

CHM2132 Midterm 2: Friday November 11th, 2011

Name: _____

Student #: _____

This is a closed book exam with no notes allowed.

Calculators are permitted.

Write all the formulas that you use to solve the questions and show all your work.

Remember to include units in all your calculations. Marks will be deducted if units are not shown in your final answer.

Constants and equations are on page 8 – this page can be removed from the rest of the exam and does not have to be handed in.

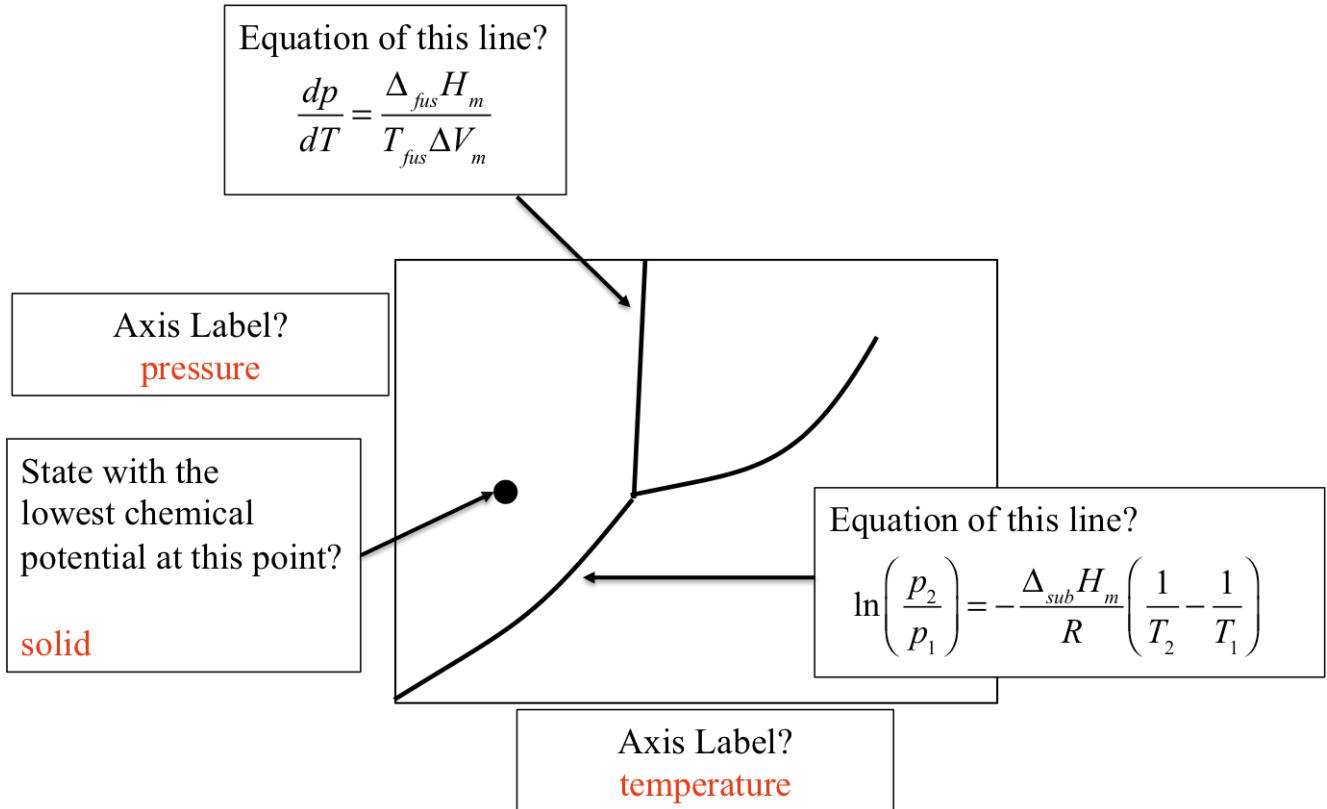
Q1: _____/7 Q2: _____/7 Q3: _____/6 Q4: _____/11

Q5: _____/9

Total = _____/40

Question 1

a) For the phase diagram of a pure substance shown below, fill in each box with the information requested. The equations you write **must be specific for the indicated line (e.g. vaporization, sublimation etc...)**. (6 marks):



1 mark for each box correctly filled in, plus 0.5 marks for correct transitions in two equations (fusion and sublimation)

b) Is this a phase diagram for water? How can you tell if it's a phase diagram for water? (1 mark)

No, a phase diagram for water would have a negative slope for the phase transition boundary between liquid and solid phases.

(1 mark, no part marks for guessing the answer...)

