

\* For Adiabatic,

system in which heat given is 0

∴ dq = 0

∴ ds =  $\frac{dq}{T}$

ds = 0

change in entropy = 0

Statements of 2nd law of Thermodynamics:  
Planck

Kelvin statement

↓

It is impossible to construct an engine which operates in a complete cycle, will absorb heat from a single body & convert it completely into work without leaving changes in the working system.

In short heat cannot be completely (100%) converted into work. In other words no heat engine is 100% efficient.

Clausius Statement

↓

It is impossible to transfer for a self acting machine, ~~unaided~~ unaided by any external agency to convert transfer heat continuously, from one body

at lower temp. to a body at higher temp.  
 In short,  
 heat does not flow from cold system to hot system without any external support

\* Calculation of entropy for Ideal Gases.  
 for irreversible.

According to 1st law,

$$dU = dq + w$$

$$dU = dq - w \quad [\text{work done by system}]$$

$$dq = dU + w$$

$$T ds = dU + w \quad \text{since we know,}$$

$$T ds = C_v dT + P dV \quad \frac{dq}{T} = ds, \quad dU = C_v dT$$

Dividing whole eq. by T

$$w = P dV \quad (\text{Expansion work})$$

$$ds = \frac{C_v dT}{T} + \frac{P dV}{T}$$

as, for ideal gas,  $PV = RT$

$$ds = \frac{C_v dT}{T} + \frac{R dV}{V}$$

Integrating both side

$$\int_{s_1}^{s_2} ds = \int_{T_1}^{T_2} \frac{C_v dT}{T} + \int_{V_1}^{V_2} \frac{R dV}{V}$$

$$\Delta s = C_v \ln \left( \frac{T_2}{T_1} \right) + R \ln \left( \frac{V_2}{V_1} \right)$$

$$\Delta S = C_v \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1}$$

for n moles

$$\Delta S = n C_v \ln \frac{T_2}{T_1} + n R \ln \frac{V_2}{V_1}$$

as for ideal gas,  $PV = RT$

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$\frac{V_2}{V_1} = \frac{P_1 T_2}{P_2 T_1}$$

Now,  $\Delta S = n C_v \ln \frac{T_2}{T_1} + n R \ln \frac{P_1 T_2}{P_2 T_1}$

$$\Delta S = C_v \ln \frac{T_2}{T_1} + R \ln \frac{P_1}{P_2} + R \ln \frac{T_2}{T_1}$$

$$\Delta S = (C_v + R) \ln \frac{T_2}{T_1} + R \ln \frac{P_1}{P_2}$$

as,  $C_v + R = C_p$

$$\Delta S = C_p \ln \frac{T_2}{T_1} + R \ln \frac{P_1}{P_2}$$

for n moles,

$$\Delta S = n C_p \ln \frac{T_2}{T_1} + n R \ln \frac{P_1}{P_2}$$

(B)

For Isothermal,

$$\Delta S = nR \ln \frac{V_2}{V_1}$$

$$\text{or } \Delta S = nR \ln \frac{P_1}{P_2}$$

For Isochoric,

$$\Delta S = n C_V \ln \frac{T_2}{T_1}$$

For Isobaric,

$$\Delta S = n C_P \ln \frac{T_2}{T_1}$$

★  $\Delta S$  for Isobaric  $>$   $\Delta S$  for Isochoric at same temp. range

Ques:- 10 mole of ideal gas is allowed to expand from 10 atmosphere @ at 300 K to 100 atm at 600 K. If the value of  $C_p$  is 6.9 cal/mole. Calculate  $\Delta S$ .

→  $n = 10$  moles,  $T_1 = 300$  K,  $T_2 = 600$  K,  
 $P_1 = 10$  atm,  $P_2 = 100$  atm,  
 $C_p = 6.9$

$$\Delta S = n C_P \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2}$$

$$\Delta S = 10 \times 6.9 \times 2.303 \times \log \frac{600}{300} + 10 \times 2.303 \times \log \frac{10}{100}$$

