國立成功大學

115學年度碩士班招生考試試題

編　號：56

系　所：化學工程學系

科　目：物理化學

日　期：0203

節　次：第 3 節

注　意：1.可使用計算機
2.請於答案卷(卡)作答，於試題上作答，不予計分。

1. Considering Ar gas as an ideal gas, **(16%)**

(a) calculate the Gibbs energy change (ΔG) and entropy change (ΔS) for the adiabatic free expansion from 300 K and 1 bar to 0.1 bar. (8%)

(b) calculate the excess work done for the isothermal compression from 300 K and 1 bar to 10 bar at a constant external pressure of 10 bar as compared to the work done for the reversible process (5%), and explain where this excess work is used (3%).

2. For the decomposition of ammonia into nitrogen and hydrogen gases on a Pt catalyst ($2\,NH_3 = N_2 + 3\,H_2$), it was found that ammonia adsorbed on the Pt surface at first and then the decomposition reaction occurred. Moreover, the resulting hydrogen gas also could adsorb on the Pt surface but the adsorption of nitrogen gas could be ignored.

(a) Assuming Langmuir adsorption isotherm is applicable, prove that the fraction coverages for the adsorption of ammonia (θ_A) and hydrogen gas (θ_H) on the Pt surface can be expressed as follows:

$$\theta_A = \frac{K_A[NH_3]}{1 + K_A[NH_3] + K_H[H_2]} \quad ; \quad \theta_H = \frac{K_H[H_2]}{1 + K_A[A] + K_H[H_2]}$$

where K_A and K_H are the adsorption equilibrium constants related to ammonia and hydrogen gas. (10%)

(b) If the decomposition of ammonia on the Pt catalyst is proportional to θ_A , write the rate expression and estimate the reaction orders related to ammonia concentration in the early period and final period. (6%) **(16%)**

3. The electromotive force of the cell

$$Zn \,|\, ZnCl_2(0.555\ mol\ kg^{-1}) \,|\, AgCl \,|\, Ag$$

is 1.015V at 25°. The temperature coefficient is -4.02×10^{-4} V K^{-1}. (a) Write the half-cell reaction and the cell reaction (6%); (b) Calculate $\Delta G°$, $\Delta H°$, and $\Delta S°$ for the cell reaction (9%). **(15%)**

4. The conversion of A to B obeys a first-order rate equation. The influence of temperature on the rate constant k (unit: s^{-1}) can be expressed as: $k = 2\times10^{-3}\ T^2 e^{-3000/RT}$ (i.e., unit)

where the units of k, T and R are s^{-1}, K and J mol^{-1} K^{-1}, respectively.

(a) Determine the activation energy (4%) and pre-exponential factor (4%) at 300 K for the Arrhenius equation. (b) Calculate the half-life (3%) and relaxation time (3%) at 300 K. (c) How long will it take to achieve a 90% of conversion at 300 K (4%)? **(18%)**

5. Derive the following relationships: **(13%)**

(a) $\left(\frac{\partial(A/T)}{\partial(1/T)}\right)_V = U$ (6%)

(b) For a van der Waals gas, $\left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{V_m^{\,2}}$ (7%)

where A, T , V, U, a, and V_m denote the Helmholtz energy, temperature, volume, internal energy, van der Waals gas constant for intermolecular attraction, and molar volume, respectively.

6. Answer the following questions: (22%)

(a) Explain the supersaturation phenomenon during the condensation process using Kelvin equation. (5%)

(b) Describe the retrograde condensation phenomenon. (5%)

(c) Determine the number of degrees of freedom and suggest the required variables for the solution mixture of ice, water, and alcohol in equilibrium. (6%)

(d) For $ZnCl_2$ at infinite dilution, the molar conductivities of $\frac{1}{2}Zn^{2+}$ and Cl^- ions at 25°C are 52.8 and 76.31 $S\ cm^2 mol^{-1}$, respectively. Determine the transport number and the speed under a potential gradient of 100 $V\ cm^{-1}$ for Zn^{2+} ions. (6%)