

SOLUTIONS

READ THIS FIRST

Do not enter your answers on this insert. Enter your answers in the space provided with each question. Show your work in order to receive credit on questions involving calculations. This examination is worth a total of 200 points.

1) Useful Constants

$$R = 8.31451 \text{ J/K-mole} = 0.082058 \text{ L-atm/K-mole}$$

$$F = 96485.3 \text{ C/mole}$$

$$N_A = 6.0221367 \times 10^{23} \text{ molecules/mole}$$

2) Ethanol is now being used as anti-knocking additive to gasoline. The following data which you use in Problem 1 have been published for the system ethanol-octane at 338.15 K.

vapor pressure of pure ethanol: 0.5768 atm

vapor pressure of pure octanol: 0.1279 atm

vapor pressure of ethanol and octane in equilibrium with a solution of the two

<u>Solution</u>	<u>X(ethanol)</u>	<u>p(ethanol) [atm]</u>	<u>p(octane) [atm]</u>
I	0.9833	0.5694	0.0249
II	0.5734	0.4976	0.1130

1) (75 points) Using the data on the insert, answer the following questions dealing with the system ethanol-octane at 338.15 K.

a) Calculate the activity coefficient of the ethanol in solution I **and** in solution II.

The Raoult's Law Standard State is the natural choice for this problem. For an ideal solution, Raoult's Law predicts $p_E = X_E p_E^\bullet$. We modify this for a real solution by inserting an activity coefficient so $p_E = \gamma_E X_E p_E^\bullet$. This yields $\gamma_E = p_E / (X_E p_E^\bullet)$.

$$\text{solution I: } \gamma_E = (0.5694 \text{ atm}) / (0.5768 \text{ atm})(0.9833) = 1.004$$

$$\text{solution II: } \gamma_E = (0.4976 \text{ atm}) / (0.5768 \text{ atm})(0.5734) = 1.505$$

b) Discuss the physical significance and ramifications of the results obtained in part (a). A thoughtful, thorough but succinct essay is expected.

γ_E of solution I is close to unity as expected. With the choice of a Raoult's Law Standard State, the activity coefficient rapidly approaches 1 as X_E approaches one. γ_E of solution II where X_E is not close to one differs significantly from unity so the system ethanol-octane is non-ideal. In fact, it is greater than one so ethanol shows a positive deviation from Raoult's Law. The other component will also show a positive deviation. Hence, the vapor pressure of each component and the total vapor pressure will be greater than expected from the Raoult's Law prediction. This increase in the vapor pressure has consequences for the use of ethanol as an additive in gasoline. The positive deviation suggests that the origin of non-ideality lies in repulsions between the ethanol and octane molecules in the solution. The non-ideality of the solution has a further consequence; the enthalpy and volume of mixing are not zero.

c) Calculate the change in the Gibbs free energy for the transfer of one mole of liquid ethanol from solution I to solution II.

$$\mu_E = \mu_E^\circ + RT \ln(a_E) \text{ and } a_E = \gamma_E X_E \text{ so}$$

$$\Delta\mu = RT \ln[a_E(\text{II})/a_E(\text{I})] = RT \ln[\gamma_E(\text{II})X_E(\text{II}) / \gamma_E(\text{I})X_E(\text{I})]$$

$$\Delta\mu = (8.31451 \text{ J/K})(338.15 \text{ K}) \ln[(1.505)(0.5734) / (1.004)(0.9833)] = -379 \text{ J/mol}$$

d) A tank consists of two chambers separated by a membrane permeable to ethanol and octane. Suppose that the two chambers are loaded with solutions I and II at 338.15 K. In what direction will the ethanol flow? Why?

Ethanol will flow to the region with the lower chemical potential. $\Delta\mu$ calculated in part (c) is negative so the ethanol will flow from the chamber containing solution I to that containing solution II.

2) (35 points) A single cell is immersed in plasma. The concentrations of the chloride anion **interior** to and **exterior** to the cell are 1.50 mM and 3.00 mM, respectively.

a) Is the pH higher inside or outside the cell? Explain.

