# THE UNIVERSITY OF BRITISH COLUMBIA

CHEMISTRY 123 Midterm

28 February 2012

This examination consists of **8** numbered pages.

**PLEASE CHECK THAT YOU HAVE A COMPLETE PAPER**

**TIME LIMIT:**
**1.0 HOURS**

GIVEN NAME(S): ____ANSWER KEY________________ (IN INK)
SURNAME: ________________________ (CAPITALS) (IN INK)
STUDENT NUMBER: ________________________ (IN INK)
SIGNATURE: ________________________ (IN INK)

**The only calculator allowed is the Sharp EL-510RB. All other calculators will be confiscated. Cell phones or other electronic communication devices are not permitted. Molecular models are allowed and may be pre-built.**

Lecture Section (check √ your section)

___ 201 (MWF 1:00) Bizzotto/Sammis
___ 202 (MWF 2:00) Addison/Ryan
___ 203 (MWF 3:00) Addison/Ryan
___ 210 (MWF 10:00) Grant/Kunz
___ 211 (MWF 11:00) Grant/Sammis
___ 299 (T,Th 9:30) Lekhi
___ 222 (T,Th 2:00) Bizzotto/Kunz

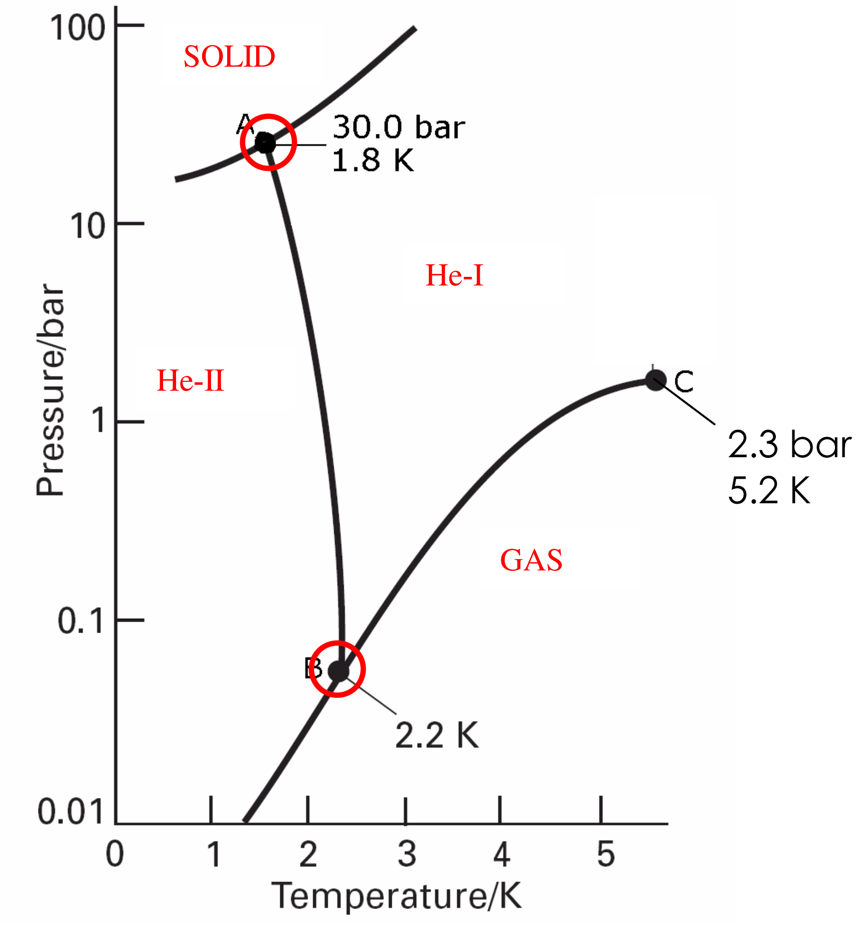
| Question | Maximum | Obtained | Code |
|---|---|---|---|
| 1 | 12 | | |
| 2 | 5 | | |
| 3 | 8 | | |
| 4 | 8 | | |
| 5 | 6 | | |
| 6 | 6 | | |
| TOTAL | 45 | | |

## REGULATIONS FOR EXAMINATIONS

1. Each candidate must be prepared to produce upon request, a Library/AMS card for identification.
2. Candidates are not permitted to ask questions of the invigilators, except in cases of supposed errors or ambiguities in examination questions.
3. No candidates shall be permitted to enter the examination room after the expiration of one half hour from the scheduled starting time, or to leave during the first half hour of the examination.
4. Candidates guilty of any of the following, or similar, dishonest practices shall be immediately dismissed from the examination and shall be liable to disciplinary action:
   (a) Having at the place of writing any books, papers or memoranda, calculators, audio or visual cassette players or other memory aid devices, other than those authorized by the examiners.
   (b) Speaking or communicating with other candidates.
   (c) Purposely exposing written papers to the view of other candidates. The plea of accident or forgetfulness shall not be received.
5. Candidates must not destroy or mutilate any examination material; must hand in all examination papers; and must not take any examination material from the examination room without permission of the invigilator.

