

LAST Name: \_\_\_\_\_

FIRST Name: \_\_\_\_\_

Student #: \_\_\_\_\_

# CHM2132 Exam

## Fall 2013

This is a closed book exam with no notes allowed. Non-graphing, non-programmable calculators are permitted. Data, constants and equations are provided on the last two pages of the exam. You may rip these 2 pages off of the exam and use them for rough work.

**You must show all work to receive partial credit.**

Remember to include units in all your calculations. **Marks will be deducted if units are not shown in your final answer. Marks will be deducted if an unreasonable number of sig figs is shown in final answer.**

If data calculated in previous sections of a multi-part question and used for subsequent calculations is incorrect, no additional mark deductions will be applied.

Q1: \_\_\_\_\_/10    Q2: \_\_\_\_\_/10    Q3: \_\_\_\_\_/11    Q4: \_\_\_\_\_/10

Q5: \_\_\_\_\_/12    Q6: \_\_\_\_\_/10    Q7: \_\_\_\_\_/9    Q8: \_\_\_\_\_/11

Q9: \_\_\_\_\_/6    Q10: \_\_\_\_\_/5    Q11: \_\_\_\_\_/6

Total = \_\_\_\_\_/100

**Question 1.** Answer 10 of the following 11 questions (1 mark each)

- a) Is a sealed glass tube containing a real gas an open, closed or isolated system?
- b) If 1 mole of  $N_2$  is isothermally introduced into a rigid-walled flask containing 1 mole of  $H_2$  at room temperature, will the partial pressure of  $H_2$  increase, decrease, or stay the same?
- c) What is the change in internal energy for an ideal gas that releases 350 J of heat when 300 J of work is done on it?
- d) Is the process described in part c) physically possible? Why or why not?
- e) Circle all the term(s) below that do NOT represent a state function:
- i) Gibbs energy      ii) entropy      iii) heat capacity      iv) enthalpy      v) heat
- f) If the internal pressure ( $\pi_T$ ) of a real gas is positive, are intermolecular interactions repulsive or attractive?
- g) If the internal pressure ( $\pi_T$ ) of a real gas is positive, does the gas release or absorb heat when it expands freely ( $p_{ext} = 0$ )?
- h) For what type of process can Helmholtz energy calculations be used to find the maximum work that can be done by the system?
- i) If a dissolved substance precipitates from solution, does the entropy of this substance increase or decrease?
- j) What equation from the equation sheet would you use to calculate the molar Gibbs energy of mixing for one component of a binary solution? (Just give the equation as it appears on the equation sheet.)
- k) According to the Debye-Huckel model, is the chemical potential of an ion lower or higher than it would be if it were in an ideal solution?

**Question 2.** Answer 5 of the following 6 questions. (2 marks each)

- a) Rank the three isothermal processes below performed at 298 K on 1 mole of an ideal gas in terms of magnitude of work from smallest (1) to largest (3).

Rank:

irreversible compression from 4 L to 2 L \_\_\_\_\_

reversible expansion from 2 L to 4 L \_\_\_\_\_

irreversible expansion from 2 L to 4 L \_\_\_\_\_

- b) Write the formation reaction for solid alanine ( $C_3O_2H_7$ ). Be sure to include the phases in your equation.
- c) Why is the enthalpy of vaporization always greater than the internal energy change for vaporization?
- d) Is it possible to change the entropy of an ideal gas trapped inside a perfectly insulated sealed container? Why or why not?
- e) If a heat engine operating between  $4.0^\circ\text{C}$  and  $100.0^\circ\text{C}$  absorbs 55.0 kJ of heat, what is the maximum amount of work that can be done?
- f) Solve  $\left(\frac{\partial p}{\partial T}\right)_V$  for a van der Waals gas.

**Question 3.**

a) Sketch a phase diagram for a pure substance, and label the axes, triple point and critical point. Draw an arrow to the liquid-solid phase transition boundary and label it with the equation of this line. Indicate the region of the phase diagram where the chemical potential of the gas phase will be lower than the chemical potential of the other 2 phases. (6 marks)

b) Suppose a 5.450 g piece of ice is put into a 10.0 L freezer containing only dry air that is kept at  $-20.0^{\circ}\text{C}$ . After the system is allowed to come to equilibrium, what will the new mass of the ice be? (5 marks)

**Question 4.** Calculate the following for the combustion of phenol ( $C_6H_6O$ ) in a bomb calorimeter at 298.15 K. (Bomb calorimeter means it is sealed, with rigid walls.) Some useful data is provided on page 12.

