

EXAM 3

November 6, 2015

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) 20 points

i) Imagine mixtures of two liquids A and B form an ideal solution. What does that imply for the combined total vapor pressure as a function of composition, and what is the implication for intermolecular forces in the mixture?

ii) 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 $d(\ln p)/d(1/T)$. Show work.

i) The individual partial pressures will be proportional to the mole fractions. The total pressure will vary linearly with composition.

The A-B molecular interactions are similar to the A-A and B-B interactions.

$$\text{ii) } \Delta S \approx \frac{\Delta_{\text{vap}}H}{T} \text{ and } \Delta V \approx \text{vol of 1 mol of gas} = \frac{RT}{P}$$

$$\therefore \frac{dp}{dT} = \frac{\Delta_{\text{vap}}H}{T} \div \frac{RT}{P} = \frac{P \Delta_{\text{vap}}H}{RT^2}$$

$$\frac{d \ln p}{d(1/T)} = \frac{dp}{dT} \times \frac{d \ln p}{dp} \times \frac{dT}{d(1/T)}$$

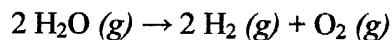
$$\frac{d \ln p}{dp} = \frac{1}{p}$$

$$\frac{dT}{d(1/T)} = -\frac{1}{T^2} \therefore \frac{dT}{d(1/T)} = -T^2$$

$$\therefore \frac{d \ln p}{d(1/T)} = \frac{P \Delta_{\text{vap}}H}{RT^2} \times \frac{1}{P} \times -T^2 = -\frac{\Delta_{\text{vap}}H}{R}$$

(2) 20 points

Consider this dissociation reaction of water vapor at 3000 K, and suppose $\Delta G^\circ = +48 \text{ kJ mol}^{-1}$:



- i) Is the reaction spontaneous from left to right if the initial activity of each species is 1?
ii) Is the reaction spontaneous from left to right if the initial activity of each species is 0.1?

Show work and justify your answers.

i) If all species have unit activity then ΔG° controls spontaneity and because it is positive, the answer is No.

If you prefer, $\Delta_r G = \Delta G^\circ + RT \ln Q$ and $\ln Q = 0$ here,

$$\text{so } \Delta_r G = \Delta G^\circ,$$

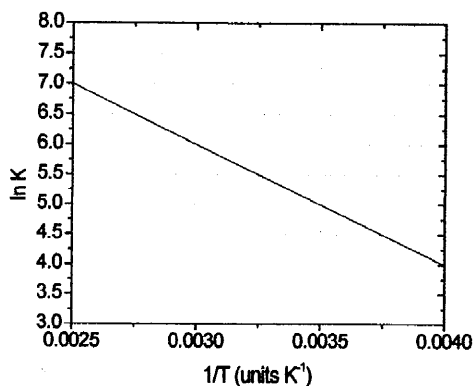
$$\text{ii) } Q = \frac{0.1^2 \times 0.1}{0.1^2} = 0.1. \quad RT \ln Q = -57.4 \text{ kJ mol}^{-1}$$

$$\therefore \Delta_r G = \Delta G^\circ + RT \ln Q = 48 - 57.4 \text{ kJ mol}^{-1} < 0$$

\therefore YES.

(3) 30 points

Given that $d(\ln K)/d(1/T) = -\Delta H/R$, use the information about the equilibrium constant K measured as a function of temperature and plotted in the graph to estimate ΔH and ΔS (you can assume these two quantities do not vary significantly with temperature).



$$\text{Slope} = \frac{4 - 7}{(0.0040 - 0.0025) \text{ K}^{-1}} = -2000 \text{ K} = -\frac{\Delta H}{R}$$

$$\begin{aligned}\therefore \Delta H &= 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 2000 \text{ K} \\ &= 16628 \text{ J mol}^{-1} \\ &= 16.6 \text{ kJ mol}^{-1}\end{aligned}$$

Pick any point;

