D. B. College (Jaynagar) chemistry department
Thermodynamics. B.Sc.(II) Sub.
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Condition for gas:—

- $n\uparrow$ $\Delta S > 0$
- $T\uparrow$ $\Delta S > 0$ $Fe(300K) \rightarrow Fe(400K)$
- $V\uparrow$ $\Delta S > 0$ $CO_2(10atm) \rightarrow CO_2(1atm)$
- $P\uparrow$ $\Delta S < 0$

$CO_2(1atm) \rightarrow CO_2(8atm)$ $\Delta S < 0$

Example:—

1. $\Delta S_{graphite} > \Delta S_{diamond}$
   (Free $^{\ominus}$ more)

During boiling of egg $\Delta S > 0$
due to denaturation of proteins

Stretching of rubber $\Delta S < 0$

Coiled (disordered) $\xrightarrow{\Delta S < 0}$ uncoiled ordered

Mixture formation

gas + gas
gas + liq
liq + liq
liq + solid
solid + solid

] randomness $\Delta S\uparrow$

(2) Gas + Solid absorb $\Delta S \downarrow$

$$H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(g) \quad \Delta S < 0$$

Eg :- Rusting of Iron : $\Delta S > 0$

Fe + rust / m'n

Precipitation :- $\Delta S < 0$

$$Ag^+(aq) + Cl^-(aq) \rightleftharpoons AgCl(s)$$

Crystallisation $\Delta S < 0$

Polymerisation $\Delta S < 0$

Entropy change in Physical reacn :-

1. Heat of fussion / Enthalpy of fusion (ΔH_{fusion}) when 1 mole of liquid is converted into liquid at its M.P. Then heat change is c/a ΔH_{fusion}.

$$Solid \rightleftharpoons liquid \quad (M.P)$$

$$\Delta S = \frac{\Delta H_{fusion}}{T} \qquad J K^{-1} mol^{-1}$$

2. Heat / Enthalpy vapourisation ($\Delta H_{vap.}$)

$$liq \rightleftharpoons gas \quad B.P.$$

$$\Delta S = \frac{\Delta H_{vap.}}{T}$$

③

3. Heat / Enthalpy Sublimation

$$\text{Solid} \rightleftharpoons \text{gas}$$

$$\Delta S_{sub} = \frac{\Delta H_{sub}}{T}$$

Ques: For a sample of perfect gas when its Pressure is changed isothermally from P_i to P_f then entropy change is given by -

① $\Delta S = nRT \ln \frac{P_i}{P_f}$ ② $\Delta S = nRT \ln \frac{P_f}{P_i}$

③ $\Delta S = nR \ln \frac{P_i}{P_f}$ ④ $\Delta S = nR \ln \frac{P_f}{P_i}$

$T \rightarrow$ Const.

$$\Delta S = nR \ln \frac{V_2}{V_1} \qquad P \propto \frac{1}{V}$$

$$\Delta = nR \ln \frac{P_i}{P_f}$$

Ques:- $\Delta S > 0$ for

① $CaO(s) + CO_2(g) \rightleftharpoons CaCO_3(s)$ $\Delta n_g < 0$, $\Delta S < 0$

② $Nacl(aq) \rightleftharpoons Nacl(s)$ $\Delta S < 0$

③ $NaNO_3(s) \rightleftharpoons Na^+(aq) + NO_3^-(aq)$ $\Delta S > 0$

④ $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ $\Delta n_g = 2 - 4 = -2$, $\Delta S < 0$

(4) Ques:- $\Delta S < 0$ for.

(1) $H_2O(l) \longrightarrow H_2O(g)$ Δn_g

(2) $H_2O(g) \longrightarrow H_2O(s)$

(3) $H_2O(s) \longrightarrow H_2O(l)$

(4) $H_2O(s) \longrightarrow H_2O(g)$

Ques:- The entropy change involved in isothermal & reversible expansion of 2 mol of an ideal gas from a volume of 1 cm^3 to 10 cm^3 at 27°C in $JK^{-1} mol^{-1}$

$$\Delta S = 2.303\, nR \log_{10} \frac{V_2}{V_1}$$

$$= 2.303 \times 2 \times 8.3 \log_{10} \frac{10}{1}$$

$$= 2.3 \times 2 \times 8.3 \log_{10} 10^1$$

$$= 4.6 \times 8.3$$

$$\Delta S = 38.18 \ JK^{-1} mol^{-1}$$

8.3
4.6
498
332 ×
3818

Ques:- The enthalpy of vap. for water is 185 KJ mol^{-1}. Then calculate entropy change.

$$\Delta S = \frac{\Delta H_{vap}}{T}$$

$$= \frac{185 \times 10^3}{373} = \frac{18500}{373}$$

$$= 495.9 \ J\,mol^{-1}K^{-1}$$