

INDIAN INSTITUTE OF SCIENCE EDUCATION AND RESEARCH MOHALI

Mid-Term 2 2022-2023

CHM202: ENERGETICS AND DYNAMICS OF CHEMICAL REACTIONS

DURATION 1 HR

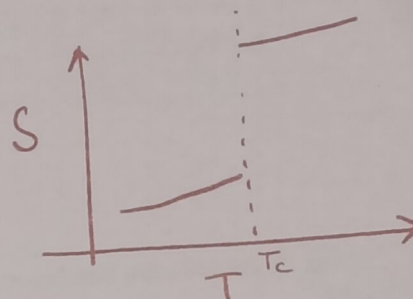
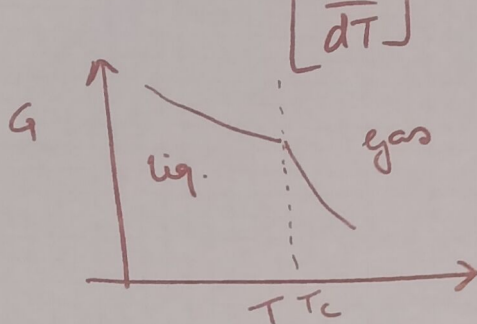
FULL MARKS 20

1. One mole of a gas system is changed from $A \equiv (P_1, V_1)$ to $B \equiv (P_2, V_2)$ by first changing pressure at constant volume and then volume at constant pressure. Show that,
 - (a) $S_2 - S_1 = C_P \cdot \ln \frac{T_2}{T_1} - R \cdot \ln \frac{P_2}{P_1}$
 - (b) Write the expression for the entropy-change if the process goes other way, first change in V at constant P followed by a pressure-change at constant V , and via an intermediate of $I \equiv (P_0, V_0)$.
 - (c) Show from the above equation in (a), the entropy-change in adiabatic process leads to no-entropy change. $3 + 1 + 2 = 6$
2. Using Maxwell's relations, derive the Clapeyron equation. 2
3. Depict the change in entropy and free-energy as a liquid is heated and transformed to gas in S vs T and G vs T diagrams, respectively. $2 + 2 = 4$
4. What is the absolute entropy of 1 mole of water at 546 K? [Given: $C_P^{ice} = 0.5 \text{ cal/g.K}$ and $C_P^w = 1.0 \text{ cal/g.K}$, L_f (at 273 K) = 80 cal/g] 4

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5. (a) Show that free-energy of mixing decreases in mixing ideal gases. $2+2 = 4$
(b) The decrease in the free-energy of mixing is largest when equimolar quantities of two components are mixed. Show in a diagram.

(3)

Phase-transition from liquid \rightarrow gas
is a 1st order phase-transⁿ \Rightarrow means
 $\left[\frac{\partial G}{\partial T}\right]$ is discrete. & dS is continuous.



(4)

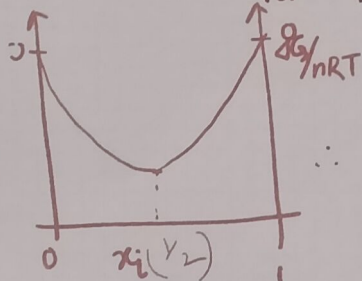
1 mole of water at 546 K \Rightarrow

$$S(546K) = S(0) + \int_0^{T_i} C_p(\text{ice}) \cdot \frac{dT}{T} + \frac{\Delta H_{\text{melt}}}{T} + \int_{T_i}^{T_b} C_p(\text{H}_2\text{O}) \frac{dT}{T} \\ + \frac{\Delta H_{\text{vap}}}{T_b} + \int_{T_b}^{546} C_p(\text{vap}) \cdot \frac{dT}{T} \rightarrow (2)$$

