of organic is natural matter or compounds with a carbon base and also refers to food and meat grown or raised without chemicals or pesticides.

Ex: Fats, sugars, Protiens, enzymes, hydrocarbon fuels, etc.

Inorganic

The defination of inorganic is something unrelated to organic matter or organic life, not animal or vegetable, or a chemical compound that does not contain carbon.

Ex: Plastic, salts, Metals, etc.

Ductility

Ductility is the property of deforming of a material.

Ex: Steel rod, etc.

Brittleness

Brittleness is the property of a material of fracturing or break-down without appreciable deformation

Ex: Chalk. Glass, etc.

Conductor

Conductors are the materials or substances which allows electricity or heat to pass through them. It is happen due to flow of electron.

Ex: Iron rod, water, etc.

Insulator

Insulators are the materials or substances which do not allows electricity or heat to pass through them. It is happen due to no flow of electron.

Ex: Plastic, wood, etc.

Dt- 10-12-19

✓Mineral

Minerals are the naturally occuring inorganic compound of one or more metals associated with the non-metals such as oxygen, sulphur, etc.

✓Ores.

Ores are the metal bearing minerals from which the metal can be extracted economically.

ex: Haematite, Bauxite, etc.

✓Alloys.

These are obtain by the mixing of two or more metals, with or without non-metals. Especially to give greater strength or resistance to corrosion.

Ex: Steel → content: Fe (Iron)
C (carbon)
Cr. (Chromium)
Mo (Molybdenum)
Ni (Nickel).

Alloys with their elements (Assignment No. 02)

Alloy

1. Aluminium → ~~Bim~~ Birmabright (Magnesium, Manganese)
★ Used in car bodies. mainly used in Land Rover cars.
→ Duralumin (copper)
→ ~~Hindu~~ Hiduminium (2% copper, iron, nickel)
★ used in aircraft pistons
→ Hydronalium (upto 12% magnesium, 1% manganese)
→ Ni-Ti-Al (Titanium 40%, Aluminium 10%)
→ Y-alloy (4% copper, nickel, Magnesium)

2. Chromium → Nichrome (Nickel)
Ferrochrome (Iron)

3. Beryllium → Lockalloy (62% Beryllium, 38% Aluminium)

4. Bismuth → Rose metal (lead, tin)
Cerrosafe (lead, tin, cadmium)

5. ~~Megallium →~~

5. cobalt → Megallium (cobalt, chromium, molybdenum)
Vitallium (cobalt, chromium, molybdenum)
Stellite (chromium, tungsten, carbon)
Talonite (Tungsten, molybdenum, carbon)

6. copper → Brass (zinc)
Gun metal (tin, zinc)
Bell metal (tin)
Guanin (gold, silver)
copper hydride (hydrogen)

7. Gallium → Al Ga (Aluminium, gallium)
Galinstan (Indium, tin)
Galfenol (Iron)

8. Gold → Rhodite (Rhodium)
Rose gold (copper)
Crown gold (silver, copper)
colored gold (silver, copper)
white gold (nickel, palladium).

9. Indium → Field's metal (bismuth, tin)

10. Iron → Elinvar (Nickel, chromium)
Fernico (nickel, cobalt)
Invar (nickel)
cast iron (carbon)
Steel (carbon)
High speed steel (Tungsten 18%, chromium 4%, vanadium 1%)

11. Mercury → Amalgum
Ashtadhatu

12. Nickel → Alnico (Aluminium, cobalt)
Chromel (Chromium)
Nichrome (chromium)
Ferronickel (Iron)
Hastealloy (Molybdenum, chromium, tungsten)

13. Silver → Goloid (copper, gold)
Electrum (gold)
Sterling silver (copper)
Tibetan silver (copper)

14. Titanium → Ni - Ti - Al (Titanium 40%, Aluminium 10%).
6al - 4v (Aluminium, Vanadium)
Titanium hydride (hydrogen)
Titanium gold (gold).

15. Tin → Babbitt (copper, antimony, lead)
Solder (lead, antimony)
Queen's metal (antimony, lead, Bismuth)
White metal (copper or lead)

16. Uranium → Staballoy (depleted uranium with other metals, usually titanium or molybdenum)

17. zinc → Zamak (aluminium, magnesium, copper)
Electroplated zinc alloys.

iium) 1%.)

Occurance Of Minerals

Minerals mostly occurs in the nature in the form of oxide, sulphide and halides.

Minerals : 1) Oxide
2) sulphide
3) halides.

Ex. Cinnabar → HgS
Beryl → $Be_3 Al_2(SiO_3)_6$
Chalcopyrite → $CuFeS_2$
Dolomite → $CaMg(CO_3)_2$
Tourmaline → $((Na Li K)_6 (Mg Fe Ca)_3 (Al Cr Fe)_2 B_2 SiO_5)$

Assignment No: 03.

THE PERIODIC TABLE

Assignment No: 03.

THE PERIODIC TABLE

magnetic property

1 H 1																	2 He 4
3 Li	4 Be											5 B	6 C 12	7 N 14	8 O 16	9 F	10 Ne
11 Na	12 Mg											13 Al 27	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe 56	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 - 71	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au 197	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 - 103	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn						

Noble gases

57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

CHAPTER NO: 02.

Agglomeration

It is process where high value of fines materials are made into lumpy mass which is suitable for charging into furnace.

There different process of agglomeration.

(a) Briquetting
(b) Nodulising
(c) Vaccum extrusion
(d) Sintering
(e) Pelletising

Briquetting

It consists of pressing of ore fines with or without a binder in to a block or Briquette of some suitable size and shape and then subjecting to a hardening process.

→ A wide range of organic and inorganic binder like tar, pitch, sodium silicate, limestone, cement, etc have been used.

→ Fine ore mixed with water was pressed into blocks which were hardened in a tunnel kiln heated to about 1350°C

→ These are produce from DRI fines generated during handling and it is also used in solid charge in electric steel making

Nodulising

In the nodulising process flue dust, pyrite residue or fine ore concentrate along with some carbonaceous materials like tar are passed through a rotatory kiln heated by gas or oil.

→ The feed travels counter-current to the gases.

→ The kiln is inclined slightly to the horizontal

→ It rotate at 1-2 r p m, 30-60 m in length, diameter of the feed end is 3m.

→ Time taken about $1\frac{1}{2}$ to 2 hour

Vaccum extrusion

It is basically used in ceramic industry.

→ Moist ore with or without bentonite as a binder is feed in the de-airing chamber and extruded into a cylindrical product which is cut into desired small size

→ This product is dried and fired before use in the blast furnace.

Sintering

It is a process of heating a mass of fines particles to the stage of incipient fusion for the purpose of agglomeration then in to lumps

→ Metal powder compact are sintered to obtain desired solid shapes.

→ The main aim is to produce a strong but porous agglomerate from a sandy mass.

→ Heating the entire bed of fine particles to the temperature required for sintering as is done in powder metallurgy.

Pelletising

It is a process consist of rolling of moist iron ore fines of less than 100 mesh size, with or without a binder into balls of usually 7-20 mm in size

→ This green balls lack necessary strength these are dried, preheated and fired to produce hardened balls which are an excellent feed for a blast furnace

10/10

V. Good

→ Disc Pelletizer. - 3rd sem note.

→ DL sinter machine - 3rd sem note.

Drying

Drying means the removal of moisture or water from any material. Generally, solid materials are dried by heating so that water present in it, is evaporated.

Calcination

Calcination is a thermal treatment of an ore where it is heated to required temperature in the absence of air or limited amound of air to eliminate moisture and volatile matter as well as decomposition of ore takes place

Eq: $CaCO_3 \xrightarrow[840^\circ C]{\Delta} CaO + CO_2\uparrow$.

→ It is an endothermic reaction and it is carried out inside the kiln.

→ It require fuel for decomposition

Roasting

→ Roasting of an ore is a concentration process in which ore is heated in the presence of air for the conversion of sulphide nature ore to oxide nature ore.

→ Oxide ore is ~~more~~ easy to reduce the metal than sulphide, so all the sulphide ores are heated to proper roasting temperature for converted into another chemical form.

→ In roasting sulphur is removed. Simultaneously other volatile matter like Arsenic, Tellurium volatilised

Catalyst: Alter the rate of reaction.
→ Increase in the rate of reaction.

Types of roasting

1) Oxidising roasting
2) Volatilising roasting
3) Chloridising roasting.

some other kind of roasting are,

1- Sulphatic roasting
2- Magnetic roasting
3- Reduction roasting
4- Blast roasting or sinter roasting.

1. Oxidising roasting

→ It is the most important roasting process where sulphur is replaced by oxygen.

→ The general reaction is.

$$\text{Metal sulphide} + \tfrac{3}{2}O_2 \longrightarrow \text{Metal oxide} + SO_2.$$

As example:

$$ZnS + \frac{3}{2} \cdot O_2 \longrightarrow ZnO + SO_2.$$

Note:

Dead roast: When the sulphide ore is roasted to a point where almost the entire sulphur is eliminated then the residue is called dead roast.

→ During roasting some sulphates are also formed which required high temprature for its break up. So, roasting is depends on factors such as time, temp^{r} & availability of O_2 in air.

(2) Volatilising Roasting

→ In this roasting volatile oxides are eleminated such as As_2O_3, Sb_2O_3 & ZnO from an ore.

→ During roasting oxygen should be care controlled otherwise higher oxides are formed those are non-volatile oxide and remain in the ores.

(3) Chloradising Roasting

→ Chlorodising roasting is carried out to convert metal compounds to chlorides under oxidising or reducing condition.

→ Many metals are extracted from their chloride Uranium, Berilium, Neobium (Nb), Zirconium (Zr), Titanium (Ti)

→ Some chlorodising reactions are

$$2NaCl + \underset{\text{Metal sulphate}}{\underline{MS}} + 2O_2 = Na_2SO_4 + MCl_2$$

$$4NaCl + \underset{\text{Metal Oxide}}{\underline{2MO}} + S_2 + 3O_2 = 2Na_2SO_4 + 2MCl_2.$$

→ In the 1st reaction, sulphide nature of material is converted into chloride nature and in the 2nd reaction oxide nature of material is converted into chloride nature.

(4) Sulphatic roasting

In this roasting, sulphide ore is converted to sulphate.

(5) Magnetic roasting

In this roasting, hematite is converted to magnetite

(6) Reduction roasting

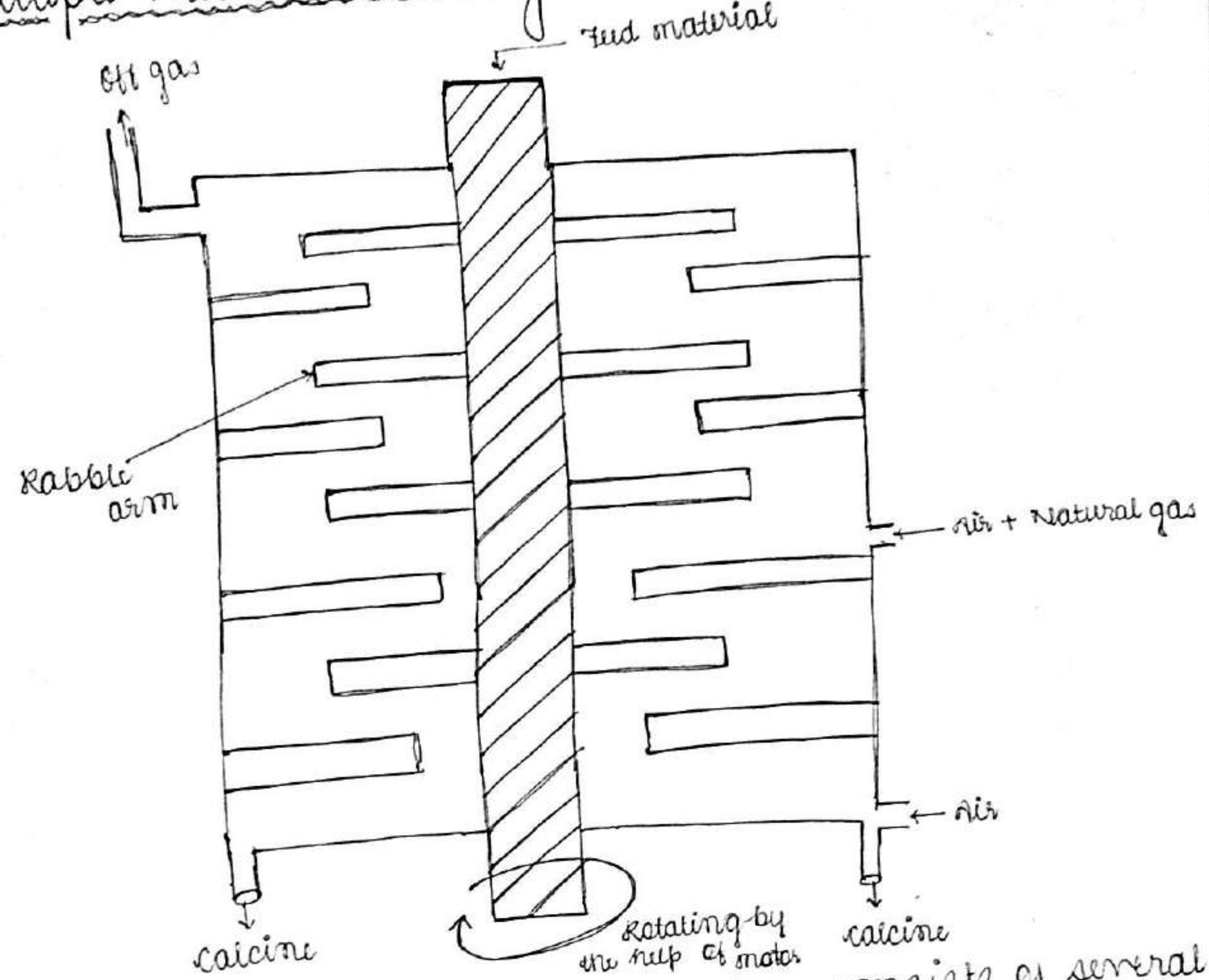
In this roasting, ore are reduce and removal of oxygen is takes place.

⇒ Different types of roasting practices :-

Generally roasting is carried out by 4 units

1.) Multiple hearth roasting
2.) Flash roasting
3.) Fludised bed roasting
4.) Sinter roasting.

1) Multiple hearth roasting



→ It is a MC dougall type roaster consists of several circular brick hearth

→ The entire structure is enclosed in a cylindrical brick steel shell

→ Revolving mechanical rabbles are attached with the central shaft which is always rotated in its own axis.

→ The feed is given at the top which is distributed on the top rabble.

→ Gradually, the materials are moves downward & finally reach to the bottom.

→ The oxidising gas/air flow upward from bottom to top and counter current in nature with the materials.

