

Exam 2
CHM 3400, Dr. Chatfield

Read through the questions thoroughly, set up the answers carefully, show your work, and be neat. There are 5 questions; each is worth 20 points. Partial credit will be given when the instructor can follow your train of thought. Credit will not be given for answers without work or reasoning. If you have difficulty with a question, go on and return to it later. Check your work.

GOOD LUCK!

1. Provide descriptions or definitions of the following. Employ graphs and equations where helpful.

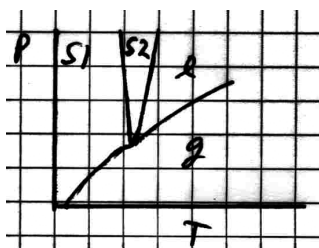
a) 2nd Law of Thermodynamics

The entropy of the universe increases in a spontaneous process.

b) 3rd Law of Thermodynamics

The entropy of a pure crystal at 0 K is zero.

c) Below is a phase diagram proposed for pure compound X. Is it plausible (i.e., can it possibly be correct)? Why or why not? [Reasoning must be given for credit.]



Not plausible. At most three phases of a single, pure compound can co-exist at equilibrium. This phase diagram has a quadruple point, i.e., a point at which 4 phases are in equilibrium. This would predict -1 for the number of 'degrees of freedom' from the Gibbs' phase rule, which is impossible:

$$f = c - p + 2 = 1 - 4 + 2 = -1$$

d) When we discussed properties of neutral solutes, we often ignored activity coefficients. We recently began discussing properties of ions in solution, and we are not ignoring activity coefficients. Explain why.

It is the strong, coulombic forces between charged ions, and between charged ions and the diple of water, that leads to large activity coefficients that cannot be ignored. The interactions between neutral species are much smaller.

e) We have described the ideal gas law, Raoult's law, and Henry's laws as "limiting laws." Explain why.

Each of these laws describes an 'ideal' that real systems approach more and more closely in a particular *limit*, but never reach. For a gas, this is the *limit* as the pressure approaches zero [ideal gas law]. For a solvent, this is the *limit* as the solvent's mole fraction approaches 1 (i.e. infinitely dilute in terms of the solute) Raoult]. For a solute, again, it is the *limit* as the solution approaches infinite dilution[Henry].

2.

- (a) An aqueous solution of an unknown compound is prepared by dissolving 0.125 g of the unknown in water so that the total volume of the solution is 100.0 mL. The osmotic pressure at 298 K is measured to be $\Pi = 58.0$ Torr. Determine the molar mass of the unknown.

$$\Pi = [B]RT \Rightarrow n = \frac{\Pi V}{RT}$$

$$= \frac{m}{M}$$

$$M = \frac{m}{n} = \frac{m RT}{\Pi V}$$

$\frac{0.125 \text{ g}}{\quad} \quad \frac{0.08206 \text{ L-atm K}^{-1} \text{ mol}^{-1}}{\quad} \quad \frac{298 \text{ K}}{\quad}$
 $\frac{58.0 \text{ Torr}}{\quad} \quad \frac{100.0 \text{ mL} = 0.1000 \text{ L}}{\quad}$

$$58.0 \text{ Torr}$$

$$= \frac{58.0}{760} \text{ atm}$$

$$M = 400. \text{ g/mol}$$

3.

(a) The standard boiling point is the temperature at which a substance boils when the pressure is 1 bar. The standard boiling point of water is $T_b = 373$ K. Determine the vapor pressure of water at $T = 323$ K (this is also the pressure at which water would boil at a temperature of $T = 323$ K). Given: $\Delta_{\text{vap}}H^\circ(\text{H}_2\text{O}) = 40.7$ kJ/mol.

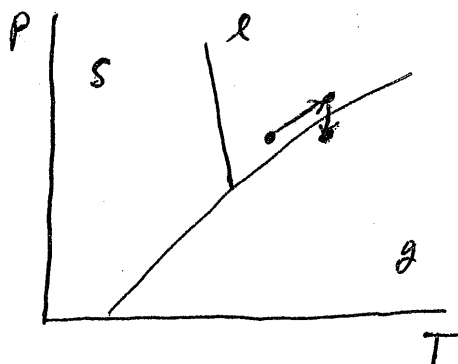
$$\ln \frac{p_2}{p_1} = \frac{\Delta_{\text{vap}}H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) = -2.03$$

$\begin{matrix} 1 \text{ bar} & & 8.314 \text{ J K}^{-1} \text{ mol}^{-1} & & 373 \text{ K} & & 323 \text{ K} \end{matrix}$

$$p_2 = p_1 e^{-2.03} = 0.13 \text{ bar}$$

$\begin{matrix} 1 \text{ bar} \end{matrix}$

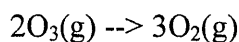
(b) A person heated water in a closed bottle in a microwave oven for tea. After removing the bottle from the oven, she added a tea bag to the hot water. To her surprise, the water started to boil violently. Explain what happened, making use of a phase diagram.