GOOD WRITE

$$\Delta S = 10 \times 6.9 \times 2.303 \times \log 2 + 10 \times 2.303 \times \log \frac{10}{100}$$

$$\Delta S = 158.907 \times \log 2 +$$

Ques 9. 6 mole of ideal gas expanded isothermally & reversibly from vol. of 1 dm<sup>3</sup> to 10 dm<sup>3</sup> at 27°C. what is ΔS

$$\rightarrow \Delta S = nR \ln \frac{V_2}{V_1} = 6 \times 0.821 \times 2.303 \times \log 10$$

$$\Delta S = 11.34 \text{ caloric.}$$

Ques 10. Calculation of Entropy during Reversible phase transformation.

$$s \rightleftharpoons l \quad \Delta S_f = \frac{\Delta H_f}{T_m}$$

boiling\*  $l \rightleftharpoons g \quad \Delta S_v = \frac{\Delta H_v}{T_b}$

$$s \rightleftharpoons c \quad \Delta S_{sub} = \frac{\Delta H_{sub}}{T_{sub}}$$

\* Trouton assumed that ratio of enthalpy of vapourisation to boiling point of any liquid, or entropy of vapourisation.

$$\Delta S_v = \frac{\Delta H_v}{T_b} \approx 88 \text{ J/kmole}$$

provided that there is no hydrogen bonding in liquid.

Ques: Calculate the ent \$\Delta S\$ in evaporation of 1 mole of water at its boiling point given that \$\Delta H\_v\$ at boiling pt is 2259 J/g

\$\rightarrow\$  $\Delta S_{vap} = \frac{\Delta H_{vap}}{T_b}$

$$\Delta S_v \text{ for 1 mole} = 2259$$

$$\Delta S_v \text{ for 18g or 1 mole} = 2259 \times 18$$

$$\Delta S_v \text{ for 273K or } 100^\circ\text{C} = \frac{2259 \times 18}{373}$$

\$\Rightarrow\$

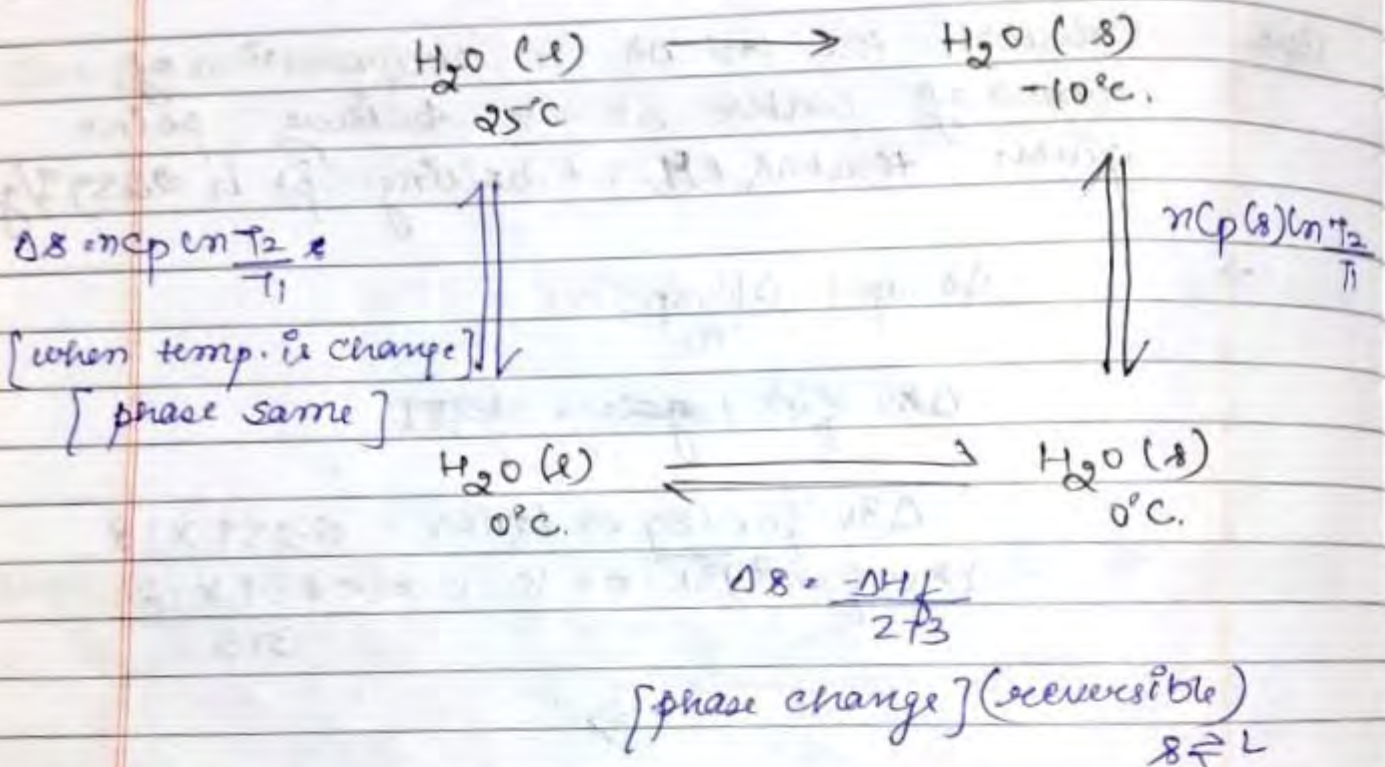
★ Calculation of Entropy for irreversible phase transformation.

