國立中央大學109學年度碩士班考試入學試題

所別： 化學工程與材料工程學系 碩士班 甲組(一般生)　　　共2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%) For each of the following 25 statements from a. to y. indicate whether it is true (T) or false (F).
   - a. The compressibility factor is always less than or equal to unity.
   - b. For any real gas at constant temperature, as the pressure approaches zero the residual volume approaches zero.
   - c. A closed system is one of a constant volume.
   - d. The Redlich / Kwong equation is superior to the van der Waals equation because its mixing rules are exact.
   - e. All property-changes of mixing are zero for an ideal solution.
   - f. The bubblepoint curve of a binary vapor/liquid equilibrium system represents the states of saturated vapor mixtures.
   - g. The activity coefficient is zero for a component in an ideal solution.
   - h. Lost work is a quantity devised to account for exceptions to the first law of thermodynamics.
   - i. Frictional effects are difficult to incorporate explicitly in the energy equations because such effects constitute violations of the second law of thermodynamics.
   - j. The use of activity coefficients based on the Lewis/Randall rule is necessarily more realistic than the use of activity coefficients based on Henry's law.
   - k. The fugacity coefficient has units of pressure.
   - l. In the limit as $P \to 0$, the ratio f/P for a gas goes to infinity, where f is the fugacity.
   - m. A total property of a homogeneous mixture is always equal to $\Sigma n_i M_i$, where n_i is the number of moles of species i and M_i is the corresponding molar property of pure i.
   - n. A steady-flow process is one for which the velocities of all streams may be assumed negligible.
   - o. All real fluids become simple fluids in the limit as the pressure approaches zero.
   - p. All ideal gases have the same molar heat capacity at constant pressure (C_P).
   - q. For a closed system, the value of $\int P dV$ for the change of the gas from one given state to another is independent of the path so long as all processes are reversible.
   - r. Work is always given by the integral $\int P\, dV$.
   - s. When a molten salt crystallizes, the atoms arrange themselves in a highly ordered lattice structure; since increasing order is associated with decreasing entropy, we must conclude that the entropy of the universe decreases as a result of this process.
   - t. Heat is always given by the integral $\int T\, dS$.
   - u. The equation $dH = T\, dS + V\, dP$ can be applied only to reversible processes.
   - v. Cyclic processes get work from heat in defiance of the qualitative expression of the second law of thermodynamics.
   - w. The entropy of an isolated system must be constant.
   - x. The equation PV^γ = constant is valid for any adiabatic process in an ideal gas where $\gamma = C_p/C_V$.
   - y. Liquid-phase activity coefficients are generally less than zero for systems which exhibit negative deviations from Raoult's Law.

參考用

2. Polymer-polymer and polymer-solvent systems are important in the chemical industry, and typically the Flory-Huggins model is used to describe the activity coefficients in such systems. Assuming the vapor phase is ideal, and that the vapor pressure of the polymer is negligible, (a) (7%) develop the equations that should be solved for the bubble point pressure as a function of temperature for polymer-solvent mixtures using the Flory-Huggins model; (b) (6%) develop the equations that should be solved for the molten polymer-molten polymer liquid-liquid immiscibility region as a function of temperature using the Flory-Huggins model.

3. Warfarin, marketed as Coumadin, is used to prevent blood clots in humans and also, at high body doses, as a rat poison by promoting internal bleeding. Warfarin binds with human plasma albumin, a family of proteins in

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blood plasma, in the reaction W + A $\overset{K}{\leftrightarrow}$ WA. The following measured or apparent (not standard-state) data at 25°C are available for this binding reaction, $\Delta_{\text{bnd}}G = -30.8\ \text{kJ mol}^{-1}$, $\Delta_{\text{bnd}}H = -13.1\ \text{kJ mol}^{-1}$, and $\Delta_{\text{bnd}}C_p \sim 0$, where these apparent changes are for the equilibrium constant, $\Delta_{\text{bnd}}G = RT\ \ln K$, where $K = M_{\text{WA}}/(M_{\text{W}}M_{\text{A}})$, with M being the concentration in molality. (a) (6%) What is the entropy change for this reaction at 25°C? (b) (6%) Starting with concentrations of warfarin and human plasma albumin of 0.1 mM, what is the fraction of unbound (unreacted) albumin at the temperatures of 30°C and 40°C?

4. (8%) Experiment shows that the homogeneous decomposition of ozone proceeds with a rate

$$-r_{O_3} = k[O_3]^2[O_2]^{-1}$$

(a) What is the overall order of reaction?
(b) Suggest a two-step mechanism to explain this rate and state how you would further test this mechanism.

5. (7%) Enzyme E catalyses the fermentation of substrate A (the reactant) to product R. Find the size of mixed flow reactor needed for 95% conversion of reactant in a feed stream (25 liter/min) of reactant (2 mol/liter) and enzyme. The kinetics of the fermentation at this enzyme concentration are given by

$$A \xrightarrow{\text{enzyme}} R, \qquad -r_A = \frac{0.1C_A}{1+0.5C_A}\ \frac{\text{mol}}{\text{liter}\cdot\text{min}}$$

6. (10%) The kinetics of the aqueous-phase decomposition of A is investigated in two mixed flow reactors in series, the second having twice the volume of the first reactor. At steady state with a feed concentration of 1 mol A/liter and mean residence time of 96 sec in the first reactor, the concentration in the first reactor is 0.5 mol A/liter and in the second is 0.25 mol A/liter. Find the kinetic equation for the decomposition.

7. To remove NO from automobile exhaust, it has been proposed that uses unburned CO in the exhaust to reduce the NO over a solid catalyst, according to the reaction
$CO + NO \rightarrow$ Products (N_2, CO_2)

(a) (10%) Write the possible reaction mechanism of the catalytic reaction, involved adsorption and surface reaction (dual-site mechanism)

(b) (10%) What is the rate limiting step that gives the rate law of the form:

$$-r'_{\text{N}} = \frac{kP_{\text{NO}}P_{\text{CO}}}{\left(1+K_1P_{\text{NO}}+K_2P_{\text{CO}}\right)^2}$$

where P_{NO} = gas-phase partial pressure of NO
P_{CO} = gas-phase partial pressure of CO
k, K_1, K_2 = coefficients depending only on temperature

(c) (5%) A certain engineer thinks that it would be desirable to operate with a very large stoichiometric excess of CO to minimize catalytic reactor volume. Please give you opinion and explain the reason why.

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