$-1366.5\,kJ = \Delta U - RT$

$\Delta U = -1366.500 + 2494.2$

$\Delta U = -1364.0\,kJ$

→ Spontaneous and non-Spontaneous Process →

1) Spontaneous process - The process which has a natural tendency to occur in a particular direction either of its own or after initiation under the given set of condition.
All natural process ~~of~~ are irreversible and spontaneous

2) Non - spontaneous process - The process which does not occur of its own in a particular direction.
→ This process does not have tendency to occur in a particular direction either of its own or after initiation.
→ No - spontaneous process may be made to occur when energy from external source is supplied continuously throughout the process like refrigrator.

Example of spontaneous process -
a) Process that need no initiation like diffusion of gases, flow of water from high level to low level, Melting at 25°C, Evaporation.
b) Process that need initiation - Burning of candle, combustion of hydrocarbon in presence of Oxygen.

Criteria for process to be spontaneous :-
a) Tendency to attain max. energy (max. stability)
b) Tendency to attain max. disorder or randomness (entropy factor)

→ Entropy (S) :—

It is state function and extensive property used for measure randomness or dis-orderness

$$\Delta S_{system} = S_{final} - S_{initial}$$

Mathematically it can be calculated as —

$$\Delta S_{system} = \frac{dq}{T}$$ (at constant temp.)

$$\Delta S_{system} = \int \frac{dq}{T}$$ (at variable temp)

$$\Delta S_{total} (\Delta S_{universe}) = \Delta S_{system} + \Delta S_{surrounding}$$

$\Delta S > 0$ or +ve. → spontaneous process

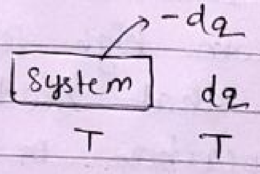
$\Delta S < 0$ or −ve. → non-spontaneous process

unit of entropy = cal / molK

$\Delta S = 0$ → equillibrium condition

→ Total change in Entropy (ΔS) for reversible process at constant temperature :

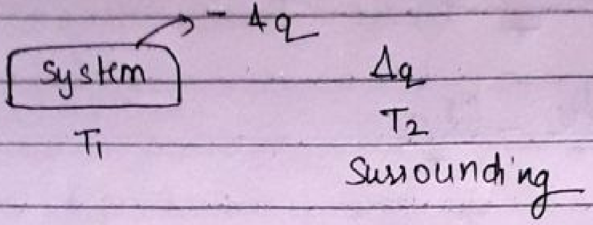
$$\Delta S_{system} = \frac{-dq}{T} \neq 0$$



$$\Delta S_{surrounding} = \frac{dq}{T} \neq 0$$

$$\Delta S_{total} = \frac{-dq}{T} + \frac{dq}{T} = 0$$

→ Total change in entropy $(\Delta S)_{total}$ for irreversible process (non- isolated).



$$\Delta S_{system} = \frac{-\Delta q}{T_1} \neq 0$$

$$\Delta S_{surrounding} = \frac{\Delta q}{T_2} \neq 0$$

$$\Delta S_{total} = -\frac{\Delta q}{T_1} + \frac{\Delta q}{T_2} \neq 0$$

$$\Delta S_{total} = \Delta q \left(\frac{T_1 - T_2}{T_1 T_2} \right)$$

Here $T_1 > T_2$
So $\Delta S_{total} > 0$
(spontaneous) (System अपने आप ठंडा हो रहा है।)

If $T_2 > T_1$
So $\Delta S < 0$
(non-spontaneous)

→ ΔS for diff. To system (Process) —

$$\Delta S_{system} = \int \frac{dq}{T} \quad \text{——} ①$$

$du = dq + dw$
$dq = du - dw$ —— ②

put ⑪ in eq ①

$$\Delta S_{system} = \int \frac{dU - dw}{T}$$

$$\Delta S_{system} = \int \frac{dU}{T} - \int \frac{dw}{T}$$

$$\Delta S_{system} = \int \frac{nC_v dT}{T} - \int \frac{p \cdot dv}{T}$$

$$\Delta S_{system} = nC_v \int_{T_1}^{T_2} \frac{dT}{T} - nR \int_{V_1}^{V_2} \frac{dv}{V}$$

$$\Delta S_{system} = nC_v \log_e (T_2 - T_1) - nR \log_e (V_2 - V_1)$$

$$\Delta S_{system} = nC_v \log_e \left(\frac{T_2}{T_1}\right) - nR \log_e \left(\frac{V_2}{V_1}\right)$$

a) ΔS for isothermal system —

$dT = 0$ So, $dU = 0$

$$\Delta S_{system} = -nR \log \frac{V_2}{V_1}$$

b) ΔS for isochoric system —

$dv = 0$ $dw = 0$

$$\Delta S_{system} = nC_v \log_e \left(\frac{T_2}{T_1}\right)$$

c) ΔS for Adiabatic System (insulated system)

