UNIVERSITY OF TORONTO

FACULTY OF APPLIED SCIENCE AND ENGINEERING

FINAL EXAMINATION, DECEMBER 2001

SECOND YEAR – PROGRAM 08

MSE202F – Thermodynamics 1

EXAM TYPE: C

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ANSWER ANY FIVE (5) QUESTIONS.

<u>If you answer question 7, part (c), please hand in that page with your answer booklet.</u>

Wherever appropriate, make full use of balanced chemical reactions, thermodynamic equations and carefully drawn diagrams.

1. Calculate the final volume and work done in the expansion of 15 litres of an ideal gas at 0°C and 15 atm to 1 atm in an
   (a) isothermal reversible expansion, **(4 marks)**
   (b) adiabatic reversible expansion, **(6 marks)**
   (c) irreversible adiabatic expansion in which pressure is suddenly released to 1 atm, and then the gas expands adiabatically against this constant pressure. **(6 marks)**

   Calculate the change in internal energy of the system during processes (a) and (b). **(4 marks)**

2. Calculate $\Delta H°$ for the following reaction at 1300K:

   $ZnS_{(s)} + CaO_{(s)} + C_{(s)} = Zn_{(g)} + CaS_{(s)} + CO_{(g)}$

   Data:
   $\Delta H°(ZnS, s, 298K) = -48.2$ kcal/mol
   $\Delta H°(CaO, s, 298K) = -151.6$ kcal/mol
   $\Delta H°(CaS, s, 298K) = -110.0$ kcal/mol
   $\Delta H°(CO, g, 298K) = -26.4$ kcal/mol
   The melting point of Zn is 419.6°C
   The enthalpy of fusion is 1.74 kcal/mol
   The boiling point of Zn is 900°C
   The enthalpy of vaporization is 27.3 kcal/mol **(20 marks)**

   $Cp\ (ZnS, s) = 12.16 + 1.24 \times 10^{-3}T - 1.36 \times 10^{5}T^{-2}$ cal/(deg.mol)
   $Cp\ (C, s) = 4.10 + 1.02 \times 10^{-3}T - 2.10 \times 10^{5}T^{-2}$ cal/(deg.mol)
   $Cp\ (CaO, s) = 11.86 + 1.08 \times 10^{-3}T - 1.66 \times 10^{5}T^{-2}$ cal/(deg.mol)
   $Cp\ (CaS, s) = 10.20 + 3.80 \times 10^{-3}T$ cal/(deg.mol)
   $Cp\ (CO, g) = 6.79 + 0.98 \times 10^{-3}T - 0.11 \times 10^{5}T^{-2}$ cal/(deg.mol)
   $Cp\ (Zn, s) = 5.35 + 2.40 \times 10^{-3}T$ cal/(deg.mol)
   $Cp\ (Zn, l) = 7.50$ cal/(deg.mol)
   $Cp\ (Zn, g) = 5.00$ cal/(deg.mol)

3. It has recently been suggested that molybdenum could be produced from its sulphide by using the reaction

$$\frac{1}{2}MoS_{2\,(s)} + CaO_{(s)} + C_{(s)} = \frac{1}{2}Mo_{(s)} + CaS_{(s)} + CO_{(g)}$$

A thermodynamic study of this reaction has yielded the following results:

Temperature (°C)	310	437	560	683	810
p_{co} (atm)	10^{-4}	2.6×10^{-2}	1.10	17.9	163.6

By a suitable plot, determine the $\Delta H°$of this reaction. **(12 marks)**

By interpolation, determine the $\Delta G°$ and hence the $\Delta S°$ of this reaction at 1000K, and hence express $\Delta G°$ as a function of temperature. **(5 marks)**

Calculate the minimum temperature at which this reaction would occur when pco = 1 atm **(3 marks)**

4. Below the triple point (-56.2°C) the vapour pressure of solid CO_2 is given as

$$\ell n\, p\,(\text{atm}) = -\frac{3116}{T} + 16.01$$

The molar heat of melting of CO_2 is 8330 joules. Calculate the vapour pressure exerted by liquid CO_2 at 25°C and at the triple point **(17 marks)**, and hence deduce why solid CO_2, sitting on the laboratory bench, evaporates rather than melts **(3 marks)**.

5. Consider a system consisting of a liquid A, another heavier liquid B and a solid C. Surface tensions of liquid A, liquid B and solid C are 500 mN/m, 700 mN/m and 1200 mN/m respectively. The interfacial tension between liquid A and liquid B is 250 mN/m. The contact angle of liquid B on solid C in air is 106.6^{O}. The contact angle of liquid B on solid C while immersed in liquid A is 60^{O}. All data is at a constant temperature.

