

## Comments 2012:

- This exam turned out to be too short – almost all of the class had left after 2 ½ hours or so. For this year, then, expect a somewhat longer exam (with a few more questions and/or somewhat longer questions – at least, that’s my intent.)
- Q 3 of this exam concerns material *not* covered in 2012.

Name:

Student ID:

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## UNIVERSITY OF MANITOBA, DEPARTMENT OF CHEMISTRY Chemistry 2290, Winter 2011, Dr. H. Georg Schreckenbach

### Final Examination April 12, 2011 (3 hours)

Make sure the exam has 5 pages. Read the questions carefully!!!! Answer **ALL** questions. The questions that are marked '**Bonus**' are the only exception: These particular questions are *optional* and tend to be more involved but may earn you extra points (questions 1c, 4d, 14, 15).

Most questions have *multiple* parts. Note that the questions aren't necessarily ordered by *difficulty* (or any other *criteria*).

For numerical problems, all mathematical steps must be shown. A formula sheet will be provided that contains all the key equations of the course, and that can be taken home afterwards. However, this **question sheet must be handed in** at the end of the exam.

(Total marks in the exam: 53; additionally, up to 4 *bonus* marks.)

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### **1. Laws of thermodynamics**

*(3 marks – parts a and b; 1 bonus mark – part c)*

Give a concise verbal formulation of (a) the Zeroth Law of Thermodynamics, (b) Third Law of Thermodynamics.

(c **Bonus**) Give a 2<sup>nd</sup>, different formulation of the Third Law and prove the equivalence of your two formulations.

### **2. Some definitions and concepts across the board – part 1**

*(5 marks)*

(a) Define “thermodynamic equilibrium”.

(b) What if any is the connection between “thermodynamic equilibrium” and “reversible process”?

(c) What is an “isolated system”? (Definition.)

(d) Can an isolated system change its internal energy? Explain!

### **3. Mesophases**

**(2 marks)**

With an example, explain what is meant by the statement that “a mesophase shows liquid-like behavior in some directions but crystal-like behavior in other directions.”

*Please be concise, though.* [Comment 2012: This material was *not* covered in 2012.]

### **4. Carnot cycle**

**(4 marks – parts a to c; 1 bonus mark, part d)**

(a) In a p–V diagram, draw a qualitative representation of a reversible Carnot cycle involving an ideal gas. In the diagram, mark the direction of change for the system (e.g. using arrows).

(b) For each step of the Carnot cycle (part a), state which properties if any are kept constant.

(c) What is the overall change in Gibbs free energy for an entire cycle? Provide a *brief* explanation of your answer.

(d **Bonus**) Explain the connection between your Carnot cycle and the definition of the entropy.

### **5. Ideal gas**

**(3 marks)**

Using the ideal gas law, calculate the average molar mass of air at sea level (assume standard conditions; 1.00 atm pressure) and 0.00°C if the density of air is 1.29 kg m<sup>-3</sup>.

### **6. Real gases**

**(4 marks)**

(a) Derive an expression for the compression factor Z of a gas that obeys the van der Waals equation of state.

(b) Show what happens to Z for very small values of a, b.

### **7. Some definitions and concepts across the board – part 2**

**(4 marks)**

(a) In the context of the “phase rule”, what are “thermodynamic degrees of freedom”? (Definition.)

(b) If two phases are in equilibrium with each other, what follows for the chemical potentials?

(c) Is it possible to measure the activity coefficient of Na<sup>+</sup>(aq)? Explain.

### **8. Ideal gas, First and Second Laws**

**(10 marks)**

Consider 1.50mol of an ideal gas initially at 1.10atm pressure and a temperature of 25.0°C. The temperature is held constant. This gas is allowed to expand against a constant external pressure of P<sub>ext</sub> = 0.500atm until the volume has doubled.

(a) For this process, calculate the work w, heat q, change in internal energy of the gas ΔU, change in enthalpy ΔH.