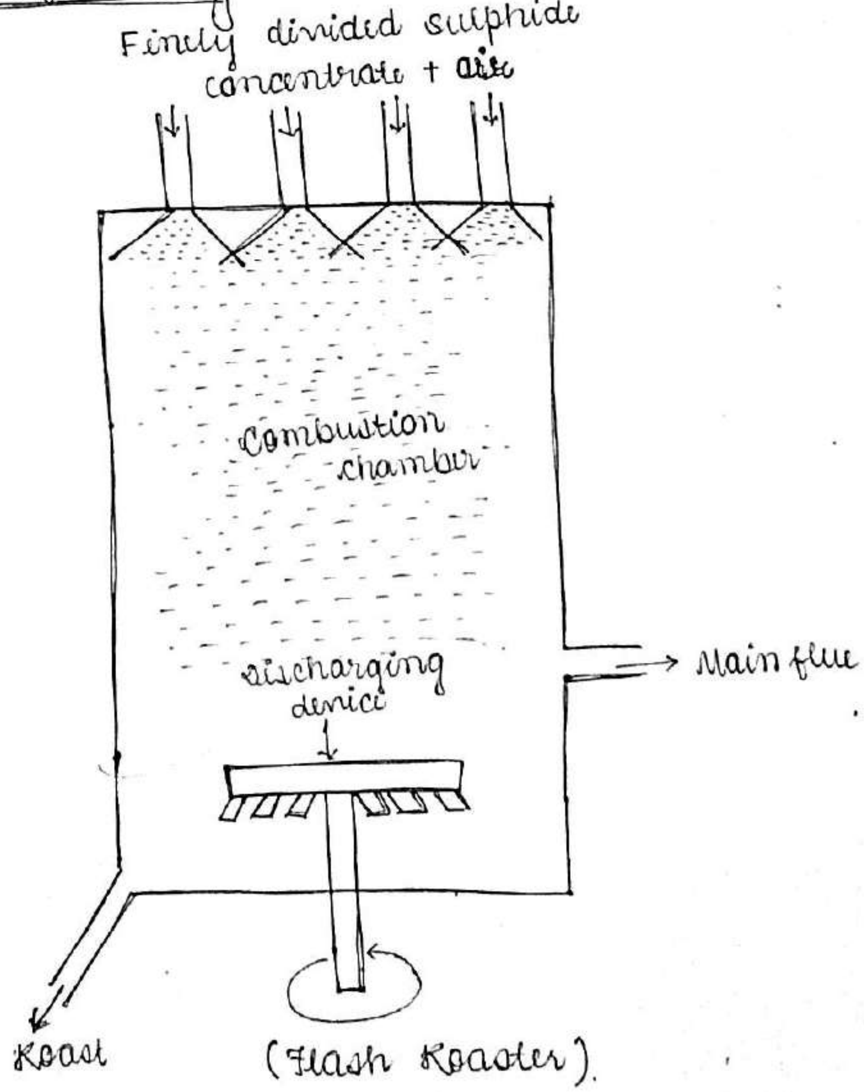
→ Air and natural gas is given to increase the temp$^{\circ}$ of the chamber as required.

→ All the roasting reaction takes place during the movement of material from top to bottom.

→ Finally roasting product / calcine collected at the bottom and the gaseous product SO_2 collected in the top as off gas.

✱ SO_2 is used to manufacturing of H_2SO_4 (Sulphuric Acid)

2) Flash Roasting



(Flash Roaster).

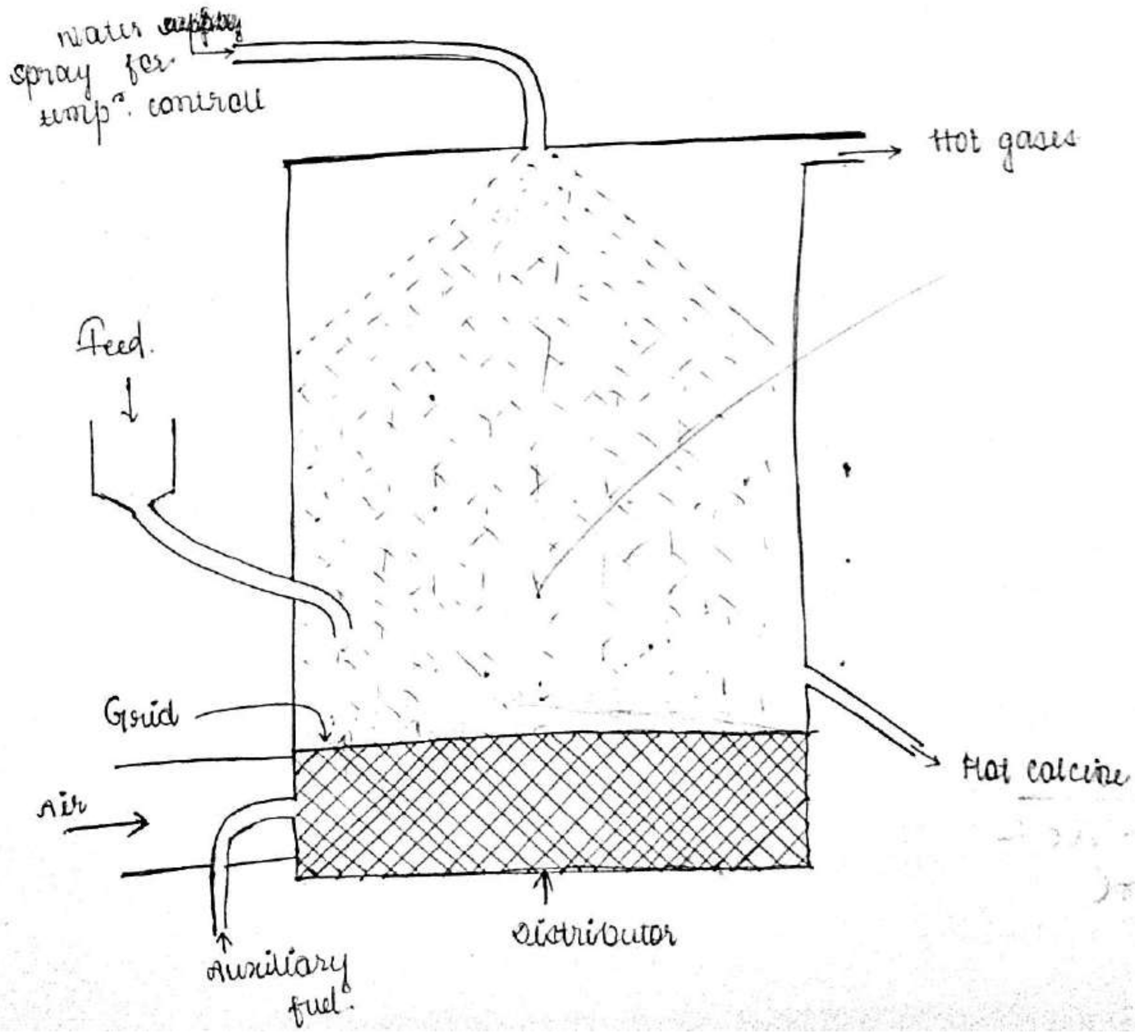
→ In flash ~~smelting~~ roasting pre-heated ore particles are fall with the hot air. So, instantaneous oxidation or flashing type of combustion takes place inside the combustion chamber.

→ sulphide nature is converted to oxide nature during the flashing.

→ Finally roasted product fall on the bottom and out from the chamber by discharge device.

→ The product gas comes out as a main flue from the chamber.

3.) Fluidised bed roasting :-



→ When the gas is pass upward through solid bed particle of small diameter about (0.005 to 0.05)cm

→ The behaviour of bed changes w.r.t the velocity of gas passing through it.

→ This roasting followed 5 stages.

Stage - 1:

when the gas flow rate is very low, gas can move easily through the porous of fine particle without disturbing it. so, there is no pressure drop in this stage

Stage - 2

As the gas velocity increases the bed expands upward due to the force of gas stream

→ There is some pressure drop in this stage

Stage - 3

When the gas velocity further increase a stage will reached where the pressure drop across the bed is equal to the weight of the particle of the bed

Now, the particles are individually in suspended state

Stage - 4.

again increase in pressure the bed continue to expand due to increase in inter particle distance

Good Work

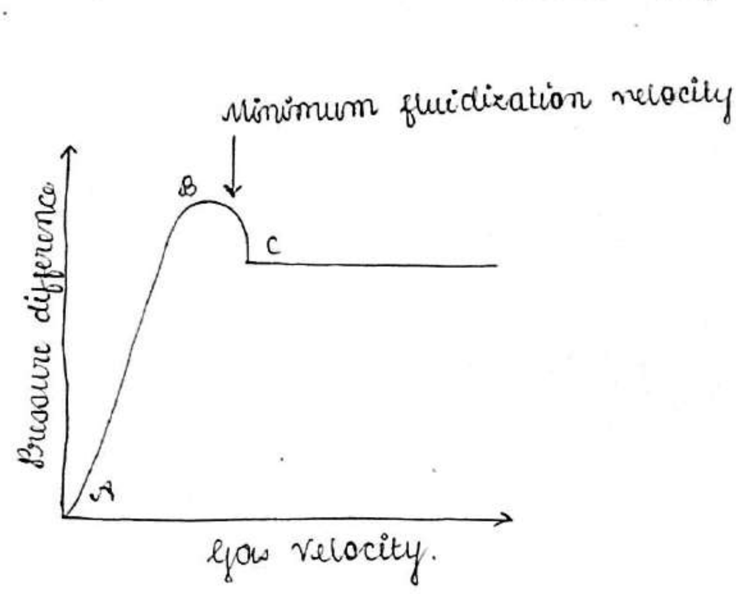
Stage - 5

Finally a stage will reached when the expansion of bed becomes independent of gas velocity.

Now, the out coming gas appears in the form of bubble, bursting on the surface of ~~[illegible]~~ bed which looks like a well stired boiling liquid

In this condition the bed is said to be fluidised and all the roasting reaction takes place during this stage

Relationship between pressure drop and gas velocity.



→ This is a fluidisation curve where fluidization behaviour is graphically represented.

→ In this figure AB represent the pressure drop for the stationary bed before fluidization occurs.

→ As the pressure drop across the bed reaches to the lifting point the bed is rearranged to provide minimum resistance to the gas flow as indicated by the segment BC.

→ Point C indicate the maximum void of the bed beyond C the pressure drop independent of the gas velocity and became constant graph on the curve.

Sinter roasting / Blast Roasting

→ Ore fines are agglomerated before they can be charged into the B.F. otherwise dust may loss or choke the furnace.

→ Sinter roasting is the treatment of sulphide ore in the sintering machine where roasting and agglomeration takes place simultaneously.

→ It is carried out in Dwight-Lloyd sintering machine.

→ The fine concrete is large as a layer of (15-20) cm thick on to an endless reclaiming grates pellets which move over the wind box.

→ At the start of the bed charge material are charged and combust-ion takes place.

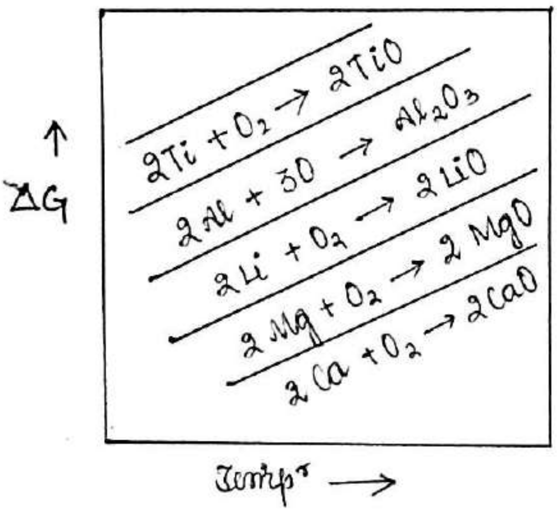
→ Then the combustion propagate through out the mass with the help of wind box which suck the air in down draught state.

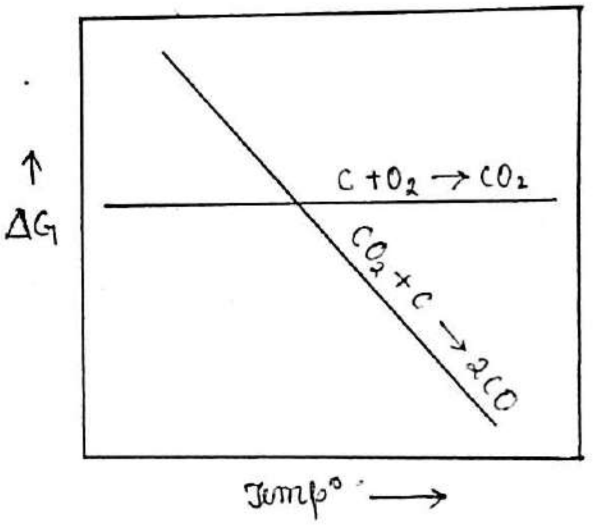
→ The combustion zone temperature is about incipient fussion temperature of the ore.

→ Finally due to the high temperature bonding takes place between the particle as well as roasting occurs.

→ So, large sulphur free mass is discharged at the other end of the sintering machine.

Ellingham Diagram





→ Ellingham diagram used to represent the data in between temperature versus free energy of oxides and sulphides.

→ It is developed by ellingham in 1944 with the formation of oxides and sulphide represented in form of linear plot in a wide range of temperature.

→ This diagram is plotted by taking one mole of gaseous oxidation at one atmospheric pressure combined with pure element to form an oxide.

→ These diagram helps to known stability an oxide at different temp° over another as well as it help to compare the relative reducing or oxidising tendency of different element of different temperature.

→ Highly stable oxides are found at the bottom and less stable oxides are occupy high position.

→ Therefore an element occupying the lower position the diagram can always reduce the oxides of another metal line material above it.