***ANSWER ALL QUESTIONS***

1. [12 marks] The phase diagram for helium has two distinct liquid phases (He-I, He-II), one solid phase, and one gas phase. The solid phase has a higher density than both the liquid and gas phases. The transition from the liquid He-I phase to the He-II phase is an exothermic process.



a. On the phase diagram, label the states present in each region of the phase diagram:

b. What is the temperature of the normal boiling point for helium.

~4.5 K

c. Which form of helium in the liquid phase, He-I or He-II, has a higher density? Explain.

He-I has higher density. Increasing pressure at a constant temperature leads to He-II → He-I phase transition.

d. How many triple points are in the phase diagram for helium? Clearly circle the triple points on the phase diagram.

\# of triple points: ___2________________

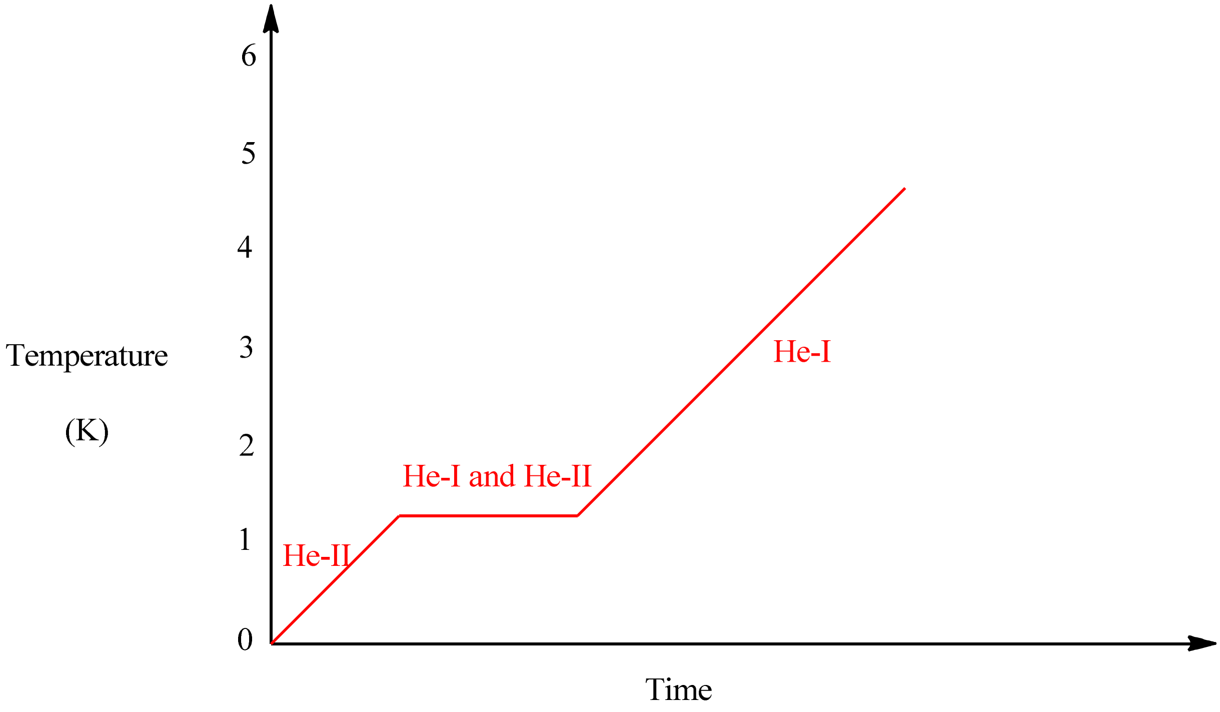
e. Explain the significance of point C.

Critical point; beyone this termperature and pressure the liquid and the gas phases become indistinguishable.

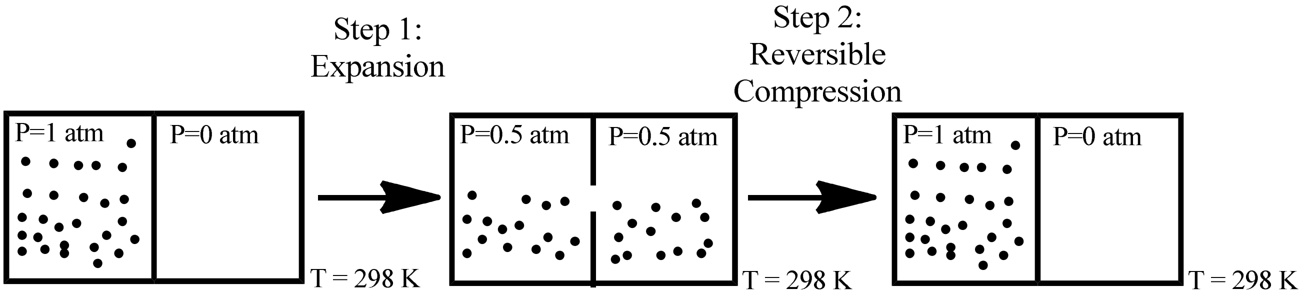
f. Can helium undergo sublimation? Explain.