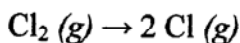
$$\text{When } \frac{1}{T} = 0.0025 \text{ K}^{-1}, T = \frac{1}{0.0025 \text{ K}^{-1}} = 400 \text{ K} \text{ and } \ln K = 7$$

$$\begin{aligned}\Delta G^\circ &= -RT \ln K = -8.314 \times 400 \times 7 \text{ J mol}^{-1} \\ &= -23279 \text{ J mol}^{-1} \\ &= \Delta H - T\Delta S\end{aligned}$$

$$\begin{aligned}\therefore \Delta S &= \frac{\Delta H - \Delta G}{T} = \frac{16628 + 23279 \text{ J mol}^{-1}}{400 \text{ K}} \\ &= 99.8 \text{ J mol}^{-1} \text{ K}^{-1}\end{aligned}$$

(4) 30 points

At 800 K, $\Delta_f G^\circ$ of atomic chlorine is 77 kJ mol^{-1} . Calculate the degree of dissociation α of Cl_2 in a container where $3 \times 10^3 \text{ Pa}$ of initially pure Cl_2 vapor at 800 K comes to equilibrium:

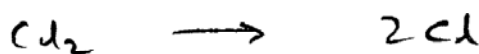


Short cut: you may assume that α is small compared to 1.

Qualitatively, explain how you expect α to behave if some Cl_2 is then removed and a new equilibrium is established.

$$\begin{aligned}\Delta_r G^\circ &= 2 \times \Delta_f G^\circ(\text{Cl}) - \Delta_f G^\circ(\text{Cl}_2) \\ &= 2 \times 77 \text{ kJ mol}^{-1} - 0 = -RT \ln K_{\text{eq}}\end{aligned}$$

$$\therefore K_{\text{eq}} = \exp\left(-\frac{154000}{8.314 \times 800}\right) = e^{-23.15} = 8.80 \times 10^{-11}$$



initial
activity

$$\frac{3 \times 10^3}{10^5} = 0.03 \quad 0$$

equilibrium
activity

$$0.03(1-\alpha) \quad 2 \times 0.03\alpha = 0.06\alpha$$

$$K_{\text{eq}} = \frac{a_{\text{Cl}}^2}{a_{\text{Cl}_2}} = \frac{0.06^2 \alpha^2}{0.03(1-\alpha)} \approx \frac{0.0036 \alpha^2}{0.03} = 0.12 \alpha^2$$

$$\therefore \alpha^2 = \frac{8.80 \times 10^{-11}}{0.12} = 7.33 \times 10^{-10}$$

$$\therefore \alpha = \underline{2.71 \times 10^{-5}}$$

Loss of Cl_2 would reduce the pressure, so by Le Chatelier's principle the equilibrium shifts to the side that increases pressure i.e., to the atoms, so α will increase.

Further comments on this question (which were not expected on the test)

The final activities are $a_{Cl_2} \approx 0.03$ and $a_{Cl} = 0.06\alpha = 1.63 \times 10^{-6}$.

Now some Cl_2 is removed. Imagine this lowers a_{Cl_2} to 0.02 (say).

You might think this causes the $Cl_2 \rightleftharpoons 2Cl$ reaction to move to the left (correct) and this makes α smaller (wrong).

Suppose the activity of Cl goes down by x (if we had the wrong direction for reaction then x would be negative, but it isn't):

	Cl_2	Cl
initial activities	0.02	1.63×10^{-6}
new equilibrium activities	$0.02 + \frac{x}{2}$	$1.63 \times 10^{-6} - x$

$$K_{eq} = \frac{a_{Cl}^2}{a_{Cl_2}} = \frac{(1.63 \times 10^{-6} - x)^2}{0.02 + \frac{x}{2}} \approx \frac{(1.63 \times 10^{-6} - x)^2}{0.02} = 8.80 \times 10^{-11}$$

$$\text{so } 1.63 \times 10^{-6} - x = 1.33 \times 10^{-6} \text{ so } x = 3.0 \times 10^{-7}$$

what is α ? By the arguments on the previous page,

$$2 \times 0.02x = a_{Cl} = 1.33 \times 10^{-6}$$

$$\therefore \alpha = 3.33 \times 10^{-5}, \text{ which is bigger than before.}$$