Entropy change for irreversible process can be calculated by changing initial state to final state through reversible path because.

entropy change is defined for reversible process.

for example:- if we want to calculate  $\Delta S$  during conversion of water at  $25^\circ\text{C}$  into ice at  $-10^\circ\text{C}$ .

We need to convert the irreversible (~~system~~) process into number of reversible process.



Ex

Ques:- Calculate the entropy change of 1 mole of water at  $25^\circ\text{C}$  transforming into ice irreversibly at  $-10^\circ\text{C}$  given that  $C_p(\text{liquid})$   
 $C_p(l) \Rightarrow 75.32 \text{ J/Kmole}$ ,  $\Delta H_f = 6 \text{ KJ/mole}$  &  
 $C_p(s) = 36.7 \text{ J/Kmole}$ .

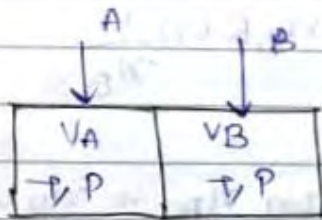
### Thermodynamics



## Entropy of mixing :-

→ CONDITIONS :-

- \* all considered gases are ideal in nature.
- \* There is no chemical rxn during mixing of gases.
- \* There is no change in volume of during mixing of gases,  $\Delta V_{mix} = 0$ .
- \*  $\Delta U_{mix} = 0$
- \*  $\Delta H_{mix} = 0$
- \* Isothermal (temp. constant)
- \* Isobaric (to pressure, const)



consider, two gases A, B are separate by partition.

$$\Delta S_{mixing} = nR \ln \frac{V_{total}}{V_i}$$

$$\text{for } \Delta S_A = n_A R \ln \frac{V_{total}}{V_A}$$

$$\Delta S_B = n_B R \ln \frac{V_{total}}{V_B}$$

$$\Delta S_{mix} = n_A R \ln \frac{V_{total}}{V_A} + n_B R \ln \frac{V_{total}}{V_B} \quad \text{--- (1)}$$

∴ for ideal gas,

$$P V_A = n_A R T$$

$$P V_B = n_B R T$$

$$P V_{\text{total}} = n_{\text{total}} (n_A + n_B) R T$$

from above eq. we get

$$\frac{V_A}{V_{\text{total}}} = \frac{n_A}{n_A + n_B} = n_A \quad (\text{mole fraction})$$

$$\frac{V_B}{V_{\text{total}}} = \frac{n_B}{n_A + n_B} = n_B$$

put value in Eq (1)

$$\Delta S_{\text{mix}} = n_A \cdot R \ln \frac{1}{n_A} + n_B \cdot R \ln \frac{1}{n_B}$$

$$\Delta S_{\text{mix}} = -R [n_A \ln n_A + n_B \ln n_B]$$

for a system containing  $i$  no. of gases.

