Name key

CEM 484 SS13 Exam 3A

Instructions: You have fifty minutes to complete this exam. Please place your name on all pages of this exam. Exams submitted without a name will not be graded. Show all work when calculating answers. You are allowed to use a calculator for the exam.

1. (10 points, true/false) Determine whether each of the following statements regarding a pure liquid in equilibrium with its vapor at 298 K is true or false. Write the entire word TRUE or FALSE or else no credit will be give.
   a. Before equilibrium, the greater the value of $\Delta_r G^0_{298}$ the faster equilibrium was obtained. FALSE
   b. At equilibrium the chemical potentials of the liquid and gas phases are equal. TRUE
   c. At equilibrium the rate of evaporation is greater than the rate of condensation. FALSE
   d. At equilibrium the value of $\Delta_r \overline{G}^0_{298}$ is equal to 0. FALSE
   e. If heat is added slowly so that the system remains at equilibrium, the temperature will not rise until all the liquid has evaporated. TRUE

2. (10 points) While you are working at the U.S. patent office an application comes across your desk. A heat engine is described which operates between a hot reservoir of 600 K and a cold reservoir of 300 K. The inventor claims that for 500 J of heat put into the engine, 200 J is exhausted while 300 J is converted to work.
   a. What is the theoretical maximum efficiency for the heat engine described?

$$\epsilon = 1 - \frac{T_C}{T_H} = 1 - \frac{300}{600} = 0.5$$

   b. Would you believe the claim from the inventor that 300 J can be converted to work? Explain.

$$\epsilon = \frac{-w}{q_H} = \frac{300}{500} = 0.6$$

do not believe the inventor, efficiency is too high

3. (35 points) One mole of NH_3 (g) is expanded reversibly adiabatically from an initial state of P_1 = 21.58 bar, V_1 = 1 L, and T_1 = 300 K to a final state of P_2 = 1.62 bar, V_2 = 10 L, and T_2 = 200 K against a constant external pressure of 3.45 bar. The gas can be treated using the van der Waals equation of state with a=4.3 L^2bar/mol^2 and b=0.038 L/mol.

$$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$$

a. Calculate the work performed by the gas.

$$w = -\int_{V_1}^{V_2} P_{ext}\, dV = -3.45\text{ bar}\,(10 - 1\text{ L}) = -31.05\text{ Lbar}$$

b. What is the change in the internal energy, ΔU, for the process?

$$\Delta U = q + w \qquad q = 0 \qquad \Delta U = -31.05\text{ Lbar}$$

c. What is the entropy change, ΔS, for the process?

$$\Delta S = 0$$

d. Calculate the heat capacity of NH_3(g).

$$\Delta S = 0 = \int_{T_1 V_1}^{T_2 V_2} \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV \qquad \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \qquad \left(\frac{\partial P}{\partial T}\right)_V = \frac{nR}{V - nb}$$

$$0 = \int_{T_1 V_1}^{T_2 V_2} \frac{C_V}{T} dT + \frac{nR}{V - nb} dV = C_V \ln\frac{T_2}{T_1} + nR\ln\left(\frac{V_2 - nb}{V_1 - nb}\right)$$

$$C_V = \frac{-nR\ln\left(\frac{V_2 - nb}{V_1 - nb}\right)}{\ln\frac{T_2}{T_1}} = \frac{(-1\text{mol})(8.3145\text{ J/Kmol})\ln\left(\frac{10L - 1mol(0.038\text{ L/mol})}{1L - 1mol(0.038\text{ L/mol})}\right)}{\ln\frac{200\text{ K}}{300\text{ K}}} = 47.9\text{ J/Kmol}$$

e. What is the enthalpy change, ΔH for the process?

$$\Delta H = \Delta U + \Delta(PV)$$

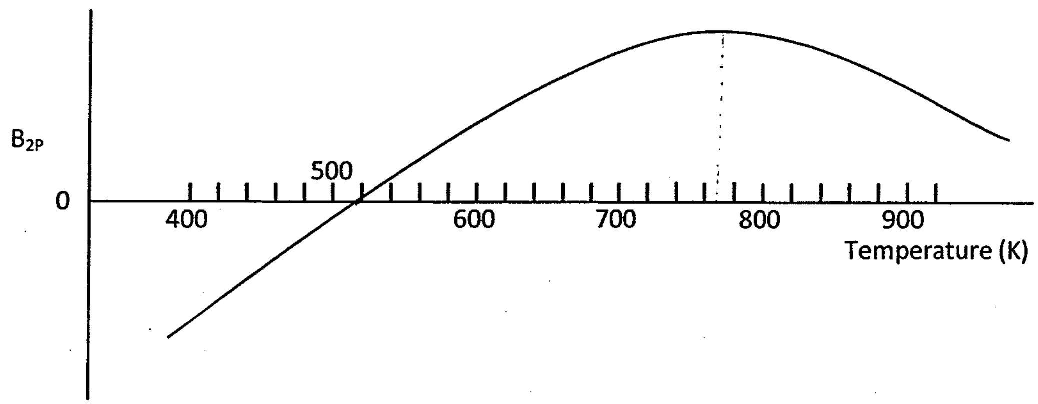
$$\Delta H = -31.05\text{ Lbar} + (\overset{P_2}{(1.62\text{ bar})}\overset{V_2}{(10L)}) - (\overset{P_1}{(21.58\text{ bar})}\overset{V_1}{(1L)}))$$

