國立中正大學 114 學年度碩士班招生考試

試題

[第4節]

| 科目名稱 | 化工熱力學與化工動力學 |
|------|-------------|
| 系所組別 | 化學工程學系 |

-作答注意事項-

- ※作答前請先核對「試題」、「試卷」與「准考證」之<u>系所組別、科目名稱</u>是否相符。
- 1. 預備鈴響時即可入場,但至考試開始鈴響前,不得翻閱試題,並不得書寫、書記、作答。
- 2. 考試開始鈴響時,即可開始作答;考試結束鈴響畢,應即停止作答。
- 3.入場後於考試開始 40 分鐘內不得離場。
- 4.全部答題均須在試卷(答案卷)作答區內完成。
- 5.試卷作答限用藍色或黑色筆(含鉛筆)書寫。
- 6. 試題須隨試卷繳還。

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1. (10%) Briefly explain the following terms

- (A) Gibbs phase rule (with reaction term) (3%), and determine the degrees of freedom of the system for liquid water in equilibrium with a mixture of water vapor and nitrogen (3%)
- (B) Colligative properties of solutions (solutions of solids in liquids) (4%)
- 2. (20%) One mole of an ideal gas (with specific heat $c_v=2R$ and $c_p=3R$) starts at a state with initial pressure (P_0) , volume (V_0) , and temperature (T_0) and then undergoes the following sequence of mechanically reversible processes in a closed system. (a) From the initial state, it is compressed adiabatically to $2T_0$, (b) it is then cooled from $2T_0$ at a constant pressure, and (c) finally, it is expanded isothermally to its original state. Question: (A) draw the pressure-volume (P-V) diagram of the processes (a), (b), and (c), and (B) calculate the change in the internal energy (ΔU) , the heat added to the system (Q), the work done by the system (W), and the change in enthalpy (ΔH) , for each of the processes in the cycle.

EXPRESS ALL YOUR ANSWERS IN TERMS OF "To" AND "R" ONLY.

| Military III | | | | | | |
|------------------------|------|------|------|------|--|--|
| Process | ΔU | Q | W | ΔΗ | | |
| (a) | (1) | (2) | (3) | (4) | | |
| (b) | (5) | (6) | (7) | (8) | | |
| (c) | (9) | (10) | (11) | (12) | | |
| Total for entire cycle | (13) | (14) | (15) | (16) | | |

3. **(20 %)** Assuming a mixture of benzene and toluene behaves as an ideal gas in the vapor phase and as an ideal solution in the liquid phase, (A) calculate the temperature and composition of the vapor in equilibrium with a liquid that is 30.0 mole% benzene and 70.0 mole% toluene at 760 mmHg. Is the calculated temperature a bubble-point or dew point temperature? (using Regula-Falsi method, start trial–error searches of temperature in the range of 95.0 °C to 100.0 °C. The precision of T_{bubble} needs to be one digital place), and (B) a gas mixture consisting of 15.0 mole% benzene, 10.0 mole% toluene, and 75.0 mole% nitrogen is compressed isothermally at 80.0 °C until condensation occurs. At what pressure will condensation begin? What will be the composition of the initial condensate?

$$log_{10}p_{benzene}^{*}(mmHg) = 6.89272 - \frac{1203.531}{T(\ ^{o}C) + 219.888}$$

$$log_{10}p_{toluene}^{*}(mmHg) = 6.95805 - \frac{1346.773}{T({}^{o}C) + 219.693}$$

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- 4. (15%) A unimolecular reaction $A \rightarrow P$ has a rate constant $k=10 \text{ h}^{-1}$. We wish to process 0.05 m³/h of a solution containing species A at a concentration of 0.12 kmole/m³. We have four reactors available:
 - 1. A CSTR (continuous stirred-tank reactor) of volume 0.005 m³.
 - 2. A PFR (plug-flow reactor) of volume 0.005 m³.
 - 3. A CSTR of volume 0.0025 m³.
 - 4. A PFR of volume 0.0025 m³.
 - (A) Compare the 0.005 m³ CSTR and the 0.005 m³ PFR. Which reactor achieves the higher conversion? (5%)
 - (B) If a 0.0025 m³ PFR is placed in series after a 0.0025 m³ CSTR, what is the overall conversion? (5%)
 - (C) What is the best conversion if we could only select three of the reactors? Give reasons. (5%)
- 5. (20%) Consider the following mechanistic scheme for an enzyme catalyzed reaction

$$E + S \rightleftharpoons ES \xrightarrow{k_2} EP \xrightarrow{k_3} E + P$$

(A) Show step by step how the following equation can be derived (10%):

$$v = \frac{\binom{k_2 k_3}{(k_2 + k_3)} [E]_0 [S]}{\binom{k_2 k_3}{(k_2 + k_3)} \cdot K_D + [S]}$$

Make the following assumptions:

- The last step shall be rate limiting, so that $v = k_3[EP]$
- The steady state approximation is valid for EP
- There is a rapid pre-equilibrium among ES, E, S with a dissociation constant $K_D = \frac{[E][S]}{[ES]}$
- S shall be present in large excess, so that $[S]_0 = [S]$, but $[E]_0 = [E] + [ES] + [EP]$.
- (B) What happens if [S] is large? Write out an expression for a rate law that an experimentalist should observe upon working with a large excess of substrate. (5%)
- (C) What happens if [S] is tiny? What type of rate law would an experimentalist observe in this case? (5%)
- 6. (15%) A liquid phase first order reaction was carried out isothermally in three CSTR reactors in series. It was known that the second reactor was as large as the first reactor and the third reactor as χ times larger than the first one. It was also assumed that the density was constant throughout the system. If 35% conversion was achieved in the first reactor. What should the χ be to achieve a total conversion of 91.2%?