

Homework 5

Problem 1, 5 marks

Starting from $A = U - TS$, differentiate both sides with respect to V at constant T and use a Maxwell relation to prove that

$$\left(\frac{\partial U}{\partial V}\right)_T = -P + T \left(\frac{\partial P}{\partial T}\right)_V \quad (1)$$

$$\left(\frac{dA}{dV}\right)_T = \left(\frac{dU}{dV}\right)_T - \left(\frac{dT}{dV}\right)_T S + \left(\frac{dS}{dV}\right)_T T$$

$$\left(\frac{dA}{dV}\right)_T = \left(\frac{dU}{dV}\right)_T - T \left(\frac{dS}{dV}\right)_T$$

using $\left(\frac{dU}{dV}\right)_T = -P + T \left(\frac{\partial P}{\partial T}\right)_V$
 $-T \left(\frac{\partial P}{\partial T}\right)_V \quad -T \left(\frac{\partial P}{\partial T}\right)_V$

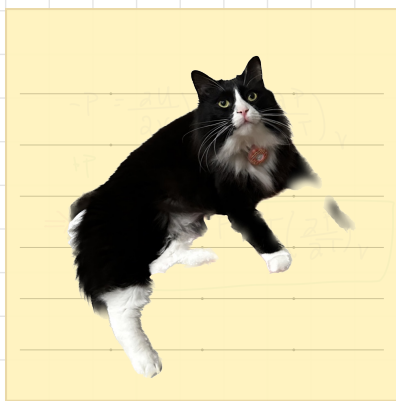
$$-P = \left(\frac{dU}{dV}\right)_T - T \left(\frac{\partial P}{\partial T}\right)_V$$

so $\left(\frac{dA}{dV}\right)_T = -P$

$$\left(\frac{dA}{dV}\right)_T = \left(\frac{dU}{dV}\right)_T - T \left(\frac{dS}{dV}\right)_T$$

Maxwell relation:

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



at this point you should have enough info to prove.
(show me how you manipulate at end!)

Problem 2, 10 marks

(a) Starting from $G = H - TS$, differentiate both sides with respect to P at constant T and use a Maxwell relation to prove that

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T \left(\frac{\partial V}{\partial T}\right)_P \quad (2)$$

a)

$$\left(\frac{\partial G}{\partial P}\right)_T = \left(\frac{\partial H}{\partial P}\right)_T - \cancel{\frac{\partial T}{\partial P}}_T \cdot S + \frac{\partial S}{\partial P}_T T$$

$$\left(\frac{\partial G}{\partial P}\right)_T = \left(\frac{\partial H}{\partial P}\right)_T - T \left(\frac{\partial S}{\partial P}\right)_T$$

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T \left(\frac{\partial V}{\partial T}\right)_P$$

Maxwell relation (given)

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

$$+V = \left(\frac{\partial H}{\partial P}\right)_T - T \left(\frac{\partial V}{\partial T}\right)_P$$

$$\left(\frac{\partial G}{\partial P}\right)_T = V$$

$$\left(\frac{\partial G}{\partial P}\right)_T = \left(\frac{\partial H}{\partial P}\right)_T - T \left(\frac{\partial S}{\partial P}\right)_T$$



at this point you should have enough info to prove.
(show me how you manipulate at end!)

(b) Starting from Equation (2), show that

$$\left(\frac{\partial C_P}{\partial P}\right)_T = -T \left(\frac{\partial^2 V}{\partial T^2}\right)_P \quad (3)$$

b)

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P$$

$$\left(\frac{\partial C_P}{\partial P}\right)_T = \left(\frac{\partial}{\partial P}\right)_T \left(\frac{\partial H}{\partial T}\right)_P$$

$$= \left(\frac{\partial}{\partial T}\right)_P \left(\frac{\partial H}{\partial P}\right)_T$$

$$= \left(\frac{\partial}{\partial T}\right)_P \left(v - T \left(\frac{\partial V}{\partial T}\right)_P \right)$$

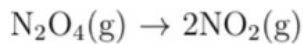
Part A

then, differentiate again with respect to T at constant P



Problem 3 – 10 marks

(a) Use Table 26.1 to find K_P for the following reaction at 298 K and 1 bar



$\frac{1}{2}\text{N}_2 + \text{O}_2 \rightarrow \text{NO}_2 \Rightarrow \Delta G_{f,1}$	nitrogen oxide	NO(g)	86.600
$\text{N}_2 + 2\text{O}_2 \rightarrow \text{N}_2\text{O}_4 \Rightarrow \Delta G_{f,2}$	nitrogen dioxide	NO ₂ (g)	51.258
	dinitrogen tetraoxide	N ₂ O ₄ (g)	97.787
		N ₂ O ₄ (l)	97.521

$$\Delta G^\circ = -\Delta G_{f,2} + 2\Delta G_{f,1} = \text{answer}$$

and

$$\Delta G^\circ = -RT \ln K_P \quad \text{and solve for } K_P$$

(b) Solve for ξ , the extent of reaction, assuming one mole of reactant and no product is initially present.

