

### EXAM 3

November 5, 2018

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

$$dU = dq + dw$$

$$dS = dq_{\text{rev}}/T$$

$$\gamma = C_p/C_v$$

$$C_p - C_v = nR$$

$$dw = -p_{\text{ex}} dV$$

$$\text{Heat engine } \varepsilon = (T_h - T_c)/T_h$$

$$\text{adiabat: } pV^\gamma = \text{const}$$

$$H = U + pV$$

$$G = H - TS$$

$$A = U - TS$$

(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  $dp/dT = p \Delta_{\text{vap}}H/(RT^2)$ .  $\Delta_{\text{vap}}H$  is the enthalpy of vaporization. Hence prove that for two temperatures  $T_1$  and  $T_2$ , the corresponding vapor pressures  $p_1$  and  $p_2$  obey the relation  $\ln(p_2/p_1) = -(\Delta_{\text{vap}}H/R)(1/T_2 - 1/T_1)$ . *Show work.*
- ii) Use the results above to deduce the temperature at which the vapor pressure of water is  $2 \times 10^4$  Pa, given that it is  $10^5$  Pa at 373 K and  $\Delta_{\text{vap}}H$  is 41 kJ mol<sup>-1</sup>. You may treat water vapor as a perfect gas and assume that  $\Delta_{\text{vap}}H$  does not vary with temperature.
- iii) Water is part of an ideal solution with a mole fraction of 0.7 at 373 K. What partial pressure of H<sub>2</sub>O(g) do you expect? Suppose instead this solution is non-ideal and exhibits a negative deviation from Raoult's Law. What would be the effect on the partial pressure of H<sub>2</sub>O(g)?

$$i) \Delta S = \Delta H/T; \quad \Delta V = V_{\text{gas}} - V_{\text{liquid}} \approx V_{\text{gas}} = \frac{RT}{p}$$

$$\frac{dp}{dT} = \frac{\Delta S}{\Delta V} = \frac{\Delta H}{T} \div \frac{RT}{p} = \frac{p\Delta H}{RT^2}$$

$$\therefore \frac{1}{p} dp = \frac{\Delta H}{R} \frac{1}{T^2} dT \quad \therefore \int_{p_1}^{p_2} \frac{1}{p} dp = \frac{\Delta H}{R} \int_{T_1}^{T_2} \frac{1}{T^2} dT$$

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

$$ii) \ln \left( \frac{10^5 \text{ Pa}}{2 \times 10^4 \text{ Pa}} \right) = -\frac{41000 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1}} \left( \frac{1}{373} - \frac{1}{T} \right)$$

$$\therefore 1.61 = -4930 \text{ K} \left( \frac{1}{373} - \frac{1}{T} \right)$$

$$\therefore \frac{1}{373} - \frac{1}{T} = -0.000326 \quad \therefore T = 333 \text{ K}$$

iii) Ideal solution so  $p \propto$  mol. fraction  $\therefore 0.7 \times 10^5 \text{ Pa} = 7 \times 10^4 \text{ Pa}$ .

Negative deviation means a lower pressure.

(2) 40 points

i) Starting with the definition of  $A$ , and through consideration of  $A$  as a function of  $T$  and  $V$ , show that

$$(\partial S / \partial V)_T = (\partial p / \partial T)_V. \text{ Be sure to justify each step.}$$

ii) Hence determine  $\Delta S$  for the isothermal compression of 1 mole of a non-ideal gas accomplished by increasing the pressure from  $p_1$  to  $p_2$  and decreasing the volume from  $V_1$  to  $V_2$ . The equation of state for 1 mole of this gas is  $p = (RT/V) + aT^2/V^2$  where  $a$  is a constant.

$$\begin{aligned} \text{i) } A &= U - TS \quad \text{so } dA = dU - TdS - SdT \\ &= dq + dw - TdS - SdT \\ &= TdS - pdV - TdS - SdT \\ &= -pdV - SdT. \end{aligned}$$

$$\text{For } A(T, V), \quad dA = \left(\frac{\partial A}{\partial T}\right)_V dT + \left(\frac{\partial A}{\partial V}\right)_T dV \quad \therefore \left(\frac{\partial A}{\partial T}\right)_V = -S \quad \text{and} \quad \left(\frac{\partial A}{\partial V}\right)_T = -p$$

