國立成功大學

112學年度碩士班招生考試試題

編　號：79

系　所：化學工程學系

科　目：物理化學

日　期：0206

節　次：第 3 節

備　註：可使用計算機

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※ 考生請注意：本試題可使用計算機。　請於答案卷(卡)作答，於本試題紙上作答者，不予計分。

1. (a) For the reversible and adiabatic expansion/compression of an ideal gas, prove that $\frac{T_1}{T_2}=\left(\frac{P_1}{P_2}\right)^{\gamma-1/\gamma}$, in which $\gamma = C_P / C_V$ (6%). (b) For a monoatomic ideal gas at 300 K and 1 bar, calculate the work (4%) and entropy change (4%) for its reversible and adiabatic compression to 5 bar. **(14%)**

2. Consider the concentration cell $Cu\,|\,CuCl_2(0.005\ m)\,\vdots\,CuCl_2(0.01\ m)\,|\,Cu$ in which two $CuCl_2$ solutions are separated by a partition. The partition is permeable to both Cu^{2+} and Cl^- ions, and the speed ratio of Cu^{2+} and Cl^- ions through the partition equals to the ratio of their transport numbers (t_+ and t_-). (a) Assuming the junction potential for the partition is zero and the activity coefficients are unity, derive the expression for the electromotive force (emf) of this cell. (6%) (b) Calculate the transport number of Cu^{2+} ions (3%) and the emf of this cell (4%). (i.e., the molar conductivities of $\frac{1}{2}Cu^{2+}$ and Cl^- ions at infinite dilution of 25°C are 56.6 and 76.31 $S\ cm^2 mol^{-1}$, respectively) **(13%)**

3. Consider the consecutive first-order reaction $A \xrightarrow{k_1} B \xrightarrow{k_2} C$

Neither B nor C is present initially. It has been proven that $[B]=\frac{k_1[A]_0}{k_2-k_1}\left(e^{-k_1 t}-e^{-k_2 t}\right)$

(a) Under what condition is the induction period for the formation of C clearly observed? (3%)

(b) Under what condition does the existence of B become invisible (i.e., very short life)? (3%)

(c) Calculate the time to reach the maximum B concentration if the initial concentration of A ($[A]_0$) is 1.0 $mol\ dm^{-3}$, $k_1 = 5\ s^{-1}$ and $k_2 = 2\ s^{-1}$. (5%)

(d) If the consecutive reaction becomes reversible ($A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} C$) with $k_{-1} = 4\ s^{-1}$ and $k_{-2} = 1\ s^{-1}$, derive the equilibrium B concentration and calculate the value (4%). **(15%)**

4. The right figure is the solid-liquid phase diagram of Zn and Mg at a constant pressure.

(a) Explain what is the congruent melting compound and determine its chemical formula (4%)

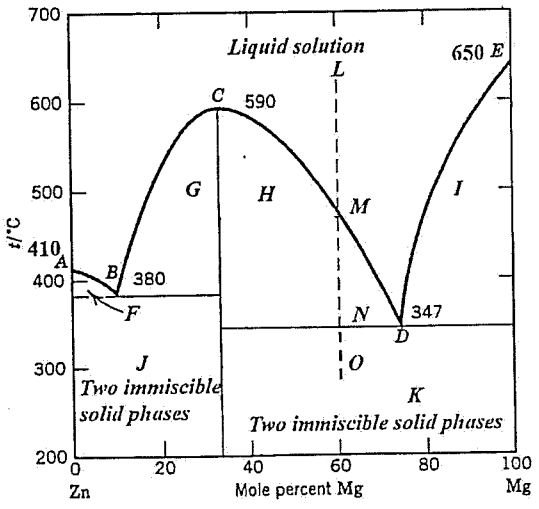
(b) Write the eutectic composition(s) (2%)

(c) Draw the cooling curve (temperature vs. time) for the liquid solution from L to O (2%)

(d) Write the composition for area G (2%)

(e) Determine the number of degrees of freedom (3%) and suggest the required variables for the curve C-M-D (2%)

(15%)



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5. (a) Prove that $\Delta_{mix}H = 0$ and $\Delta_{mix}S = -R\sum x_i \ln x_i$ for ideal solutions. (8%)

(b) Explain why $\Delta_{mix}H = 0$ but $\Delta_{mix}S \neq 0$ for ideal solutions from the microscopic viewpoint. (4%)

(12%)

6. Answer the following questions: **(31%)**

(a) An electrolyte exhibits lower molar conductivity at higher concentrations. Why? (4%)

(b) For the isothermal expansion of an ideal gas, the work done by the irreversible process is less than that by the reversible process. Where does the lost work go (3%), and what kind(s) of energy (U, H, A, G) decrease(s) in the system? (2%)

(c) What is the Joule-Thomson inversion temperature? (3%)

(d) For the following compounds: CO, CO_2, H_2O, N_2O, and O_2, whose residual entropy at the absolute zero temperature is zero? (4%)

(e) A first-order surface reaction occurs on the surface of a spherical vessel of radius 10 cm with a rate of $2.5\times10^{-3}\, mol\ dm^{-3}\ s^{-1}$ and a rate constant of $7.5\times10^{-4}\ s^{-1}$. What will be the rate and the rate constant if the radius is increased to 50 cm at the same pressure and temperature? (4%)

(f) For the isothermal expansion/compression of a real gas, prove that $\Delta H = -C_P \mu_{JT} \Delta P$, where C_P (heat capacity at constant pressure) and μ_{JT} (Joule-Thomson coefficient) are independent of pressure. (5%)

(g) The following figure shows the vapor-liquid phase diagram of a binary system. During the pressure reduction of the liquid solution at x_1=0.2 from 90 bar, what is the pressure at which the liquid starts to generate bubbles and what is the composition of bubbles (i.e., y_1=?)? Also, what is the activity coefficient? (6%)