Name: _____

Question 2 (7 marks)

For **seven of the eight** scenarios described below, write the equation (as it appears in the equation sheet), that you would use to calculate:

- a) The **mass of salt** that it would take to lower the boiling point of water by 1°C.

$$\Delta T_b = K_b \times m_{\text{solute}}$$

- b) The **partial pressure of nitrogen** in the air (comprised of 80% N₂) at the top of Mount Everest.

$$p_i = \chi_i P$$

- c) The **mass of a volatile polychlorinated biphenyl (PCB) compound** dissolved in 1 L of a water sample taken from a polluted river.

$$m_A = K_A p_A$$

- d) The **molar Gibbs energy change** for the combustion of 1 mole of CH₄ (g) in an open flask. (Air contains ~20% oxygen and trace amounts of water.)

$$\Delta G_m = \Delta G_m^o + RT \ln Q$$

- e) The **standard molar entropy change** for the sublimation of solid CO₂ (dry ice).

$$\Delta_{\text{trs}} S^o = \frac{\Delta_{\text{trs}} H^o}{T_{\text{trs}}}$$

- f) The **maximum work** that can be done by an isothermal chemical reaction.

$$A = U - TS$$

- g) The **vapour pressure of water** over a solution made from 1 gram of sugar dissolved in 1 L of water.

$$p_i = \chi_i p_i^*$$

- h) The **Gibbs energy change** for compression of a liquid.

$$\left(\frac{\partial G}{\partial p} \right)_T = V$$

Name: _____

Question 3 (6 marks)

Provide short answers for *six of the seven* questions below:

- a) If an isothermal chemical reaction run in an open flask occurs spontaneously, will the Gibbs energy be less than, greater than, or equal to zero?

Less than zero

- b) What is the specific name of the phenomenon that prevents spontaneous mixing of oil and water?

Hydrophobic effect

- c) If the reaction $A(g) + B(g) \rightleftharpoons C(g)$ is at equilibrium, and then is compressed isothermally and reversibly, will the equilibrium constant increase, decrease or stay the same?

Stay the same

- d) What is the value of the equilibrium constant (K) for a phase transition at the phase transition temperature?

$K=1$

- e) If a solution of 1 mM ethyl acetate in water hydrolyzes to form acetic acid and ethanol, then will the osmotic pressure increase, decrease or stay the same?

Increase

- f) Suppose a wall separating two sides of an isolated system is removed. If both sides contain 2 L of the same type of ideal gas at 298 K, does the entropy of the gas increase, decrease or stay the same after the barrier is removed?

Increase

- g) If a solution of methanol (M) in ethanol (E) is ideal then is μ_M greater than, less than or equal to μ_M^* ?

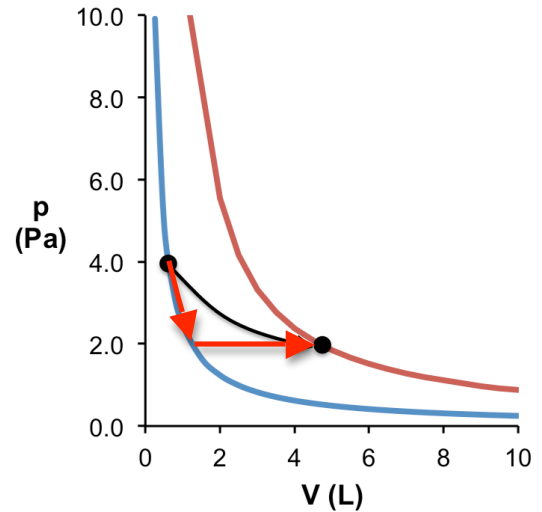
$\mu_M < \mu_M^*$

Question 4

Heat is transferred into a piston containing 1.00 mol of nitrogen gas at 4.0 Pa, 298 K until it reaches 2.0 Pa, 1.0×10^3 K via the path shown in the p-V diagram (right).

a) What is the entropy change of the nitrogen gas ($C_{p,m}^o = 29.125 \text{ J K}^{-1} \text{ mol}^{-1}$) for this process? Draw the path that you used to calculate this entropy change on the p-V diagram shown on the right. (6 marks)

Correctly drawn processes that correspond to calculations: 1 mark



This process must be broken down into two steps, isothermal expansion:

$$\Delta S = nR \ln \left(\frac{V_2}{V_1} \right) \quad (1 \text{ mark})$$

$$\Delta S = nR \ln \left(\frac{p_1}{p_2} \right) \quad (\text{since } p_1 V_1 = p_1 V_2 \text{ for isothermal processes}) \quad (1 \text{ mark})$$

and constant pressure heating:

$$\Delta S = nC_{p,m}^o \ln \left(\frac{T_2}{T_1} \right) \quad (1 \text{ mark})$$

$$\text{Add the two terms: } \Delta S = nR \ln \left(\frac{p_1}{p_2} \right) + nC_{p,m}^o \ln \left(\frac{T_2}{T_1} \right) \quad (1 \text{ mark})$$