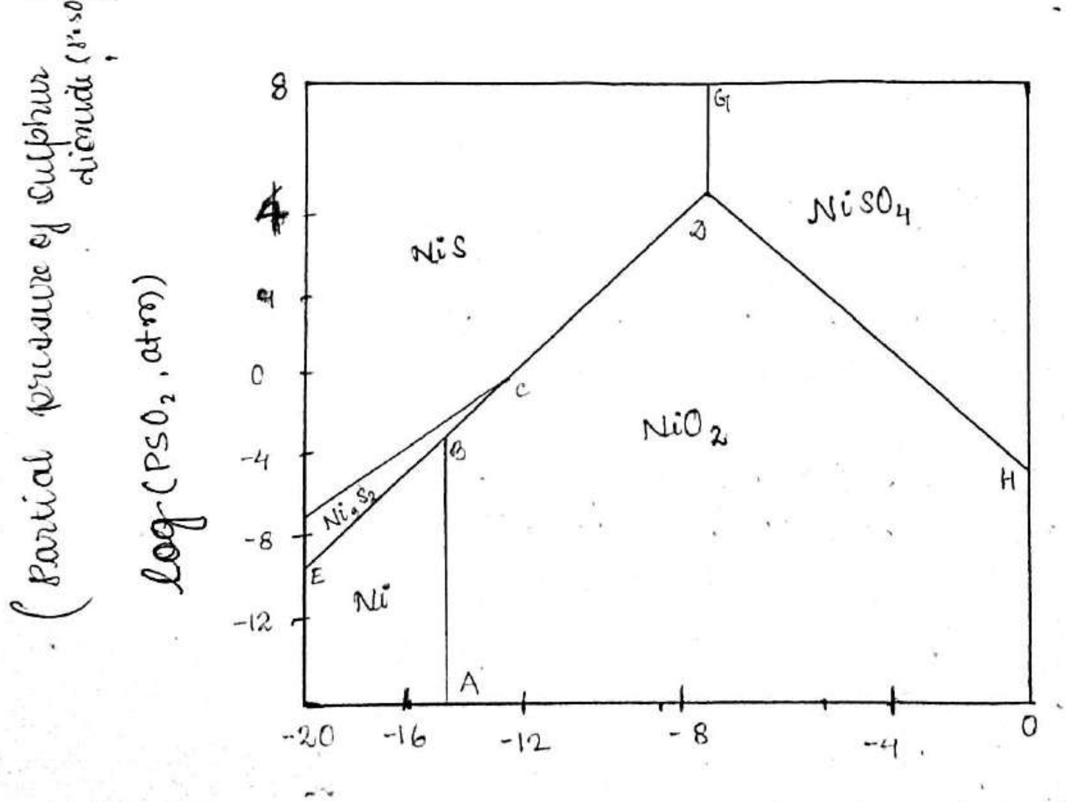
→ CO_2 line is parallel to the temperature axis because their is no increases in free energy with increasing temperature. similarily, CO decreases in slope with increase in temperature. That define the stability of CO increases with increase in temperature.

→ So, CO has tendency to reduces all the oxides at different temperature.

→ Similarily the hydrogen is also a reducer for some oxide but it slope rapidly increases with temperature. So it is a good reducer at low temperature but poor reducer at high temperature.

→ But CO is opposite in nature.

Predominance area diagram



a) Ni-S-O system at 1000 K

(Partial pressure of Oxygen = $P.O_2$)

→ In this M-S-O system we can determine the nature of the product obtained during the roasting and also we can determine the best operating temperature for the roasting.

→ In this diagram the relative stability of different phases can be determine.

→ This diagram is drawn by taking the partial pressure of oxygen and partial pressure of SO_2 in the system.

→ In this ~~system~~ diagram Ni-S-O system is taken as an example at thousand kelvin.

→ The different phases are made of during the roasting are obtain such as NiS, NiS_2, Ni, $NiSO_4$, NiO, etc.

→ The iron oxide reduction by aluminium may be called as aluminothermic reduction.

Smelting

→ It is a heating process for the production of metals and matte.

→ Generally the process is one of the reduction of the oxide of the metal with carbon, sulphur, sulphide in a suitable furnace (B.F., Electric arc furnace, Reverbarotory furnace).

→ During smelting the gangue present in the ore is generally less fusible than the metal.

→ So flux may be added to reduce the melting point of the gaunge and form slag.

→ The smelting process for the metal extraction can be written as.

Minerals + gangue + Reducing agent = Metal/matte + slag + gas

Characteristics of the smelting

→ Reduction smelting is carried out in a B.F. and matte smelting is carried out in reverbaratory furnace.

→ The material to be smelted are usually charge in solid state.

→ The heat required for smelting is usually supplied by external source.

→ The product of smelting furnace are in liquid state.

→ The solid material that escape in the dust that is carried away by the furnace gas.

→ In reduction smelting the ore is reduce by carbon in the presence of flux produce molten metal and slag.

→ sometimes reduction is brought about by another metal whose oxides are much more stable than those of the metal being extracted then

→ In the other hand in matte smelting reducing agent is not used

→ The sulphide itself act as a reducing agent in this operation metal is not produce. The product is molten matte or molten slag.

Matte

→ It is a term used in the field in the pyrometallurgy given to the molten metal sulphide phases. Typically form during smelting of Cu, Ni and other base metal.

→ A matte is a phase in which principle metal being extracted is recovered prior to a final reduction process to produce a crude metal.

→ Matte is also used to collect impurities from a metal phase such ~~in~~ the case of antimony smelting.

✓ Flux

→ In smelting a flux is used to low both the liquidious temperature and viscosity of the slag.

→ Flux is classified according to their chemical nature.

- i) Acidic flux (SiO_2)
- ii) Basic flux (CaO, MgO)
- iii) Neutral flux (CaF_2, Na_2SO_4).

Slag

The two main function of a slag are to collect the unreduce gangue material and form a separate layer in metal extraction process.

→ slag have following properties

i> The difference between the specific gravity and the slag metal should be sufficiently high so that one can easily separated from the other.

ii> The slag must be fluid enough to permit is easy separation from the metal and also mass transformation between the metal and slag.

Smelting furnace

→ The Blast furnace has must popular furnace for reduction smelting where smelting of iron ore is carried out.

→ simultaneously lead is also a metal which is extracted in the B.F.

→ For sulphide smelting reduction is not necessary so it is carried out in Reverberatory furnace.

→ No special furnace is required for the metallo-thermic reduction.

→ It is carried out by using B.F.

Converting of Matte

Converting of matte provide conversion of metal sulphide to metal.

→ In this process ~~metal~~ matte is oxidised by blowing oxygen into the matte.

→ The oxygen purity is about 99.99%.

→ During blowing the unwanted impurities and sulphur react with the oxygen and oxides because it has higher affinity towards oxygen than other metals.

→ Sulphur oxides to form sulphur dioxide with high exothermic reaction.

→ Other impurities are also oxides with exothermic reaction.

↔ This exothermic make the process Autogenious.

Converting of Pig Iron

→ Pig iron which is obtained from the B.F during Iron making.

→ It contains so many impurities like C, P, Si, Mn, Al, S.

→ All these impurities are mixed up in the iron during iron making. so it should be eleminated to get pure iron.

→ According to Ellingham diagram all impurities has the maximum affinity toward oxygen than Iron.

→ so in converting process 99.99% pure oxygen is blown.

→ During ~~[illegible]~~ blowing all the impurities are oxidised and escape out as a slag when mixed with the flux.

→ carbon and sulphur oxide product is CO. and SO_2 which comes out in the form of gas.

→ After removal of this impurities 'Fe' becomes converted to steel because it contain 'Fe' and some amount of carbon.

Hydrometallurgy

→ Hydrometallurgical treatment was originally for low grade ore.

→ The different steps are form in hydrometallurgical process are

i) Preperation of ore for leaching.

ii) leaching.

iii) Separation of leach liquior

iv) Recovery of metalic value for leach liquor.

v) Recycling of leach liquior.

1. Preparation of ore from leaching

→ It include crushing, grinding and concentration or removal of unwanteds.

→ The separation may be carried out by physical method or by chemical method. such as froth floatation, calcination and rusting.

2. Leaching

In Leaching the metallic value is an ore selectively dissolves using a suitable liquid reagent.

→ The selectivity depends on cost of agent rate of dissociation, temperature, pressure and density of the leaching agent.

3. Separation of leaching liquior

→ The leach liquior is separated from the residue after the leaching by settling thickning, washing (filtering)

4. Recovery of metallic value ~~of~~ for leach liquior

→ The metallic value are recover from the leach liquior by employing one of the following process namely.

a.) Precipitation
b.) Cementation
c.) Electrolysis
d.) Ion exchange
e.) Solvent extraction

5. Recycle of leach ~~liquior~~ liquior

Leach liquior is recycle after it has been purified and its composition and readjusted.

Objective of hydrometallurgy

→ To produce a pure compound which can later be proceed by pyrometallurgical process.

→ To produce metal from the crude metal or crude metal, compound

→ To produce the metal directly from the ore or concentration

Advantage of hydrometallurgy

→ This are ideal for lean and complex ore.

→ It has greater control on the process than other method

→ Pyrometallurgical process developed by-product are not environmental friendly. but hydrometallurgical leaching process eliminate this.

→ Pyrometallurgical process use metallurgical coke as a heating & reducing agent source which is costly, it can be eliminated by aqueous solution process.

→ Now a day, demands for both quality and quantity of metals.

→ Hydrometallurgical can produce metals of different physical form such as powders, nodules, etc.

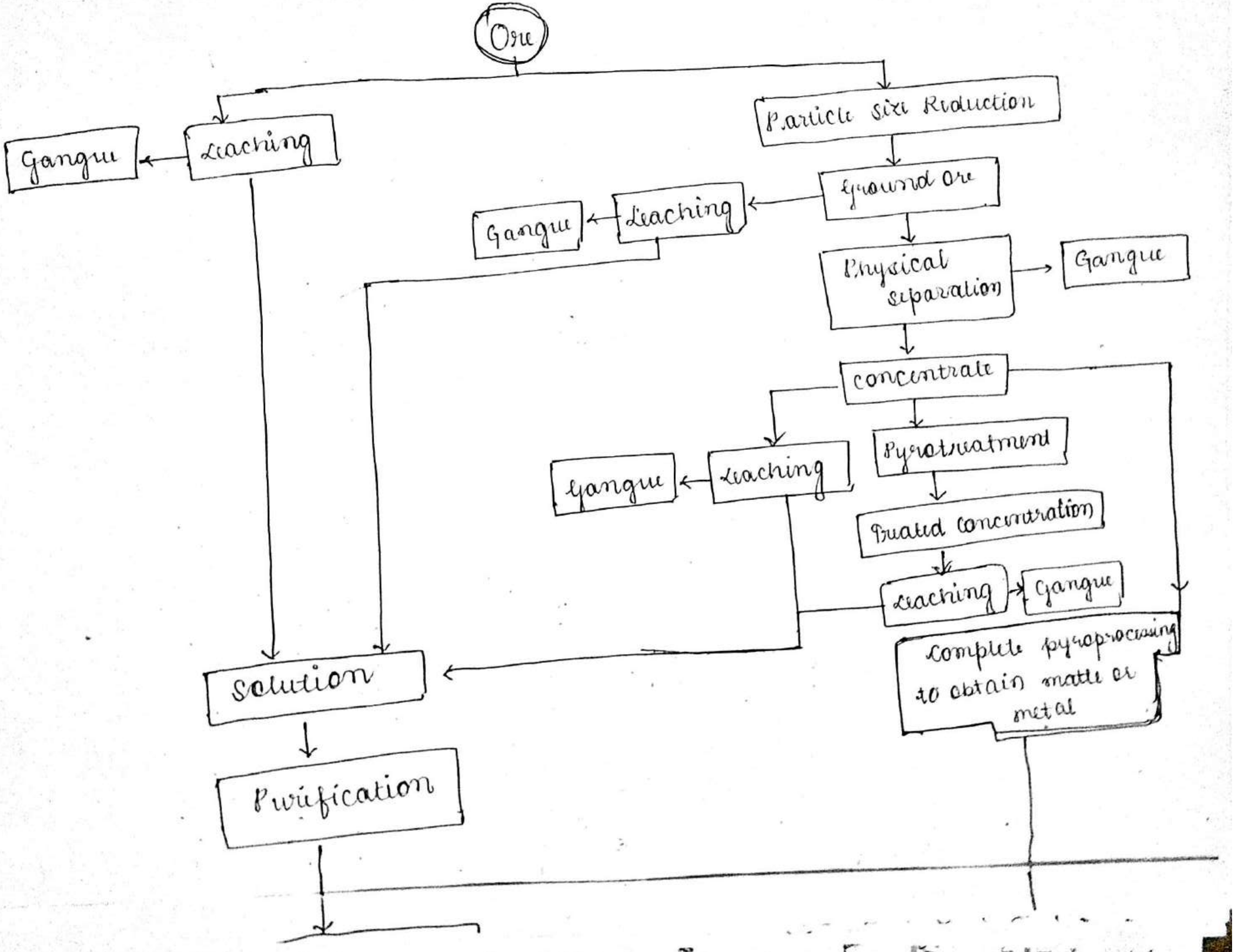
→ (Pyrometallurgical process required to liberate temp°

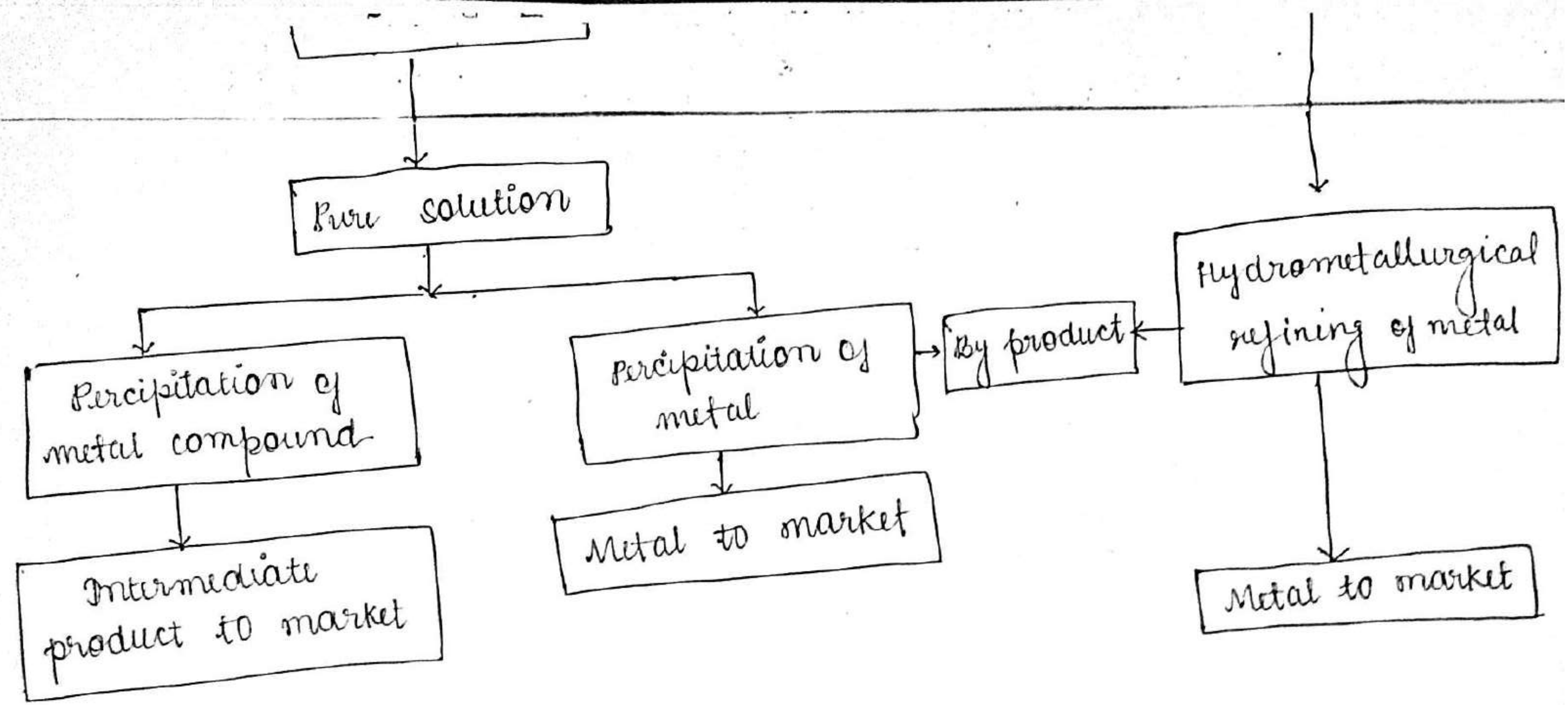
Pyrometallurgical process required temp°)*

but hydrometallurgical process required temp°

→ Hydrometallurgical leaching operation are carried out at room temp° or at slightly elevated temperature.

