

Answers - problem set 5

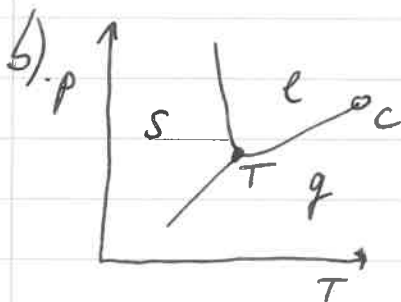
(2) a) in equil: $\mu_\alpha = \mu_\beta \rightarrow d\mu_\alpha = d\mu_\beta$

$d\mu = -S_m dT + V_m dp$, so

$-S_m^\alpha dT + V_m^\alpha dp = -S_m^\beta dT + V_m^\beta dp$

$(S_m^\beta - S_m^\alpha) dT = (V_m^\beta - V_m^\alpha) dp$

$\Rightarrow \frac{dp}{dT} = \frac{\Delta S_m}{\Delta V_m}$



slope $\rightarrow \frac{dp}{dT} = \frac{\Delta S_m}{\Delta V_m}$

s-l boundary:

• s \rightarrow l: $\Delta S_m > 0$, but $\Delta V_m < 0$!, hence $\frac{dp}{dT} < 0$, which is unusual.

• usually ΔV_m is small \rightarrow steep slope of s-l phase boundary.

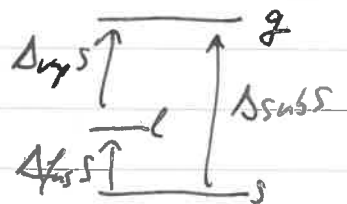
s-g & l-g boundaries:

$\frac{dp}{dT} > 0$, as s/l \rightarrow g $\Delta S_m > 0$ & $\Delta V_m > 0$. Less steep than s-l as $|\Delta V_m|$ is larger than for s-l.

c) \rightarrow see part b) negative s-l boundary

\hookrightarrow see part b)

d) Why is $(\frac{dp}{dT})_{sub} > (\frac{dp}{dT})_{vap}$?



$\Rightarrow \Delta_{sub} V \approx V_{m,g}$ & $\Delta_{vap} V \approx V_{m,g}$, but $\Delta_{sub} S = \Delta_{fus} S + \Delta_{vap} S$ so $\Delta_{sub} S > \Delta_{vap} S$

$\Rightarrow (\frac{dp}{dT})_{sub} \approx \frac{\Delta_{sub} S}{V_{m,g}} = \frac{\Delta_{vap} S}{V_{m,g}} + \frac{\Delta_{fus} S}{V_{m,g}} \sim > 0 (+ve)$

$= (\frac{dp}{dT})_{vap} + \frac{\Delta_{fus} S}{V_{m,g}} \sim > 0 (+ve)$

$\rightarrow (\frac{dp}{dT})_{sub} > (\frac{dp}{dT})_{vap}$

d) start from: $\frac{dp}{dT} = \frac{\Delta S_m}{\Delta V_m} \Rightarrow \Delta S_m = \Delta S_{tr} S$
 $\Delta V_m = \Delta S_{tr} V$

$$\frac{dp}{dT} = \frac{\Delta S_{tr} S}{\Delta S_{tr} V} = \frac{\Delta S_{tr} H}{T \Delta S_{tr} V}$$

$$\boxed{dS = \frac{dq_{rev}}{T} \xrightarrow{cstp} \frac{dH}{T} \rightarrow \Delta S = \frac{\Delta H}{T}}$$

since if gas is involved:

① $\Delta S_{tr} V = V_{m,g} - V_{m,ls} \approx V_{m,g}$

② perfect gas assumption: $V_{m,g} = \frac{RT}{P}$

$\Delta S_{tr} V \approx \frac{RT}{P}$

$$\Rightarrow \frac{dp}{dT} = \frac{\Delta S_{tr} H}{T \cdot \left(\frac{RT}{P}\right)} = \frac{P \cdot \Delta S_{tr} H}{RT^2}$$

$$\Rightarrow \frac{1}{P} \frac{dp}{dT} = \frac{\Delta S_{tr} H}{RT^2} \Rightarrow \frac{d \ln p}{dT} = \frac{\Delta S_{tr} H}{RT^2}$$

finally, for vapour pressure of liquid: $\Delta S_{tr} H = \Delta_{vap} H$:

$$\Rightarrow \frac{d \ln p}{dT} = \frac{\Delta_{vap} H}{RT^2}$$

✓

22) a) $\Delta_{\text{vap}}H = 44.0 \text{ kJ mol}^{-1}$, we need p_2 @ $T_2 = 393 \text{ K}$.