$dq = 0$

$\Delta S_{system} = 0$

d) ΔS for isobaric system

$$dp = 0$$

$$\Delta S = \int \frac{dq}{T}$$

$$\Delta S = \int ncp\, dT$$

At constant pressure $dq = ncp\, dT$

$$\Delta S = \int_{T_1}^{T_2} \frac{ncp\, dT}{T}$$

$$\Delta S_{system} = ncp \int_{T_1}^{T_2} \frac{dT}{T}$$

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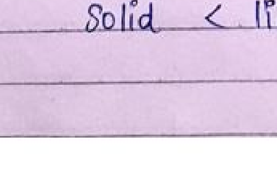
$$\Delta S_{system} = ncp\, [T]_{T_1}^{T_2}$$

$$\boxed{\Delta S_{system} = ncp\, \Delta T}$$

Note – In below Adiabatic system, after open the value $\Delta S > 0$ (positive) due to intermixing of gases randomness $\uparrow$ses



$dq = 0$

but

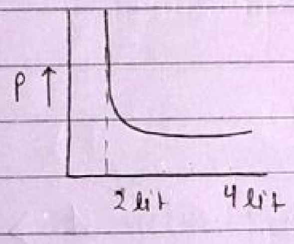
$\Delta S > 0$

The order of entropy for diff. matter

Solid < liq < Gas

Que 2 mole of Oxygen gas in a closed container is heated so temp. rise from 0° to 273°C. find out the change of entropy for system.

Que find out the change in entropy in following ~~terms~~ curve



Cv value is 1.5 R and no. of mole is 2.

→ Change in Entropy for different phase change –

a) Molar entropy of fusion –

The entropy change when 1 mole of solid change into liquid, its melting point temp.

$$\Delta S = \frac{dq}{T}$$

$$\Delta S_{fusion} = \frac{\Delta H}{T_{m.p}}$$ (due to rxn is carried out at constant T and P)

b) Molar entropy of Vapourisation –

$$\Delta S_{vap} = \frac{\Delta H}{T_{B.P}}$$

c) Molar entropy of Sublimation –

$$\Delta S_{sub} = \frac{\Delta H}{T_{sub.}}$$

Que ΔH_f = 1.43 kcal/mol

ΔS_{fusion} = 5.26 cal/mol k

find out the melting point

Que find out change in entropy for conversion of 1 gm ice to water at 273 K and 1 atm pressure. Enthalpy of fusion is 6.02 cal/mol k

★ Second law of Thermodynamics —

$$\Delta S_{total} \text{ or } \Delta S_{universe} > 0 \text{ or } (+ve)$$
$$\Delta S_{system} + \Delta S_{surrounding} > 0 \quad (+ve)$$

a) It tell us about the direction of flow of heat.
b) All natural process in universe are irreversible process or natural process are spontaneous in nature.
c) Due to spontaneous process, entropy of universe ↑ing continuously

GIBB'S FREE ENERGY (G)

a) Gibb's energy is defined at constant temp and pressure to predict spontanity of a process (system)
b) It is a thermodynamic quantity which is used to measure the capacity of system to do useful work OR it is the part of total energy of system which can be convert into useful work

c) Mathematically, It is expressed as

$$G = H - TS$$

d) Enthalpy (H), ~~and~~ temp., entrophy (S) are state function so gibb's free energy is also state function. so, above reaction can also be written as — $\Delta G = \Delta H - T\Delta S$

This reaction is also known as Helmholtz Gibbs eq reaction.

$\Delta G < 0$ (-ve) ⟶ spontaneous

$\Delta G > 0$ (+ve) ⟶ non-spontaneous

$\Delta G = 0$ ⟶ at equillibrium

ΔH	ΔS	ΔG	Process
−ve	+ve	−ve	Spontaneous at all temp.
+ve	−ve	+ve	non-spontaneous —"—
−ve	−ve	−ve	Spontoneous at low temp.
−ve	−ve	+ve	Non-spontaneous at high temp.
+ve	+ve	−ve	Spontaneous at high temp.
+ve	+ve	+ve	Non-spontaneous at low temp.

Que $A \rightarrow 2B + C$

$\Delta H = 30\ kJ/mole$

$\Delta S = 60\ J/mol$

find out the temp. above which reaction should be spontaneous

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

−ve $\quad 30000 - T \times 60$

$T > \frac{30000}{60}$

$T > 500\ K$

T above 500 K

Relation between change in Gibb's free Energy (standard) and standard cell potential.

$\Delta G^\circ = - nFE^\circ cell$

Here ; n = n factor

F = faraday constant = 96500 coulomb / mole

E° = standard cell potential

Relation between ΔG° and Equillibrium constant -

$$\Delta G^\circ = - 2.303\ nRT \log kc$$

$$- 2.303\ nRT \log \frac{(Product)}{(Reactant)}$$

$$\Delta G^\circ = - 2.303\ nRT \log \frac{[Anode]}{[cathode]}$$