No. The solid and gas phases are not directly adjacent to each other on the phase diagram.

g. Consider a sample of helium initially at **0 K** and **5.0 bar**. Complete the isobaric heating curve, using the axis below, as the temperature is increased from 0 K to 6 K at 5.0 bar. Label each segment of the curve with the phases present.



2. [5 marks] Consider the following two-step isothermal ($\Delta T = 0$) cycle shown below:



Initially, one mole of an ideal gas at 298 K and at 1 atm is separated by a closed valve from an evacuated chamber. In step 1, the valve opens and the gas expands against a zero opposing pressure. Therefore, $P_{ext}\Delta V = 0$, with $\Delta T = 0$.

In step 2, a piston reversibly compresses the system back to a pressure of 1 atm. The change in internal energy ($\Delta E$ or $\Delta U$) is zero.

a. During the second step of this cycle, the piston does 1.72 kJ of work on the system. Calculate $\Delta S$ for the second step.

$$\begin{aligned}\Delta E &= q + w = 0\\ &= q + (1.72 kJ) = 0\\ q &= -1.72 kJ\end{aligned}$$

$$\Delta S = \frac{q_{rev}}{T} = \frac{-1720 J}{298 K} = -5.77 J\,K^{-1}$$

b. Using your answer from part (a), calculate $\Delta S$ for the first step.

$$\begin{aligned}\Delta S_{cycle} &= \Delta S_{step1} + \Delta S_{step2} = 0\\ &= \Delta S_{step1} + (-5.77 J\,K^{-1}) = 0\\ \Delta S_{step1} &= 5.77 J\,K^{-1}\end{aligned}$$

3. [8 marks] Cesium metal spontaneously reacts with liquid water to form cesium oxide and hydrogen:

$$Cs(s) + \frac{1}{2}H_2O(l) \rightarrow \frac{1}{2}Cs_2O(s) + \frac{1}{2}H_2(g)$$

| | $H_2O(l)$ | $Cs_2O(s)$ |
|---|---|---|
| $\Delta H^0_{f,298}$ (kJ mol$^{-1}$) | –285.8 | –345.8 |
| $\Delta G^0_{f,298}$ (kJ mol$^{-1}$) | –237.1 | –308.1 |

a. Calculate the enthalpy of this reaction at 298 K. Does the reaction of cesium with water release heat or absorb heat?

$$\begin{aligned}\Delta H^o{}_{rxn} &= \sum \Delta H^o_{f,prod} - \sum \Delta H^o_{f,prod} \\ &= \frac{1}{2}(\Delta H^o_{f,H_2(g)} + \frac{1}{2}\Delta H^o_{f,Cs_2O(s)} - [\frac{1}{2}\Delta H^o_{f,H_2O(l)} + \Delta H^o_{f,Cs\ (s)} \\ &= -172.9kJ - (-142kJ) \\ &= -30kJ\end{aligned}$$

Heat is released.

b. Calculate the equilibrium constant for the given reaction at 298 K.

$$\begin{aligned}\Delta G^o{}_{rxn} &= \sum \Delta G^o_{f,prod} - \sum \Delta G^o_{f,prod} \\ &= \frac{1}{2}(\Delta G^o_{f,H_2(g)} + \frac{1}{2}\Delta G^o_{f,Cs_2O(s)} - [\frac{1}{2}\Delta G^o_{f,H_2O(l)} + \Delta G^o_{f,Cs\ (s)} \\ &= -35.5kJ\end{aligned}$$

$$\Delta G^o_{rxn} = -RT\ln K$$

$$K = e^{\frac{-\Delta G}{RT}} = e^{\frac{35500J}{(8.314J\,mol^{-1}K^{-1}}} = 1.67\times10^6$$

c. What is the partial pressure of $H_2(g)$, $P_{H_2}$ for equilibrium at 298 K?

$$K = \frac{a_{CsO}^{1/2}a_{H_2}^{1/2}}{a_{Cs}a_{H_2O}^{1/2}} = \frac{p_{H_2}^{1/2}}{1}$$

$$p_{H_2}^{1/2} = (1.67\times10^6)^2 = 2.79\times10^{12}\,atm$$

d. What happens to the equilibrium constant for the reaction of cesium metal with liquid water at an elevated temperature of 1843 K? Circle the correct answer.