a)  $\Delta H_m^\circ$  (3 marks)

b)  $\Delta S_m^\circ$ . (1 mark)

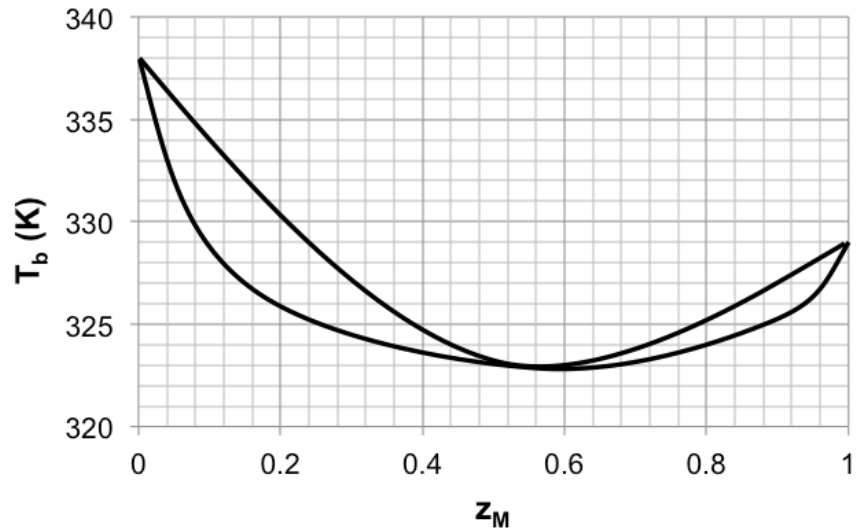
c)  $\Delta G_m^\circ$ . (1 mark)

d) The heat of this reaction for 1 mol of phenol. (3 marks)

e)  $\Delta G_m^\circ$  at 50°C. Assume that the reaction enthalpy is temperature independent. (2 marks)

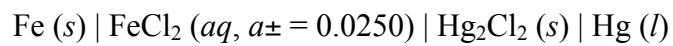
**Question 5.** The normal boiling point of a methanol (M) – chloroform (C) solution was measured for a range of compositions to give the 2-component phase diagram shown below. (12 marks)

- a) What is the boiling point of pure chloroform?
- b) Label the pure liquid and pure vapour regions of the phase diagram.
- c) Is the boiling point of this real solution greater than or less than the boiling point would be for an ideal solution?



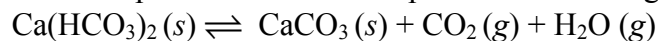
- d) Suppose 0.6 mol of methanol is added to 4.4 mol of chloroform. At what temperature will it begin to boil?
- e) What is the composition of the vapour phase of the solution in d) when it just begins to boil?
- f) What is the composition of the vapour at the azeotrope?
- g) Which component is more volatile, methanol or chloroform?
- h) According to this phase diagram, do methanol and chloroform interact more favourably with each other, or with themselves? Justify your answer with ~1 sentence.
- i) Is it possible to isolate pure methanol from the solution made in d) by fractional distillation? Why or why not?

**Question 6.** For the cell run at 298.15 K:



- a) Write the balanced chemical equation that would result in the transfer of two molar equivalents of electrons. (3 marks)
- b) What is the equilibrium constant for this reaction? (4 marks)
- c) Calculate the cell potential. (3 marks)

**Question 7.** Calcium bicarbonate decomposes at elevated temperatures according to the stoichiometric equation:



Pure calcium bicarbonate is put into a sealed vessel and the air is pumped out. When the vessel and its contents are heated to 500 K the total pressure is 0.290 bar.

a) Calculate  $K_p$ . (2 marks)

b) What will happen to the partial pressure of  $\text{CO}_2$  if 0.120 bar of  $\text{H}_2\text{O}$  gas is added to this equilibrium mixture, and the system is allowed to come to equilibrium again? Justify your answer with one sentence. (2 marks)

c) If the air was not pumped out of the reaction vessel before heating the reaction, how would this affect  $K_p$ ? Briefly explain your answer. (2 marks)

d) Calculate the temperature that will increase the final pressure of the system by 2-fold. Assume that the enthalpy of the reaction (32.8 kJ/mol) is temperature independent. (3 marks)

