

10.213 Fall 2005
Final (5 problems, 100 points total)

- *Write your name on all blue books.*
- *Clearly show your work, your reasoning, and state all assumptions.*
- *Include units for all numerical calculations.*

Problem 1 (25 points)

Consider a steady-state, reversible, adiabatic mixing device with two inlets and a single outlet. The temperature of the surroundings is 300 K.

The conditions at the inlets are:

Inlet 1: 1.0 mol/min, 300 K, 1 bar

Inlet 2: 4.0 mol/min, 400 K, 1 bar

Both inlets are composed of the same pure liquid oil "A". Over the temperature range of interest, this oil has a constant pressure heat capacity of 30 J/mol K. The outlet pressure is 1 bar.

- a) (10 points) Determine the outlet temperature and the work rate of the device.
- b) (3 points) Indicate if work is being produced or consumed by the device.
- b) (12 points) Repeat the calculation of part a) if the composition of the second inlet is changed to a different pure liquid oil "B". Oil "B" also has a heat capacity of 30 J/mol K over the temperature range of interest. The other conditions at inlet 2 remain the same: a flow rate of 4.0 mol/min, temperature of 400 K, and pressure of 1 bar. You can assume that oils "A" and "B" form an ideal solution at the outlet and that no chemical reactions occur between the two oils.

Problem 2 (15 points)

Spray cans contain liquid under elevated pressure. Common household examples include spray paints and spray on oils used for cooking. Depressing the nozzle on the can allows liquid to exit through small orifices, forming a fine mist of droplets in the surroundings at a pressure of 1 bar and a temperature of 300 K.

- a) (12 points) Calculate the minimum work per mole of oil required to produce a steady state mist containing 10 micron size droplets of oil from bulk oil at the same temperature

and pressure. The oil has a surface tension of 20 mN/m, a molecular weight of 0.20 kg/mol, and a density of 1000 kg/m³.

- b) (3 points) To decrease droplet size, should the pressure inside the can be increased or decreased? Why?

Problem 3 (15 points)

Proteins can sometimes be purified from other contaminating proteins by denaturation. If the contaminating protein denatures at a lower temperature than the desired protein, it can be selectively denatured and precipitated from solution. You have a solution of chymotrypsin that is contaminated with a protein in which ΔG^0 for the denaturing reaction is known to be 8.5 kJ/mol less than ΔG^0 for the denaturation of chymotrypsin at all temperatures. You wish to remove 99% of the contaminating protein by denaturation. What temperature should be used and what percentage of the chymotrypsin will be denatured? The proteins are in dilute aqueous solution.

TABLE: Representative Thermodynamic Parameters for Thermal Protein Denaturation in Aqueous Solution at 298 K

Protein	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (J/molK)	ΔC_p (kJ/molK)
Barnase	48.9	307	866	6.9
Chymotrypsin	45.7	268	746	14.1
Cytochrome-c	37.1	89	174	6.8
Lysozyme	57.8	242	618	9.1
Ribonuclease A	27.0	294	896	5.2
λ Repressor _{G-85} ^a	17.7	90.4	244	6.0

Source: Adapted from G.I. Makhatadze and P.L. Privalov, Adv. Pros. Chem., 47, 307 (1995).

^aSee G.S. Huang and T.G. Oas, Biochemistry 35, 6173 (1996)

Problem 4 (15 points)

- (i) (4 Points) The partial molar property of a particular component is defined as the differential change in that property with a differential change in the number of moles of that component, holding the mole numbers of all other components constant, i.e.,

$$\bar{M}_i = \left(\frac{\partial n M_m}{\partial n_i} \right)_{T, P, n_{j \neq i}}$$

where M_m is the property value per mole of solution at the given composition. A common error among those new to thermodynamics is to assume that

$$\bar{M}_i = \left(\frac{\partial M_m}{\partial x_i} \right)_{T,P}$$

Explain why this cannot be true, and show that $\bar{M}_i = M_m + (1 - x_1) \left(\frac{\partial M_m}{\partial x_1} \right)_{T,P}$

(ii) (4 points) The partial molar heat of mixing of water in a solution of water and a non-volatile substance has been determined from the temperature dependence of water partial pressures. These data can be represented by the simple algebraic expression

$$\Delta \bar{H}_w = b(1 - x_w)^2$$

Use this information to determine the heat of mixing per mole of solution, ΔH_{mix} , as a function of composition x_w .