Increase [✓ Decrease] Stay the same

e. What happens to the equilibrium constant for the reaction of cesium metal with liquid water when $P_{H_2}$ is increased by a factor of 10? Circle the correct answer.

Increase Decrease [✓ Stay the same]

4. [8 marks] An alternative fuel cell design using sodium borohydride/sodium metaborate is currently being designed. The relevant electrochemical reduction reactions are:

$$O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq) \qquad (\Delta\varepsilon^0 = +0.40V)$$
$$BO_2^-(aq) + 6H_2O(l) + 8e^- \rightarrow BH_4^-(aq) + 8OH^-(aq) \qquad (\Delta\varepsilon^0 = -1.24\ V)$$

a. Write out the net overall reaction in the direction of spontaneous change.

$$2O_2(g) + 4H_2O(l) + 8e^- \rightarrow 8OH^-(aq)$$
$$BH_4^-(aq) + 8OH^-(aq) \rightarrow BO_2^-(aq) + 2H_2O(l) + 8e^-$$

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$$2O_2(g) + BH_4^-(aq) \rightarrow BO_2^-(aq) + 2H_2O(l)$$

b. What is the potential of the cell written in part (a) at standard states (ie standard potential, $\Delta\varepsilon^0$)?

$$\Delta\varepsilon^o_{cell} = 1.64V$$

c. Calculate the cell potential in a typical borohydride fuel cell at 298 K when $[BO_2^-]$ is 0.25 M, $[BH_4^-]$ is 0.50 M, $P_{O_2}$ is 0.20 atm and pH is 14.

$$\Delta\varepsilon = \Delta\varepsilon^o - \frac{RT}{nF}\ln Q$$

$$\Delta\varepsilon = 1.64V - \frac{(8.314 Jmol^{-1}K^{-1})(298K)}{(8mol)(96500Cmol^{-1})}\ln\frac{[BO_2^-]}{[BH_4^-]P_{O_2}^2}$$

$$\Delta\varepsilon = 1.64V - 3.21\times10^{-3}V(\ln\frac{0.25}{0.5(0.2)^2})$$

$$\Delta\varepsilon = 1.632V$$

5. [6 marks] A solution is made by combining formic acid, HCOOH and 0.020 mols of NaOH to a final volume of 150 mL at room temperature. The pH of the solution after it reaches equilibrium is 4.046. The $pK_a$ of formic acid at 298 K is 3.745.

   a. Calculate the number of moles of formic acid that was added initially.

   $$HCOOH + OH^- \rightleftharpoons HCOO^- + H_2O$$

   Let x be the initial mols of HCOOH.

   Since NaOH is a strong base, it completely reacts with HCOOH to form $HCOO^-$.

   At equilibrium:
   mols of HCOOH is x-0.02
   mols of $HCOO^-$ is 0.02
   $[H^+] = 10^{-pka} = 10^{-4.046}$

   $$K_a = 10^{-pK_a} = 10^{-3.745} = 1.8\times10^{-4}$$

   $$K_a = \frac{[H_3O^+][HCOO^-]}{[HCOOH]}$$

   $$1.8\times10^{-4} = \frac{(8.99\times10^{-5})(0.02mol/0.150L)}{(x-0.02)/(0.150L)}$$

   $Solve\ for\ x:$

   $x = 0.03mols$

   b. Is this solution a buffer? Briefly explain.

   Yes it is a buffer. There is an appreciable amount of both conjugate acid and base present at equilibrium (0.03-0.02 = 0.01 mols of HCOOH at equilibrium and 0.02 mols of $HCOO^-$).

6. [6 marks] A small sample of t-butyl bromide, $(CH_3)_3CBr$ is added to solvent at 90 °C and slowly fragments into reactive $(CH_3)_3C^+$ cations and $Br^-$ anions. As they form, the $(CH_3)_3C^+$ cations collide with abundant $Cl^-$ anions in solution to form t-butyl chloride, $(CH_3)_3CCl$.
   a. Write down the elementary reactions for these two steps in the overall conversion of $(CH_3)_3CBr$ to $(CH_3)_3CCl$. You do not need to include phases.

   $$(CH_3)_3CBr \longrightarrow (CH_3)_3C^+ + Br^-$$

   $$(CH_3)_3C^+ + Cl^- \longrightarrow (CH_3)_3CCl$$ Bimolecular reaction

   b. Identify the reaction intermediate(s).

   $(CH_3)_3C^+$

   c. Label the bimolecular reaction in part (a).

   d. Write down the rate law for the bimolecular elementary reaction in part (a).

   Rate = $k[(CH_3)_3C^+][Cl]$

END OF EXAMINATION