Name _____

Student Number ___ _____

University of Toronto

Faculty of Applied Science and Engineering

Final Examination, April 2001

Second Year -- Program 5

ChE219S Engineering Thermodynamics

Examiner: Y.-L. Cheng

Instructions:

1. Type D: one aid sheet and one pre-specified sheet of notes allowed.
2. Calculator Type 2: Any non-programmable calculator allowed.
3. Do all work on these sheets.

Problem 1	/20
Problem 2	/20
Problem 3	/20
Problem 4	/20
Problem 5	/20
Total	/100

Problem 1 [20 marks total]

Provide brief answers to the following questions. Each is worth 5 marks.

(a) On the P-$\underline{V}$ diagram shown, provide a sketch that shows:

    (i)   a saturated liquid curve (sat'd L)

    (ii)   a saturated vapor curve (sat'd V)

    (iii) liquid-vapor coexistence regions (L + V)

    (iv) liquid region (L)

    (v)   vapor region (V)

    (vi) critical point (C)

    (vii) five isotherms that cover temperatures ranging from below the critical temperature to above the critical temperature: $T_1 < T_2 < T_3 < T_c < T_5$
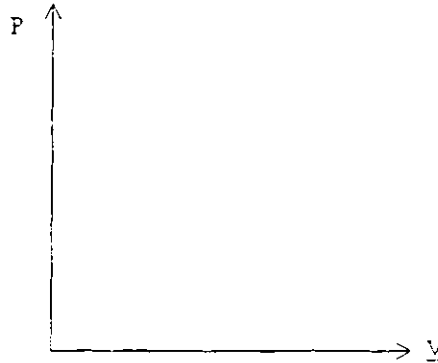
(b) The total volume of a mixture is related to the partial molar volume of each of the components as follows: $V = \sum_{i=1}^{c} N_i \overline{V}_i$. Consider a mixture that contains N_1 moles of component "1" with partial molar volume $\overline{V}_1$. Does $N_1 \overline{V}_1$ represent the fraction of the total mixture volume occupied by component "1"? Explain your answer.

(c) In words, describe the meaning of departure functions, e.g. entropy departure.

(d) The Clausius-Clapeyron equation describing liquid-vapor equilibrium of a pure component is sometimes written as:

$$\ln\left[\frac{P^{sat}(T_2)}{P^{sat}(T_1)}\right] = -\frac{\Delta H^{vap}}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

Give the fundamental equilibrium criterion that forms the basis of this relationship, and state all the assumptions that were made to get to the above equation.

Problem 2 [20 marks]

[Marks]

[10] (a) Prove that $\left(\dfrac{\partial \underline{U}}{\partial T}\right)_{\underline{S}} = C_V \left(\dfrac{\partial \ln T}{\partial \ln P}\right)_{\underline{V}}$

The following relationships that we have derived in class may be used without proof. (You don't need all of them.)

$$d\underline{U} = T d\underline{S} - p d\underline{V}$$

$$d\underline{H} = T d\underline{S} + \underline{V} dp$$

$$d\underline{A} = -\underline{S}\, dT - p d\underline{V}$$

$$d\underline{G} = -\underline{S}\, dT + \underline{V} dp$$

$$d\underline{U} = C_V dT + \left[T\left(\frac{\partial p}{\partial T}\right)_{\underline{V}} - p \right] d\underline{V}$$

$$d\underline{H} = C_p dT + \left[\underline{V} - T\left(\frac{\partial \underline{V}}{\partial T}\right)_p \right] dp$$

$$d\underline{S} = \frac{C_V}{T} dT + \left(\frac{\partial p}{\partial T}\right)_{\underline{V}} d\underline{V}$$

$$d\underline{S} = \frac{C_p}{T} dT - \left(\frac{\partial \underline{V}}{\partial T}\right)_p dp$$

<u>Problem 2. continued [20 marks total]</u>

<u>[Marks]</u>

[10] (b) The following pair of equations has been suggested for representation of partial molar volume data for a binary system at constant T and P:

$$\overline{V}_1 - \underline{V}_1 = a + (b-a)x_1 - bx_1^2 \qquad \text{and} \qquad \overline{V}_2 - \underline{V}_2 = a + (b-a)x_2 - bx_2^2$$

Are these equations thermodynamically sound? Explain.

Problem 3 [20 marks]

One mole of ethylene is contained in a closed, rigid vessel. Initially, the temperature in the vessel is 282.4K, and the pressure is 2 MPa. The ethylene is heated until the temperature reaches 423.6K.

[Marks]
[6] (a)   What is the pressure in the vessel when the temperature is 423.6K?
[14] (b)   How much heat was added in this process?