$$\Delta S_{\text{mix}} = -R \left[ \sum n_i \ln n_i \right]$$

$$\text{Total } \Delta S_{\text{mixing}} \left\{ \Delta S_{\text{mix}} = -2.303 R \left[ \sum n_i \log n_i \right] \right\}$$

$$\text{Total } (\Delta S_{\text{mix}})_{\text{molar}} \left\{ (\Delta S_{\text{mix}})_{\text{molar}} = -2.303 R \sum \frac{n_i \log n_i}{n} \right\}$$

$$(\Delta S_{mix})_{molar} = -2.303 R \left[ \sum n_i \log n_i \right]$$

So,  $(\Delta S_{mix})$  always ~~for~~ +ve.  
because  $\log n_i$  is -ve

$$\therefore (\Delta S_{mix})_{molar} = +ve$$

Ques:- 1 mole of  $N_2$  is mixed with 3 moles of oxygen.  
Calculate  $(\Delta S)_{molar}$

$$\rightarrow (\Delta S_{mix})_{molar} = 2.303 \times 8.314 \left[ \sum \frac{n_i}{4} \log \frac{4}{n_i} \right]$$

$$(\Delta S_{mix})_{molar} = -2.303 \times R \left[ \frac{1}{4} \log \frac{1}{4} + \frac{3}{4} \log \frac{3}{4} \right]$$

$\Rightarrow$

Ques:- 2 mole of  $H_2$  mix with 3 mole of  $N_2$  calculate  $(\Delta S)_{mix}$

$\rightarrow$

$$\Delta S_{mix} = -R \left[ 2 \log \frac{2}{5} + 3 \log \frac{3}{5} \right]$$

$$\Delta S_{mix} = -2.303 R \left[ 2 \log \frac{2}{5} + 3 \log \frac{3}{5} \right]$$

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

$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$

$\Delta G_{mix} = -T\Delta S$

$\therefore \Delta G_{mix} = +2.303RT \left[ \sum n_i \log \pi_i \right]$

$(\Delta G_{mix})_{molar} = 2.303RT \left[ \sum \pi_i \log \pi_i \right]$

$(\Delta G_{mix})_{molar} < 0$

H<sub>2</sub>O

Answer:-

To find  $\Delta S = ?$

water  $\rightarrow$  ice.

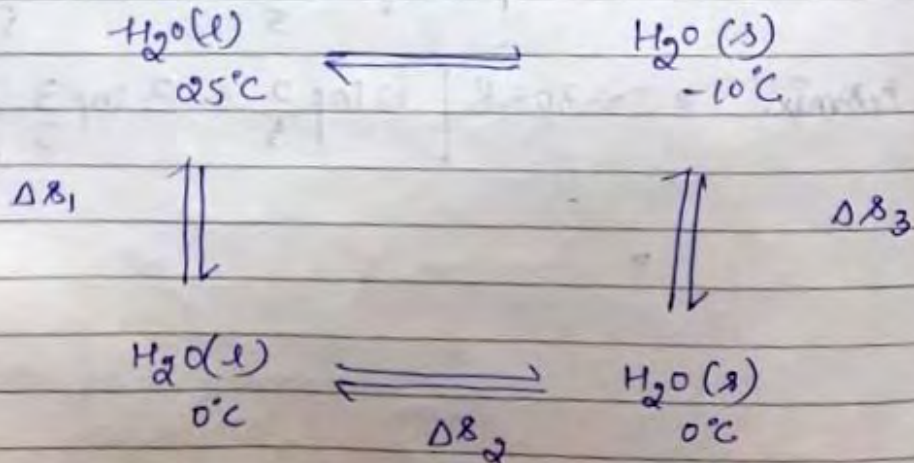
$n = 1 \text{ mole}$

$\Delta T = -10^\circ\text{C}$ .  $25^\circ\text{C} \rightarrow -10^\circ\text{C}$

$C_p(l) = 75.32 \text{ J/K mole}$

$\Delta H_f = -6 \text{ KJ/mole}$

$C_p(s) = 36.7 \text{ J/K mole}$



$$\Delta S_{total} = \Delta S_1 + \Delta S_2 + \Delta S_3$$

$$\Delta S_1 = \eta C_p \ln \frac{T_2}{T_1} = 1 \times 75.32 \times 2.303 \times \log(0-25)$$

$$\Delta S_1 = -75.32 \times 2.303 \times \log 25 = -173.46 \times 1.397$$
$$\Delta S_1 = -242.32$$

$$\Delta S_2 \text{ (phase change)} \quad S \rightleftharpoons L$$

$$\Delta S_2 = \frac{-\Delta H_f}{273}$$

$$\Delta S_2 = \frac{-6000}{273}$$

$$\Delta S_2 = -21.97$$

$$\Delta S_3 = \eta C_p \ln \frac{T_2}{T_1} = 1 \times 36.7 \times 2.303 \times \log(-10-0)$$

$$\Delta S_3 = -36.7 \times 2.303 \times \log 10$$

$$\Delta S_3 = -84.5201$$

$$\Delta S_3 =$$

$$\Delta S_{Total} = -242.32 + 21.97 - 84.52$$

$$= -348.81$$

Ques 2- On boiling an egg, entropy increases as due to denaturation the helical structure of protein become more complicated & random coiled structure. You would have thought that on boiling the liquid protein gets solidifies & thus entropy decreases.

