國立高雄應用科技大學
101 學年度碩士班招生考試
化學工程與材料工程系

准考證號碼□□□□□□□□□□ （考生必須填寫）

物理化學

注意：a. 本試題共 6 題，每題　分，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. **An ideal gas expands from 10 to 2 bar at 298 K. Calculate q (heat) per mole, w (work) per mole and each of the thermodynamic quantities, ΔS (change in molar entropy), ΔA (change in molar Helmholtz energy) and ΔG (change in molar Gibbs energy) (a) for a reversible expansion and (b) for an expansion against a constant external pressure of 2 bar. (Work done in the system is considered to be positive). (20%)**

2. **What is the activity, a, of liquid water at 1 and 10 bar at 25℃, assuming that the molar volume is constant. *Hint*: Use the equation of $\mu = \mu^o + RT \ln a$, where μ and μ^o are chemical potential and chemical potential at a = 1. (10%)**

3. **What is the freezing point of water under a pressure of 100 bar? (The heat of fusion of ice is 333.5 J g^{-1}, the density of water is 0.9998 g cm^{-3}, and the density of ice is 0.9168 g cm^{-3}, all at 0℃ and 1 bar) (10%)**

4. **The reaction**

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

Comes to equilibrium at 1 bar total pressure and 227℃ when the partial pressure of the nitrosyl chloride, NOCl, is 0.64 bar. Only NOCl was present initially. (a) What is the equilibrium constant? (b) Calculate ΔG^o for this reaction. (c) At what total pressure will the partial pressure of NO be 0.2 bar? (d) What is the value of the equilibrium constant and ΔG^o when the reaction is reversed? (20%)

5. For the cell (20%)

Zn (s)| Zn^{2+} (a = 0.0004)| | Cd^{2+} (a = 0. 2) | Cd (s). (a: activity)

(a) What is the cell reaction? (b) What is the standard electromotive force (E^o) of the cell at 25℃? (c) What is the electromotive force of the cell at 25 ℃? (d) What is the equilibrium constant for the cell reaction? (e) Calculate ΔG^o for the cell reaction from the standard electromotive force.
The standard electrode potentials at 25℃ are given as:

$Cd^{2+} + 2e^- = Cd$	$E^o = -0.403$ V
$Zn^{2+} + 2e^- = Zn$	$E^o = -0.763$ V

6. The gas-phase decomposition of N_2O_5 with overall reaction $2N_2O_5 = 4NO_2 + O_2$ occur by the following multistep mechanism:

Step 1: $N_2O_5 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NO_2 + NO_3$

Step 2: $NO_2 + NO_3 \xrightarrow{k_2} NO + O_2 + NO_2$

Step 3: $NO + NO_3 \xrightarrow{k_3} 2NO_2$

(a) Show that $r = k[N_2O_5]$, where $k = k_1k_2/(k_{-1} + 2k_2)$. *Hint*: Use the steady-state approximation for both intermediates. (15%) (b) If $k = 2.05 \times 10^{13} \exp(-103135.6\ J\ mol^{-1}/RT)\ (s^{-1})$. Calculate k and $t_{1/2}$(half-life) at 0℃. (5%)