**Question 8.** Suppose a sample of liquid water at 273.15 K is put into a freezer at  $-20.0^{\circ}\text{C}$ .

a) What is the entropy change for 2.50 mol of water? (5 marks)

b) Is the freezing of water spontaneous in this situation? Provide support for your answer with a calculation. (6 marks)

**Question 9.**

- a) Assuming ideal behaviour, what is the solubility of  $\text{Ca}(\text{OH})_2$ , ( $K_{sp}=6.50 \times 10^{-6}$ )? (2 marks)
- b) Calculate the mean activity coefficient for a saturated  $\text{Ca}(\text{OH})_2$  solution using the solubility calculated in a). (4 marks)

**Question 10.**

The dissolution of 7.75 g of a substance in 825 g of benzene at 298 K raises the boiling point by  $0.575^\circ\text{C}$  ( $K_b = 2.53 \text{ K kg mol}^{-1}$ , density of benzene is  $876.6 \text{ kg/m}^3$ ). What is the osmotic pressure of this solution? (5 marks)

**Question 11.**

Calculate the standard entropy at 870 K for the dissociation of bromine:  $\text{Br}_2(\text{g}) \rightarrow 2 \text{Br}(\text{g})$  given that: (6 marks)

$$\frac{C_{p,m}(\text{Br}_2)}{\text{J K}^{-1} \text{ mol}^{-1}} = 36.05 + 30.11 \frac{\text{T}}{\text{K}}$$
$$C_{p,m}(\text{Br}) = 20.79 \text{ J K}^{-1} \text{ mol}^{-1}$$



## Constants and Conversion Factors

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

$$F = 96485 \text{ C mol}^{-1} \quad N_A = 6.022 \times 10^{23} \text{ mol}^{-1} \quad e^- = 1.6022 \times 10^{-19} \text{ C}$$

$$1 \text{ L} = 1 \text{ dm}^3 = 10^{-3} \text{ m}^3 \quad 1 \text{ kJ} = 1000 \text{ J} \quad 1 \text{ atm} = 101325 \text{ Pa} \quad 760 \text{ Torr} = 1 \text{ atm}$$

$$1 \text{ bar} = 10^5 \text{ Pa} \quad 1 \text{ L atm} = 101.325 \text{ J} \quad 1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2} \quad 1 \text{ Pa} = 1 \text{ kg m}^{-1} \text{ s}^{-2}$$

$$1 \text{ C s}^{-1} = 1 \text{ amp}$$

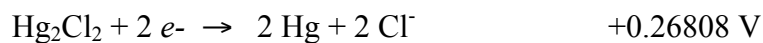
## Data for H<sub>2</sub>O

$$\Delta H_{vap}^{\circ} = 40.65 \text{ kJ mol}^{-1} \quad \Delta H_{sub}^{\circ} = 46.66 \text{ kJ/mol} \quad T_{vap} = 373.15 \text{ K} \quad T_{fus} = 273.15 \text{ K}$$

$$T_{triple\ point} = 273.16 \text{ K} \quad p_{triple\ point} = 611 \text{ Pa} \quad M = 18.01 \text{ g mol}^{-1} \quad m_{H_2O}^* = 55.555 \text{ mol kg}^{-1}$$

$$\rho_{ice} = 920 \text{ kg m}^{-3} \quad \rho_{liquid\ water} = 997 \text{ kg m}^{-3} \quad p_{H_2O}^* = 3200 \text{ Pa at } 298 \text{ K}$$

## Standard Reduction Potentials



## Thermodynamic Data at 298.15 K

Substance	$\Delta H_f^{\circ}$ (kJ mol <sup>-1</sup> )	$S_m^{\circ}$ (J K <sup>-1</sup> mol <sup>-1</sup> )	$C_{p,m}^{\circ}$ (J K <sup>-1</sup> mol <sup>-1</sup> )
Br <sub>2</sub> (g)	30.9	245.5	36.0
Br (g)	111.9	175.0	20.79
Ca <sup>2+</sup> (aq)	-542.8	-53.1	99.7
CaCO <sub>3</sub> (s)	-1206.9	92.9	83.5
C (s, graphite)	0	5.74	8.52
C <sub>6</sub> H <sub>6</sub> O (s)	-165.1	144.0	127.4
CO <sub>2</sub> (g)	-393.5	213.8	37.1
H <sub>2</sub> (g)	0	130.7	28.8
H <sub>2</sub> O (g)	-241.8	188.8	33.6
H <sub>2</sub> O (l)	-285.8	70.0	75.3
H <sub>2</sub> O (s)	--	48.0	36.2
O <sub>2</sub> (g)	0	205.2	29.4
OH <sup>-</sup> (aq)	-230.0	-10.9	--