(a) Calculate the interfacial tension between liquid A and solid C. **(5 marks)**
(b) Calculate the interfacial tension between liquid B and solid C. **(5 marks)**
(c) Calculate the contact angle of liquid A on solid C in air. **(5 marks)**
(d) Calculate the visible contact angle, if a drop of liquid A is placed on bulk liquid phase B. **(5 marks)**

6. **Construct a hypothetical binary phase diagram for the system A-B with the following conditions:** **(5 marks)**

a) *Component A melts at 1850°C and component B melts at 1700°C.*
b) *Compound AB_4 (80 mole % B) melts incongruently at 1500°C.*
c) *Compound AB (50 mole % B) melts congruently at 1600°C.*
d) *There is eutectic reaction, E1, between solid solutions α and β at 20 mole % B and 1400°C.*
e) *There is another eutectic reaction, E2, between β and γ at 60 mole % B and 1200°C.*
f) *There is a peritectic reaction involving γ and δ at 1500°C and liquid with a composition of 30 mole % A.*
g) *The amount of α in equilibrium with β at the E1 eutectic temperature contains 10 mole % B.*
h) *The amount of β in equilibrium with α at the E1 eutectic temperature contains 35 mole % B.*
i) *The amount of α in equilibrium with β at room temperature contains 98 mole % A.*
j) *The amount of β in equilibrium with α at room temperature contains 55 mole % A.*
k) *The amount of β in equilibrium with γ at the E2 eutectic temperature contains 55 mole % B.*
l) *The amount of γ in equilibrium with β at the E2 eutectic temperature contains 76 mole % B.*
m) *The amount of β in equilibrium with γ at room temperature contains 52 mole % B.*
n) *The amount of γ in equilibrium with β at room temperature contains 78 mole % B.*
o) *The amount of δ in equilibrium with γ and the liquid at the peritectic temperature contains 10 mole % A.*
p) *The minimum amount of A soluble in γ at room temperature is 15 mole %.*
q) *The minimum amount of A soluble in δ is 5 mole %.*

Use the diagram you have constructed to answer the following:

(i) Label all phase fields. **(3 marks)**

(ii) Describe the solidification path (include changes occurring at phase boundaries and all invariant reactions) of an alloy, x, containing 75% B starting from 2000°C. **(3 marks)**

(iii) Perform a phase analysis of alloy x at 1550°C. **(3 marks)**

(iv) Describe the solidification path (include changes occurring at phase boundaries and all invariant reactions) of an alloy, y, containing 40% B starting from 1700°C. **(3 marks)**

(v) Perform a phase analysis of alloy y at 1000°C. **(3 marks)**

Please answer any **TWO** out of the three parts of this question.

7. (a) The following free energies of formation are given in KJ per mole of oxygen:

Temperature (°C)	0	500	1000	1700
CO	-275	-360	-445	-560
H_2O	-460	-405	-350	-275
XO	0	50	105	
YO	-625	-520	-415	-275
ZO	-815	-740	-665	-560

Calculate the range of temperatures (within the given range) over which the metal oxides can be reduced, to yield the metals X, Y and Z respectively, by (a) carbon and (b) hydrogen.

