

- Various System

① System - The part of universe under study

② Surrounding - The part outside system in universe

③ Open - Transfer of energy & Mass

Closed - Exchange of Heat but not Mass

Isolated - No exchange

Homogeneous - All reactants in single phase

④ State function - function does not depend on path to achieve final state

eg, enthalpy, entropy, etc

Path function - function depends on path

eg Heat, Work, etc

⑤ Intensive variable - does not depend on quantity

eg:- temp, density, refractive index, etc

Extensive Variable - depends

eg :- Volume, moles, etc

## • Thermody. Process

① Isothermal ( $\Delta T = 0$ )

② Isochoric ( $\Delta V = 0$ )

③ Isobaric ( $\Delta P = 0$ )

④ Adiabatic ( $\Delta Q = 0$ )

⑤ Reversible / Irreversible

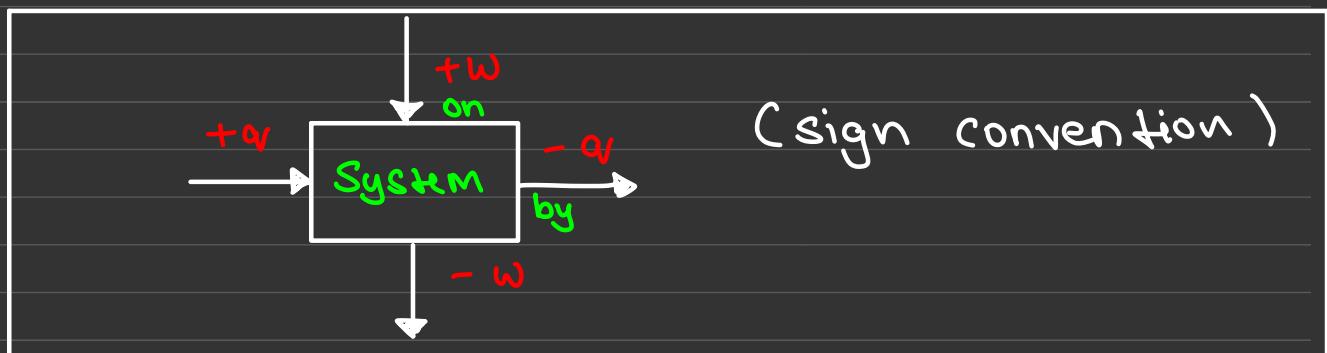
⑥ Internal energy: Sum of Translational, Rotational and Vibrational energy

State function, extensive,  $-\Delta V \rightarrow$  endo

## • 1<sup>st</sup> law

↳ nor can be created, nor be destroyed.

$$q_v = \Delta U + w$$



e.g. A container has a sample of N<sub>2</sub> gas and tightly fitting movable piston that does not allow any of the gas to escape during a thermodynamic process 200 J of Heat enter the gas and the gas does 300 J of work  
Find  $\Delta U$

$$q_v = +200 \text{ J} \quad \Delta U = -100 \text{ J}$$

$$w = -300 \text{ J}$$

eg 4 identical containers have eq. amt. of He<sub>2</sub> gas that all start at same T, containers of the gas tightly filling movable piston (no gas escape) each sample of the gas is taken to diff thermo process as below

- i) 500J of Heat releases , 300J work done - 800
- ii) 500J of Heat enters , 300J work done 200
- iii) 500J of Heat exceeds , 300J work on - 200
- iv) 500J of Heat enters , 300J work on 800

∴ Temp order = iv > ii > iii > i

## • Enthalpy (H)

$$H = U + PV$$

State func / Extensive

$$\Delta H = \Delta H_{\text{prod}} - \Delta H_{\text{react}}$$

$$\begin{aligned}\Delta H &= +ve = \text{endo} \\ &= -ve = \text{exo}\end{aligned}$$



eg Using std. Thermo values, calc. the enthalpy of reaction of comb of  $C_4H_{10}(g)$  with  $O_2(g)$  to form  $CO_2 + H_2O$

