國立雲林科技大學 108 學年度 碩士班招生考試試題

系所：化材系

科目：物理化學

1. For the reversible process of the gas [C_V (heat capacity of constant volume) = constant] which is in a closed system and obeys the following equation of state:

$$P(V-b)=nRT \qquad \text{where } b \text{ is a constant}$$

according to the first law of thermodynamics and Maxwell relation (obtained from $dA=-SdT-pdV$), show that $\Delta U = C_V \Delta T$, where ΔU is the changes of internal energy for the gas and ΔT is the changes of temperature for the gas. (24 %)

2. For a regular solution in which the mole fraction of A is x_A and the mole fraction of B is x_B, show that the Gibbs energy of mixing (its temperature is T, n is total moles, and β is a parameter) is $\Delta_{\text{mix}}G = nRT(x_A ln x_A + x_B ln x_B + \beta x_A x_B)$. (12%)

3. The following consecutive reactions are elementary:

$$\text{A} \overset{k_a}{\rightarrow} \text{I} \overset{k_b}{\rightarrow} \text{P}$$

If the initial concentration of A is $[\text{A}]_0$ and no I as well as P are present initially. When $\text{A} \rightarrow \text{I}$ is the rate-determining step ($k_a \ll k_b$). Find an approximate expression for the concentration of P as a function of the time. (14%)

4. Two mole of a perfect gas at 300 K is allowed to expand reversibly and isothermally from 10 dm^3 to 100 dm^3. (a) What is the change of entropy of the gas and its surroundings? (b) The same gas is expanded adiabatically and irreversibly from 10 dm^3 to 100 dm^3 with no work done. What is the final temperature of the gas? What is the change of entropy of the gas and its surroundings? (12%)

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5. The partial molar volumes of water and ethanol in a solution with at 303K are 16.2 and $58.8\,\mathrm{cm^3\ mol^{-1}}$, respectively. The mole fraction of ethanol is 0.42. Calculate the volume change upon mixing sufficient ethanol with 2.65 mol of water to give this concentration. The densities of water and ethanol are 0.992 and $0.7823\,\mathrm{g\,cm^{-3}}$, respectively, at this temperature. (12%)

6. The value of the equilibrium constant for the reaction $\mathrm{A(g) + B(g) \rightleftharpoons C(g)}$ is 10.36 at 400K and 7.24 at 500K. Determine (a) the standard reaction enthalpy, (b) equilibrium constant, (c) standard reaction Gibbs energy and (d) standard reaction entropy for this reaction at 450K. (14%)

7. The rate equation for the chemical reaction: $\mathrm{A \rightarrow B + C}$ is first-order with $k_r = 9.82\times10^{-6}\ \mathrm{s^{-1}}$ at 300K and $2.84\times10^{-4}\ \mathrm{s^{-1}}$ at 328K. Determine (a) the energy of activation and (b) the pre-exponential factor (frequency factor) for the reaction. (12%)