國立高雄應用科技大學
107 學年度研究所碩士班招生考試
化學工程與材料工程系碩士班
物理化學

注意：a.本試題共　題，共 100 分
b. 作答時不必抄題
c. 考生作答前請詳閱答案卷之考生注意事項

Given: R = 8.314 J $K^{-1}mol^{-1}$ = 8.314x10^{-2} L bar $K^{-1}mol^{-1}$ = 8.206 x10^{-2} L atm $K^{-1}mol^{-1}$; 1 atm = 1.013 bar; 1bar = 10^5 Pa; 1F = 96485 C mol^{-1}.

1. **What is the molar volume of methane at 300 K and 50 bar according to (a) the ideal gas law and (b) the virial equation? The second virial coefficient B of methane is -0.04 L mol^{-1} at 300 K.** **10%**

2. **The combustion of ethanol in a constant-volume calorimeter produces 1364.34 kJmol^{-1} at 25°C. What is the value of $\Delta_r H^o$ for this combustion reaction? Assuming that the combustion reaction produces water is liquid state. (The quantity $\Delta_r H^o$ is the reaction enthalpy)** **8%**

3. **Calculate the $\Delta_{mix}S$ and $\Delta_{mix}G$ for the formation of a quantity of air containing 1 mol of gas by mixing nitrogen and oxygen at 30°C. Air may be taken to be 80% nitrogen and 20% oxygen. (The quantity $\Delta_{mix}S$ and $\Delta_{mix}G$ is the mixing entropy and mixing Gibbs energy)** **8%**

4. **A mole argon is allowed to expand adiabatically and reversibly from a pressure of 10 bar and 300 K to 2 bar. Calculate the final temperature and the molar quantities of ΔU and ΔH. (The quantity U is the internal energy, $\overline{C}_V$ = 2/3 R).** **12%**

5. **The transition of one mole of supercooled water at -10℃ and 1 bar to ice at -10℃ and 1 bar is given as:**

$$H_2O\ (l, -10℃) = H_2O\ (s, -10℃)$$

For the crystallization of liquid water at 0℃, $\Delta H = -6004$ J mol^{-1}. The heat capacity of water may be taken to be 75.3 J K^{-1} mol^{-1}, and that of ice may be taken to be 36.8 J K^{-1} mol^{-1} over this range. (a)What is the molar quantity of ΔS for the water (denoted as system)? (b) What is the molar quantity of ΔS for the heat reservoir at -10℃(denoted as surrounding)? (c) Is the process reversible or irreversible? 12%

6. For the reaction

$$H_2O\,(g) = H_2\,(g) + 1/2O_2\,(g)$$

At 2000°C water is 4% dissociated into oxygen and hydrogen at a total pressure of 1 bar. (a) Calculate the equilibrium constant K and $\Delta_r G^o$. (b) Will the extent of reaction increase or decrease if the pressure is reduced? Why? (C) Will the extent of reaction increase or decrease if argon is added, when the total pressure is held equal to 1 bar? Why? (d) Will the extent of reaction change if pressure is raised by the addition of argon at constant volume to the closed system containing partially dissociated water vapor? Why? (The quantity $\Delta_r G^o$ is the reaction Gibbs energy) 16%

7. For the cell

$$Cl^-|\,AgCl\,(s)\,|Ag\,(s)$$

Chemical thermodynamic properties at 298 K and 1 bar are given as:

	$\Delta_f H^o$/kJ mol^{-1}	$\Delta_f G^o$ /kJ mol^{-1}
Cl^-	-167.159	-131.228
AgCl	-127.068	-109.789

(a) What is the cell reaction? (b) Calculate the molar quantities of ΔH^o and ΔG^o for the cell reaction at 25℃. (c) What is the standard electromotive force of the cell at 25℃? (d) Calculate the molar quantity of ΔG^o for the cell reaction at 100℃ by using Giggs-Helmholtz equation ($[\partial(\Delta G^0/T)/\partial T]_p = -\Delta H^0/T^2$) if $\Delta_r Cp^0 = 0$. (e) What is the standard electromotive force of the cell at 100℃? 20%

8. For the decomposition reaction

$$2HI\,(g) = H_2\,(g) + I_2\,(g)$$

At 508°C has a half-life of 135 min when the initial pressure of HI is 0.1 atm and 13.5 min when the pressure is 1 atm. (a) Show that this proves that the reaction is second order. (b) What is the value of the rate constant in L mol^{-1} s^{-1}? 14%