→ In hydrometallurgical process the waste liquid can be completed recycle.


Ore
Particle size Reduction
Leaching
Gangue
Ground Ore
Leaching
Gangue
Physical separation
Gangue
concentrate
Pyrotreatment
Leaching
Gangue
Treated concentration
Leaching
Gangue
Complete pyroprocessing to obtain matte or metal
Solution
Purification



* Flow sheet of Hydrometallurgical process

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This are ideal for lean and complex ore.

→ It has greater control on the process than other method

→ Pyrometallurgical process developed by-product are not environment friendly but hydrometallurgical leaching process eliminate this.

→ Pyrometallurgical process use metallurgical coke as a heating and reducing agent source which is costly, It can be eliminated by aqua solution process.

→ Now a days demands for both quality and quantity of metals.

→ Hydrometallurgical can produce metals of different physical forms such as powder, nodules, etc.

→ Hydrometallurgical leaching operation are generally carried out at room temperature or at slightly elevated temp°.

→ In hydrometallurgical process the waste liquid can completely recycle.

Different types of leaching process

There are several type of leaching operation.

- i) In-situ leaching.
- ii) Dump leaching.
- iii) Heap leaching.
- iv) Percolation leaching.
- v) Agitation leaching.
- vi) Bacteria leaching.
- vii) Pressure leaching.

In-situ leaching

It is a leaching carried out of the shatter rock reduce left behind in a mine after the major mining operation.

Dump leaching

It is a leaching of off grade are required from normal mining operation is called dump leaching.

Heap leaching.

When high grade ores are leached then it is called heap leaching.

Percolation leaching

In this, leach solution perculated upward and downward through an ore which has crushed and proper bedded in a tank.

→ The bed should have proper permeability for better leaching operation.

Agitation leaching

→ In agitation leaching, stirring is used to aid the dissolution process.

→ There could be variations; for example, atmospheric or high pressure operation, continuous cocurrent or continuous counter current modes. and single-stage or multistage leaching

Bacterial or Microbial leaching

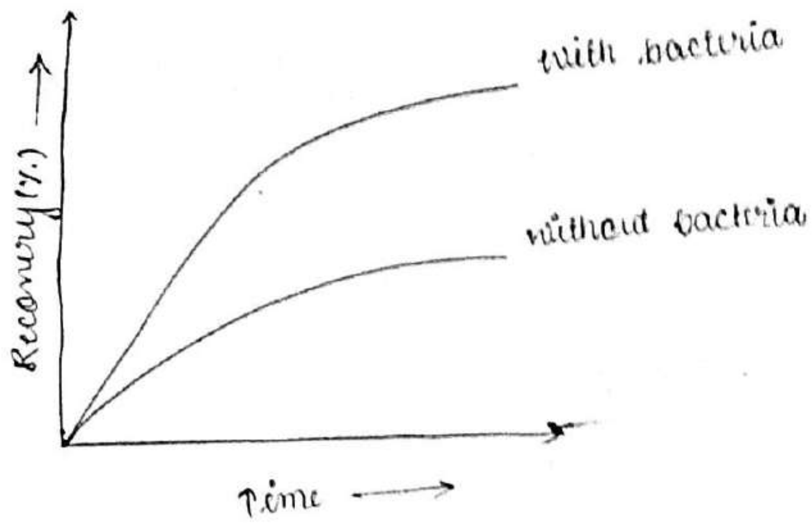
Natural leaching process are very slow and takes year to year for dissolution. so it can not be used for effective commercial process.

→ However in the early part of twenty century it was accidently discovered that certain type of bacteria speed up the natural conversion process.

→ The mineral sulphide that leach faster in the presence of suitable type of bacteria are bornite, chalcopyrite, galena, pyrite, stichnite, sphalerite.

→ Bacteria leaching not only enhance the dissolution rate but also increases the recovery rate.

→ Bornite (Cu_5FeS_4)
Arsenopyrite (FeS_2)
Galena (PbS)
Chalcopyrite ($CuFeS_2$)
Covellite (CuS)
Tetrahydrite ($Cu_8Sb_2S_7$)



→ The three important Bacterias are
- i.) Thiobacillus thioxidans
- ii) Ferrobacillus Ferro- oxidans
- iii) Thiobacillus Ferro- oxidans

→ These bacterias are capable to grow inorganics media sometime enzyme is used to act as a catalyst for the leaching process.

Pressure leaching

When a solid dis- solvent in leaching reagent the change in total volume takes place.

→ Pressure is a unit which has influence on leaching process.

→ Pressure shift the equillibrium condition and favour for better disolution.

→ Beside the reason in many leaching process are increased ~~by leaching~~ pressure is advantageous.

→ We know that rate of dis- solution is increased by leaching at a high temperature.

→ Some leaching process are carried out at a tempr of 200 °C. So, pressure is applied to maintain it in liquid state without vapourization. So in most of the cases pressure is applied for the better leaching process.
Ex: Leaching of bauxite with leaching reagent NaOH at a temperature of 220 °C and pressure 25 atm.

ZONE REFINING

→ Zone refining principle based on the solubility of impurity in the solid and liquid.

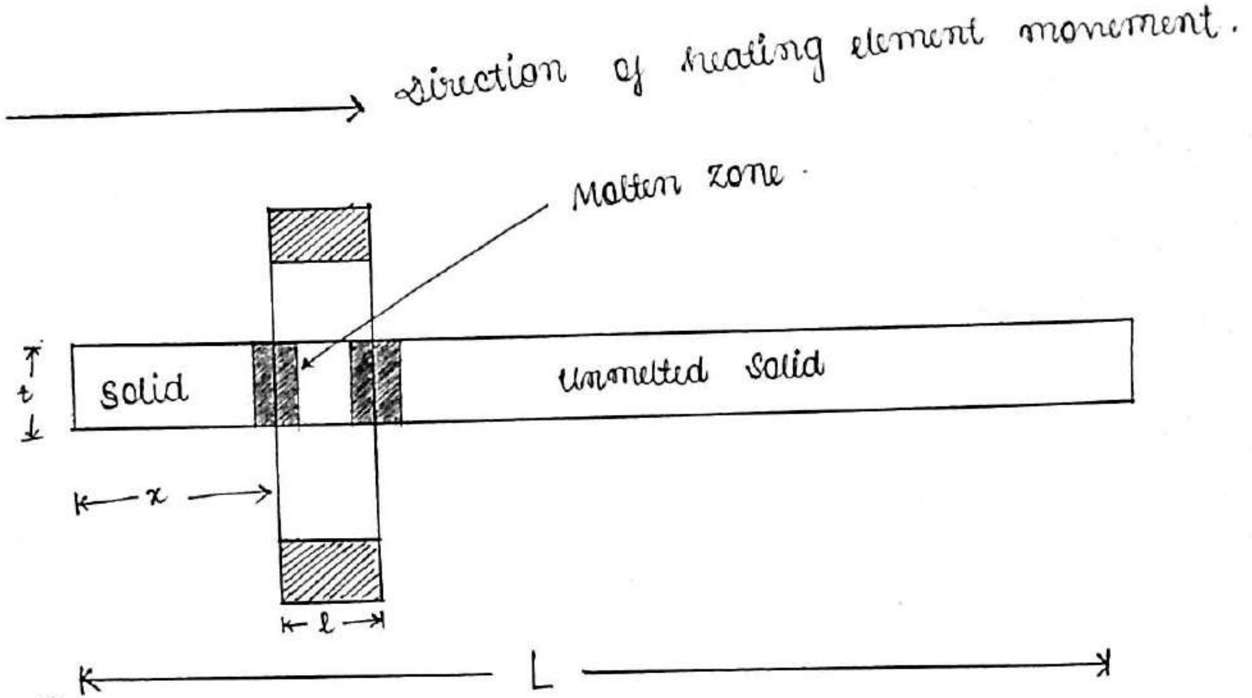
→ According to the Isomorphous system, we can determine that at a particular temperature the alloy can be found solid as well as liquid state.

→ This depends on the impurities or solute content in the pure metal.

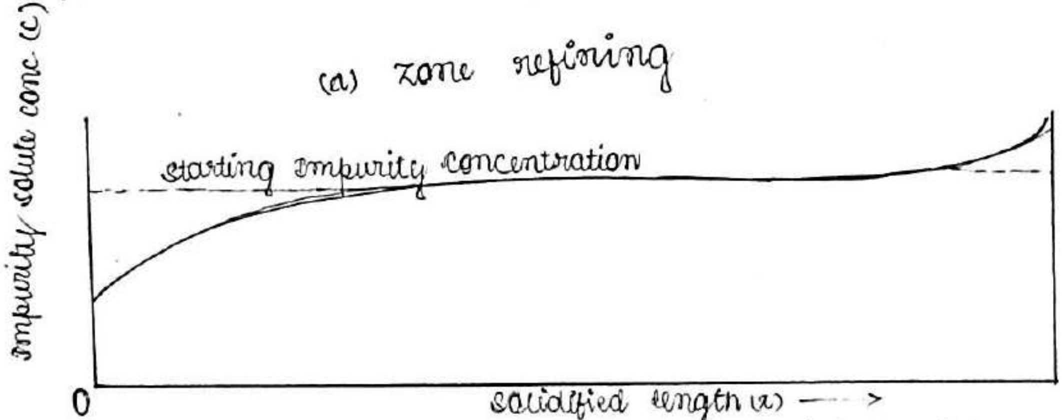
→ This diagram reveals if the solute content is more, than the metal has lower melting point and when the solute content decreases the melting point of pure metal increases.

→ From this principle, we conclude that, the alloy liquid has the maximum solubility with the impurities as compare to solid.

→ In zone refining same principle is carried out.



(a) zone refining



→ Let us consider a rod of ~~[illegible]~~ element 'a' which content ~~[illegible]~~ element 'b' as an impurities.

→ The length of the bar 'L' and it is thickness 't'

→ The zone heating eleminate move gradually from Left to Right.

→ At the initial position, all the same zone of rod liquified and when it move to the nearest zone the previous zone get solidified and create a solid-liquid interface with the heating zone.

→ Due to solubility differentiation between the solid and liquid at the solid and liquid interface impurities moves from solid to liquid zone and this is gradually move to end of the rod.

→ The solute concentration of left the bar decreases and it ~~incr~~ increases at the end of the bar.

→ In a single pass all the solute can not be eleminated. so no passage is given to the rod for complete elemination of impurity and get ultra pure rod.

→ Finally all the impurities deposited at the end side of the bar which trimmed out.

→ It is used for the purification of germanium to manufacture of transistor.

FIRE REFINING.

→ Fire refining technic is used to remove more reactive element from a molten metal by preferential oxidation.

→ This techique is suitable for refining Iron, Pb, Sn and Cu.

→ The cheapest reagent available for oxidation is atmospheric oxygen is blown through the metal.

→ Flux is added so that the impurity oxide is removed not as a solid. it reduce the melting point and form liquid oxide.

→ This technique is used for the hot metal refining in open hearth furnace, LD process, in which hot metal or pig iron from B/F. refined by oxygen blowing.

→ In non ferrous industry 'Cu' also refined by fire refining process.

→ In some cases oxygen is provided not from the atmosphere but in the form of salt added to the melt.

Ex: $NaNO_3$ when added decomposed to form Nescent oxygen for the refining.

Faraday's Law of Electrolysis

Electrolysis

Electrolysis is the passage of electricity through an electrolyte with cation moning to the cathode to get reduced. and anions moning towards the anode to get oxidised.

→ An electrolyte is a liquid that conduct electricity

1st law of Electrolysis

The mass of the substance deposited or liberated (cathode / anode) at any electrode is directly proportional to the quantity of electricity passed through the electrolyte

Mathematically,

$$w \propto Q.$$

$$\Rightarrow \boxed{w = zQ.}$$

where, w = weight of the substance deposited or liberated - chemically.

z = coulombs constant or electro equivalent

Q = Quantity of charge.

2nd law of electrolysis

It states that when the same quantity of electricity is passed through several electrolytes the mass of the substance deposited are proportional to their respective electro-chemical equivalent or equivalent weight.

$$\text{Chemical Equivalent} = \frac{\text{Atomic weight}}{\text{valency}}$$

Electrometallurgy

→ It includes all metallurgical process which utilize electricity and electrical effects.

→ A large number of operation is carried out.

→ process use electricity supply like electrowinning, electrorefinning and electro-deposition.

Electrowinning

The process that produces a metal by the electrolysis of an aqueous solution or a fused salt.