$$= -36.43\text{ Lbar}$$

4. (15 points) O_2 can be liquefied through successive Joule-Thompson expansions. During class we derived an expression for the Joule-Thompson coefficient in terms of B_{2P}:

$$\mu_{JT} = \frac{RT^2\left(\frac{\partial B_{2P}}{\partial T}\right)_P}{\bar{C}_P}$$

A plot of B_{2P} as a function of temperature is given below.



a. What is the maximum allowable initial temperature for the Joule-Thompson expansion to lead to a drop in temperature of the gas?

~765

b. At what temperature would O_2 behave most like an ideal gas?

~520

c. O_2 undergoes a Joule-Thompson expansion from 100 bar to 1 bar. If the initial and final temperatures are 400 K and 350 K what is the Joule-Thompson coefficient.

$T_2 - T_1 = \mu_{JT}(P_2 - P_1)$

$\mu_{JT} = \frac{(350\text{K} - 400\text{K})}{(1 - 100\text{ bar})} = 0.505\ \text{K/bar}$

5. (15 points) A short duration instant heat pack used by athletes to quickly treat injuries work by dissolving a substance in water. A heat pack is constructed by placing 1 mol of magnesium sulfate ($MgSO_4$) in a vial in a plastic pouch with 300 g of water. $MgSO_4$ dissolves in water according to the reaction given below

$$MgSO_4\,(s) + H_2O(l) \rightarrow Mg^{2+}\,(aq) + SO_4^{2-}\,(aq) + H_2O\,(l)$$

After breaking the vial and mixing the chemicals what is the highest temperature that can be reached by the hot pack if the pack is initially at 298 K?

Substance	$\Delta_f\bar{H}^0_{298}$ (kJ/mol)
$MgSO_4$	-1278.2
Mg^{2+}	-462.0
SO_4^{2-}	-907.5

You may assume that the heat capacity of the water, pouch, vial, and aqueous $MgSO_4$ is 1053 J/K after the dissolution and does not vary as a function of temperature.

$$\Delta_r \bar{H}^\circ_{298} = \Delta_f \bar{H}^\circ_{298}(SO_4^{2-}) + \Delta_f \bar{H}^\circ_{298}(Mg^{2+}) - \Delta_f \bar{H}^\circ_{298}(MgSO_4)$$

$$= -907.5 - 462.0 + 1278.2 = -91.3\ \text{kJ/mol}$$

for 1 mole 91.3 kJ released by rxn and absorped by pouch, vial, solution, ...

$$91.3\ \text{kJ/mol} = \int_{298}^{T_2} C_p\, dT = C_p(T_2 - 298)$$

$$T_2 = \frac{91.3\ \text{kJ/mol}}{C_p} + 298\text{ K} = \frac{91.3\ \text{kJ/mol}}{1.053\ \text{kJ/K}} + 298\text{ K}$$

$$= 384.7\text{ K}$$

6. (15 points) The vapor pressure of benzaldehyde is 0.533 bar at 427 K and its normal boiling point is 452 K (the normal boiling point is the temperature at which the vapor pressure is equal to 1 bar). What is the molar enthalpy of vaporization?

$$\ln \frac{P_2}{P_1} = \frac{\Delta_{vap}\bar{H}^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\Delta_{vap}\bar{H}^\circ = \frac{R \ln \frac{P_2}{P_1}}{\left(\frac{1}{T_1} - \frac{1}{T_2}\right)} = \frac{(8.3145\ \text{J/K mol})\left(\ln \frac{1\ \text{bar}}{0.533\ \text{bar}}\right)}{\left(\frac{1}{427\text{K}} - \frac{1}{452\text{K}}\right)} = 40390\ \text{J/mol}$$