Substitute values into equation:

$$\begin{aligned} \Delta S &= (1.00 \text{ mol}) (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \ln \left(\frac{4.0 \text{ Pa}}{2.0 \text{ Pa}} \right) \\ &\quad + (1.00 \text{ mol}) (29.125 \text{ J K}^{-1} \text{ mol}^{-1}) \ln \left(\frac{1000 \text{ K}}{298 \text{ K}} \right) \end{aligned} \quad (1 \text{ mark})$$

$$\Delta S = 41 \text{ J K}^{-1}$$

Name: _____

b) If the temperature of the surroundings is constant at 1000 K, how much heat must be transferred from the surroundings in order for this process to occur spontaneously? *For this question please give your final answer in the form of a sentence.* (3 marks)

For a spontaneous process: $\Delta S_{\text{Total}} = \Delta S_{\text{System}} + \Delta S_{\text{Surroundings}} > 0$ (1 mark)

$$\Delta S_{\text{Surroundings}} > -\Delta S_{\text{System}}$$

$$\frac{-q_{\text{irr, system}}}{T_{\text{Surroundings}}} > -\Delta S_{\text{System}} \quad (1 \text{ mark})$$

$$q_{\text{irr, system}} > \Delta S_{\text{System}} T_{\text{Surroundings}}$$

$$q_{\text{irr, system}} > (41 \text{ J K}^{-1})(1000 \text{ K}) = 41 \text{ kJ} \quad (0.5 \text{ marks})$$

Therefore the system must absorb more than 41 kJ of heat from the surroundings. (0.5 marks)

c) Suppose after this process has occurred, the system is allowed to cool to 298 K under constant volume conditions, and then is isothermally compressed to bring the gas back to its initial state at 4.0 Pa. Calculate the maximum theoretical work that could be done by this heat engine over one cycle if 31 kJ of heat was absorbed in the first step of this cycle. (2 marks)

Maximum theoretical work for a heat engine = efficiency x absorbed energy

$$\varepsilon = \frac{T_{\text{high}} - T_{\text{low}}}{T_{\text{high}}}$$

$$\varepsilon = \frac{1000 \text{ K} - 298 \text{ K}}{1000 \text{ K}} = 0.702 \quad (1 \text{ mark})$$

$$\begin{aligned} w_{\text{max}} &= q_{\text{absorbed}} \times \varepsilon \\ &= 0.702 \times 31 \text{ kJ} \quad (1 \text{ mark}) \\ &= 22 \text{ kJ} \end{aligned}$$

Name: _____

Question 5

Molecular bromine is 24 percent dissociated at 1600 K and 1.50 bar in the equilibrium

 $\text{Br}_2(\text{g}) \rightleftharpoons 2\text{Br}(\text{g})$. $\Delta_r H_m^\circ$ for this reaction is 112 kJ/mol.a) Calculate K at 1600 K. (6 marks)

	$\text{Br}_2(\text{g})$	$2\text{Br}(\text{g})$	
Initial	1	0	(1 mark)
Change	-x	2x	(1 mark)
Final	1-x	2x	(1 mark)
Mole fraction	$\chi_{\text{Br}_2} = \frac{1-x}{1+x} = \frac{1-0.24}{1+0.24} = 0.613$	$\chi_{\text{Br}} = \frac{2x}{1+x} = \frac{2(0.24)}{(1+0.24)} = 0.387$	(1 mark)
Partial pressure	$p_{\text{Br}_2} = \chi_{\text{Br}_2} p = (0.613)(1.50 \text{ bar})$ $p_{\text{Br}_2} = 0.919 \text{ bar}$	$p_{\text{Br}} = \chi_{\text{Br}} p = (0.387)(1.50 \text{ bar})$ $p_{\text{Br}} = 0.581 \text{ bar}$	(1 mark)

$$K = \frac{\left(\frac{p_{\text{Br}}}{p^\circ}\right)^2}{\frac{p_{\text{Br}_2}}{p^\circ}} = \frac{0.581^2}{0.919} = 0.37 \quad (1 \text{ mark})$$

b) Calculate ΔS_m° for this reaction at 1600K. (3 marks)

$$\Delta G_m^\circ = \Delta H_m^\circ - T\Delta S_m^\circ \quad (1 \text{ mark})$$

$$\Delta G_m^\circ = -RT \ln K \quad (1 \text{ mark})$$

$$\Delta S_m^\circ = \frac{\Delta H_m^\circ}{T} - \frac{\Delta G_m^\circ}{T}$$

$$\Delta S_m^\circ = \frac{\Delta H_m^\circ}{T} + R \ln K \quad (0.5 \text{ marks})$$

$$\Delta S_m^\circ = \frac{(112 \text{ kJ mol}^{-1})(10^3 \text{ J kJ}^{-1})}{(1600 \text{ K})} + (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \ln(0.367) \quad (0.5 \text{ marks})$$

$$= 62 \text{ J K}^{-1} \text{ mol}^{-1}$$

CHM2132 Midterm 2 Equations and Constants

This sheet can be removed from the rest of the midterm.