Electro refining

It is a refining process based on electrolytic phenomenon

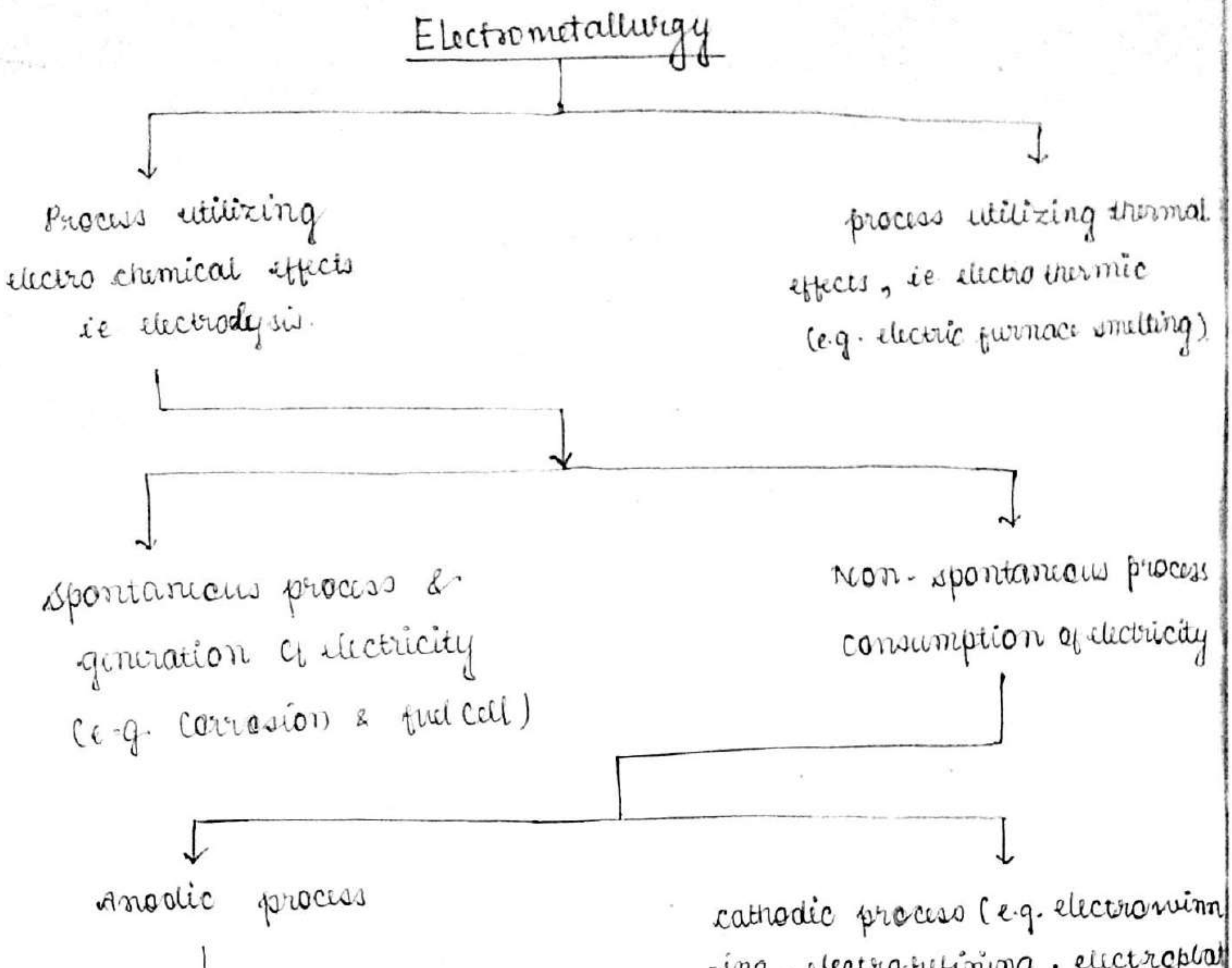
Electrodeposition

The technique of deposition of one metal on another at the cathode.

* some important metal by electrolysis are

Aluminium - 100, sodium - 100, Magnesium - 80, Chromium - 70, zinc - 50, Copper - 10,

* Other metal also extracted Be, Ta, Nb, Ga, Ti, Zr, Hf, B.



(Classification of Electrometallurgical Process)

Electrowinning

→ Electrowinning refers to process that produced a meta by the electrolysis ~~of~~ in an aqueous solution or fuse salt

→ The step involved in the extraction process leading to electrowinning of metal from aqueous solution are leaching of roasted ore to form a soluble in an acid.

$$MO + 2H^+ \longrightarrow M^{2+} + H_2O$$

→ Purification and concentration of leaching liquid.

→ Anode and cathode reaction during electrolysis. at anode (

$$H_2O \longrightarrow H_2O_2 + 2H + 2e^-$$

at cathode, (-)

$$M^{2+} + 2e^- \longrightarrow M.$$

→ During electrolysis the reaction take place at cathode and anode.

→ At cathode the metal ion is discharge and the metal deposit at anode.

Electro Refining

→ Electro- refining is a refining process based on the electrolytic phenomenon.

→ In electro-refining the metal to be refining ~~the metal~~ ~~to be refining~~ is made by anode and the pure metal is deposited on the cathode by taking a suitable electrolyte

→ during passing of current through shell the impurity associated with parent metal dissolve in the electrolytic if there more reaction then the primary metal

Difference betn Electrowinning and Electro Refining

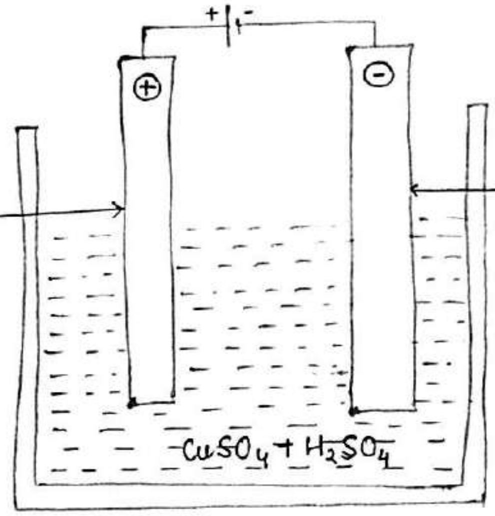
ELECTRO - WINNING	ELECTRO - REFINING
→ Electrowining refers to a process that produces metal by the electrolysis of aqueous solution or fused salt.	→ Electro refining is a refining process based on electrolysis phenom-enon
→ Nature of anode is insoluble.	→ Nature of anode is soluble.
→ Electrochemical reaction is irrever-sible	→ Electrochemical reaction is reversible.
→ More energy is required.	→ Less energy is required.
→ Cell Efficiency is lower	→ Cell efficiency is higher.
→ Power consumption is high- (2-5 v)	→ Power consumption is low (small voltage)
→ Anode product is oxygen.	→ Oxygen is not produces in charge refining.

ELECTRO-REFINING OF COPPER 'Cu'

→ During electro refining of Cu a impure Cu is taken as anode an placed in a tank filled with solution of $CuSO_4$ and H_2SO_4 as electroly

→ The cathode is either pure [illegible] component or stainless steel.

→



$$CuSO_4 \rightleftharpoons Cu^{2+} + SO_4^{2-}$$

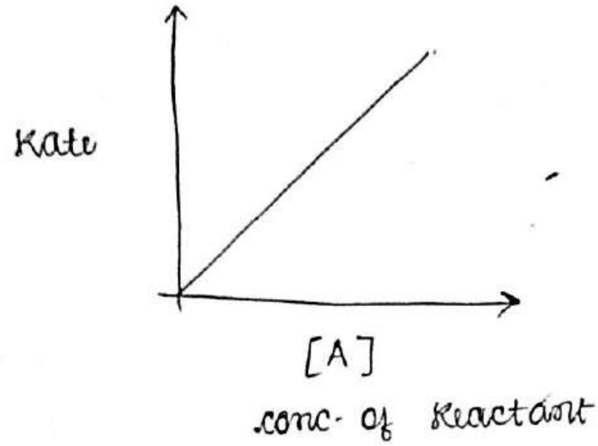
→

1st order Reaction or Kinetics

In zero order $K[A]^0$

$$A \longrightarrow \text{Products}$$

Rate of Reaction (ROR) = r = $K[A]^1$



$$\boxed{\log_e x = 2.303 \log_{10} x}$$

$$A \longrightarrow \text{Products}$$

rate = r = $K[A]^1$

rate = r = $-\frac{1}{1}\frac{dA}{dt}$

$$-\frac{1}{1}\frac{dA}{dt} = K[A]$$

$$\int_{A_0}^{A} \frac{dA}{A} = -\int_0^t K\,dt$$

Let. at $t = 0$, $A = A_0$ (initial)

$t = t$, $A = A$ (remaining)

$$(\log_e A)_{A_0}^{A} = -K(t)_0^t$$

$$\log_e A - \log_e A_0 = -K(t-0)$$

$$\boxed{\log_e A = \log_e A_0 - Kt}$$

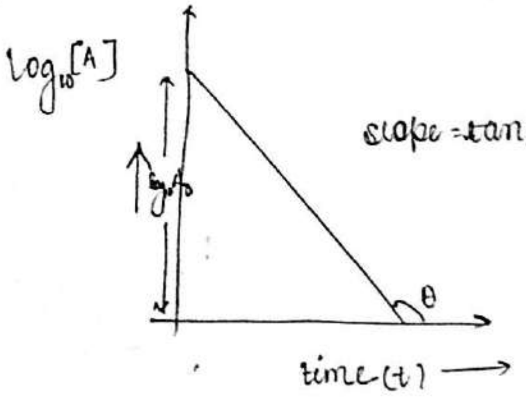
Integrated Rate law

$$2.303 \log_{10} A = 2.303 \log_{10} A_0 - Kt$$

$$\boxed{\log_{10} A = \log_{10} A_0 - \frac{Kt}{2.303}}$$

Integrated Rate law.

Log. of conc. v/s time



slope = tan θ = $\frac{-K}{2.303}$.

First order

$$\log_{10} A = \frac{-Kt}{2.303} + \log_{10} A_0$$
$$y = mx + C$$

Other forms of rate law

$$\boxed{\begin{aligned} \log_e x &= y \\ x &= e^y \end{aligned}}$$

(1) use to solve numericals.

$$\log_{10} A_0 - \log_{10} A = \frac{Kt}{2.303}$$

$$\log_{10} \frac{A_0}{A} = \frac{Kt}{2.303}.$$

$$\boxed{t = \frac{2.303}{K} \log_{10} \frac{A_0}{A}}$$

A_0 → Initial concentration

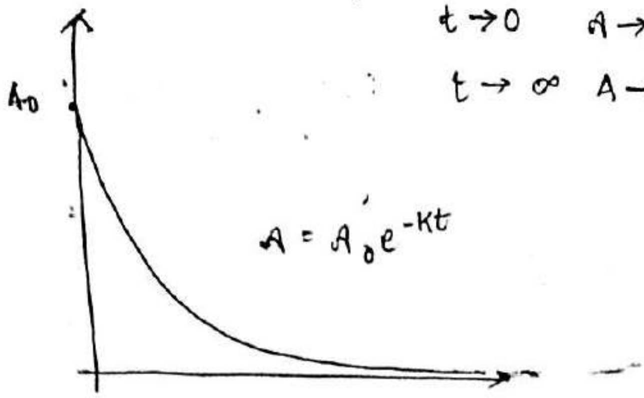
A → Remaining concentration.

(2) $\log_e A - \log_e A_0 = -Kt$

$$\log_e \frac{A}{A_0} = -Kt$$

$$\frac{A}{A_0} = e^{-Kt}$$

$$\boxed{A = A_0 e^{-Kt}}$$ → exponential form.



$t \to 0 \quad A \to A_0$

$t \to \infty \quad A \to 0$

$$\boxed{t = \frac{2.303}{K} \log_{10} \frac{A_0}{A}}$$

$\log_{10} 2 = 0.3$
$\log_{10} 3 = 0.48$
$\log_{10} 5 = 0.7$
$\log_{10} 7 = 0.85$

Half life of Reaction ($t_{1/2}$)

Time in which reaction complete 50%

at. $t = t_{1/2}$

$A = \frac{A_0}{2}$

$$t = \frac{2.303}{K} \log_{10} \frac{A_0}{A}$$

$$t_{1/2} = \frac{2.303}{K} \log_{10} \frac{\cancel{A_0}}{\frac{\cancel{A_0}}{2}}$$

$$t_{1/2} = \frac{2.303}{K} \log_{10} 2$$

$$t_{1/2} = \frac{2.303 \times 0.3}{K} \approx \frac{0.693}{K}$$

$\ln 2$
$\log_e 2$
$= 2.303 \log_{10} 2$

$$\boxed{t_{1/2} = \frac{\log_e 2}{K}}$$

$$\boxed{t_{1/2} = \frac{0.693}{K}}$$

[→ Radioactive element based on 1st order reaction]

Zero order

$$\boxed{t_{1/2} = \frac{A_0}{2K}}$$

First order

$$\boxed{t_{1/2} = \frac{0.693}{K}}$$

Lifetime of Reaction (t_{lf}) ⟶ ∞ (complete at ∞)

time in which reaction completes 100%

at $t = t_{lf}$

$A = 0$

$$t = \frac{2.303}{K} \log_{10} \frac{A_0}{A}$$

$$\boxed{t_{lf} = \frac{2.303}{K} \log_{10} \frac{A_0}{0}}$$

*(1st order reaction never complete to 100%)

*(zero order reaction complete)

$$t_{1/2} = \frac{0.693}{K}$$

$$\boxed{t_{1/2} = \frac{\log_e 2}{K}} \rightarrow \text{used in Radioactivity}$$

$$t_{lf} \longrightarrow \infty$$

$$\boxed{Rate = K[A]^1}$$

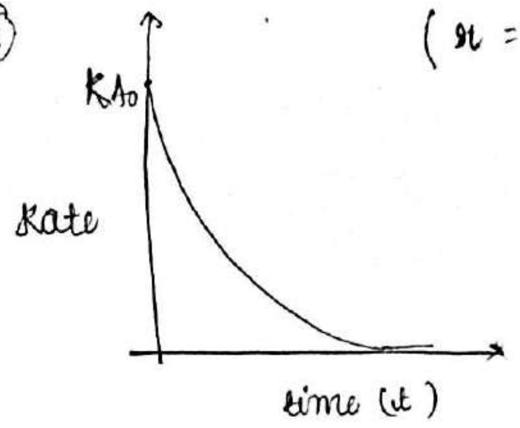
Graphs of 1st order Kinetics

(1)

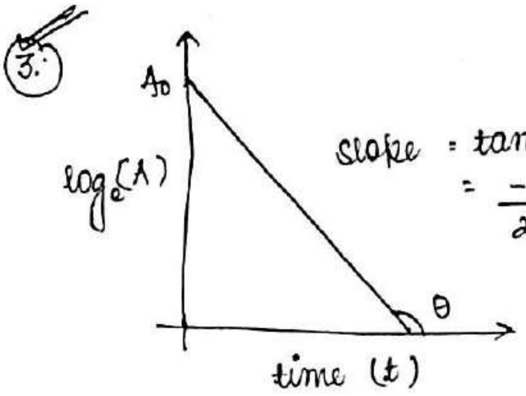
$(r = K[A])$

②

$(r = K A_0 e^{-Kt})$

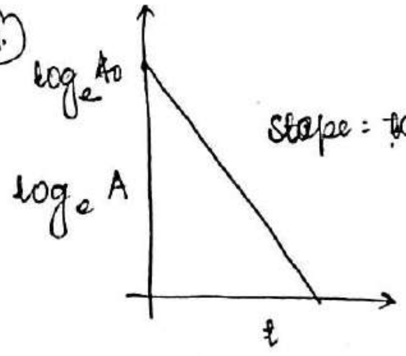


③



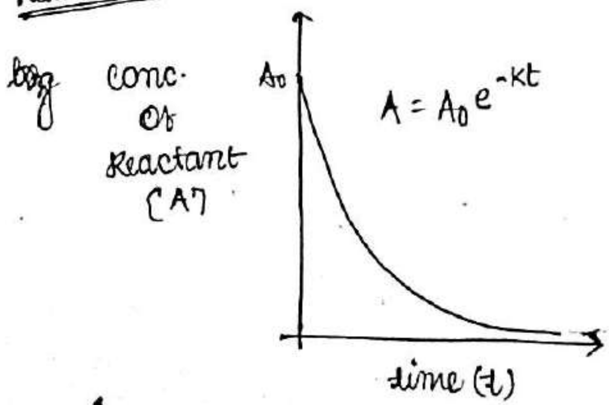
Slope = tan θ
$= \frac{-K}{2.303}$

④



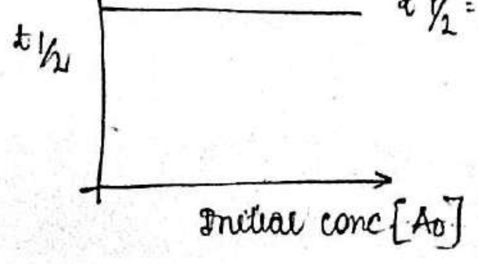
Slope : tan θ = K.