(5)

$$\Delta G_{\text{mixing}} = nRT \sum_i x_i \ln x_i \rightarrow (1)$$

For two gases $x_1 + x_2 = 1$; as $x_i < 1$
 $x_2 = 1 - x_1$ $\Delta G_{\text{mixing}} < 0$ (2)



$$\Delta G_{\text{mixing}} = RT [x_1 \ln x_1 + (1-x_1) \ln (1-x_1)]$$

$$\frac{d \Delta G_{\text{mixing}}}{d x_1} = 0 \text{ at minimal.}$$

$$\therefore \frac{d \Delta G_{\text{mixing}}}{d x_1} = RT \left[\dots \right] = 0$$

(2)

$$\begin{aligned}
 &= C_p (\gamma - 1) \ln \frac{V_1}{V_2} - R \gamma \ln \frac{V_1}{V_2} \\
 &= C_p \left(\frac{C_p - C_v}{C_v} \right) \ln \frac{V_1}{V_2} - R \cdot \frac{C_p}{C_v} \ln \frac{V_1}{V_2} \\
 \therefore \Delta S &= \left(\frac{C_p}{C_v} \right) R \ln \frac{V_1}{V_1} - \left(\frac{C_p}{C_v} \right) R \ln \frac{V_1}{V_2}
 \end{aligned}$$

$$\boxed{\Delta S = 0} \Rightarrow \text{proved.}$$

(2) Clapeyron eq.ⁿ $\frac{dP}{dT} = \frac{L}{T_c \Delta V}$
 $\begin{matrix} L: \text{Latent heat} \\ \Delta V: \text{Vol. change} \\ T_c: \text{Trans}^n \text{ Temp} \end{matrix}$

Maxwell's rel.ⁿ \vdash

$$\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V$$

$$\therefore T \left(\frac{\partial S}{\partial V} \right)_T = T \cdot \left(\frac{\partial P}{\partial T} \right)_V$$

$$\therefore T \cdot \left(\frac{\partial P}{\partial T} \right)_V = T \left(\frac{\partial S}{\partial V} \right)_T$$

during for a transition, phase transition, the T remains constant. $\Rightarrow T_c$
 and heat of trans.ⁿ \approx heat-exchange in
 latent heat $\equiv L = T \cdot dS = dQ$

$$\therefore T \cdot \left(\frac{\partial P}{\partial T} \right)_V = T_c \left[\frac{dP}{dT} \right]_V = \frac{L}{\Delta V}$$

$$\therefore \boxed{\frac{dP}{dT} = \frac{L}{T_c \cdot \Delta V}} \Rightarrow \text{proved.}$$

(3)

Phase-transition from liquid \rightarrow gas

$$1. \quad dU = dQ - PdV$$

$$dQ = dU + PdV$$

For 1 mole of ideal gas,

$$\rightarrow dU = C_V dT$$

$$\frac{dQ}{T} = C_V \frac{dT}{T} + P \frac{dV}{T} \quad \text{--- (1)}$$

For ideal gas,

$$PV = RT$$

$$P = \frac{RT}{V}$$

$$\therefore dS = C_V \frac{dT}{T} + R \cdot \frac{dV}{V}$$

$$S_2 - S_1 = C_V \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1}$$

$$\frac{V_2}{V_1} = \frac{T_2 P_1}{T_1 P_2} \Rightarrow R \ln \frac{V_2}{V_1} = R \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1}$$

$$\therefore S_2 - S_1 = (C_V + R) \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1} = C_P \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1} \quad \text{--- (1)}$$

(b) Expression would remain same / unchanged.

(c) Entropy-change in an adiabatic system is '0'.

So we have to prove that, $S_2 - S_1 = 0$

$$\text{From eq}^n \text{ (1), } \Delta S = C_P \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1}$$

$$\text{For adiabatic change, } PV^\gamma = \text{Constant}; \quad \gamma = C_P / C_V$$

$$\hookrightarrow \frac{P_2}{P_1} = \left(\frac{V_1}{V_2} \right)^\gamma$$

$$\& \quad \frac{T_2}{T_1} = \left(\frac{V_1}{V_2} \right)^{\gamma-1}$$

$$\therefore \text{For eq}^n \text{ (1), } \Delta S = C_P \ln \left(\frac{V_1}{V_2} \right)^{\gamma-1} - R \ln \left(\frac{V_1}{V_2} \right)^\gamma$$