$$pV = nRT$$

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

$$\Delta U = w + q$$

$$w = \int_{x_1}^{x_2} F \cdot dx$$

$$w = \int_0^Q \phi \cdot dQ'$$

$$w = - \int_{V_1}^{V_2} p_{ext} dV$$

$$C_p - C_v = nR$$

$$\Delta U = \int_{T_1}^{T_2} C_v dT$$

$$\Delta H = \int_{T_1}^{T_2} C_p dT$$

$$H = U + pV$$

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

$$\Delta S = \int \frac{\delta q_{rev}}{T}$$

$$p_1 V_1^\gamma = p_2 V_2^\gamma \quad \gamma = \frac{C_p}{C_v}$$

$$\frac{T_2}{T_1} = \left( \frac{V_1}{V_2} \right)^{(\gamma-1)}$$

$$\Delta H_r^\circ = \sum_{\text{Products}} \nu \Delta H_f^\circ - \sum_{\text{Reactants}} \nu \Delta H_f^\circ$$

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

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

$$\Delta H_{r,T}^\circ = \Delta H_{r,298.15\text{K}}^\circ + \int_{T_1}^{T_2} \Delta C_p(T') dT'$$

$$\Delta C_p(T') = \sum_i \nu_i C_{p,i}(T')$$

$$\Delta S = \int \frac{C_v dT}{T}$$

$$\Delta S = \int \frac{C_p dT}{T}$$

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

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

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

$$\Delta S_{\text{surr}} = \frac{-q_{\text{sys}}}{T_{\text{surr}}}$$

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

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

$$\left( \frac{\partial G}{\partial T} \right)_p = -S$$

$$A = U - TS$$

$$G = H - TS$$

$$\Delta G = V \Delta p$$

$$\Delta(\Delta G) = \Delta V \Delta p$$

$$\Delta G_r^\circ = \sum_{\text{Products}} \nu \Delta G_f^\circ - \sum_{\text{Reactants}} \nu \Delta G_f^\circ$$

$$\Delta G = nRT \ln \left( \frac{p_2}{p_1} \right)$$

$$p_A = x_A p_T$$

$$x_A = \frac{n_A}{n_{\text{Total}}}$$

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

$$\Delta G^{\text{mixing}} = RT \sum_i n_i \ln x_i = nRT \sum_i x_i \ln x_i$$

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

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

$$\frac{\Delta G(T_2)}{T_2} = \frac{\Delta G(T_1)}{T_1} + \Delta H \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

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

$$K_p = \left( \frac{p_T}{p^\circ} \right)^{\Delta \nu_i} \prod_i x_i^{\nu_i} = \left( \frac{p_T}{p^\circ} \right)^{\Delta \nu_i} K_x$$

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

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

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

$$m_A = K_A p_A$$

$$p_i = \chi_i p_i^*$$

$$y_A = \frac{p_A p_T - p_A^* p_B^*}{p_T (p_A^* - p_B^*)}$$

$$F = C - p + 2$$

$$p_A = \chi_A k_A^H$$

$$\frac{n_l^{\text{Total}}}{n_v^{\text{Total}}} = \frac{(y_A - Z_A)}{(Z_A - x_A)}$$

$$\mu_i = \mu_i^* + RT \ln(a_i)$$

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

$$a_i = \gamma_i \chi_i$$

$$\mu_i = \mu_i^\circ + RT \ln(a_i)$$

$$a_i = \gamma_i \frac{m_i}{m^\circ}$$

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

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

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

$$\Pi = [B] RT$$

$$I = \frac{1}{2} \sum_i z_i^2 \frac{m_i}{m^\circ}$$

$$\log \gamma_{\pm} = - |z_+ z_-| (0.5092) \sqrt{I}$$

$$\int x^n dx = \frac{1}{n+1} x^{n+1} + c$$

$$\int \frac{dx}{x} = \ln x + c$$

$$\frac{dx^n}{dx} = \frac{1}{n} x^{n-1}$$

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

$$Q = \prod_i a_i^{\nu_i}$$

$$E^\circ = E^\circ(\text{right}) - E^\circ(\text{left})$$

$$\Delta G_m = -vFE$$

$$E = E^\circ - \frac{RT}{vF} \ln Q$$