$$\Delta H_f(H_2O)_l = -285.83 \text{ kJ/mol}$$

$$\Delta H_f(CO_2)_g = -393.5 \text{ kJ/mol}$$

$$\Delta H_f(C_4H_{10})_g = -61.87 \text{ kJ/mol}$$



$$\Delta H = \Delta H_p - \Delta H_r$$

$$= [4(-39.35) + 5(-285.83)] - [-61.87 + 0]$$

$$= -2941.28 \text{ kJ/mol}$$

Note



eg The enthalpy of form. of  $\text{CO}_2$  &  $\text{H}_2\text{O}$  &  
 $-393.5 \text{ J} - 285.83 \text{ kJ/mol resp}$  & enthalpy  
of comb of  $\text{CH}_3\text{COOH}$  is  $-869 \text{ kJ/mol}$   
find  $H(\text{form. of } \text{CH}_3\text{COOH})$

$S_{\text{std}}$



$$-869 = [2(-393.5) + 2(-285.83)] - [\Delta H_f] + 0$$

$$\therefore -489.68 \text{ kJ/mol}$$

- Entropy  $\rightarrow$  state & extensive

Heat abs/ rel by system reversibly and isothermally per unit temp is

### Physical Significance

① Measure of randomness / disorderliness

② Spontaneity of process

$$\Delta S > 0 \quad [\text{spon}]$$

$$\Delta S < 0 \quad [\text{non-spon}]$$

$$\Delta S_{\text{sys}} + \Delta S_{\text{curr}} > 0$$

$$\Delta S_{\text{adia}} = 0 \quad (\text{No heat exch})$$

$$\Delta S_{\text{irreversible}} > 0$$

$$\Delta S_{\text{reversible}} = 0$$

eg The rxn at eq<sup>br</sup> release 35J at 37°C  
what is  $\Delta S$

$$\text{Soln} \quad \Delta S = \frac{25}{310}$$

$$\approx 0.08 \text{ J/K}$$

eg Calc entropy change for foll. rxn



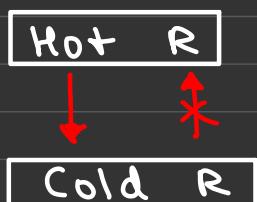
$$\begin{aligned}\text{Soln} \quad \Delta S &= \Delta S_p - \Delta_f \\ &= [214 + 140] - [410 + 186] \\ &= 354 - 596 \\ &\approx -242 \text{ J/K.mol}\end{aligned}$$

- limitations of First law

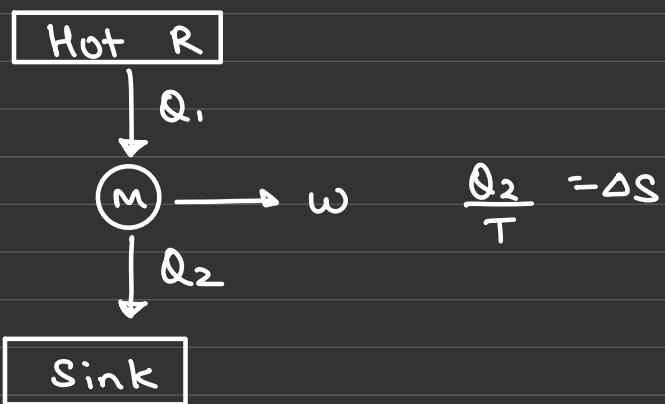
- ① Direction of flow cannot be predicted
- ② Cannot predict spontaneity / feasibility
- ③ When heat is given to system not same amt converted to work coz of efficiency

- 2nd law of thermo

- ① Clausius Statement



## ② Kelvin-Planck



③  $\Delta S_{univ} > 0$  [For spont]  
 L sys + surr

• Note

① Entropy of an isolated sys. always ↑, isolated system spontaneously evolve towards thermal eq, by i.e. the state of max<sup>m</sup> entropy of system

② Entropy is univ is constantly inc.