\* Criteria for Reversible & Irreversible process:-

①

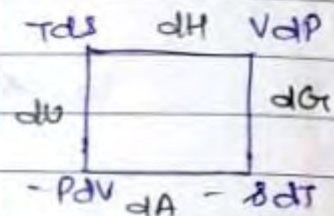
$$dH \leq Tds + VdP$$

at constant  $H, P$

$$(ds)_{H,P} \geq 0$$

at constant  $S, P$

$$(dH)_{S,P} \leq 0$$



$\Delta S \geq 0$   
 Irreversible  
 Reversible

②

$$dG \leq VdP - SdT$$

at constant  $P, T$

$$(dG)_{P,T} \leq 0$$

③

$$dA \leq -PdV - SdT$$

at constant  $T, P$

$$(dA)_{T,P} \leq 0$$

④

$$du \leq Tds - PdV$$

at constant  $u, V$

$$(ds)_{u,V} \geq 0$$

at const.  $S, V$

$$(du)_{S,V} \leq 0$$

Partial Molar Quantities & Gibbs Duhem Equation:

Thermodynamic function like  $G, U, H, S, A$  are state functions i.e. they depend on two variables out of three ( $P, V, T$ ) keeping third constant for eg:-  
at constant volume, thermodynamic function.

$$X = f(T, P) \quad \text{at constant volume}$$

All the thermodynamic functions are extensive properties so they depend on amount of substance or no. of moles.

Let  $N$  be the number of moles in a closed system such that

$$N = n_1 + n_2 + \dots + n_i + n_j$$

where  $n_1, n_2, \dots, n_i, n_j$  are no. of moles of first, second,  $i$ th &  $j$ th component respectively.

$$X = f(T, P, N) \quad \text{at constant volume.}$$

For example 2. for a heterogeneous close system containing  $\phi$  compounds. components

$$X = f(T, P, n_1, n_2, \dots, n_i, n_j)$$

For example 2. for a binary system (containing two components)

$$[n_1, n_2]$$

$$X = f(T, P, n_1, n_2)$$

Now,  $X = f(T, P, n_1, n_2, \dots, n_i, n_j)$   
complete differentiate

$$dX = \left( \frac{dX}{dT} \right)_{P, n_1, n_2, \dots, n_i, n_j} dT + \left( \frac{dX}{dP} \right)_{T, n_1, n_2, \dots, n_i, n_j} dP +$$

$$\left( \frac{dX}{dn_1} \right)_{T, P, n_2, \dots, n_i, n_j} dn_1 + \left( \frac{dX}{dn_2} \right)_{T, P, n_1, \dots, n_i, n_j} dn_2 +$$

$$\left( \frac{dX}{dn_i} \right)_{T, P, n_1, n_2, \dots, n_j} dn_i + \left( \frac{dX}{dn_j} \right)_{T, P, n_1, n_2, \dots, n_i} dn_j$$

Change in thermodynamic function w.r.t number of moles of its component in a closed heterogeneous system keeping temperature, pressure, & moles of other component ( $n_1, n_2, \dots, n_i$ ) constant is defined as partial molar quantities

For example -

$$U_i^o = \left( \frac{\partial U}{\partial n_i} \right)_{T, P, n_1, n_2, \dots, n_j} \quad \text{Partial molar internal energy.}$$

$$H_i^o = \left( \frac{\partial H}{\partial n_i} \right)_{T, P, n_1, n_2, \dots, n_j} \quad \text{Partial molar enthalpy.}$$

$$S_i^o = \left( \frac{\partial S}{\partial n_i} \right)_{T, P, n_1, n_2, \dots, n_j} \quad \text{Partial molar entropy.}$$

$$A_i^o = \left( \frac{\partial A}{\partial n_i} \right)_{T, P, n_1, n_2, \dots, n_j} \quad \text{Partial molar Helmholtz free energy.}$$