(b) For this process, calculate also the change in entropy for the system, surroundings as well as the overall change in entropy.

(c) For this process, calculate the change in Gibbs and Helmholtz free energy of the system.

(d) Is this process spontaneous? Why?

### **9. Solutions**

**(3 marks)**

The vapor pressure of benzene (molar mass: M = 78.114 gmol<sup>-1</sup>) is 400.0 Torr at 60.6°C, but it fell to 386 Torr when 19.0g of an involatile organic compound were dissolved in 500.00g of benzene. Calculate the molar mass of the compound. Assume ideal behavior for the solution.

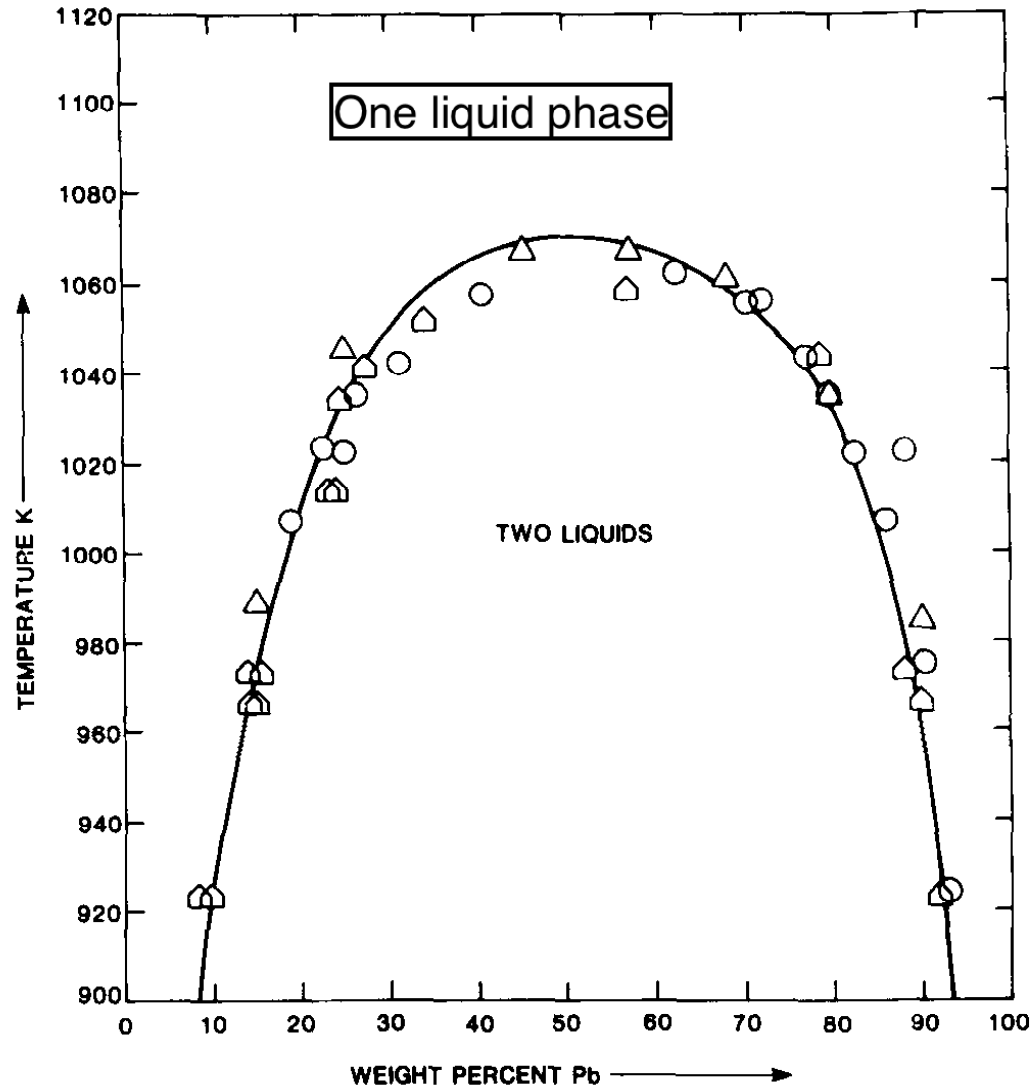
### 10. Phase diagram

(4 marks)

Consider the following experimentally determined phase diagram (Zn–Pb). Consider a mixture with an overall composition of 65% Pb by weight at 940K.

