所別：　化學工程與材料工程學系 碩士班 甲組(一般生)　　　　共 3 頁　第 1 頁

科目：　化工熱力學及化學反應工程

本科考試可使用計算器，廠牌、功能不拘　　　　　　　　　　＊請在答案卷(卡)內作答

1. **(25 pts)** Cell membrane forms the boundary of a cell and thereby defines "life" out of "lifeless". Due to its complicated functional needs, cell membrane is a liquid crystalline material whereby the biomolecules constituting cell membrane, mostly lipids and proteins, can move freely within the membrane plane, while the so-called "bilayer" structure of the membrane is still maintained. Because of the characteristics, cell membrane can be regarded as a "2-D" liquid mixture. To explore the universal mechanisms governing the properties and behavior of cell membrane, the lipid membrane systems solely composed of $1 \sim 3$ lipid species with defined compositions are studied as a simplified model for cell membrane. While cell membrane had long been considered as a uniform mixture of lipids and proteins, recent studies based on the model systems have hinted that phase separation [into the phases known as the liquid-ordered (L_o) and liquid-disordered (L_d) phases] may actually occur on cell membrane and be responsible for several cellular processes involving cell membrane. One such study was conducted on a model membrane composed of three lipid species, cholesterol (Chol), dioleoylphosphatidylcholine (DOPC) and egg sphingomyelin (eSM); and the compositional phase diagram was mapped out at $(T, P) = (23\ ^\circ C, 1\ bar)$ as follows:
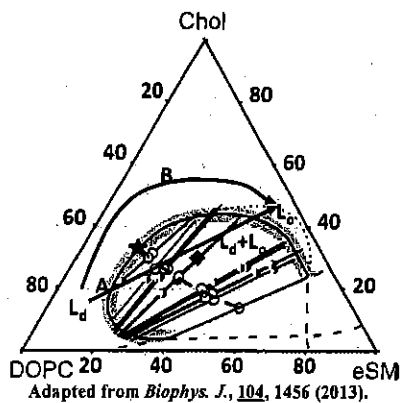
Adapted from *Biophys. J.*, **104**, 1456 (2013).

(a) **(3 pts)** Within the region of the phase diagram encompassed by the thick curve sees the lipid membrane phase-separate into the coexisting L_o and L_d phases. Is it thermodynamically reasonable to expect the observation of such a phase coexistence region at other (T, P)s? Why?

(b) **(6 pts)** The lines within the phase coexistence region are tie lines. What are the compositions of the L_o and L_d phases and of the entire mixture at the location indicated with a diamond?

(c) **(2 pts)** The tie line shrinks in the directions of increasing the Chol and DOPC molar fractions, and retreats to a point at the location indicated with a star. What is this point?

(d) **(4 pts)** Is the phase transition from L_d to L_o following Path A a first- or second-order phase transition? What about the one following Path B?

(e) **(10 pts)** Changing the temperature of the system would see the disappearance of the phase coexistence region. Assume the composition indicated with the diamond is the cell membrane composition of a specific type of human cells. At the temperature of human body, $\sim$37 $^\circ C$, the mixture of this composition is a single liquid. For the proper functioning of the cells, the membrane must phase-separate. Therefore, an additional energy has to be supplied (most likely by proteins) to force the occurrence of the phase separation. Given that the molar Gibbs energies of the three lipid species alone are $\underline{G}_{Chol}$, $\underline{G}_{DOPC}$ and $\underline{G}_{eSM}$, determine the energy needed to induce the phase separation. (Assume the mixture behaves ideally in the considered compositions.)

2. **(25 pts)** When a small amount of solid is dissolved in a liquid solvent and the temperature of the liquid mixture is lowered, the pure liquid starts to separate out as a solid at a temperature T_f. This temperature is lower than the freezing (or melting) temperature T_m of the pure solvent. This phenomenon is the depression of freezing point and one of its applications is adding antifreeze to lowers the freezing point of a water-based cooling liquid in car engines. Thus, it is useful for engineers to understand how to estimate the depression of the solvent freezing point, $\Delta T = T_m - T_f$.

(a) **(13 pts)** Please derive the following equation for the determination of ΔT and write down

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all your assumptions,

$$\Delta T = T_m - T_f = -\frac{RT_m T_f}{\Delta_{fus}\underline{H}_m}\ln(x_1\gamma_1)$$

where $\Delta_{fus}\underline{H}_m$ is the enthalpy of fusion of the pure solvent at T_m and x_1 and γ_1 are mole fraction and activity coefficient of the solvent, respectively, in the mixture at the equilibrium condition when the first liquid crystal of pure solvent forms.