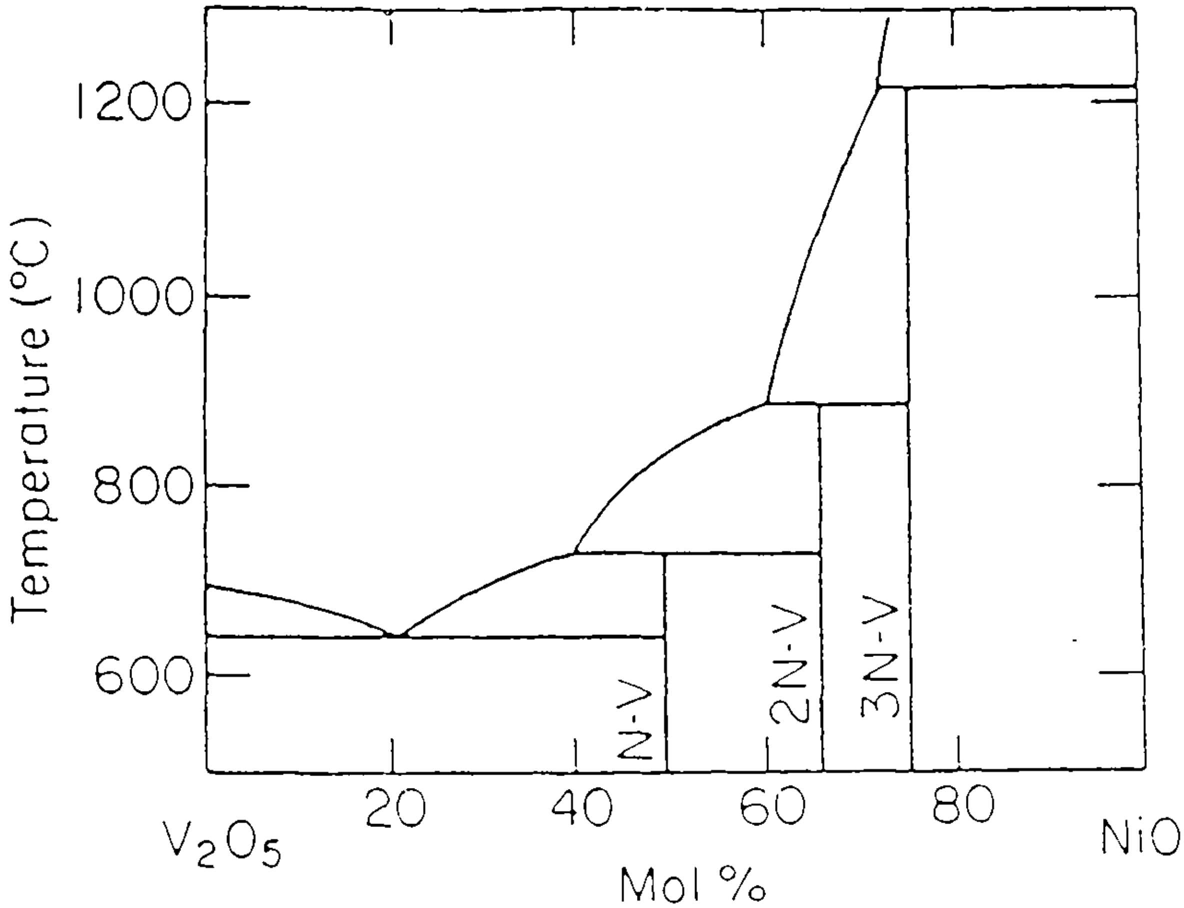
(10 marks)

7. (b) (i) A liquid aluminum alloy with a density of 2.30 g/cm^3 is held in a crucible under the cover of molten salt at 740 ^{O}C. The molten salt has a density of 1.60 g/cm^3. A capillary tube is introduced in the metallic bath covered with salt. The liquid aluminum alloy does not wet the inner walls of the tube and the contact angle between aluminum alloy and capillary tube is measured to be 130^{O} at the aluminum/salt interface. Assume that the capillary tube is of a sufficiently smaller diameter, so that the aluminum/salt meniscus can be considered to be approximately spherical. The interfacial tension between aluminum and salt is equal to 750 mN/m. The inside diameter of the capillary tube has been measured to be equal to 0.8 cm. Calculate the height of capillary rise or depression of aluminum/salt interface inside the capillary.

(5 marks)

(ii) A surface active species, 2, adsorbs on 1 by building a close-packed monolayer. The atomic radius of species 2 is 2.5 Å. Assuming that the area per atom is equivalent to a hexagon with an inscribed circle of the atomic radius, what is the value of Γ_2 at saturation coverage (in mol/m^2)? **(5 marks)**

7. (c)



Use the above phase diagram to answer the following questions

i) Label all the phase fields. **(2 marks)**

ii) Describe the solidification path of an alloy that undergoes two peritectic reactions. Show the position of the alloy you have chosen on the phase diagram. After each phase change, calculate the percentage of each phase present and determine the composition of each phase. **(2 marks)**

iii) Describe the melting process of an alloy that undergoes only one peritectic reaction. Show the position of the alloy you have chosen on the phase diagram. After each phase change, calculate the percentage of each phase present and determine the composition of each phase. **(2 marks)**

iv) Use the phase rule to show that the eutectic and peritectic reactions occur at constant temperature. **(2 marks)**

v) Draw the equilibrium cooling curve of an alloy that undergoes one eutectic and one peritectic reaction. **(2 marks)**

If you have answered this part of the question, please hand in this page with your answer booklet.

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