Information is provided about one electrolyte. However, a cell contains many electrolytes. Therefore, mass and charge balances can not be used in this problem. The Donnan condition is the key to the problem. If we assume equal but not unity activity coefficients on the two sides of the cell membrane, the Donnan Condition yields

$[Cl^-]'/[Cl^-]'' = (1.5 \text{ mM})/(3.00 \text{ mM}) = 0.5 = [H^+]'/[H^+]''$ (' for in- & '' for outside)
Therefore, $[H^+]' = 2[H^+]'' > [H^+]''$ so the cell interior has the higher hydronium concentration and the lower pH.

b) Calculate the change in pH across the cell membrane.

$$\Delta pH = (-\log_{10}[H^+]') - (-\log_{10}[H^+]'') = -\log_{10}\{[H^+]'/[H^+]''\} = -\log_{10}(2) = -0.301$$

3) (25 points) Consider a drug that can exist in two crystalline polymorphs, A and B.

The key to this problem is the differential for μ : $d\mu_i = -\bar{S}_i dT + \bar{V}_i dp$ (1).

a) Given constant temperature, how does $\Delta\mu = \mu_A - \mu_B$ depend on the total pressure p ? That is, for $d\Delta\mu = f dp$, identify the function f .

From equation (1), it follows that $f = \Delta\bar{V}$ where $\Delta\bar{V} = \bar{V}_A - \bar{V}_B$

b) Given constant pressure, how does $\Delta\mu = \mu_A - \mu_B$ depend on the temperature T ? That is, for $d\Delta\mu = g dT$, identify the function g .

From equation (1), it follows that $g = -\Delta\bar{S}$ where $\Delta\bar{S} = \bar{S}_A - \bar{S}_B$

c) Suppose that T and p are changed together so that the two polymorphs remain in equilibrium. What is the value of $\Delta\mu$ during this process?

Equilibrium is the crucial word; $\Delta\mu = 0$.

d) For the process described in part (c), derive an equation that relates the derivative dp/dT to thermodynamic state functions.

Combine the results from parts (a), (b), and (c).

$$0 = d\Delta\mu = -\Delta\bar{S}dT + \Delta\bar{V}dp. \text{ Therefore, } dp/dT = \Delta\bar{S}/\Delta\bar{V}.$$

4) (65 points) Anorthite and albite are two feldspar minerals found in granite. The phase diagram for the system albite-anorthite is displayed below.

a) Consider an equilibrium mixture of albite and anorthite with a net composition of 20 wgt.-% anorthite. What phases are present at 1300°C. Provide the composition and relative amounts of the phases.

Note the 1300°C tie line drawn below in red. The point F is determined by the temperature and the net composition of the mixture, 20 wgt.-% anorthite. The intersection of the red tie line with phase boundaries determines the identity and composition of the two phase. Point E identifies a melt; its composition, 15 wgt.-% anorthite is read from the line EE'. Point G identifies a solid solution; its composition, 54 wgt.-% anorthite, is read from the line GG'. The ratio of the tie line segments, $FG/EF = 6.2$ is the ratio of the mass of melt to the mass of the solid solution.

b) Sketch the cooling curve (T versus time) for a sample initially at 1600°C that is 50 wgt.-% anorthite. Provide values of the temperature at each break in the curve, i.e. at each point where there is a discontinuity in slope.

The sketch is given below. There is no eutectic point and therefore no eutectic halt for this system. The cooling curve will show two breaks, at the fp and the mp. The slope will be the smallest between the fp and the mp where dq/dt mostly expresses itself via the phase change, i.e. $\Delta H(dn/dt)$.

c) Provide the melting point (mp) and the freezing point (fp) of a sample that is 60 wgt.-% anorthite.

$$\text{mp} = \underline{\hspace{2cm} 1334 \text{ }^\circ\text{C} \hspace{2cm}} \quad \text{fp} = \underline{\hspace{2cm} 1474 \text{ }^\circ \hspace{2cm}}$$

Note the melting point is the lowest temperature at which the solid begins to melt upon cooling. The freezing point is the lowest temperature at which solid first forms upon cooling. For a mixture, $\text{fp} < \text{mp}$. The mp is given by point H on the phase diagram; the fp, by point H'.

d) Suppose a molten mixture of albite and anorthite is allowed to cool very slowly until it has solidified. Would one find crystals of pure albite and pure anorthite in the solid? Explain.

No. The phase diagram identifies a system in which the two components, albite and anorthite, form a solid solution. Therefore at no composition other than the components will the solid be a pure substance.