⑤ Radioactivity



$A = A_0 e^{-Kt}$

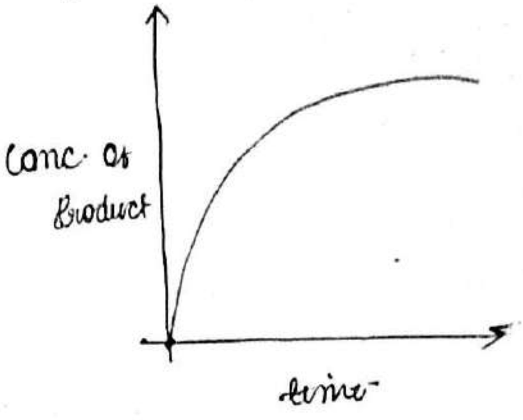
⑥



$t_{1/2} = \frac{0.693}{K}$

⑦

$[B] : x = A_0(1 - e^{-Kt})$



$A \longrightarrow B$

$t = 0 \quad A_0 \quad \cancel{A_0} \quad -$

$t = t \quad A_0 - x \quad x$

$A = A_0 e^{-Kt}$

$A_0 - x = A_0 e^{-Kt}$

$x = A_0 (1 - e^{-Kt})$

Q1. In A first order reaction the conc of reactant decreases from 800 mol/dm^3 to 50 mol/dm^3 in 2×10^4 s. Find the rate constant.

a) $2.1\times10^{-4}\ s^{-1}$ b) $2.1\times10^{4}\ s^{-1}$

✓c) $1.37\times10^{-4}\ s^{-1}$ c) $1.37\times10^{4}\ s^{-1}$

ans: $t = \frac{2.303}{K}\log_{10}\frac{A_0}{A}$

$$K = \frac{2.303}{\cancel{t}}\log_{10}\frac{A_0}{A}$$

$$= \frac{2.303}{2\times10^4}\log_{10}\frac{\cancel{800}^{16}}{\cancel{50}}$$

$$= \frac{2.303}{2\times10^4}\,4\log_{10}2$$

$$= \frac{2.303\times4\times0.3}{2\times10^4 \quad 10} = \frac{13.818}{10^5} = 1.38\times10^{-4}\ s^{-1}.$$

Q2. A first order reaction is 20% complete in 5 minutes. find the time in which it is 60% complete.

[redacted] a) 10 min ~~b)~~ 20 min

c) 30 min d) 40 min

ans $A_0 = 100\%$

$A = 80.$

$t = 5$ min

$$5\text{min} = \frac{2.303}{K}\log_{10}\frac{A_0}{A} \Rightarrow 5\text{min} = \frac{2.303}{K}\log_{10}\frac{100}{80} \quad \text{—(1)}$$

$A_0 = 100\%$

$A = 40\%$

$t = ?$

$$t = \frac{2.303}{K}\log_{10}\frac{A_0}{A} \Rightarrow t = \frac{2.303}{K}\log_{10}\frac{100}{40} \quad \text{—(2)}$$

⇒ on dividing eq^n (i) by eq^n (ii)

$$\frac{t}{5\,min} = \frac{\log_{10}\frac{10\cancel{0}}{4\cancel{0}}}{\log_{10}\frac{10\cancel{0}}{8\cancel{0}}}$$

$$= \frac{\log_{10}10 - \log_{10}4}{\log_{10}10 - \log_{10}8}$$

$$\frac{t}{5\,min} = \frac{1 - 2\times0.3}{1 - 3\times0.3}$$

$$\frac{t}{5\,min} = \frac{0.4}{0.1}$$

$$t = 4\times5 = 20\ mins \Rightarrow \boxed{t = 20\,min}$$

Q3 A ⟶ Product First order reaction. The concentration of A changes from 0.1 M to 0.025 M in 40 mins. Find the rate of the reaction when concentration of A is 0.01 M.

a) 2.79×10^{4} M min^{-1}

b) 3.47×104 M. min^{-1}

c) 2.79×10^{-4} min^{-1}

[✓ d)] 3.47×10^{-4} min^{-1}.

Ans: Rate $= K[A]^1$

$$= \frac{3.454}{100}\times\frac{0.01}{100}$$

$$= \underline{\underline{3.4\times10^{-4}}}$$

$$t = \frac{2.303}{K}\log_{10}\frac{A_0}{A}$$

$$K = \frac{2.303}{t}\log_{10}\frac{A_0}{A}$$

$$= \frac{2.303}{40\,min}\log_{10}\frac{0.1\times1\cancel{00}\;4}{0.02\cancel{5}}$$

$$= \frac{2.303\times2\times0.3}{40\times10} = \frac{13.818}{4\times100}$$

$$\boxed{K = \frac{3.454}{100}}$$

Q.4. If for a 1st order reaction $t = \frac{2.303}{K} \log_{10} \frac{A_0}{A}$.

$K = 6.93 \times 10^{-3}\ min^{-1}$

a) $t_{1/2}$ c) $t_{2/3}$

b) $t_{1/3}$ d) $t_{3/4}$.

---

ans: $\boxed{t_f = \frac{2.303}{K} \log_{10} \frac{1}{1-f}}$

Examples of 1st order reaction

1. Nuclear physics → Radioactive decay (follow 1st order kinetics)
2. Growth & decay of bacteria.
3. Inversion of cane sugar in acidic medium.

$$\underset{\text{(dextro)}}{\underset{\text{(sucrose)}}{C_{12}H_{22}O_{11}}} + H_2O \xrightarrow{H^+} \underset{\text{(dextro)}}{\underset{\text{(glucose)}}{C_6H_{12}O_6}} + \underset{\text{(laevo)}}{\underset{\text{(fructose)}}{C_6H_{12}O_6}}$$

4. acidic hydrolysis of Ester.

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH.$$

5. dissociation of N_2O_5.

$$2N_2O_5 \longrightarrow 4NO_2 + O_2.$$

6. dissociation of H_2O_2.

$$2H_2O_2 \rightarrow 2H_2O + O_2.$$

★ Important point

1. $t_{75\%} = 2\,t_{50\%} \Rightarrow$ First order kinetics
2. $t_{99.9\%} = 10\,t_{50\%}$.

Proof: (1) $t_{75\%} = 2\,t_{50\%}$

$t = \frac{2.303}{K}\log_{10}\frac{A_0}{A}$.

50%

$A_0 = 100$

$A = 50$

$t_{50\%} = \frac{2.303}{K}\log_{10}\frac{\overset{2}{\cancel{100}}}{\cancel{50}}$

75%

ics)

$A_0 = 100$

$A = 25$

$t_{75\%} = \frac{2.303}{K}\log_{10}\frac{\overset{4}{\cancel{100}}}{\cancel{25}}$

$\frac{t_{75\%}}{t_{50\%}} = \frac{\log_{10}4}{\log_{10}2} = \frac{2\cancel{\log_{10}}2}{\cancel{\log_{10}}2}$

$\boxed{t_{75\%} = 2\,t_{50\%}}$

$\boxed{t_{3/4} = 2\,t_{1/2}}$

$t_{25\%} = 0.415\,t_{1/2}$

$t_{50\%} = t_{1/2}$

$\boxed{t_{75\%} = 2\,t_{1/2}}$

$t_{99.9\%} = 10\,t_{1/2}$

Proof (2)

$t_{99.9\%} \approx 10\,t_{50\%}$

$t = \frac{2.303}{K}\log_{10}\frac{A_0}{A}$

50% $t_{50\%} = \frac{0.693}{K}$.

99.9%

$A_0 = 100$

$A = 0.1$

$t_{99.9\%} = \frac{2.303}{K}\log_{10}\frac{1000}{0.1}$

(ii) − (i)

$$\frac{t_{99.9\%}}{t_{50\%}} = \frac{\frac{2.303\log_{10}10^3}{\cancel{K}}}{\frac{0.693}{\cancel{K}}}$$

$$\frac{t_{99.9\%}}{t_{50\%}} = \frac{2.303\times 3}{0.693} = \frac{6.909}{0.693}$$

$\boxed{t_{99.9\%} = 10\,t_{50\%}}$

(#1)

Thermodynamics

Introduction

Thermo → heat

dynamic → Motion

Heat, work, different forms of energy, process feasible, heat changes, gas process → P, V, T   H,S U,G, W

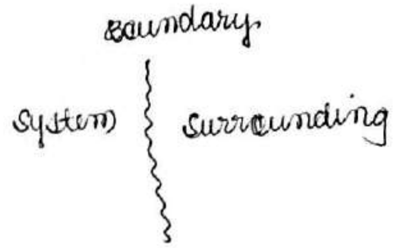
→ system + surrounding = universe

system → Observation

system ↓ (Part under investigation) → small part, calculation, interested

surrounding ↓ (anything except system)

boundary



conducting
diathermic : across heat change easily

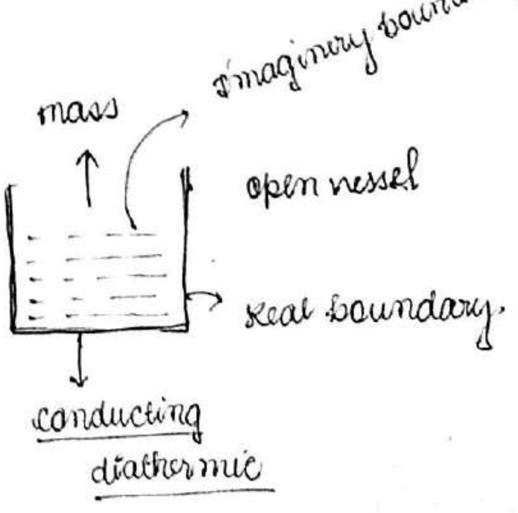
adiabatic : across heat cannot flow
↳ insulating $\boxed{\Delta q = 0}$

boundary → diathermic, adiabatic, Real, imaginary, Rigid, flexible

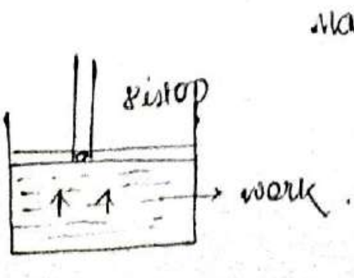
Types of system

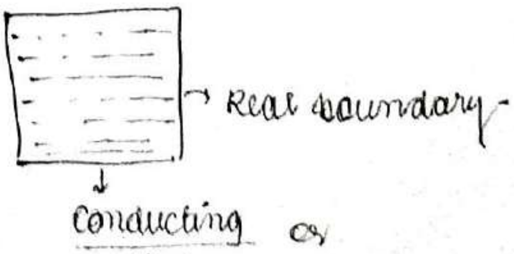
(i) open system
(ii) closed
(iii) isolated

Open system, such a system ↓ mass exchange + Energy exchange → Heat, work



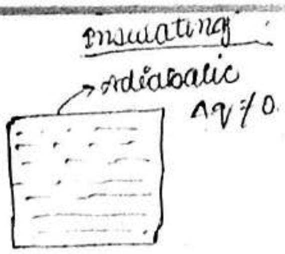
Closed System : such a system ↓ Mass exchange ✗ + Energy exchange ✓





Isolated system such a system.

no mass exchange ✗ + no energy exchange ✗



→ variable / parameter / properties → Extensive / → Intensive

system → properties

Extensive

→ depend upon amount or quantity of matter

→ (size of system / sample pe depend no)

⇒ Mass, volume, No. of moles; heat capacity.

Example

- → volume
- → Heat capacity.
- → No. of moles.
- → energy → heat, work.
  - → enthalpy
  - → entropy
  - → Gibb's free energy
  - → Internal energy

Intensive

→ doesnot depend upon size of sample or amount of matter.

→ density, Refractive index, specific heat capacity.

Example

- → Temperature, [illegible]
- → Pressure
- → density
- → Refractive index
- → viscosity.
- → specific heat capacity.
- → concentration. Molarity = $\frac{\text{No. of mo}}{\text{volume}}$ Molality, Mole fraction, Normality.

$$\boxed{\frac{\text{Extensive}}{\text{extensive}} = \text{Intensive}}$$

$$\boxed{\text{Molar Entropy} = \frac{\text{Entropy} \rightarrow E}{\text{Mole} \rightarrow E} = I}$$

pH = concentration of hydrogen

$$\boxed{pH \rightarrow \log_{10}[H^+]} \rightarrow \text{Intensive.}$$

Q1. which of the following is extensive property.

a) Specific heat capacity → I : $\frac{Q}{m\Delta T}$

b) Gibb's free energy → E

c) electro motive force → I . $\frac{W}{Q}$ → E
→ E

d) dielectric constant → I

State variable / state functions / state parameters

System का condition / state $\xrightarrow{\text{defined}}$ variables

Gas
P = 1 atm
T = 27°C
V = 30ml

$\xrightarrow{\text{state change}}$

Gas
P =
T =
V =

#Note

i) P (ii) T (iii) V iv) No. of moles, (n)
v) Enthalpy (H) (vi) entropy (S) vii) Internal Energy (U/E)
viii) Gibb's free energy (G)

State variable / state function
→ change → depends only upon initial & final condition state

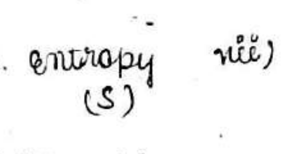
Note : Heat, work → Path function (Not a state function)

$\Delta E = E_f - E_i$

$\Delta S = S_f - S_i$

change in state function is zero in cyclic process

Cyclic process
↓ same state, variables change



$\Delta P = 0$
$\Delta E = 0$ $\Delta T = 0$
$\Delta S = 0$ $\Delta V = 0$

$\boxed{\Delta q \neq 0}$
$\boxed{\Delta w \neq 0}$ → because heat & work is a path function

Types of thermo-d process

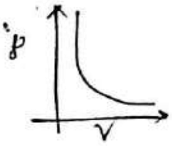
(i) Iso-thermal process

same temp (constant temp°)

$\boxed{\Delta T = 0}$

 # Note $\boxed{\text{Ideal gas}, \ \Delta T = 0, \ \Delta E = 0}$ $(E = K.E \propto T)$

Boyle's law. T= constant $P \propto \frac{1}{V}$

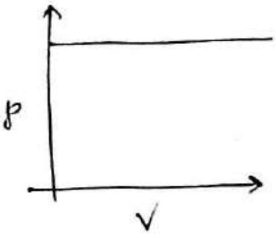


→ (Rectangular hyperbola)

(ii) Iso-baric process

→ constant pressure

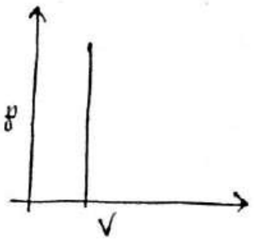
$\Delta P = 0$



(iii) Iso-choric process

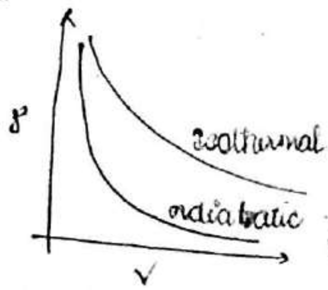
→ constant volume

$\Delta V = 0$



(iv) Adiabatic process

$\Delta q = 0$, No heat exchange.



