

### EXAM 3

November 6, 2017

*IMPORTANT: Write neatly and lay out solutions clearly. Make sure that you give some reasoning or working for each answer. Full marks will NOT be awarded for the final answer by itself, UNLESS it is supported by a brief justification or explanation.*

*Give units for all quantities!*

YOUR NAME SOLUTIONS

Some data:  $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$   $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$   $1 \text{ atm} = 101325 \text{ Pa}$

$$dU = dq + dw \quad dS = dq_{\text{rev}}/T \quad \gamma = C_p/C_v \quad C_p - C_v = nR$$

$$dw = -p_{\text{ex}} dV \quad \text{Heat engine } \varepsilon = (T_h - T_c)/T_h \quad \text{adiabat: } pV^\gamma = \text{const}$$

$$H = U + pV \quad G = H - TS \quad A = U - TS$$

$$d \ln K/d(1/T) = -\Delta H/R \quad \Delta_r G = \Delta G^\circ + RT \ln Q$$

(1) 30 points

i) Starting from the Clausius equation  $dp/dT = \Delta S/\Delta V$  for a phase transition, deduce the approximate Clausius-Clapeyron relation  $dp/dT = p \Delta_{\text{vap}}H/(RT^2)$  for a liquid to vapor transition, and hence find an expression for  $d(\ln p)/d(1/T)$ .  $\Delta_{\text{vap}}H$  is the enthalpy of vaporization. Show work.

ii) Either by using the results above, or by treating liquid  $\rightleftharpoons$  vapor

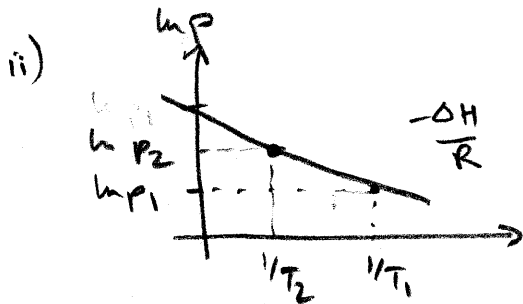
as a regular chemical equilibrium, deduce the temperature at which the vapor pressure water is  $2 \times 10^7$  Pa, given that it is  $10^5$  Pa at 373 K and  $\Delta_{\text{vap}}H$  is  $41 \text{ kJ mol}^{-1}$ . You may treat water vapor as a perfect gas and assume that  $\Delta_{\text{vap}}H$  does not vary with temperature.

$$i) \frac{dp}{dT} = \frac{\Delta S}{\Delta V} = \frac{\Delta_{\text{vap}}H/T}{V_{\text{gas}} - V_{\text{liquid}}} \approx \frac{\Delta_{\text{vap}}H/T}{V_{\text{gas}}} = \frac{\Delta_{\text{vap}}H/T}{RT/p} = \frac{p \Delta_{\text{vap}}H}{RT^2}$$

because  $V_{\text{gas}} \gg V_{\text{liquid}}$

$$\frac{dp}{p} = \frac{\Delta_{\text{vap}}H}{R} \cdot \frac{dT}{T^2} \quad \therefore d \ln p = \frac{1}{p} dp$$
$$d T^{-1} = -T^{-2} dT$$

$$\therefore d \ln p = -\frac{\Delta_{\text{vap}}H}{R} d T^{-1} \quad \therefore \frac{d(\ln p)}{d(1/T)} = -\frac{\Delta_{\text{vap}}H}{R}$$



$$-\frac{\Delta H}{R} = \text{slope} = \ln(p_2/p_1) \div \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

[As an equilibrium,  $K = P/P^\ominus$  and slope

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right), \text{ see notes}]$$

Either way,

$$\ln(p_2/p_1) = \ln\left(\frac{2 \times 10^7 \text{ Pa}}{10^5 \text{ Pa}}\right) = 5.30$$

$$\frac{\Delta H}{R} = \frac{41000 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1}} = 4931 \text{ K}$$

$$5.30 = 4931 \text{ K} \left(\frac{1}{373 \text{ K}} - \frac{1}{T_2}\right) \quad \therefore 0.00107 = \frac{1}{373} - \frac{1}{T_2} \quad \therefore T_2 = \underline{\underline{623 \text{ K}}}$$

See homework exercise 4B.6 and we did this as an example in class.

(2) 30 points

Consider the dissociation of an acid  $H_2A$  at 298 K for which  $\Delta G^\circ = +40 \text{ kJ mol}^{-1}$ :

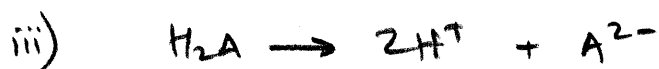


- Is the reaction spontaneous from left to right if the initial activity of each species is 1?
- Is the reaction spontaneous from left to right if the initial activity of each species is 0.001?
- If you start with pure  $H_2A$  at 1 M concentration, and assume ideal solution behavior and that after dissociation  $[H_2A]$  is still close to 1 M, what is the predicted equilibrium pH?