Equations:　$\ln\dfrac{f_1^L(T,P)}{f_1^S(T,P)} = \dfrac{\underline{G}_1^L(T,P) - \underline{G}_1^S(T,P)}{RT} = \dfrac{\Delta_{fus}\underline{G}(T,P)}{RT}$

$$\Delta_{fus}\underline{H}(T) = \int_{T_m}^{T}\Delta C_p\,dT + \Delta_{fus}\underline{H}_m$$

$$\Delta_{fus}\underline{S}(T) = \int_{T_m}^{T}\frac{\Delta C_p}{T}\,dT + \Delta_{fus}\underline{S}_m \qquad (\Delta C_p = C_p^L - C_p^S)$$

where the superscripts L and S represent the liquid and solid phase, respectively, C_p is the heat capacity, and $\Delta_{fus}\underline{S}_m$ is the entropy of fusion.

(b) **(12 pts)** While measuring the solubility of solid naphthalene in supercritical carbon dioxide (CO_2) at high pressure, it is sometimes observed that the solid naphthalene would melt at temperature lower than its melting temperature because of high solubility of carbon dioxide in liquid naphthalene. Please use the equation you derive in (a) to estimate the depression of the solvent freezing point of naphthalene at 12.5 MPa with three assumptions: (1) ideal liquid phase, (2) ideal gas phase, and (3) pure CO_2 gas phase (it is reasonable to assume only CO_2 in the gas phase because naphthalene has very low vapor pressure).

Data: The Henry's law constant for CO_2 in liquid naphthalene is 50 MPa and is assumed to be independent of temperature and pressure. $T_m = 80.2\ ^\circ C$ and $\Delta_{fus}\underline{H}_m = 18.804\ kJ/mol$.

3. **(8 pts)** A first-order, irreversible liquid-phase reaction is taking place in a CSTR and 50% conversion is obtained. If two more CSTRs of the same size are placed, in series, downstream, what is the final conversion?

4. **(17 pts)** An elementary irreversible liquid-phase reaction $A + B \to C$ is carried out in a CSTR. A and B are fed at molar rates of 1.25 mol/s and 1 mol/s respectively, at a temperature of 300 K. The reactor is jacketed and the jacket temperature can be assumed to be 310 K. An agitator contributes a work of 20.9 kW to the reactor. The volumetric flow rate is 5 lit/s. Additionally:

$$\frac{\dot{Q} - \dot{W}}{F_{A0}} - X\Delta H_{Rx} = \sum\theta_i\widetilde{C}_{pi}(T_0 - T_{i0})$$

$H_A^0(298K) = -20\ kcal/mol,\ H_B^0(298K) = -25\ kcal/mol,\ H_C^0(298K) = -60\ kcal/mol$

$C_{pA} = C_{pB} = 40\dfrac{kcal}{mol\cdot K},\ C_{pC} = 55\dfrac{kcal}{mol\cdot K}$

$k = 0.01\dfrac{lit}{mol\cdot s}$ at 300 K, $U\cdot A = 75\dfrac{kcal}{s\cdot K}$, $E = 8\ kcal/mol$

Determine the volume of the reactor for 60% conversion of A.

5. **(5 pts)** The activation of an uncatalyzed reaction is 70.0 kJ/mol. When the catalyst is added, the activation energy (at 20 $^\circ$C) is 42.0 kJ/mol. Theoretically, to what temperature ($^\circ$C) would one have to heat the hydrogen peroxide solution so that the rate of the uncatalyzed reaction is equal to the rate of the catalyzed reaction at 20 $^\circ$C?

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6. **(20 pts)** An elementary reversible liquid-phase reaction R $\rightleftharpoons$ P is carried out adiabatically with inert I in a tubular reactor at a flow rate of 15 m³/h. The reaction rate constant is 10 h⁻¹ at 300K and equilibrium constant is 3 at 330K. Heat capacities of R, P, and I are 100, 100, and 150 J/mol-K, respectively. The heat of reaction and activation energy are -25 kJ/mol and 100 kJ/mol, respectively. If equimolar of R and I are fed to the reactor at 350K (10 mole/l each),

   (a) **(8 pts)** please determine the maximum conversion.

   (b) **(12 pts)** please determine the volume of reactor which can achieve 30% conversion.