# 國立成功大學 108 學年度碩士班招生考試試題

系　　所：化學工程學系

考試科目：物理化學

考試日期：0223，節次：3



※ 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.** Answer the following questions: **(32%)**

(a) The work required for the isothermal compression of an ideal gas via an irreversible process is larger than that via a reversible process. Explain why (4%).

(b) Plot the dependence of Z (compression factor) on P for a real gas at a constant temperature below its Boyle temperature, and give the reason(s) causing the different tendencies at low P and high P. (4%)

(c) Judge the following statement is right or wrong, and explain why: Langmuir isotherm belongs to the chemical adsorption because only a monolayer is adsorbed. (4%)

(d) Explain what is the stripping mechanism, and illustrate its potential-energy surfaces for a reaction $A+B-C \rightarrow A-B+C$ (showing contour lines connecting positions of equal energy). (4%)

(e) What is the main trouble caused by azeotropes in distillation and how to overcome this problem? (4%)

(f) May a process with $\Delta S < 0$ occur spontaneously? If it is possible, give an example. (4%)

(g) Explain why $Na^+$ ion has a lower molar conductivity than $K^+$ ion, but why the molar conductivity of $H^+$ ion in water is much higher than other ions. (4%)

(h) Is the vapor pressure of a spherical droplet larger or smaller than that of a planar liquid? Why? (4%)

2. One mole of nitrogen gas at 300 K and 5 bar is considered as an ideal gas. **(15%)**

(a) Calculate $\Delta U$ while heating to 400 K at a constant pressure of 5 bar (5%);

(b) Calculate $\Delta S$ while expanding to 1 bar reversibly and adiabatically (5%);

(c) Calculate $\Delta G$ while expanding to 1 bar isothermally against a constant pressure of 1 bar (5%).

3. An aqueous solution contains 1.0 g of NaCl in 100 g water and the freezing point is –0.636°C. (a) Calculate the freezing point depression constant of water (4%) and the osmotic pressure of this solution (4%) at 300 K. (b) For an aqueous solution containing 1.0 g unknown solute in 100 g water without the occurrence of dissociation or association, its freezing point is –0.12°C. Calculate the molar mass of the unknown solute (4%). **(12%)**

4. Consider the cell $Pt,H_2(1\ bar)\,|\,HCl(m_2)::HCl(m_1)\,|\,Pt,H_2(1\ bar)$ in which the solutions are separated by a partition. Assuming zero junction potential for the partition and the activity coefficients are unity, derive the expression for the emf of this cell under the following three conditions: (a) the partition is permeable to only to $Cl^-$ ions (4%); (b) the partition is permeable to only to $H^+$ ions (4%); (c) the partition is permeable to both $H^+$ and $Cl^-$ ions and the ratio of the speeds with which these ions pass through the partition is the ratio of their transport numbers ($t_+$ and $t_-$) (6%). **(14%)**

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5. Show the partial molar properties obey the equations: (a) $dU_i = TdS_i - PdV_i$ (10%) and

(b) $\left(\frac{\partial T}{\partial V_i}\right)_{S_i} = -\left(\frac{\partial P}{\partial S_i}\right)_{V_i}$ (5%) **(15%)**

6. Y and Z are produced from A and B by the following mechanism, in which X is an unstable intermediate:

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} X$$

$$X + A \xrightarrow{k_3} Y$$

$$X + B \xrightarrow{k_4} Z$$

(a) Drive the expression for rate of production of Z by the steady-state treatment (6%); (b)What rate equations are obtained if A is present in great excess (3%)? (c) What is the product selectivity (i.e., [Y]/[Z]) (3%)? **(12%)**