Show work and justify your answers.

$$i) \Delta_r G = \Delta_r G^\circ + RT \ln Q = 40000 \text{ J} + RT \ln \frac{1^2 \times 1}{1} > 0 \quad \therefore \underline{\underline{no}}$$

$$ii) \Delta_r G = 40000 \text{ J} + RT \ln \left( \frac{0.001^2 \times 0.001}{0.001} \right) = 40000 - 34229 \text{ J} > 0 \quad \therefore \underline{\underline{no}}$$



initial activity      1                      0                      0

equilibrium activity       $1 - \frac{x}{2}$                       x                       $x/2$

$$K = e^{-\frac{40000 \text{ J mol}^{-1}}{RT}} = 9.74 \times 10^{-8} = \frac{x^2 \cdot x/2}{1 - x/2} \approx \frac{x^3}{2}$$

$$\therefore x = 5.80 \times 10^{-3}, \quad (\text{we assume } 1 - \frac{x}{2} \approx 1)$$

$$pH = -\log_{10} a_{H^+} = -\log_{10} x = 2.24$$

see homework exercises 6A.3, 6A.5 and the class examples, 6A.10

(3) 20 points

i) Starting with the definition of  $G$ , prove that  $dG = Vdp - SdT$  and hence that

$$(\partial V / \partial T)_p = -(\partial S / \partial p)_T.$$

ii) Hence determine  $\Delta S$  for the isothermal expansion of 1 mole of a non-ideal gas accomplished by reducing the pressure from  $p_1$  to  $p_2$ . The equation of state for 1 mole of this gas is  $p = (RT/V) + a$ .

$$i) \quad G = H - TS = U + pV - TS$$

$$\begin{aligned} dG &= dU + pdv + Vdp - Tds - SdT & \text{and } dU &= dq + dw \\ &= \cancel{Tds} - \cancel{pdv} + \cancel{pdv} + Vdp - \cancel{Tds} - SdT & &= Tds - pdv \\ &= Vdp - SdT. \end{aligned}$$

$$\text{Consider } G(p, T), \text{ then } dG = \left(\frac{\partial G}{\partial p}\right)_T dp + \left(\frac{\partial G}{\partial T}\right)_p dT$$

$$\begin{aligned} \text{so } \left(\frac{\partial G}{\partial p}\right)_T &= V \quad \therefore \quad \frac{\partial^2 G}{\partial p \partial T} = \left(\frac{\partial V}{\partial T}\right)_p \\ \left(\frac{\partial S}{\partial T}\right)_p &= -S \quad \therefore \quad \frac{\partial^2 G}{\partial p \partial T} = -\left(\frac{\partial S}{\partial p}\right)_T \end{aligned} \quad \left. \begin{array}{l} \leftarrow \\ \leftarrow \end{array} \right\} \text{equal.}$$

$$ii) \quad \Delta S = \int_{p_1}^{p_2} dS = \int_{p_1}^{p_2} \left(\frac{\partial S}{\partial p}\right) dp.$$

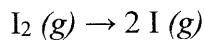
$$\text{Here } p = \frac{RT}{V} + a \quad \therefore \quad V = \frac{RT}{p-a} \quad \therefore \quad \left(\frac{\partial V}{\partial T}\right)_p = \frac{R}{p-a} = -\left(\frac{\partial S}{\partial p}\right)_T$$

$$\begin{aligned} \therefore \Delta S &= \int_{p_1}^{p_2} \frac{-R}{p-a} dp = -R \left[ \ln(p-a) \right]_{p_1}^{p_2} = -R \ln \left( \frac{p_2-a}{p_1-a} \right) \\ &= R \ln \left( \frac{p_1-a}{p_2-a} \right). \end{aligned}$$

Compare to homework problem 3D.5

(4) 20 points

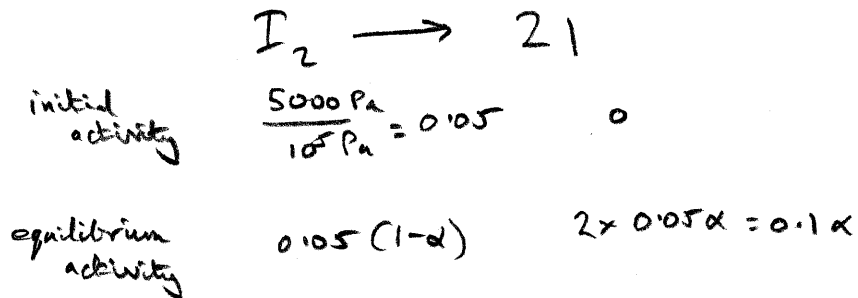
At 700 K,  $\Delta_f G^\circ$  of atomic iodine is  $3 \text{ kJ mol}^{-1}$ . Calculate the degree of dissociation  $\alpha$  of  $\text{I}_2$  in a container where 5000 Pa of initially pure  $\text{I}_2$  vapor at 700 K comes to equilibrium:



Comment: do not assume that  $\alpha$  is small compared to 1.

$$\Delta G^\circ = 2\Delta_f G^\circ(\text{I}) - \Delta_f G^\circ(\text{I}_2) = 2 \times 3 \text{ kJ mol}^{-1} - 0 = 6 \text{ kJ mol}^{-1}$$

$$\therefore K = e^{-\Delta G^\circ/RT} = e^{-\left(\frac{6000}{8.314 \times 700}\right)} = e^{-1.031} = 3.57 \times 10^{-1}$$



$$\therefore K = \frac{(0.1\alpha)^2}{0.05(1-\alpha)} = \frac{0.2\alpha^2}{1-\alpha}$$

$$\therefore K(1-\alpha) = 0.2\alpha^2 \quad \therefore \alpha^2 = 5K - 5K\alpha \quad \therefore \alpha^2 + 5K\alpha - 5K = 0$$

$$\therefore \alpha^2 + 1.785\alpha - 1.785 = 0 \quad \therefore \alpha = \frac{-1.785 \pm \sqrt{3.186 + 7.14}}{2} = \frac{-1.785 \pm 3.213}{2}$$

and  $\alpha$  must be positive so  $\alpha = \underline{\underline{0.714}}$ .

see homework exercises 6A.5 and 6B.4  
and class examples