We consider

g
e

 \rightarrow so liquid-gas eqm \rightarrow Clausius-Clapeyron!

$$\frac{d \ln p}{dT} = \frac{\Delta_{\text{vap}}H}{RT^2}$$

\rightarrow we know for H_2O : $T_1 = 100^\circ\text{C} = 373 \text{ K}$ @ $p_1 = p^\ominus = 1 \text{ bar}$.
(boiling point @ p^\ominus)

$$\int_{p_1=p^\ominus}^{p_2=p} d \ln p = \frac{\Delta H}{R} \int_{T_1}^{T_2} \frac{1}{T^2} dT \rightarrow \ln \frac{p}{p^\ominus} = -\frac{\Delta_{\text{vap}}H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\ln \frac{p_2}{p^\ominus} = -\frac{44 \cdot 10^3}{8.314} \left(\frac{1}{393} - \frac{1}{373} \right) = 0.722$$

$$p^\ominus = 1 \text{ bar} \rightarrow p_2 = 2.06 \text{ bar.}$$

b) solid-liquid equilibrium \rightarrow Clapeyron Eq.: $\frac{dp}{dT} = \frac{\Delta S_{\text{m}}}{\Delta V_{\text{m}}} = \frac{\Delta_{\text{fus}}S}{\Delta_{\text{fus}}V}$

$$\frac{dp}{dT} = \frac{\Delta_{\text{fus}}S}{\Delta_{\text{fus}}V} = \frac{\Delta_{\text{fus}}H}{T \Delta_{\text{fus}}V} = \frac{\Delta_{\text{fus}}H}{T \Delta_{\text{fus}}V}$$

$$\int_{p_1}^{p_2} dp = \frac{\Delta_{\text{fus}}H}{\Delta_{\text{fus}}V} \int_{T_1}^{T_2} \frac{1}{T} dT \rightarrow p_2 - p_1 = \frac{\Delta_{\text{fus}}H}{\Delta_{\text{fus}}V} \cdot \ln \frac{T_2}{T_1}$$

c) $\Delta_{\text{fus}}H = 6.01 \text{ kJ mol}^{-1}$



$$T_1 = 273 \text{ K} \quad p_1 = p^\ominus = 1 \text{ bar} = 10^5 \text{ Pa}$$

$$T_2 = T_{\text{TP}} \quad p_2 = 533.29 \text{ Pa}$$

temp @ triple point \rightarrow we need to calculate $T_2 = T_{\text{TP}}$, to get the answer $T_2 - T_1$.

mass density

first calculate $\Delta_{fus}V$: use $\rho = \frac{m}{V} \rightarrow V = \frac{m}{\rho}$

$$\Delta_{fus}V = \frac{m^*}{\rho_e} - \frac{m^*}{\rho_s} = m^* \left(\frac{1}{\rho_e} - \frac{1}{\rho_s} \right)$$

mass of 1 mole H_2O
(18 g mol^{-1})

$\rho_e = 1 \cdot 10^6$
 $\rho_s = 0.917 \cdot 10^6$

in g m^{-3}

same mass unit

$$\text{so: } \Delta_{fus}V = 18 \cdot \left(\frac{1}{1 \cdot 10^6} - \frac{1}{0.917 \cdot 10^6} \right) = -1.63 \cdot 10^{-6} \frac{\text{m}^3}{\text{mol}}$$

(should be -ve)

$$\Rightarrow \text{now use } p_2 - p_1 = \frac{\Delta_{fus}H}{\Delta_{fus}V} \ln \frac{T_2}{T_1}$$

$$\ln \frac{T_2}{T_1} = (p_2 - p_1) \cdot \frac{\Delta_{fus}V}{\Delta_{fus}H} = (553.29 - 10^5) \cdot \frac{-1.63 \cdot 10^{-6}}{6.01 \cdot 10^3}$$

$$\ln \frac{T_2}{T_1} = 2.697 \cdot 10^{-5}$$

$$\frac{T_2}{T_1} = 1.0000269 \rightarrow (T_1 = 273 \text{ K}) \quad T_2 = 273.007363$$

$$\Rightarrow T_2 - T_1 = 7.37 \cdot 10^{-3} \text{ K}$$

the \Rightarrow This (small difference) makes complete sense, because the slope of sea level boundary ($\frac{dp}{dT}$) is very steep:

small change in T

large change in p .

