國立成功大學

110學年度碩士班招生考試試題

編　號：79

系　所：化學工程學系

科　目：物理化學

日　期：0203

節　次：第 3 節

備　註：可使用計算機

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※ 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。

Useful constants:

F=96485 C mol^{-1}

R= 8.315 J K^{-1} mol^{-1}

1. Answer the following questions: **(20%)**
   a. A nonideal gas undergoes adiabatic expansion through a throttling valve. Is △H of this process equal to zero? **(4%)**
   b. Provide the rationale to decide the rate-determining step in a chemical reaction. **(4%)**
   c. Briefly describe the Langmuir adsorption isotherm and provide its assumptions. **(4%)**
   d. Trouton's rule suggests the entropy of vaporization of normal liquid is 88 J K^{-1} mol^{-1}. This rule may provide a good estimation for the enthalpy of vaporization of some liquids. Please give a potential molecular interpretation of Trouton's rule. Also, name some liquids that do not follow Trouton's rule and explain why such deviation occurs. **(4%)**
   e. For a system containing ice in a solution of water and alcohol, determine the degree of freedom. **(4%)**

2. A process first maintains water vapor at 100 °C, 1.8 atm, and then condense the vapor into liquid at the same condition. The $\Delta_{vap}H$ of water is 40.6 kJ/mol. We can assume the vapor behaves ideally and the liquid water is incompressible. **(20%)**
   a. Calculate ΔH, ΔS, and ΔG of this process. **(15%)**
   b. Is this process spontaneous? **(5%)**

3. Derive the following relationships: **(15%)**
   a. The entropy of a perfect gas depends on the volume, $S \propto R\ln(V)$ **(7%)**
   b. $$(\frac{\partial C_P}{\partial P})_T = -T(\frac{\partial^2 V}{\partial T^2})_P$$ **(8%)**

4. One mole of a gas at 300 K is compressed isothermally from an initial pressure of 1 bar to a final pressure of 50 bar. Calculate △H of this process for **(15%)**
   a. Ideal gas **(5%)**
   b. Van der Waals gas **(10%)**

   Equation of state: $\left(P + \frac{a}{V_m^2}\right)(V_m - b) = RT$

   a= 0.0248 Pa m^6 mol^{-2} and b=0.0266×10^{-3} m^3 mol^{-1}

Also, for Van der Waals gas, the Joule-Thomson coefficient can be expressed as:

$$\mu = \frac{\frac{2a}{RT} - b}{C_P}$$

5. An inhibitor, I, decreases the rate of product formation from the substrate by binding to the enzyme. Derive a modified Michaelis-Menten rate equation by considering the effect of the inhibitor. You may assume the complex EI is at steady-state. **(10%)**

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES$$

$$ES \xrightarrow{k_2} E + Z$$

$$E + I \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} EI$$

6. Consider the following cell: **(20%)**

$$Zn(s)|ZnCl_2(0.005\ mol\ kg^{-1})|Hg_2Cl_2(s)|Hg(l)$$

The cell reaction is $Hg_2Cl_2(s)+Zn(s) \rightarrow 2Hg(l)+2Cl^-(aq)+Zn^{2+}(aq)$

$$E^\circ(Zn^{2+}, Zn) = -0.7628\ V$$

$$E^\circ(Hg_2Cl_2, Hg) = +0.2676\ V$$

a. Calculate the electromotive force of this cell, neglecting the correction of activity coefficient. **(5%)**

b. Write the Nernst equation that includes activity coefficients for the cell reaction. **(5%)**

c. Assuming that the Debye-Hückel limiting law holds at this concentration, calculate the electromotive force again. **(5%)**

d. Calculate ΔG of this cell, using the electromotive force from part c. **(5%)**