大同大學 97 學年度研究所碩士班入學考試試題

註:本次考試 不可以參考自己的書籍及筆記；　不可以使用字典；　可以使用計算器。

1. (10%) $\left(\dfrac{\partial U}{\partial V}\right)_T = -P + T\left(\dfrac{\partial P}{\partial T}\right)_V$

   (a) Find the values of $\left(\dfrac{\partial U}{\partial V}\right)_T$ for an ideal gas and the van der Waals gas.

   (b) What is the physical meaning of (a)?

2. (15%)
   (a) Calculate q, w, ΔU, and ΔH for the reversible isothermal expansion at 300 K of 5.0 mol of a perfect gas from 500 cm^3 to 1500 cm^3.
   (b) What would ΔU and w be if the expansion connects the same initial and final states as in (a) but is done by having the perfect gas expand into vacuum?

3. (15%) The sublimation pressure of NO(solid) is given by
   $$\ln P \text{ (torr)} = 23.14 - 1975/T \text{ (K)}$$
   The vapor pressure of NO(liquid) is given by
   $$\ln P \text{ (torr)} = 19.43 - 1568/T \text{ (K)}$$
   Calculate the $\Delta_v H$, $\Delta_s H$, and $\Delta_f H$ for this material, and the temperature and pressure at the triple point.

4. (10%)
   (a) Explain how emf measurements can be used to obtain ΔG^0, ΔH^0, and ΔS^0 for a reaction.
   (b) Calculate the emf for the following cell at 25 °C
   $$Pt, H_2(1 \text{ bar}) \mid HCl(0.5m) \parallel HCl(1.0m) \mid Pt, H_2(1 \text{ bar}).$$

5. (15%) Calculate the activation energy and frequency for the decomposition of benzene diazonium chloride to give chlorobenzene and nitrogen from the following table.

$k(s^{-1})$	0.00043	0.00103	0.00180	0.00355	0.00717
T(K)	313.0	319.0	323.0	328.0	333.0

6. (20%) Given a reaction network as shown in figure, X_k is an intermediate, A is reactant and P, Q, and R are products. Denote k_{Ak} as rate constant for pathway from A to X_k and k_{kA} as rate constant for pathway from X_k to A for example.
   (1) Assume all pathways are reversible, find the reaction rate r_P.
   (2) If P is desired product and Q is unwanted side product and only pathways from X_k to P and X_k to Q are irreversible, find the selectivity r_P/r_Q.
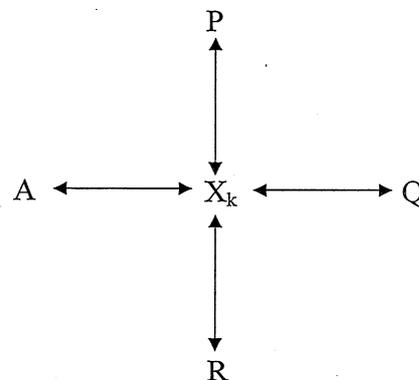

Figure for Problem 6.

7. (15%) Suppose that a large molecule, such as a protein, contains n sites to which a molecule A (ligand) can become attached. Assume that the sites are equivalent and independent, so that the reactions M + A $\longleftrightarrow$ MA, MA + A $\longleftrightarrow$ MA_2, etc., all have the same equilibrium constant K_s. Show that the average number of occupied sites per molecule is

$$\bar{v} = \frac{nK_s[A]}{1 + K_s[A]}$$