• Helmholtz free energy / Helmholtz func / Work func ( $\Delta A$ )

Helmholtz free energy is defined as the max<sup>m</sup> work done by system at const. T, V

$$A = U - TS$$

Where A =

U =

T =

S =

Initial state, at temp T

$$A_1, U_1, S_1 \quad A_1 = U_1 - TS_1$$

at final state

$$A_2, U_2, S_2 \quad A_2 = U_2 - TS_2$$

Subtracting (i) from (ii)

$$A_2 - A_1 = U_2 - U_1 - T(S_2 - S_1)$$

$$\Delta A = \Delta U - T\Delta S$$

$$\Delta A = \Delta U - \frac{T(q_{rev})}{T}$$

$$\Delta A = \Delta U - q_{rev}$$

$$\Delta A = w_{rev} \quad \text{on the sys}$$

$$\Delta A = -w_{rev} \quad \text{by the sys}$$

L or  $\downarrow$

$$-\Delta A = w_{rev}$$

dec. in Helmholtz free energy is equal to maximum work done

$$\therefore -\Delta A = \text{Total work done}$$

- **Gibb's free energy**

It is defined as max<sup>m</sup> work done by system at const. T, P

$$G = H - TS$$

Where  $G =$

H =

T =

S =

Initial state, at temp T

$$G_1, H_1, S_1 \quad G_1 = H_1 - TS_1$$

at final state

$$G_2, H_2, S_2 \quad G_2 = H_2 - TS_2$$

Subtracting (i) from (ii)

$$G_2 - G_1 = H_2 - H_1 - T(S_2 - S_1)$$

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

$$\Delta G_r = (\Delta U + P\Delta V) - T\Delta S$$

$$\Delta Q_r = \Delta U - T\Delta S + P\Delta V$$

$$\Delta G_r = \Delta A + P\Delta V$$

$$-\Delta G_r = -\Delta A - P\Delta V$$

$$-\Delta G_r = W_{rev} - P\Delta V \quad \text{work of expansion}$$

$$-\Delta G_r = W_{rev} - P\Delta V \\ = \text{Net work done}$$

Q.1 Define extensive & intensive prop. with eg

Soln Intensive prop : A Variable that does not depend on quantity

eg : Temp, density, etc

Extensive prop : A variable that does depend on quantity.

eg : moles, volume, etc.

Q.2 Short Note on Internal energy

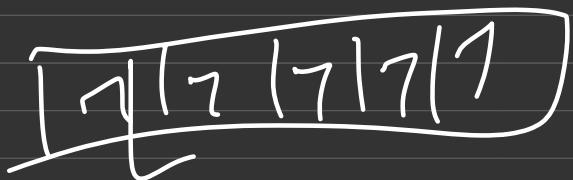
Soln Internal energy is the sum of translational, Rotational and vibrational energies

It is a state function

It is a extensive variable

Q.9

WFL Fe<sup>+2</sup>



Q.10 axial  $d(x^2-y^2)$   $d(z^2)$

Q.11 H < O < N < C

Q.12 Identify reagent

(AA<sub>2</sub>) B C

Calculate the solubility product of  $\text{PbCl}_2$  if  
50 ml of saturated soln of  $\text{PbCl}_2$  was found  
found to contain 0.2207 gms of  $\text{PbCl}_2$  dissolved  
in it.



$$(2s)^2 \cdot s$$

$$4s^2 \cdot s$$

$$K_{\text{sp}} = 4s^3$$

estimate the solubility of  $\text{Ag}_2\text{CrO}_4$  is  $K_{\text{sp}} = 1.1 \times 10^{-12}$



$$1.1 \times 10^{-12} = (2s)^2 \cdot s$$

$$1.1 \times 10^{-12} = 4s^3$$

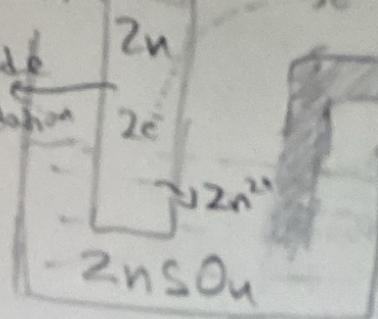
$$\frac{1.1}{4} \times 10^{-12} = s^3$$

$$\sqrt[3]{\frac{1.1}{4}} \times 10^{-4} = s$$

$$s = \dots$$

## Daniel Cell

Anode  
Oxidation

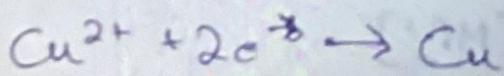
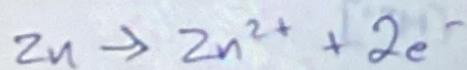


Electro-chemical

cell: Chemical energy to electrical energy, where spontaneous redox reaction is utilised to generate electricity.