- Determine the number of thermodynamic degrees of freedom under these conditions.
- Determine the composition(s) of the phase(s) present under these conditions.
- Determine the relative amounts of any phases present under these conditions.

*Note: Parts of this question may be answered directly on the sheet, using the diagram. If you choose to do so, then please don't forget your name on the question sheet.*



(Figure adapted from J. D. Esdaile and Frank Sweett, "The thermodynamic properties and phase diagram of the zinc-lead system", *Metallurgical and Materials Transactions A* 14 (1983), 2211-2218.)

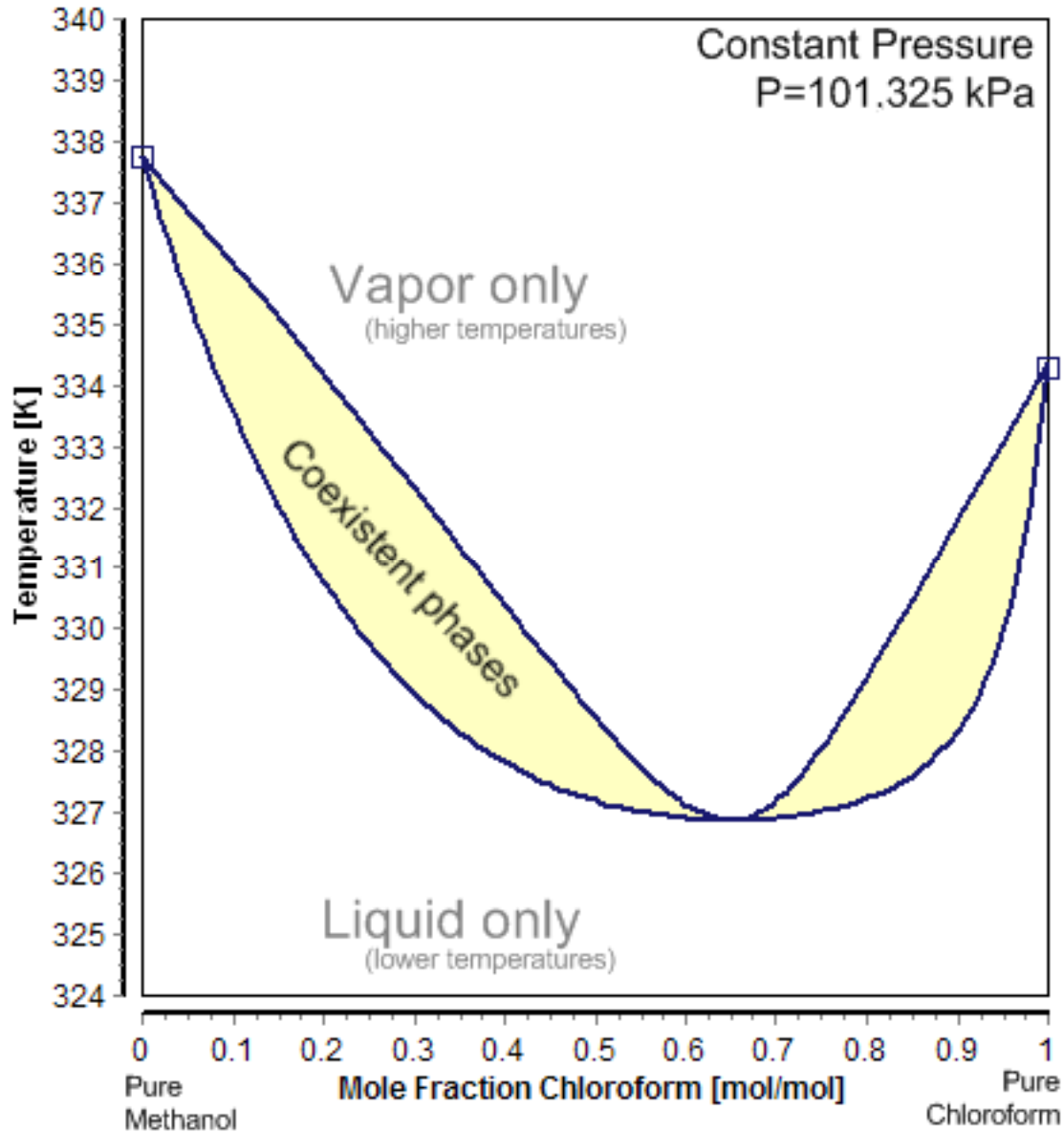
### 11. Fractional distillation

(2 marks)

Consider the following phase diagram (methanol–chloroform).

If you have a methanol–chloroform solution of  $x_{\text{chloroform}} = 0.10$ , what is the highest possible concentration of chloroform that can be obtained by fractional distillation of this solution?

Explain briefly! (You may use the diagram if you wish.)



(Figure adapted from <http://en.wikipedia.org/wiki/Azeotrope>; accessed April 6, 2011.)

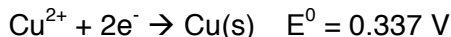
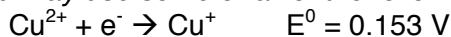
**12. Equilibrium constant; standard potential****(5 marks)**

A disproportionation reaction is a reaction in which a species is both oxidized and reduced.

(Standard temperature of 298.15 K)

- (a) Determine the standard potential for the disproportionation of  $\text{Cu}^+$  into  $\text{Cu(s)}$  and  $\text{Cu}^{2+}$ .  