(curve little sharper than the isothermal)

Cases

(i) Reversible
(ii) Irreversible

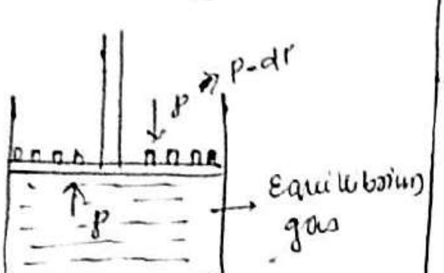
Reversible

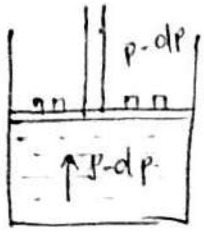
(i) which occurs in infinitely small steps →
infinite time to finish

(ii) slow process

(iii) each steps is in equilibrium with previous step.
Equilibrium exists always.

Expansion of gas





Ideal

(iv)
driving force > opposing force

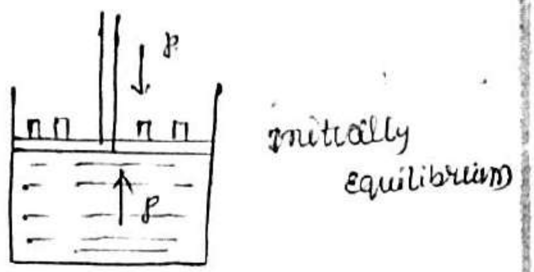
$$P > P-dp$$

Irreversible

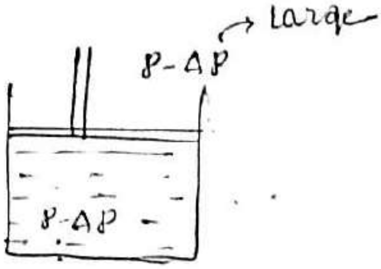
(i) at once → finite time

(ii) fast process.

(iii) Equilibrium initially & final stage → not in between.



Practical



(iv)
driving force >> opposing force

$$P > P-\Delta P$$

✓ **Heat** → Energy exchange between system and surrounding.

#2

└→ form of transfer of energy

(where there is temp^r. difference) (zeroth law)

Symbol → Q.

unit → Joule

└→ Calorie

common unit

$\boxed{1C = 4.182J}$

\# Heat given to the system ⟶ +ve

note Heat given by the system ⟶ -ve

$\frac{\text{something}}{0} = \infty$

$\frac{0}{\text{something}} = 0$

Specific heat capacity of gases $[0, \infty)$

$$\boxed{C = \frac{Q}{m\Delta T}}$$

Amount of heat required to raise the temp^r of unit mass by unit degree centigrad

$\boxed{C = 4.2J/g°C \text{ water}}$

i) Isothermal process

T → constant

$\Delta T \Rightarrow 0$

ii) adiabatic process

$Q = 0$ (Heat Exchange)

\# $C_{isothermal} \longrightarrow \infty$

$C_{adiabatic} \longrightarrow 0$

Two specific heat capacities of gases

i) At constant volume

SHC $\boxed{C_V = \frac{Q}{m\Delta T}}$

1g gas $\xrightarrow[1°C]{\text{Temp}\uparrow}$ $\boxed{Q = C_V}$

ii) At constant pressure

$$\boxed{C_p = \frac{Q}{m\Delta T}}$$

1g gas $\xrightarrow[1°C]{\text{Temp}\uparrow}$

$\boxed{Q = C_p}$

Unit

$$\boxed{C_v = J/g^\circ C}$$

$$\boxed{C_p = J/g^\circ C}$$

* Molar specific heat capacity

amount of heat required to raise the temperature of 1 mole of gas by 1°C.

Molar SHC at constant volume $\boxed{C_v = \dfrac{Q}{n\Delta T}}$

Molar SHC at constant volume $\boxed{C_p = \dfrac{Q}{n\Delta T}}$

Example O_2 gas ← $\boxed{1\,\text{mole} = 32\,g}$

Note#

$C_v = x$ → for 1g of O_2 to raise the temp^r by 1°C, amount of heat = C_v

$C_v = ?$ $32C_v = 32x$

for 1 mole of O_2. amount of heat req. to raise temp^r by 1°C

$$\boxed{\begin{aligned} C_v &= M_{c_v} \\ C_p &= M_{c_p} \end{aligned}}$$

Imp. Relation

$\boxed{C_p - C_v = R}$ for any gas

Q) For N_2 the value of $C_p - C_v$ = ?

a) 14R b) $\frac{R}{14}$ c) 28R ✓ d) $\frac{R}{28}$

ans $C_p - C_v = R.$

$M_{c_p} - M_{c_v} = R$

$28\,c_p - 28\,c_v = R$

$c_p - c_v = \frac{R}{28}$

$\boxed{Q_v = n C_v \Delta T}$

$\boxed{Q_p = n C_p \Delta T}$

$\boxed{C_v = \frac{f}{2} R}$

$C_p = R + C_v$

$C_p = R + \frac{f}{2} R$

$\boxed{C_p = \cancel{R} \left(\frac{f}{2} + 1\right) R}$

f: degree of freedom.

↳ depends upon atomicity of gas

mono-atomic	dia. atomic	Polyatomic
$f = 3$ (He, Ne, Ar)	$f = 5$ (O_2, N_2)	$f = 6$ (O_3) (BF_3)

$\boxed{\gamma = \frac{C_p}{C_v}}$

	f	$C_v = \frac{f}{2}R$	$C_p = C_v + R$	$\gamma = \frac{C_p}{C_v}$	$C_p - C_v = R$
mono-atomic	3	$C_v = \frac{3}{2} R$	$C_p = \frac{3}{2}R + R$ $= \left(\frac{3}{2}+1\right)R$ $= \frac{5}{2}R$	$\gamma = \frac{(3/2+1)R}{3/2 R}$ $\gamma = \frac{5}{3} = 1.66$	
dia.-atomic	5	$C_v = \frac{5}{2} R$	$C_v = \frac{7}{2} R$	$\gamma = \frac{7}{5}$ $\gamma = 1.4$	
Tri-atomic	6	$C_v = 3R$	$C_p = 4R$	$\gamma = \frac{4}{3}$ $\gamma = 1.333$	

#

$$\boxed{\begin{matrix}\gamma_m & > & \gamma_d & > & \gamma_p. \\ \downarrow & & \downarrow & & \downarrow \\ 1.66 & > & 1.4 & > & 1.33\end{matrix}}$$

$$\boxed{\gamma = 1 + \frac{2}{f}}$$

$$\boxed{Q = nC\Delta T}$$

$Q \rightarrow$ To system $\rightarrow$ ⊕
$Q \rightarrow$ By system $\rightarrow$ ⊖

(#3)

Energy exchange
- work → Mechanical
- Heat → Non- mechanical

WORK

↳ Mechanical way of transfer of energy

$$\boxed{W = F \times \text{displacement}}$$

$$\boxed{\text{Electrical work} = Q \times V}$$

$$\boxed{\text{gravitational work} = mgh}$$

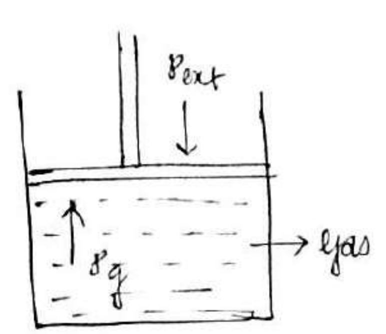
$$\boxed{\text{Spring work} = \frac{1}{2}kx^2}$$

Mechanical work in gaseous system

$$= -\underset{\substack{\downarrow \\ \text{External pressure}}}{P_{ext}}\ \overset{\text{change in volume}}{\Delta V}$$

$$\boxed{W = -P_{ext}\Delta V}$$

(valid when pressure is constant)



If gas, expand $\Delta V = +ve$

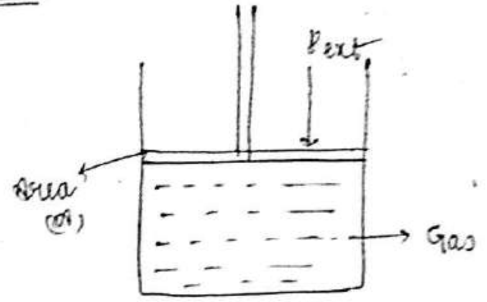
$W = -ve$
work done by gas.

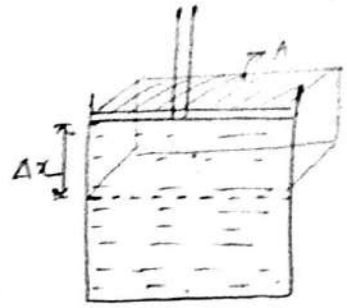
compressed $\Delta V = -ve$

$W = +ve$
work done on the gas

derivation

$P = \frac{F}{A}$





work done in expansion = $-F \times$ displacement

$= -PA \times \Delta x$

$= PA\underbrace{\Delta x}$

$$\boxed{W = -P_{ext}\Delta V}$$

Ques A gas expands by 0.5 l against an external pressure of 1 atm calculate the work done.

$\Rightarrow \quad W = -P_{ext}\,\Delta V$

$= -1\text{ atm} \times 0.5\text{ l}$

us

rge
volume

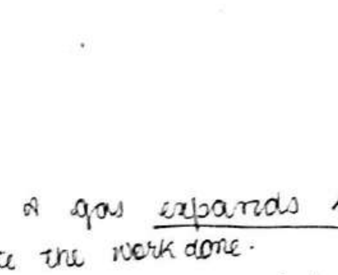
$w = -0.5\text{ atm l}$ work is done by gas ✓

$$\boxed{w = -0.5 \times 101.3\text{ J}}$$

Note

$$\boxed{1\text{ atm l} = 101.3\text{ J}}$$

Ques



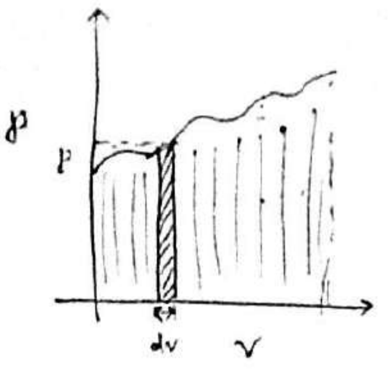
A gas expands from A to B. find the work done

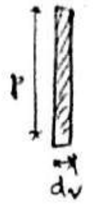
$w =$ ~~$P_{ext}\Delta V$~~ area under curve

$= \frac{1}{2}(a+b) \times h$ (trapezium)

$= \frac{1}{2}(2+4) \times 2$

$= -6$ atm l





strip area = P dv

$$\int |dW| = \int P\,dV$$
= area of strip

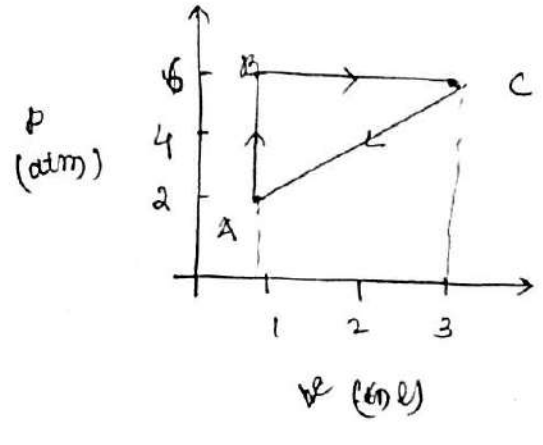
Total work done = Total area.

$$\boxed{|W| = \int_{V_1}^{V_2} P\,dV}$$

P → constant $\boxed{W = -P_{ext}\Delta V}$

P → variable $\boxed{W = -\int_{V_1}^{V_2} P_{ext}\,dV}$

Graph, $\boxed{W = \text{area under P-V curve}}$



Q1 Find work done in
1) W_{AB} ii) W_{BC} iii) W_{CA}
iv) W_{ABCA}

ans

$W_{AB} = -P_{ext}\Delta V$
$= -P_{ext}(1-1)$
$= 0$

(ii) $W_{BC} = -\cancel{P_{ext}\Delta}\ 2\times 6 = -12$ atm L.

(iii) $W_{CA} = \frac{1}{\cancel{2}}(2+6)\cancel{2} = 8$ atmL.

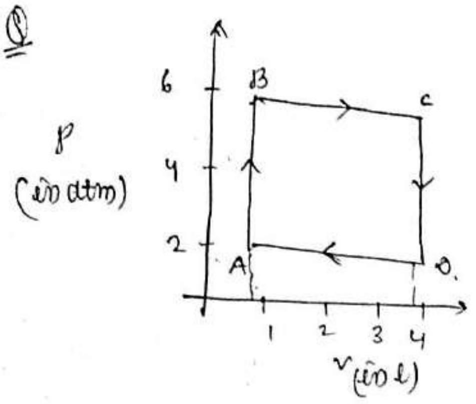
(iii) $W_{ABCA} = 0 - 12 + 8$
$= -4$ atmL

$W_{cycle} = \frac{1}{2}\times b\times h$
$= \frac{1}{2}\times 2\times 4$
$= -4$ atmL

Path function
↑
$\boxed{W_{cyclic_{ABCA}} \neq 0}$

W cyclic = area of cycle
Clockwise W → -ve
Anti clockwise W → +ve

Q



Ans

(i) $w_{AB} = 0$

(ii) $w_{BC} = 6 \times 3 = -18$ atm l

(iii) $w_{CD} = 0$

(iv) $w_{DA} = 2 \times 3 = 6$ atm l

(v) $w_{ABCDA} = 4 \times 3 = -12$ atm l.

