

THERMODYNAMICS

$$\Delta S_r = \frac{\Delta H}{T} = \frac{6000}{273}$$

at 0°C



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

Calculation of ΔG : \rightarrow Case-I for a substance not undergoing any chemical & phase change

$$G = H - TS$$

$$G = U + PV - TS$$

$$dG = dU + PdV + VdP - TdS - SdT$$

$$dG = \cancel{q} + \cancel{W_{PV}} + \cancel{PdV} + \cancel{VdP} - \cancel{TdS} - SdT$$

for a rev path

$$\boxed{dG = VdP - SdT}$$

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

(a) At constant Temp

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

(i) for ideal gas

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

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

$$\Delta G = -nRT \ln P_1 / P_2$$

= work done

(ii) for solid/liq

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

$$\Delta G = V(P_2 - P_1)$$

(b)

At const Pressure

$$dG = -S dT$$

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

THERMODYNAMICS

Case-II for chemical & phase c

$$G = H - TS$$

at const T

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

(12) ΔG_r at 1 atm, 300 K $\rightarrow \Delta G_r =$

(13) " " 1 atm, 600 K

(14) " " 10 atm, 300 K

(15) " " 10 atm, 600 K

$$\begin{aligned} (14) &= 50 \text{ kJ} - \frac{300}{1000} (-50 + R \ln 10) \\ &= 65 \text{ kJ} - \frac{3}{10} R \ln 10 \end{aligned}$$

$$= 50 \text{ kJ} - \frac{300(-50)}{1000} = 65 \text{ kJ}$$

$$= 47 \text{ kJ} - \frac{600(-50 - 10 \ln 2)}{1000}$$

$$(15) = 47 - \frac{600}{1000} (-50 - 10 \ln 2 + R \ln 10)$$

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

ΔH_{sys}	ΔS_{sys}	ΔG	
-ive	+ive	-ive	feasible at any temperature
+ive	-ive	+ive	not " " " "
+ive	+ive	-ive	feasible at high temperature
-ive	-ive	+ive	not " " low "
		-ive	feasible at low temp
		+ive	not " " high temp

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Q. for a reaction $(A \rightarrow B)$ find equilibrium temperature.
 $\Delta H_r = \underline{100 \text{ kJ}}$, $\Delta S_r = 25 \text{ J/K/mol}$

Solⁿ: for equilibrium temp

$$\Delta G_r = 0$$

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



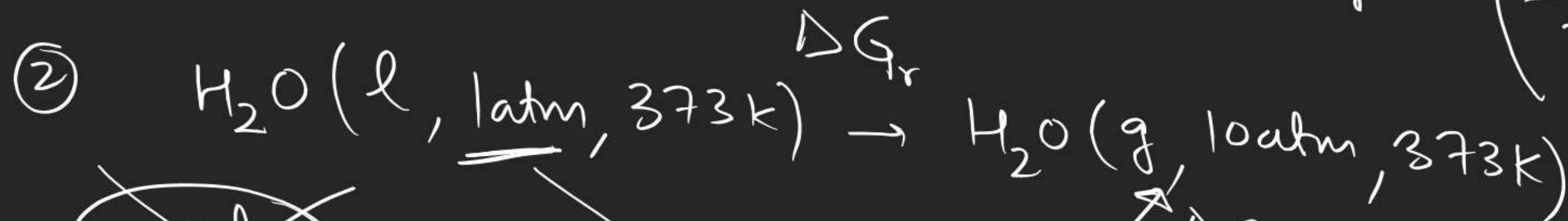
THERMODYNAMICS



$$\Delta G_r = 0$$

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

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



~~$-SdT$~~

$$\Delta G_1 = 0$$



$$\Delta G_2 = nRT \ln P_2/P_1$$

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

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Relationship betn ΔG & non-PV work: \rightarrow

$q \leq T ds$ (Clausius Inequality)
from 1st law of T.D

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

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

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

$$dU + P dV - T ds \leq W_{non-PV}$$

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

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

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

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

Work done by the system = 50 kJ

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

$-dG \geq W_{non-PV}$, by
for a rev change

$$-dG = W_{non-PV, by}$$

(useful work)

THERMODYNAMICS

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

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