$$K_P = \frac{P_{\text{NO}_2}^2}{P_{\text{N}_2\text{O}_4}}$$

where

$$P_{\text{N}_2\text{O}_4} = X_{\text{N}_2\text{O}_4} P_{\text{total}} = \frac{1-\xi}{1+\xi}$$

$$P_{\text{NO}_2} = X_{\text{NO}_2} P_{\text{total}} = \frac{2\xi}{1+\xi}$$

So, $K_P = \frac{\left(\frac{2\xi}{1+\xi}\right)^2}{\frac{1-\xi}{1+\xi}} = \frac{4\xi^2}{1-\xi^2}$

from part A

and solve for ξ

Problem 4 – 10 marks

Use the data in Table 19.2 to find K_P and K_C for the reaction in problem 3 at 1000 K and 1 bar. Rationalize your answer in terms of Le Chatelier's Principle.

$$\Delta_{\text{rxn}} H^\circ_{298} = 58.04 \text{ kJ/mol}$$

$$\Delta_{\text{rxn}} G^\circ_{298} = 4.729 \text{ kJ/mol}$$

$$\text{from 3a} \rightarrow \ln \frac{K_{P2}}{K_{P1}} = -\frac{\Delta H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

From reactants to products, $\Delta n = 1$, so use eq. 26.17 from textbook

$$K_C = K_P \left(\frac{P^\circ}{c^\circ RT} \right) = \text{answer}$$

Problem 5 – 10 marks

At 900 K, the reaction $\text{C}_2\text{H}_6(\text{g}) \rightarrow \text{C}_2\text{H}_4(\text{g}) + \text{H}_2(\text{g})$ has $\Delta H^\circ = 24.42 \text{ kcal/mol}$ and $\Delta G^\circ = 5.35 \text{ kcal/mol}$. Calculate the percent H_2 present at equilibrium if pure C_2H_6 is passed over a dehydrogenation catalyst at this temperature and 1 atm pressure. (b) Estimate the percent H_2 at equilibrium at 1000 K.

$$K_P = e^{-\Delta G / RT} = \text{answer}$$

$$P_{\text{C}_2\text{H}_4} = X_{\text{C}_2\text{H}_4} P_{\text{total}} = \frac{\xi}{1+\xi} P_{\text{total}}$$

$$P_{\text{H}_2} = \frac{\xi}{1+\xi} P_{\text{total}} \quad \text{and} \quad P_{\text{C}_2\text{H}_6} = \frac{1-\xi}{1+\xi} P_{\text{total}}$$

since $P_{\text{total}} = 1 \text{ atm}$

$$K_P = \frac{P_{\text{C}_2\text{H}_4} P_{\text{H}_2}}{P_{\text{C}_2\text{H}_6}} = \frac{\xi^2}{1-\xi^2} \Rightarrow \xi = \sqrt{\frac{K_P}{1+K_P}} = K_P$$

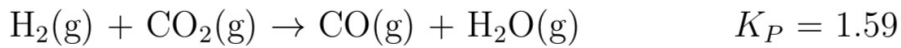
$$\text{and } \% \text{H}_2 = \frac{\xi}{1+\xi} \times 100 = \text{answer}$$

$$\text{at } 1000 \text{ K, } \ln \frac{K_{P1000\text{K}}}{K_P} = -\frac{\Delta H}{R} \left(\frac{1}{1000} - \frac{1}{900} \right)$$

$$\xi = \sqrt{\frac{K_P}{1+K_P}} \quad \text{and} \quad \% \text{H}_2 = \frac{\xi}{1+\xi} \times 100 = \text{answer}$$

Problem 6 – 5 marks

Suppose that we have a mixture of the gases $\text{H}_2(\text{g})$, $\text{CO}_2(\text{g})$, $\text{CO}(\text{g})$ and $\text{H}_2\text{O}(\text{g})$ at 1260 K, with $P(\text{H}_2) = 0.3$ bar, $P(\text{CO}_2) = 0.5$ bar, $P(\text{CO}) = 2.5$ bar and $P(\text{H}_2\text{O}) = 0.5$ bar. Is the reaction described by the equation



at equilibrium under these conditions? If not what direction will the reaction proceed to attain equilibrium?

$$Q = \frac{P(\text{CO})P(\text{H}_2\text{O})}{P(\text{H}_2)P(\text{CO}_2)} = \text{answer}$$

if $Q > K$, reaction goes backwards to reach equilibrium.