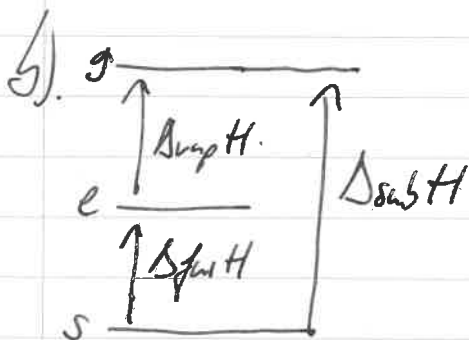
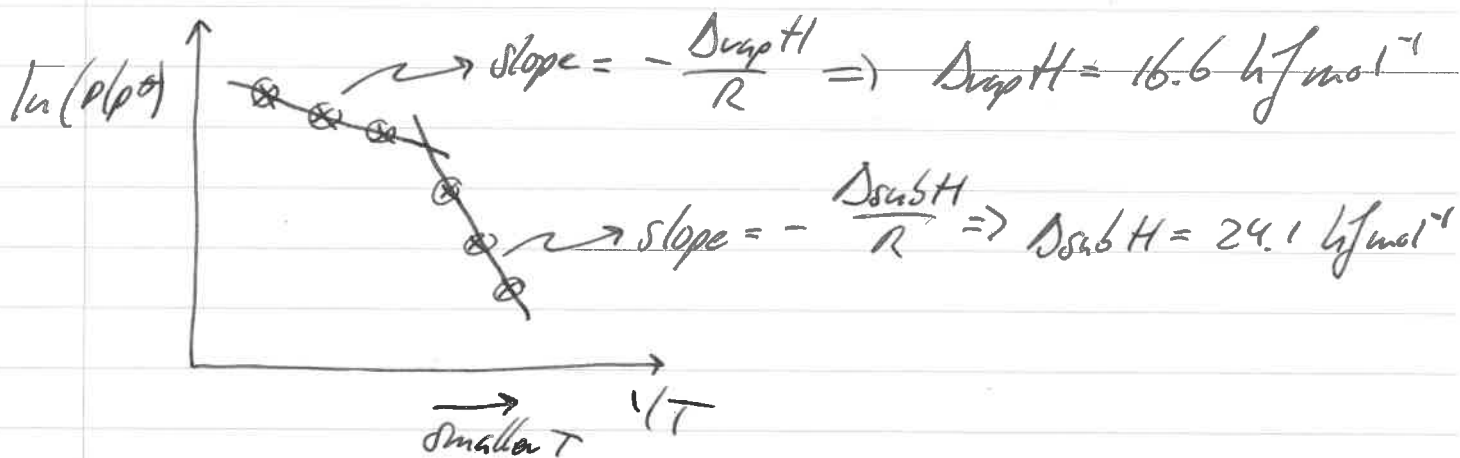
23) \Rightarrow vapour pressure of $\text{CO}_2 \rightarrow$ so gas involved
 a) \rightarrow solid-gas and/or liquid-gas involved

\Rightarrow Clausius-Clapeyron:

$$\frac{d \ln p}{dT} = \frac{\Delta_{\text{str}} H}{RT^2} \rightarrow \text{integrated form: } \ln \frac{p}{p^\ominus} = - \frac{\Delta_{\text{str}} H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

(see Exercise 22)

\Rightarrow plot of $\ln p/p^\ominus$ vs $\frac{1}{T} \rightarrow$ slope = $-\frac{\Delta_{\text{str}} H}{R}$



$$\Delta_{\text{fus}} H = \Delta_{\text{sub}} H - \Delta_{\text{vap}} H$$

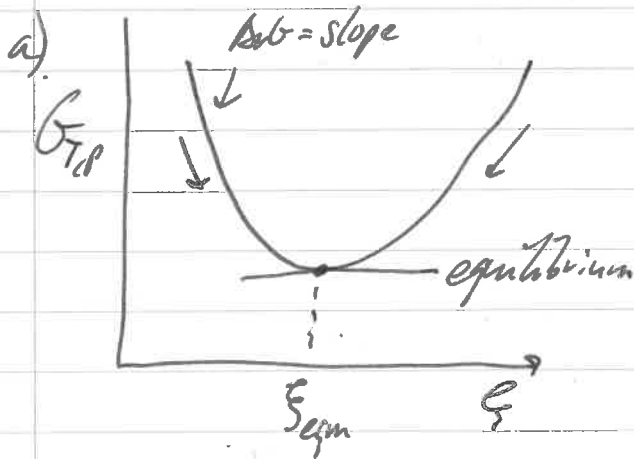
$$= 7.5 \text{ kJ mol}^{-1}$$

H: state function

(24)

$$\Delta_r G = \left(\frac{\partial G}{\partial \xi} \right)_{T,P}$$

see lecture:



- $\Delta_r G < 0$: forward reaction is spontaneous ($\xi \uparrow$)
- $\Delta_r G > 0$: backward reaction is spontaneous ($\xi \downarrow$)
- $\Delta_r G = 0$: equilibrium ($dG_{T,P} = 0 @ \text{eqm.}$)

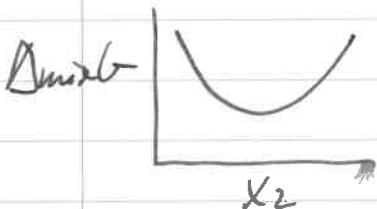
shape: minimum is due to mixing effects!

