

THERMODYNAMICS

$$\Delta S_r = \frac{\Delta H}{T} = \frac{6000}{273} \quad S \rightarrow l$$

at 0°C

$$(\Delta S_r)_{273} - (\Delta S_r)_{263} = (75-36) \ln \frac{273}{263}$$

Calculation of ΔG :-

Case - I for a substance not undergoing any chemical & phase change

$$G = H - TS$$

$$G = U + PV - TS$$

$$dG = dU + PdV + Vdp - Tds - SdT$$

$$dG = \cancel{q_r} + \cancel{W_{PV}} + \cancel{PdV} + Vdp - \cancel{Tds} - SdT$$

for a rev path

$$dG = Vdp - SdT$$

for rev as well as
irrev change
from A to B

for a rev path

$$q_{rev} = Tds$$

$$W = -P_{ext} dV$$

$$= -PdV$$

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$$\{ dG = \int V dp - \int S dT$$

(a) At constant Temp

$$\Delta G = \int V dp$$

i) for ideal gas

$$= \int \frac{nRT}{P} dp$$

$$= nRT \ln \frac{P_2}{P_1}$$

$$\boxed{\Delta G = -nRT \ln \frac{P_1}{P_2}}$$

= work done

(b) At const Pressure

$$dG = -SdT$$

ii) for solid/lig

$$\Delta G = \int V dp$$

$$\boxed{\Delta G = V(P_2 - P_1)}$$

$$\begin{pmatrix} \Delta U \\ \Delta H \\ \Delta S \\ \Delta G \end{pmatrix}$$

THERMODYNAMICS

Case-II for chemical & phase c | (14) $= 50 \text{ kJ} - \frac{300}{1000} (-50 + R \ln 10)$

$$G = H - TS$$

at const T

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

(12) ΔG_r at 1 atm, 300 K $\rightarrow \Delta G_r = 50 \text{ kJ} - \frac{300(-50)}{1000} = 65 \text{ kJ}$

(13) " " 1 atm, 600 K $= 47 \text{ kJ} - \frac{600(-50 - 10 \ln 2)}{1000}$

(14) " " 10 atm, 300 K

→ (15) " " 10 atm, 600 K | (15) $= 47 - \frac{600(-50 - 10 \ln 2 + R \ln 10)}{1000}$

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$$\Delta G = \underline{\Delta H} - T \underline{\Delta S}$$

ΔH_{sys}
-ive

+ive

+ive

-ive

ΔS_{sys}
+ive

-ive

+ive

-ive

ΔG
-ive

+ive

-ive

+ive

-ive

+ive

feasible at any temperature

not " " "

feasible at high temperature

not " " low "

feasible at low temp.

not " " high temp.

THERMODYNAMICS

Q. for a reaction $(A \rightarrow B)$ find equilibrium temperature.

$$\Delta H_r = \underline{100 \text{ kJ}}, \quad \Delta S_r = 25 \text{ J/K/mol}$$

Soln: for equilibrium temp

$$\Delta G_r = 0$$

$$\Delta S_r = \frac{\Delta H}{T} = \frac{100 \times 10^3}{25} = 4000 \text{ K}$$



THERMODYNAMICS

①

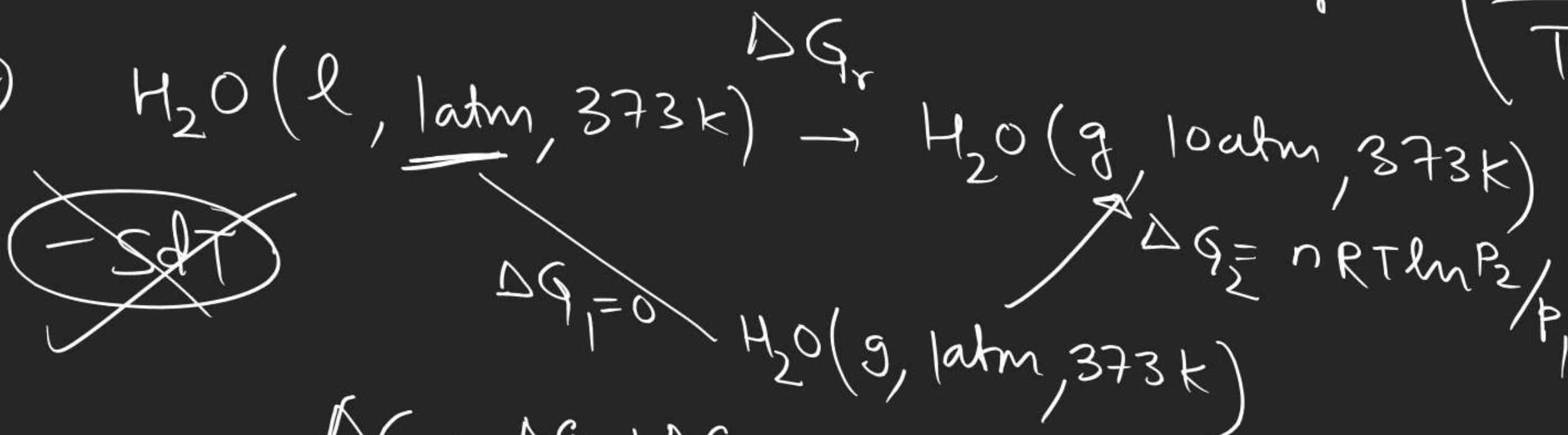


$$\Delta G_r = 0$$

$$\Delta G = \Delta H_r - T \Delta S_r$$

$$= \Delta H_r - T \left(\frac{\Delta H_r}{T} \right) = 0$$

②



$$\begin{aligned}\Delta G_r &= \Delta G_1 + \Delta G_2 \\ &= 0 + RT \ln 10\end{aligned}$$

THERMODYNAMICS

Relationship b/w ΔG & non-PV work \rightarrow

$$q \leq T ds \quad (\text{Clausius Inequality})$$

from 1st law of T.D

$$dU - w_{PV} - w_{non-PV} \leq T ds$$

$$dU - w_{PV} - T ds \leq w_{non-PV}$$

$$\text{at constant } T \& P \quad (P_{ext} = P)$$

$$dU + PdV - T ds \leq w_{non-PV}$$

$$d(U + PV - TS) \leq w_{non-PV}$$

$$d(H - TS) \leq w_{non-PV}$$

$$dG \leq w_{non-PV}$$

$$w = -50 \text{ kJ}$$

Work done by the system = 50 kJ

$$-dG \geq -w_{non-PV}$$

$$-dG \geq w_{non-PV}, \text{ by}$$

for a rev change

$$-dG = w_{non-PV}, \text{ by}$$

(useful work)

THERMODYNAMICS

decrease in Gibb's energy equals to the maximum amount of non-pv work which can be obtained by a system.

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