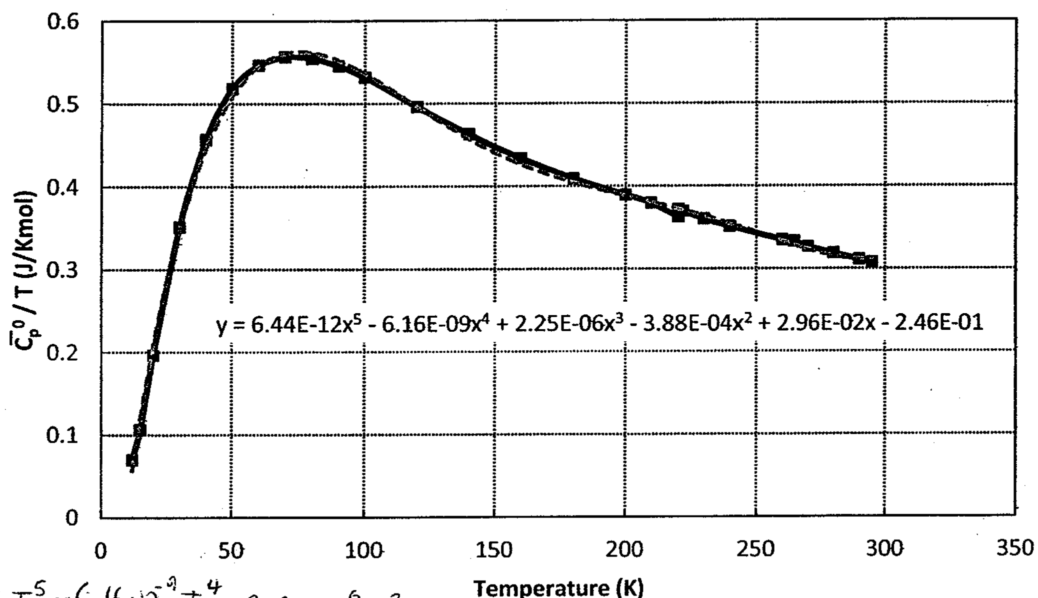
$$= 40.4\ \text{kJ/mol}$$

7. (Extra credit, 4 points) Methylammonium chloride occurs as three crystalline forms called, β, γ, and α, between 0 and 298 K. The constant pressure heat capacity divided by temperature is shown on the graph below long with a best fit polynomial expression. The β to γ transition occurs at 220.4 K with $\Delta_{trans}H$ = 1.779 kJ/mol and the γ to α transition occurs at 264.5 K with $\Delta_{trans}H$ = 2.818 kJ/mol. Approximate the molar entropy of methylammonium chloride at 298 K.

$\Delta S^{\circ} = \int_{T_1}^{T_2} \frac{C_v}{T} dT$

integrate using curve between phase transitions

At phase transitions use $\Delta S_{ph} = \frac{\Delta_{ph} H}{T}$



$\Delta S = \int_{T_1}^{T_2} 6.44\cdot10^{-12} T^5 - 6.16\cdot10^{-9} T^4 + 2.25\cdot10^{-6} T^3 - 3.88\cdot10^{-4} T^2 + 2.96\cdot10^{-2} T - 0.246$

$\Delta S = 1.073\cdot10^{-12} T^6 - 1.232\cdot10^{-9} T^5 + 5.625\cdot10^{-7} T^4 - 9.7\cdot10^{-5} T^3 + 1.48\cdot10^{-2} T^2 - 0.246 T$

There are three temperature ranges 0 → 220.4 K, 220.4 → 264.5, 264.5 → 298

Trange	T^6	T^5	T^4	T^3	T^2	T
0 → 220.4	$1.146\cdot10^{14}$	$5.2\cdot10^{11}$	$2.36\cdot10^{9}$	$1.07\cdot10^{7}$	$4.86\cdot10^{4}$	220
220.4 → 264.5	$2.278\cdot10^{14}$	$7.74\cdot10^{11}$	$2.53\cdot10^{9}$	$7.80\cdot10^{6}$	$2.14\cdot10^{4}$	44.1
264.5 → 298	$3.579\cdot10^{14}$	$1.07\cdot10^{12}$	$2.99\cdot10^{9}$	$7.96\cdot10^{6}$	$1.88\cdot10^{4}$	33.5
	$7.00\cdot10^{14}$	$2.36\cdot10^{12}$	$7.88\cdot10^{9}$	$2.65\cdot10^{7}$	$4.02\cdot10^{4}$	298

sum of area integrations 227 J/kmol

add phase trans

$\Delta S = 227 \text{ J/kmol} + \frac{1779}{220.4} + \frac{2818}{264.5} = 246 \text{ J/kmol}$

8. (Extra credit, 3 points) The value of $\Delta_r H^o_{298}$ at one bar of pressure for the reaction

$$2 ZnO (s) + 2 S (s) \rightarrow 2 ZnS (s) + O_2 (g)$$

is 290.8 kJ. Assuming ideal behavior, calculate the value of $\Delta_r U^o_{298}$ for this reaction.

$\Delta_r \bar{U}^o_{298} = \Delta_r \bar{H}^o_{298} - P\Delta V$ $P = 1 \text{ bar}$ $\Delta V \cong V_{gas} = \frac{nRT}{P} = \frac{(0.083 \frac{L\,bar}{K\,mol})(298 K)}{1 bar}$

$\bar{V} = 24.73$ L/mol.

for 1 mol of O_2 V = 24.73 L

$\Delta_r \bar{U}^o_{298} = 290.8 \text{ kJ} - (1 \text{ bar})(24.73 \text{ L})$

$= 290.8 \text{ kJ} - (1 \text{ bar})(24.73 \text{ L}) \cdot \frac{100 J}{L\,bar} \cdot \frac{kJ}{1000 J}$

$= 288.3 \text{ kJ}$