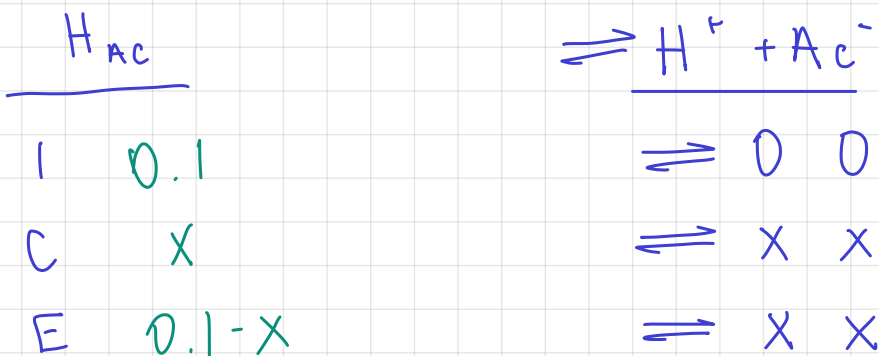
if $K > Q$, reaction goes forwards to reach equilibrium.

* Which one is it? Tell me

Problem 7 – 15 marks

Using the definition of K_a and the Debye-Hückel expression (Eq. 25.57, page 1036) for the mean ionic activity coefficient, calculate the pH of a 0.10 M acetic acid solution in (a) pure water (b) 0.1 M NaCl and (c) in 0.2 M MgSO_4 . Note: the formula for ionic strength is Eq. 25.52. The value of K_a for aqueous acetic acid is 1.74×10^{-5} .

$$a) \quad K_a = \frac{C_{\text{H}^+} \cdot C_{\text{Ac}^-} \cdot \gamma_{\pm}^2}{C_{\text{HAc}}}, \quad \text{Set } \gamma_{\pm} = 1 = K_a = \frac{C_{\text{H}^+} \cdot C_{\text{Ac}^-}}{C_{\text{HAc}}}$$



$$K_a = \frac{x^2}{0.1-x} = 1.74 \times 10^{-5}$$

Solve for x (Assuming $0.1-x \approx 0.1$)

Next, actually consider γ_{\pm} ,

$$I_c = \frac{1}{2} \cdot [C_{H^+} + C_{Ac^-}] = x$$

Then, using the Debye Huckel eq:

$$\ln(\gamma_{\pm}) = \frac{-1.173 \cdot |+1 \cdot -1| \cdot I_c^{1/2}}{1 + I_c^{1/2}}$$

$\gamma_{\pm} = \text{answer} \rightarrow$ *use K_a eq. to solve for actual x , then find pH
 $pH = -\log [H^+] =$

b) $I_c = \frac{1}{2} \times [C_{H^+} + C_{Ac^-} + C_{Na^+} + C_{Cl^-}] = \text{answer mol/L}$

$$\gamma_{\pm} =$$

$$pH =$$

c) $I_c = \frac{1}{2} \times [C_{H^+} + C_{Ac^-} + 4C_{Mg^{2+}} + C_{Cl^-}] = \text{answer mol/L}$

$$\gamma_{\pm} =$$

$$pH =$$

Problem 8 – 10 marks

Consider the dissociation reaction of $\text{I}_2(\text{g})$ to $2\text{I}(\text{g})$. The total pressure and the partial pressure of $\text{I}_2(\text{g})$ at 1400°C have been measured to be 36.0 torr and 28.1 torr, respectively. Use these data to calculate K_P (one bar standard state) and K_C (one mol/L standard state) at 1400°C .

$$P_{\text{total}} = 36 \text{ torr}$$

$$1 \text{ bar} = 750.062 \text{ torr}$$

$$- P_{\text{I}_2} = 28.1 \text{ torr}$$

$$\text{so, } P_{\text{I}} =$$

$$K_P = \frac{(P_{\text{I}} / 750.062)^2}{(28.1 / 750.062)} = \text{answer}$$

and

$$K_C = K_P \left(\frac{P^0}{c^0 RT} \right) = \text{answer}$$

↑
molar concentration