$$G = G^* + \Delta_{mix} G \quad \& \quad \Delta_{mix} G = nRT (x_1 \ln x_1 + x_2 \ln x_2)$$

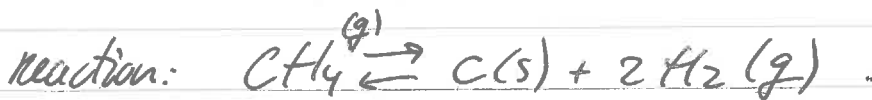
↑
pure, before mixing

< 0
as $x_i < 1$

(no need to learn $\Delta_{mix} G = \dots$)



b) $\Delta_f H^\ominus = -74.85 \text{ kJ mol}^{-1}$ & $\Delta_f S^\ominus = -80.67 \text{ J mol}^{-1} \text{ K}^{-1}$ @ 298K
@ $T = 298 \text{ K}$



elements in their reference states @ 298K

$$\Rightarrow \Delta_f G^\ominus(\text{C}) = \Delta_f G^\ominus(\text{H}_2) = 0$$

$$\Delta_r G^\ominus = \sum_i \nu_i \Delta_f G_i^\ominus = 0 + 0 - \Delta_f G^\ominus(\text{CH}_4, g)$$

$$= -\Delta_f G^\ominus(\text{CH}_4, g)$$

at constant $G = H - TS \xrightarrow{\text{const } T} \Delta G = \Delta H - T \Delta S$

$$\begin{aligned} \Rightarrow \Delta_f G^\ominus(\text{CH}_4, g) &= \Delta_f H^\ominus(\text{CH}_4, g) - T \Delta_f S^\ominus(\text{CH}_4, g) = \\ &= -74850 - 298 \cdot (-80.67) = \\ &= -5.081 \cdot 10^4 \text{ J mol}^{-1} \end{aligned}$$

$$\Delta_r G^\ominus = -\Delta_f G^\ominus(\text{CH}_4, g) = 5.081 \cdot 10^4 \text{ J mol}^{-1}$$

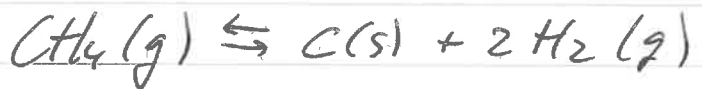
$$\begin{aligned} \Rightarrow @ \text{ equil: } \Delta_r G^\ominus &= -RT \ln K_p \\ &= -\Delta_r G^\ominus / (RT) \quad = -5.081 \cdot 10^4 / (8.314 \cdot 298) \\ K_p &= e \quad = e \end{aligned}$$

$$= 1.24 \cdot 10^{-9}$$

→ completely on CH₄-side, i.e. left-hand side

c)

$$d) K_p = \prod_i \left(\frac{p_i}{p^\ominus} \right)^{\nu_i}$$



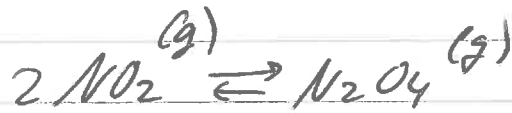
$$K_p = \left(\frac{p_{\text{H}_2}}{p^\ominus} \right)^2 \cdot \left(\frac{p_{\text{CH}_4}}{p^\ominus} \right)^{-1} = \frac{\left(\frac{p_{\text{H}_2}}{p^\ominus} \right)^2}{\left(\frac{p_{\text{CH}_4}}{p^\ominus} \right)} = \frac{p_{\text{H}_2}^2}{p_{\text{CH}_4} p^\ominus}$$

[note that solid doesn't appear as activity = 1]

$$K_p = \prod_i a_i^{\nu_i} \quad a_i \text{ for gases: } a_i = \frac{p_i}{p^\ominus}$$

→ not explained in lectures (yet!).

25



$$T = 298 \text{ K}$$

$$a) \quad K_p = \prod_i \left(\frac{p_i}{p^\ominus} \right)^{\nu_i} = \frac{\left(\frac{p_{\text{N}_2\text{O}_4}}{p^\ominus} \right)}{\left(\frac{p_{\text{NO}_2}}{p^\ominus} \right)^2} = \frac{p_{\text{N}_2\text{O}_4}}{p_{\text{NO}_2}^2} \cdot p^\ominus$$

using values from the table $\rightarrow K_p = \frac{0.031}{0.661^2} \cdot 1 =$
 $\& p^\ominus = 10^5 \text{ Pa} = 1 \text{ bar} \quad = 0.33$

$$b) \quad \Delta_r G^\ominus = -RT \ln K_p$$

$$= -0.314 \cdot 298 \cdot \ln 0.33 = -5252 \text{ J mol}^{-1}$$
$$\Delta_r G^\ominus = -5.3 \text{ kJ mol}^{-1}$$