(b) Also determine the equilibrium constant for this reaction.

*You may use some or all of the following information:*

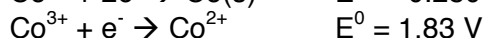
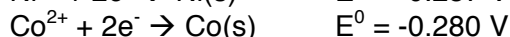
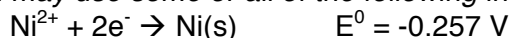
**13. Electrochemical cell****(4 marks)**

Consider the electrochemical cell  $\text{Co} | \text{Co}^{2+} || \text{Ni}^{2+} | \text{Ni}$ .

Calculate the cell potential (emf) at 298.15K if the concentrations are:

- (a)  $[\text{Ni}^{2+}] = 1.00 \text{ m}$  and  $[\text{Co}^{2+}] = 0.100 \text{ m}$ ;  
(b)  $[\text{Ni}^{2+}] = 0.0100 \text{ m}$  and  $[\text{Co}^{2+}] = 1.00 \text{ m}$ .  
(c) Write the cell reaction. Is the reaction as written spontaneous in cases (a) and (b), respectively?

*You may use some or all of the following information:*

**14 Bonus: Joule-Thomson coefficient****(1 bonus mark)**

The Joule-Thomson coefficient  $\mu_{JT}$  characterizes the adiabatic expansion of gases and is relevant for refrigeration. It is given by:

$$\mu_{JT} \equiv \left( \frac{\partial T}{\partial p} \right)_H$$

which can be calculated as

$$\mu_{JT} = \left( \frac{\partial T}{\partial p} \right)_H = \left( \frac{T(\partial V_m / \partial T)_p - V_m}{C_{p,m}} \right)$$

Using the expression above, evaluate  $\mu_{JT}$  for an ideal gas (i.e., find an expression for  $\mu_{JT}$  based on the ideal gas law).

**15 Bonus: Colligative properties****(1 bonus mark)**

Why is the magnitude of the freezing point depression less than that of the boiling point elevation?

– END OF EXAM –