Called galvanic or voltaic cell

~~Electro~~ Electrolytic cell: Electrical energy <sup>chemical</sup> converted to electrical energy where non-spontaneous redox reaction is forced to occur by applying current or voltage.



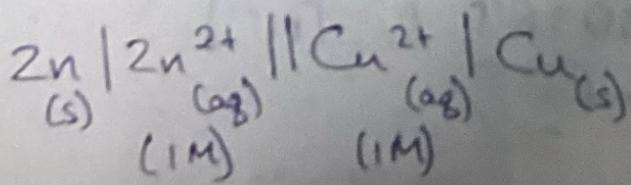
Salt bridge:

balances the charge flow,

maintains neutrality, neutralisation, completes the circuit.

Anode || Cathode

reactant | product || reactant | product



- i) Standard hydrogen electrode
- ii) Reference Electrode
- iii) Indicator/Working electrode

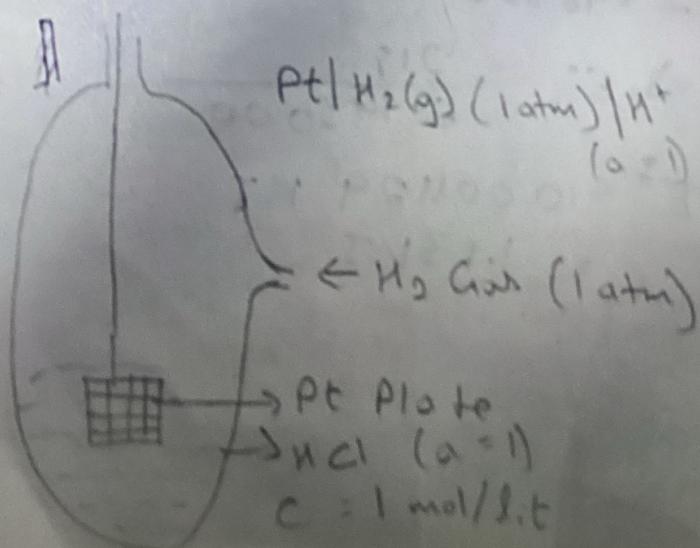
Reference Electrode : The electrode whose potential remains fixed and does not change with any change in the concentration of ions in the solution.

Eg - SHE, Standard calomel electrode  
(0.2422 V in standard KCl), Ag | AgCl.

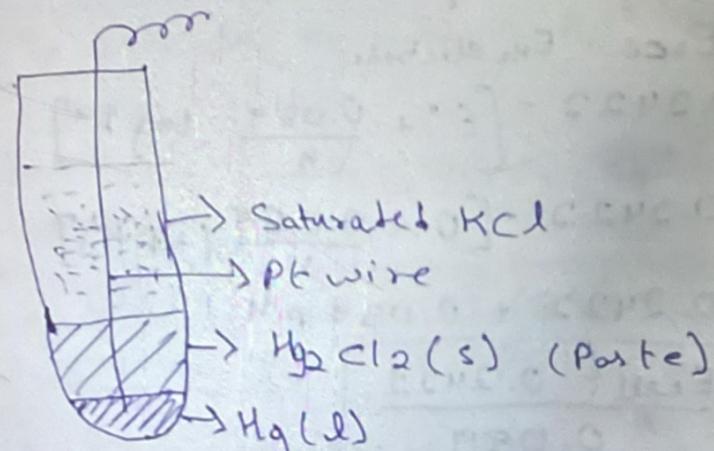
Indicator : Electrode whose potential is sensitive to the change in the working of the ion.

Eg : Plate, Carbon  
(Pt) (C)

SHE



Standard Calomel Electrode



Notation :