The pressure in the closed bottle increased during heating, so the system remained in the "l" region of the phase diagram. When lid was removed, pressure fell, so the system crossed into the "g" region. ~~However~~ However, the system remained a "superheated" liquid for a short time. This is an unstable state. Addition of the tea bag provided sites for the nucleation of gas bubbles, leading to rapid boiling.

4.

(a) Calculate $\Delta_r G$ for the reaction below at 25 °C, using the thermodynamic data given. The data pertain to 25 °C.



	$\Delta_f H^\circ$ (kJ/mol)	S° (J K ⁻¹ mol ⁻¹)	$C_{p,m}$ (J K ⁻¹ mol ⁻¹)
O ₂ (g)		205	29.4
O ₃ (g)	143	239	39.2

$$\Delta_r H^\circ = 3\Delta_f H^\circ(\text{O}_2) - 2\Delta_f H^\circ(\text{O}_3) = 3(0) - 2(143) = -286 \text{ kJ/mol}$$

$$\Delta_r S^\circ = 3S^\circ(\text{O}_2) - 2S^\circ(\text{O}_3) = 3(205) - 2(239) = 137 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta_r G^\circ = \Delta_r H^\circ - T \Delta_r S^\circ = -286 \text{ kJ/mol} - (298 \text{ K})(0.137 \text{ kJ K}^{-1} \text{ mol}^{-1}) = -327 \text{ kJ/mol}$$

(b) Calculate $\Delta_r G$ at (b) 100 °C. The heat capacity can be treated as independent of temperature up to 100 °C.

$$\Delta_f H^\circ(\text{O}_3, 373 \text{ K}) = \Delta_f H^\circ(\text{O}_3, 298 \text{ K}) + \Delta C_p \Delta T = 142.6 \text{ kJ/mol}$$

$\Delta C_p = (39.2 - \frac{3}{2} \cdot 29.4) \text{ J K}^{-1} \text{ mol}^{-1}$
 for formation of O₃
 $\frac{3}{2} \text{O}_2 \rightarrow \text{O}_3$

$$\Delta_r H^\circ = 3(0) - 2(142.6) = -285.2 \text{ kJ/mol}$$

$$S^\circ(\text{O}_2, 373 \text{ K}) = S^\circ(\text{O}_2, 298 \text{ K}) + C_p(\text{O}_2) \ln \frac{373 \text{ K}}{298 \text{ K}} = 212 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$S^\circ(\text{O}_3, -) = S^\circ(\text{O}_3, -) + C_p(\text{O}_3) \ln \frac{373 \text{ K}}{298 \text{ K}} = 248 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta_r S^\circ(373 \text{ K}) = 3S^\circ(\text{O}_2) - 2S^\circ(\text{O}_3) = 140 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$3 \Delta_r G^\circ(373 \text{ K}) = \Delta_r H^\circ - T \Delta_r S^\circ$$

$\Delta_r H^\circ = -285.2 \text{ kJ/mol}$
 $T = 373 \text{ K}$
 $\Delta_r S^\circ = 140 \text{ J K}^{-1} \text{ mol}^{-1}$

$$= -337 \text{ kJ/mol}$$

5.

(a) The Helmholtz energy, A , is defined as $A = U - TS$. The fundamental equation for a change in A , dA , is: $dA = -SdT - pdV$. Use this expression to determine ΔA for the isothermal expansion of one mole of a perfect gas at 298 K from $V_i = 25$ L to $V_f = 50$ L.

isothermal $\Rightarrow dT = 0$

$$\begin{aligned} dA &= -\int p dV \\ \Delta A &= - \int_{V_i}^{V_f} \frac{nRT}{V} dV = - \overset{1 \text{ mol}}{n} \overset{298 \text{ K}}{RT} \ln \frac{V_f}{V_i} \\ &= - \underset{8.314 \text{ J K}^{-1} \text{ mol}^{-1}}{R} \ln \frac{50 \text{ L}}{25 \text{ L}} \\ &= -1.72 \text{ kJ/mol} \end{aligned}$$

(b) Beginning with the fundamental equation for dU , derive the corresponding fundamental equation for dA given above.

$$(A + dA) = (U + dU) - (T + dT)(S + dS)$$

$$- [A = U - TS]$$

$$dA = dU - SdT - \cancel{TdS} - \cancel{dTdS}$$

$$\uparrow$$

$$\cancel{TdS} = pdV$$

$\rightarrow 0$ faster than
 $dA, dU, dT, \text{ or } dS$
individually

$$dA = -SdT - pdV \quad \text{Q.E.D.}$$