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} = 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1} = 0.08314 \text{ L bar mol}^{-1} \text{ K}^{-1}$$

$$1 \text{ L} = 10^{-3} \text{ m}^3$$

$$1 \text{ atm} = 101325 \text{ Pa}$$

$$1 \text{ L atm} = 101.325 \text{ J}$$

$$1 \text{ bar} = 10^5 \text{ Pa}$$

$$1 \text{ kJ} = 10^3 \text{ J}$$

$$10 \text{ millipedes} = 1 \text{ centipede}$$

$$pV = nRT$$

$$p = \frac{nRT}{V - nb} - a \left(\frac{n}{V} \right)^2$$

$$w = -\int pdV$$

$$\Delta U = w + q$$

$$H = U + pV$$

$$\left(\frac{\partial U}{\partial T} \right)_V = C_V$$

$$\left(\frac{\partial H}{\partial T} \right)_P = C_P$$

$$\pi_T = \left(\frac{\partial U}{\partial V} \right)_T$$

$$C_{p,m} - C_{v,m} = R$$

$$p_1 V_1^\gamma = p_2 V_2^\gamma \quad \frac{T_2}{T_1} = \left(\frac{V_1}{V_2} \right)^{(\gamma-1)} \quad \gamma = \frac{C_P}{C_V}$$

$$\varepsilon = \frac{\oint \delta w_{rev}}{q_{AB}}$$

$$\varepsilon = \frac{T_{high} - T_{low}}{T_{high}}$$

$$\Delta_r H_m^\circ = \sum_{\text{Products}} \nu \Delta_f H_m^\circ - \sum_{\text{Reactants}} \nu \Delta_f H_m^\circ$$

$$\Delta(\Delta_r H^\circ) = \Delta C_p \Delta T$$

$$\Delta S = \int_{\text{initial}}^{\text{final}} \frac{\delta q_{rev}}{T}$$

$$\Delta S = C_V \ln \left(\frac{T_2}{T_1} \right)$$

$$\Delta S = C_P \ln \left(\frac{T_2}{T_1} \right)$$

$$\Delta S = nR \ln \frac{V_f}{V_i}$$

$$\Delta S_m^\circ = -R \sum_{i=1}^N \chi_i \ln \chi_i$$

$$\Delta S = \sum_{i=1}^N n_i R \ln \left(\frac{V_{final}}{V_{i,initial}} \right)$$

$$\Delta_r S_m^\circ = \sum_{\text{Products}} \nu S_m^\circ - \sum_{\text{Reactants}} \nu S_m^\circ$$

$$\Delta S_{\text{Total}} = \Delta S_{\text{System}} + \Delta S_{\text{Surroundings}}$$

$$\Delta_{trs} S^\circ = \frac{\Delta_{trs} H^\circ}{T_{trs}}$$

$$\Delta G_m(p_2) = \Delta G_m^\circ + RT \ln \left(\frac{p_2}{p^\circ} \right)$$

$$\Delta G_m = \Delta G_m^\circ + RT \ln Q$$

$$A = U - TS$$

$$G = H - TS$$

$$\left(\frac{\partial G}{\partial p} \right)_T = V$$

$$\Delta_f G_m^\circ = \sum_{\text{Products}} \nu \Delta_f G_m^\circ - \sum_{\text{Reactants}} \nu \Delta_f G_m^\circ$$

$$\Delta G_m^\circ = -RT \ln K$$

$$\ln \left(\frac{K_2}{K_1} \right) = -\frac{\Delta_r H_m^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$K_p = \prod_i \left(\frac{p_i}{p^\circ} \right)^{\nu_i}$$

$$K_c = \prod_i \left(\frac{c_i}{c^\circ} \right)^{\nu_i}$$

$$\frac{dp}{dT} = \frac{\Delta_{trs} H_m}{T_{trs} \Delta V_m}$$

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

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{T,p,n_T}$$

$$p_i = \chi_i p_i^*$$

$$m_A = K_A p_A$$

$$p_A = \chi_A K'_A$$

$$p_i = \chi_i p$$

$$a_i = \frac{p_i}{p_i^*}$$

$$a_i = \gamma_i \chi_i$$

$$K_f = \frac{(MW) RT_f^{*2}}{\Delta_{fus} H}$$

$$\Delta T_f = K_f \times m_{\text{solute}}$$

$$\Delta T_b = K_b \times m_{\text{solute}}$$

$$\Pi = i [B] RT$$