國立高雄科技大學 108 學年度碩士班 招生考試 試題紙

系 所 別：化學工程與材料工程系碩士班　　組 別：不分組

考科代碼：1012　　考 科：物理化學

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注意事項：

1、各考科一律可使用本校提供之電子計算器，考生不得使用自備計算器，違者該科不予計分。

2、請於答案卷上規定之範圍作答，違者該題不予計分。

本試題共 5 題，每題 20 分，共 100 分。

Given: R = 8.314 J $K^{-1}mol^{-1}$ = 0.08314 L bar $K^{-1}mol^{-1}$ = 0.08206 L atm $K^{-1}mol^{-1}$

ln(2) = 0.6932, ln(3) = 1.0986, ln(5) = 1.6094, ln(7) = 1.9459

1. (a) The mechanism for the decomposition of NO_2Cl can be expressed as follows,

$$NO_2Cl \xrightarrow{k_1} NO_2 + Cl$$

$$NO_2Cl + Cl \xrightarrow{k_2} NO_2 + Cl_2$$

Assuming a steady state for the concentration of chlorine atom [Cl], what is the rate law (equation) for the reaction of NO_2Cl, and what is the order of the reaction with respect to NO_2Cl? (10%)

(b) For a first-order reaction (A → B) with a half-life of 100 s, calculate the rate constant for the reaction. (10%)

2. Ammonia (NH_3) can be used as the anodic reactant in the fuel cell. The half-cell reactions occurring at the electrodes and their standard reduction potentials are

$$N_2 + 6H_2O + 6e^- = 2NH_3 + 6OH^- \qquad E° = -0.77\ V$$

$$O_2 + 2H_2O + 4e^- = 4OH^- \qquad E° = 0.40\ V$$

All half-reactions are written as the reduction reactions. What are (a) the overall cell reaction and (b) standard electromotive force ($E°$) of this fuel cell at 298 K? (20%)

3. The vapor pressures of benzene and toluene at 363 K are 1.361 and 0.543 bar, respectively. Assuming that the liquids form ideal solutions and the gases form ideal gases. Calculate (a) the composition of the solution that will boil at 1 bar and 363 K and (b) the vapor composition. (20%)

4. The decomposition of NOCl(g) in a vessel is represented by

$$2NOCl(g) = 2NO(g) + Cl_2(g)$$

This reaction reaches equilibrium at 1 bar (total pressure) and 500 K when the partial pressure of NOCl(g) is 0.64 bar. Only NOCl(g) was present initially. All gases in this reaction obey the ideal gas law.

(a) Calculate the equilibrium constant for the reaction at 500 K. (10%)

(b) If the partial pressure of $Cl_2(g)$ reaches 0.1 bar at equilibrium, what is the total pressure at 500 K? (10%)

5. (a) Show that $\left(\frac{\partial \bar{U}}{\partial \bar{V}}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_{\bar{V}} - P$, where $\bar{U}$ and $\bar{V}$ are the molar internal energy and molar volume, respectively. (5%)

(b) Show that $\left(\frac{\partial \bar{C}_v}{\partial \bar{V}}\right)_T = 0$ for an ideal gas, where $\bar{C}_v$ is the molar heat capacity at constant volume. (5%)

(c) What is the change in molar internal energy in the isothermal and reversible expansion of a van der Waals gas form $\bar{V}_1$ to $\bar{V}_2$? The van der Waals gas equation can be expressed as $(P + \frac{a}{\bar{V}^2})(\bar{V} - b) = RT$, where a and b are the constants. (5%)

(d) One mole of an ideal gas at 2 bar and 300 K in a piston-cylinder device is isothermally and irreversibly compressed by an external pressure of 4 bar. Calculate the work done on the ideal gas. (5%)