Data for ethylene: critical temperature = 282.4K
                         critical pressure = 5.036 MPa
                         critical compressibility = 0.276
                         Ideal gas C_p^{ig} can be assumed to be constant at 49.0 J mol^{-1} K^{-1}.

Problem 4 [20 marks]

Very pure liquid water can be subcooled at atmospheric pressure to temperatures well below the 0°C freezing point at this pressure. Using a carefully conducted procedure, 1 kg of very pure liquid has been subcooled as a liquid to $-6°C$ at atmospheric pressure. A small ice crystal (of negligible mass) is added to "seed" the subcooled liquid. The subsequent change towards equilibrium occurs adiabatically and at a constant pressure of 1 atmosphere.

[Marks]

[3] (a)   On the pressure vs. temperature diagram provided, sketch the lines and curves that divide the solid, liquid and vapor regions, and indicate the following:

   (i) S – the solid region
   (ii) L – the liquid region
   (iii)   V – the vapor region
   (iv) t – the triple point
   (v) "1" – the initial state of the very pure water
   (vi) the direction that the process would take from "1"

[5] (b)   Show that when equilibrium has been reached, the vessel must contain an equilibrium mixture of solid and liquid, i.e. show that it is not possible to have either all liquid or all solid at equilibrium.

[6] (c)   What are the fractions of solid and liquid at equilibrium? W

[6] (d)   What is the total ΔS for the process?

Data and allowable assumptions:

$\Delta \hat{H}_{fw}$ = enthalpy of fusion of water at 0 °C = 335 J g^{-1} (approximately constant)

$C_P^l = C_p$ of liquid water = 4.22 J g^{-1} °C^{-1}.

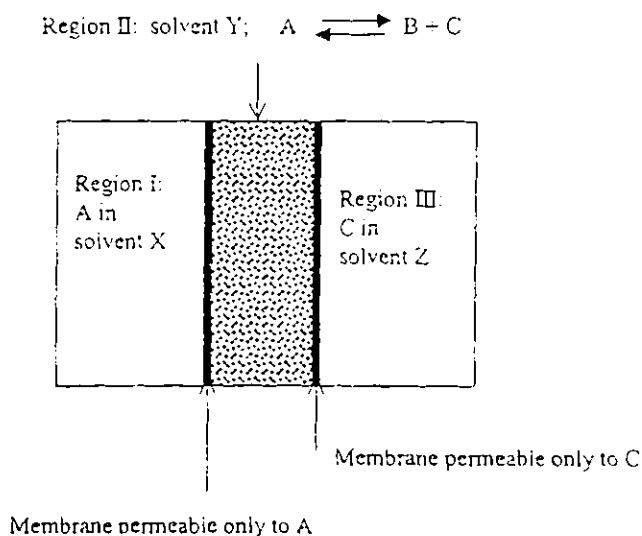$C_P^s = C_p$ of solid ice = 2.1 g^{-1} °C^{-1}

Triple point of H_2O = 273.16K, 611 Pa

The work of expansion due to the specific volume difference between solid and liquid H_2O may be neglected.

Enthalpy and internal energy may be approximated as being equal

Problem 4. continued [20 marks]

Problem 5 [20 Marks]

A proposed batch reactor for carrying out the reaction $A \leftrightarrow B + C$ is shown in the figure. B is the desired product. The reactor is divided up into three regions. Region I contains an excess of "A" in solvent X so that the chemical potential of "A" in this region, μ_A^I, may be considered constant. Region II is the reaction zone. It contains a solid catalyst for accelerating the desired reaction, and a solvent Y in which A, B and C are all soluble. Regions I and II are separated by a semi-permeable membrane that is only permeable to "A" – so you may think of Region I as providing a source of "A" to the reaction zone. Region III contains a solvent Z in which C is very soluble. Regions II and III are separated by a second semipermeable membrane that is only permeable to "C" so that "C" may diffuse into Region III. This serves two purposes: (1) it allows for the removal of C from the desired product B so that B can be more easily purified once the reaction is complete, and (2) it drives the reaction in the forward direction by removing one of the products from the reaction zone. The very high solubility of C in solvent Z in Region III keeps the chemical potential of C in Region III at a very low level throughout the reaction. The entire reactor is maintained at constant temperature and pressure.

Region II: solvent Y; $A \rightleftharpoons B + C$

Region I: A in solvent X

Region III: C in solvent Z

Membrane permeable only to C

Membrane permeable only to A

[Marks]

[10] (a) Derive the overall condition for the approach to equilibrium, and the corresponding equilibrium criterion for the reaction zone Region II.

[10] (b) State all the the equilibrium criteria between the regions and within regions in terms of T, P, and the chemical potentials of A, B, C, X, Y and Z. If you are confident of your answers, you may state them without derivation.

Problem 5. continued [20 Marks]