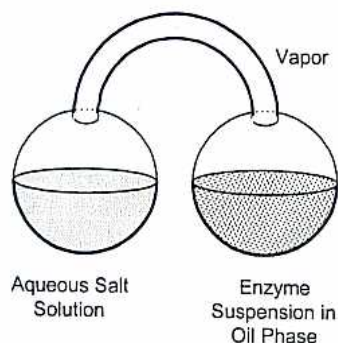
(iii) (4 points) Derive an expression for the partial pressure of the water above the solution as a function of temperature and composition, assuming that the constant b is independent of temperature, and assuming ideal vapor phase behavior. You may also assume that $\bar{S}_i^E = 0$ for all components in the mixture (This is the basis of the well-known Regular Solution theory)

(iv) (3 Points) What is the Henry's law constant for water in this non-volatile liquid phase?

You may find it useful to recall that $\frac{d}{dx} \left(\frac{y}{x} \right) = \frac{1}{x} \frac{dy}{dx} - \frac{y}{x^2}$

Problem 5 (30 Points)

Enzymes are generally thought to function only in aqueous phases, and are commonly believed always to denature when placed in a non-aqueous environment. It has been shown, however, that when dispersed as small solid aggregates in oils, these enzymes can retain their activity, and in fact, can catalyze important reactions that are not feasible in a totally aqueous environment, although a certain level of hydration of the enzymes dispersed in the oil phase is essential for the functioning of the enzyme. You wish to conduct a fundamental study of these hydration effects by exploring the reaction behavior as a function of water activity. You recognize that it is difficult to control the activity of water in the oil phase directly, but know that you can control the water partial pressure in the vapor phase by contacting it with an aqueous electrolyte solution of known ionic strength. The device you have set up is shown in the figure given below. You have two chambers, one of which contains the aqueous electrolyte solution, and the other the enzyme particles suspended in the oil phase. The water has some solubility in the oil phase, but the oil itself has a very low vapor pressure and has such limited solubility in the aqueous phase that it can be neglected. There is a vapor phase connecting the two chambers.



- (i) (3 points) Explain why you can use this set-up to control the water activity in the oil phase. Would you get the same results if you just contacted the water and oil phases directly?
- (ii) (2 Points) Show that the following expressions for the Gibbs-Duhem equation are equivalent:

$$\sum_i x_i \ln \gamma_i = 0; \quad \sum_i c_i \ln \gamma_i = 0; \quad \text{and} \quad \sum_i m_i \ln \gamma_i = 0.$$

What is the form of the Gibbs-Duhem equation for an electrolyte dissolved in an aqueous solution?

- (iii) (12 points) Assume that the Debye-Huckel theory holds so that the activity coefficient for the salt can be determined using

$$\ln \gamma_{\pm} = -A_{\gamma} |z_+ z_-| I^{1/2}$$

Show that the activity of water as a function of the molality m of a solution of a strong electrolyte CaCl_2 is given by

$$a_w = m_w \exp \left(\frac{2(4)^{1/3} A_{\gamma} m^{3/2}}{3^{1/2} m_w} \right)$$

Note that the salt concentration effect on the activity is expressed in terms of m and not m_{\pm} .

- (iv) (5 points) If the Henry's law constant is $k_{H,w}$ (in units of $\text{bar}/(\text{mol kg}^{-1})$), determine an expression for the mole fraction of water in the oil phase in terms of the salt concentration in the aqueous phase.
- (v) (8 points) Suppose that you have a base solution of NaCl of constant concentration m_{NaCl} . Show how the addition of the second electrolyte, CaCl_2 , will affect the water activity in this three-component system.