Internal Energy:

-> It is defined as the inbuilt energy that responsible for existence of the matter

Charecteristic :-

i) It depends on state variables P, T, V, n.

ii) It is a state property and since the state of internal energy is same as the state of the dependent parameters. so it is known as single valued function

iii) Internal energy is the sum of the energy associated with translation motion, vibration motion and electronic configuration.

iv) For a cyclic process, change in internal energy (ΔU) becomes zero.

v) Internal energy is perfect differential ie.

$$U_i = f(P_i, V_i, T_i)$$

a. At constant temperature,

$$\Delta U = \left(\frac{\partial U}{\partial V}\right)_P dV + \left(\frac{\partial U}{\partial V}\right)_P dV = f(V, P)_T$$

b. At constant volume.

$$\Delta U = \left(\frac{\partial U}{\partial P}\right)_T dP + \left(\frac{\partial U}{\partial T}\right)_P dT = f(P, T)_V.$$

c. At constant pressure

$$\Delta U = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT = f(V, T)_P.$$

Enthalpy

It is a defined thermodynamics potential designated by the letter 'H', that consists of the internal energy (U) of the system with the product of the pressure (P) & volume (V) of the system. Mathematically, it is given by

$$\boxed{H = U + PV}$$

At constant pressure process,

$$\int_{H_1}^{H_2} \Delta H = H_2 - H_1 = (\Delta q)_P = \int_{U_1}^{U_2} \Delta U + P \int_{V_1}^{V_2} \Delta V$$

$$\Rightarrow H_2 - H_1 = (\Delta q)_P = (U_2 - U_1) + P(V_2 - V_1).$$

At constant volume process,

$$\int_{H_1}^{H_2} \Delta H = H_2 - H_1 = (\Delta q)_V = \int_{U_1}^{U_2} \Delta U$$

(since at constant volume work done PdV becomes zero).

$$\Rightarrow H_2 - H_1 = U_2 - U_1$$

ENTROPY

entropy is a measure of randomness of a system. entropy increases as the number of possible microstates increases where microstate is the microscopic arrangement of atoms or particles.

→ symbolically represented by 'S'.

→ Standard Entropy (S°) :- The absolute entropy of a substance at 1 atm pressure and 298K temperature.

→ unit : J/K.mol.

→ Trends for standard entropy values.

a. entropy of solid < liquid < gas

b. More complexes molecules have higher entropy.

Characteristics :-

i> It depends on state variables.

ii> It is a perfect differential since it is a state property.

iii> It is mathematically expressed as

$$dS = \frac{\delta q_{rev}}{T} .$$

iv> For absorption of heat δq is positive. so entropy change dS is positive. similarily for release of heat δq is negative. so entropy change dS is negative.

v> For adiabatic process, δq is equal to zero. Hence, dS is equal to zero. So adiabatic process also known as isotropic process.

" "

constant pressure $\boxed{w = -P_{ext}\Delta V}$ gas expand.

compress

$\Delta V \rightarrow -ve$

$w = +ve$

work done on gas.

expansion $\Delta V \rightarrow +ve$

$w \longrightarrow -ve$

workdone by gas.

1) Isochoric process

constant volume

$w = -P_{ext}\,\Delta V$

$\boxed{w = 0}$ Isochoric

ii) Isobaric Expansion

constant pressure

$\boxed{w = -P_{ext}\,\Delta V}$

$$\boxed{w = -\int_{V_1}^{V_2} P_{ext}\,dV}$$

original formula

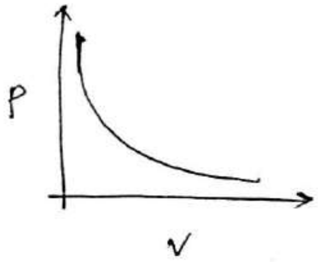
ISOTHERMAL PROCESS (Expansion) [constant tempr]

same

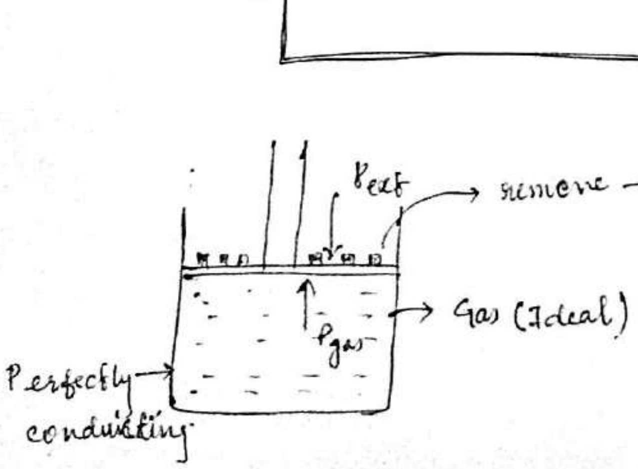
Boyle's law . $P \propto \frac{1}{V}$, $P_1V_1 = P_2V_2$

i) Reversible Isothermal expansion

workdone, $\boxed{w = -nRT\log_e\left(\frac{V_2}{V_1}\right)}$ Isothermal rev.



$$\boxed{w = -2.303\,nRT\log_{10}\left(\frac{V_2}{V_1}\right)}$$



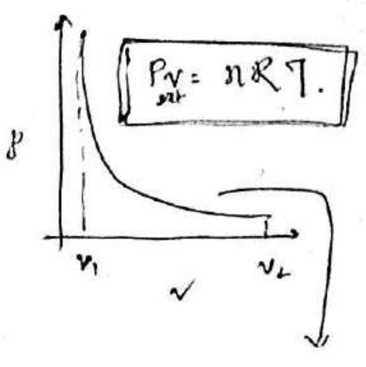
$P_{gas} > P_{ext}$

$P_{gas} = P_{ext} + dP$.

gas expands → & it cools.

Tempr of gas fall → Gas absorbs heat from surrounding → tempr remains constant

$$w = -\int_{v_1}^{v_2} P_{ext}\,dv$$



$$w \quad = -\int_{v_1}^{v_2} \frac{nRT}{V}\,dv$$

$$= -nRT \int_{v_1}^{v_2} \frac{dv}{v}$$

$$= -nRT\left[\log_e v\right]_{v_1}^{v_2} = -nRT\left[\log_e v_2 - \log_e v_1\right].$$

$$\boxed{w = -nRT \log_e\left(\frac{v_2}{v_1}\right)}$$

$$w = -2.303\, nRT \log_{10}\left(\frac{v_2}{v_1}\right)$$

$$\boxed{w = -2.303\, nRT \log_{10}\left(\frac{P_1}{P_2}\right)}$$

\# $$\boxed{w = -2.303\, P_1 v_1 \log_{10}\left(\frac{v_2}{v_1}\right)}$$

when 'n' and 'T' are not given

(2) <u>Irreversible Isothermal Expansion</u>

1) <u>vaccum</u>: free expansion

$P_{ext} = 0$ $\boxed{w = 0}$

ISO thermal free expand.

2) $P_{ext} << P_{gas}$.

$w = -P_{ext}\Delta V$ Intermediatory expansion.

ADIABATIC EXPANSION

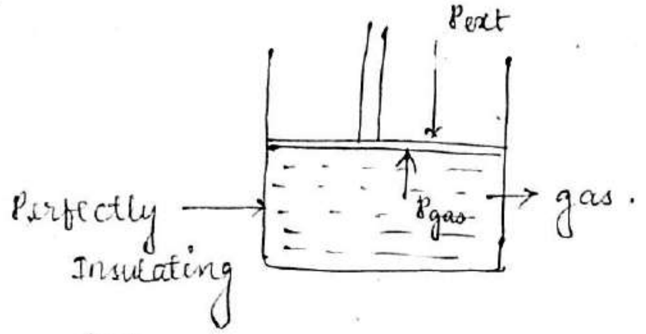
(Heat exchange = 0)
$q = 0$

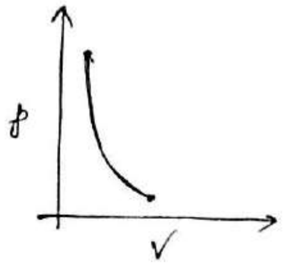
Poission's equation

$$\boxed{P_1 V_1^{\gamma} = P_2 V_2^{\gamma}}$$

Adiabatic

$\gamma \rightarrow$ monoatomic (1.66)
diatomic (1.4)
Triatomic (1.33)





Slope of adia > Slope of Iso

$W = -P_{ext} \Delta V$

$$W = -\int_{V_1}^{V_2} P_{ext}\, dV$$

$$= -\int_{V_1}^{V_2} \frac{K}{V^{\gamma}}\, dV$$

$$= -K \int_{V_1}^{V_2} V^{-\gamma}\, dV$$

$$= -K \left(\frac{V^{-\gamma+1}}{-\gamma+1} \right)_{V_1}^{V_2}$$

$$= \frac{K}{\gamma-1} \left(V_2^{-\gamma} \cdot V_2 - V_1^{-\gamma} \cdot V_1 \right)$$

$$= \frac{K V_2^{-\gamma} V_2 - K V_1^{-\gamma} V_1}{\gamma - 1}$$

$$\boxed{W = \frac{nR}{\gamma-1} (T_2 - T_1)}$$

Reversible adiabatic

$$\boxed{PV^{\gamma} = \text{constant}}$$

$(PV^{\gamma} = K)$

$(P_1 V_1^{\gamma} = P_2 V_2^{\gamma} = K)$

$$= \frac{P_2 v_2^{\gamma} v_2^{-\gamma} v_2 - P_1 v_1^{\gamma} \cdot v_1^{-\gamma} v_1}{\gamma - 1}$$

$$= \frac{P_2 \cdot v_2 - P_1 v_1}{\gamma - 1} = \frac{nR(T_2 - T_1)}{\gamma - 1}.$$

#5.

FIRST LAW OF THERMODYNAMICS

↳ conservation of energy.

$$\boxed{M = \frac{E}{c^2}}$$

ΔE or ← $\boxed{\Delta U = \Delta q + \Delta w}$ → workdone on the system

↳ Heat given to the system

Change in Internal Energy of system.

$$\boxed{dU = dq + dw}$$

INTERNAL ENERGY

Total energy = K E (motion) + P E + I.E (U)

↓ due to some gravitational / Electrostatic field

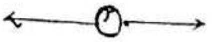
Condⁿ

* system: Rest
* Absence of external field

$\boxed{\text{Total Energy} = \text{I.E}}$.

→ Internal Energy is due to molecules, atoms, electron, neutrons, nucleus, etc.

→



K.E. of molecule.

[Molecule level energy = Internal Energy]

I.E (U) = K.E. Transitional (molecule) + K.E vibrational (molecules) + K.E Rotational (Molecules)

+ P.E. ($\bar{e}$ & nucles) + P.E. (F.O.A) + Bond energy. (O=O)

→ It is impossible to determine internal energy of a system.

⇒ Not necessary.

⇒ Important ⟶ calculate ΔU

change in Internal Energy

$$\boxed{\Delta U = \Delta q + \Delta w}$$

1.) It is an extensive property
↓
amount of matter pe depend kare.

2.) It is a state function.

ΔU → depend only on initial & final points.
↳ doesn't depend on path.

$$\boxed{\Delta U = U_f - U_i}$$

3.) In a cyclic process. $\boxed{\Delta U = 0}$

1) $\Delta U = \Delta q + \Delta w$

2) Ideal gas.

$$\boxed{\Delta U = n C_v \Delta T}$$

for variable Cv value.

$$\boxed{dU = n C_v dT}$$

For small change.

3.) $\boxed{I.E \propto T}$

only for Ideal gas

where, $C_v = \frac{f}{2} R$

f = degree of freedom

f = 3 Monoatomic (He, Ne, Ar)

f = 5 diatomic (O_2, N_2)

f = 6 Polyatomic (O_3, SO_3)

R = Universal gas constant.

R = 8.314 J/mole K.

R ≈ 2 calorie/mole K.

)-

Q) why Internal energy of gas is said to be only K.E. ?

I.E. all of ideal gas = K.E. of its molecules. ?

→ Because in the Ideal gas there is no force of attaraction. so. no P.E.

$\Delta U = \underline{\Delta q} + \Delta w.$

$C_p = C_v + R$

$C_v = \frac{f}{2} R$

Heat ⟶ form of energy exchange.

Heat given to the system → +ve

" " by " . " → -ve

* for solid, liquid, gas

$\boxed{Q = mC\Delta T}$

* for Ideal gas

$\boxed{Q = nC\Delta T}$

Work

⟶ workdone on the system → +ve

workdone by the system ⟶ -ve

variable Cv value.

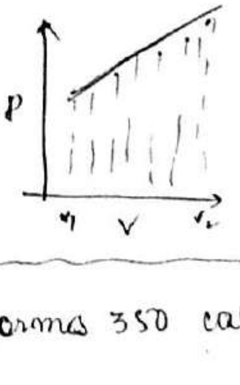
$w = F \times$ displacement

$= mgh$

$= \frac{1}{2}kx^2$ (spring)

$= Q \times \Delta V$

gases $\boxed{w = -P_{ext}\Delta V}$



w = Area under P-V curve

ll
ange-
)

Q) 500 Calorie of heat is given to a system and system performs 350 calorie work. Calculate the Internal energy of the system.

ans $\Delta U = \Delta q + \Delta w.$

$= 500 + 350 = +850$ calorie.

Q) 0.5 mole of O_2 is heated from 25°C. to 120°C at constant pressure calculate. (Cp = 7 calorie/mole K)

1) Q 2) ΔU 3) w

⇒ $Q = nC_p\Delta T.$

$= 0.5 \times 7 \times 100$

$= 50 \times 7$

$= 350$ Calorie

$nR\Delta T$

$\Delta U = \Delta q + \Delta w.$

=

(ii) ΔU

$\Rightarrow$ $\Delta U = n C_v \Delta T.$

$= 0.5 \times 5 \times 100$

$\boxed{\Delta U = 250 \text{ calorie}}$

(iii) ΔW.

$\Rightarrow$ $\Delta U = \Delta Q + \Delta W$

$250 = 350 + \Delta W$

$\boxed{\Delta W = -100 \text{ calorie}}$

$C_v = \frac{f}{2} R.$

$C_v = \frac{5}{2} R.$

$C_p = C_v + R.$

$= \frac{5}{2} R + R$

$C_p = \frac{7R}{2} = 7$ calorie/mol

$C_v = 5$ calorie/mol k

Q) 1 mole of He is heated from 27°C to 327°C at -

1) constant pressure 2) constant volume

Find for i) & ii) Heat exchange & work done.

ans

1) constant pressure (H.E.).

$Q = n C_p \Delta T.$

$= 1 \times 5 \times 300$

$= 1500$ calorie

2) constant volume

$Q = n C_v \Delta T.$

$= 1 \times 3 \times 300$

$= 900$ calorie.

$C_v = \frac{f}{2} R.$

$= \frac{3}{2} R = 3$

$C_p = C_v + R.$

$C_p = 5.$

W.D.

1) constant pressure

$\Delta U = \Delta q + \Delta W.$

$900°C = 1500 + \Delta W$

$\Delta W = 0$

2) constant volume.

$\Delta W = 0$

I.E.

1) At constant volume

$\Delta U = n C_v \Delta T.$

$= 1 \times 3 \times 300$

$= 900°C$

2) C.P $\Delta U = 1200°C$