$$\text{Take second derivatives:} \quad -\left(\frac{\partial p}{\partial V}\right)_T = -\left(\frac{\partial S}{\partial T}\right)_V$$

$$\text{ii) } \Delta S = \int dS = \int_{V_1}^{V_2} \left(\frac{\partial S}{\partial V}\right)_T dV = \int_{V_1}^{V_2} \left(\frac{\partial p}{\partial T}\right)_V dV$$

$$p = \frac{RT}{V} + \frac{aT^2}{V^2} \quad \therefore \left(\frac{\partial p}{\partial T}\right)_V = \frac{R}{V} + \frac{2aT}{V^2}$$

$$\begin{aligned} \Delta S &= \int_{V_1}^{V_2} \left(\frac{R}{V} + \frac{2aT}{V^2}\right) dV = \left[ R \ln V - \frac{2aT}{V} \right]_{V_1}^{V_2} \\ &= \underline{\underline{R \ln \left(\frac{V_2}{V_1}\right) - 2aT \left(\frac{1}{V_2} - \frac{1}{V_1}\right)}}. \end{aligned}$$

(3) 30 points

i) For 1 mol of a perfect gas,  $\mu = \mu^0 + RT \ln(p/p^0)$ .

Imagine making a mixture of  $n_A$  mol of gas A with  $n_B$  mol of gas B, with a total amount  $n = n_A + n_B$  of the two combined, from pure components. The initial pressures of the separate components are both  $p$  and the total pressure of the final mixture is also  $p$ . Show that the change in  $G$  upon mixing is  $\Delta_{\text{mix}}G = nRT(x_A \ln x_A + x_B \ln x_B)$ , where  $x_A$  is the mole fraction of A in the mixture, etc. for  $x_B$ .

ii) What value of  $x_A$  makes  $\Delta_{\text{mix}}G$  most negative? *HINT*:  $x_A + x_B = 1$ .

iii) Knowing that the entropy of mixing  $\Delta_{\text{mix}}S = -nR(x_A \ln x_A + x_B \ln x_B)$ , deduce  $\Delta_{\text{mix}}H$ .

i) For gas A, the initial pressure is  $p$  and the final is  $p_A$ , the partial pressure in the mixture.

$$\begin{aligned} \text{For } n_A \text{ mol, } \Delta G_A &= n_A \mu_A^0 + n_A RT \ln(p_A/p^0) - [n_A \mu_A^0 + n_A RT \ln(p/p^0)] \\ &= n_A RT (\ln p_A/p^0 - \ln p/p^0) \\ &= n_A RT (\ln p_A/p) \end{aligned}$$

$$p_A = x_A p \quad \text{so } \Delta G_A = n_A RT \ln(x_A p/p) = n_A RT \ln x_A.$$

$$\text{Similarly, } \Delta G_B = n_B RT \ln x_B.$$

$$\begin{aligned} \Delta_{\text{mix}}G &= \Delta G_A + \Delta G_B = n_A RT \ln x_A + n_B RT \ln x_B \\ &= RT (n_A \ln x_A + n_B \ln x_B) \\ &= nRT \left( \frac{n_A}{n} \ln x_A + \frac{n_B}{n} \ln x_B \right) \\ &= nRT (x_A \ln x_A + x_B \ln x_B). \end{aligned}$$

ii) Two possible arguments:

a) Nothing special about  $x_A$  vs  $x_B$  in  $\Delta_{\text{mix}}G$  so  $x_A = x_B \therefore$  both equal 0.5.

b)  $\Delta_{\text{mix}}G$  minimized when  $x_A \ln x_A + x_B \ln x_B$  is minimized.

$$\text{write } x = x_A = (1 - x_B) \text{ so } x_B = 1 - x.$$

$$\begin{aligned} \text{we want } \frac{d}{dx} (x \ln x + (1-x) \ln(1-x)) &= 0 = x \cdot \frac{1}{x} + \ln x + (1-x) \cdot \frac{-1}{1-x} - \ln(1-x) \\ &= 1 + \ln x - 1 - \ln(1-x) = \ln x - \ln(1-x) \\ &= \ln \left( \frac{x}{1-x} \right) \end{aligned}$$

$$\therefore \frac{x}{1-x} = 1 \therefore x = 1-x \therefore x = \underline{\underline{0.5}}$$

iii)  $\Delta G = \Delta H - T\Delta S \therefore \Delta H = \Delta G + T\Delta S = 0$  here.