1. Prove that, for a gas obeying the van der Waals equation

$$\left(P + \frac{a}{V_m^2}\right)(V_m - b) = RT, \qquad \left(\frac{\partial U}{\partial V_m}\right)_T = \frac{a}{V_m^2}$$

   Where u is the internal energy.   (10%)

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

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

   (10%)

3. The mole fraction of a nonvolatile solute dissolved in water is 0.010.   If the vapor pressure of pure water at 293 K is 2.339 kPa and that of the solution is 2.269 kPa, calculate the activity and activity coefficient of water.(10%)

4. In the system A-B a line of three-phase equilibrium occurs at 900 K as determined by thermal analysis. A second three-phase equilibrium occurs at 500 K. Only one halt is observed for any one cooling curve.   The compound AB_2 is known and melts at 600 K.   If A melts at 1200 K and B at 700 K, sketch the simplest phase diagram consistent with the given data. Label each region.(10%)

5. The molar conductivity at 18 ℃ of a 0. 0100 M aqueous solution of ammonia is $9.6\Omega^{-1}cm^2mol^{-1}$.   For NH_4Cl, $\Lambda_0 = 129.8\Omega^{-1} cm^2mol^{-1}$ and the molar ionic conductivities of OH^- and Cl^- are 174 and $65.6\Omega^{-1}cm^2mol^{-1}$, respectively. Calculate Λ_0 for NH_3 and the degree of ionization in 0.01 M solution.(10%)

6. a. Calculate the standard emf E^0 for the reaction

fumarate^{2-} + lactate$^-$ →succinate^{2-} + pyruvate$^-$

on the basis of the following information:

fumarate^{2-} + 2H$^+$ +2e$^-$→succinate^{2-} $\qquad$ $E^{0'}= 0.031V$

pyruvate$^-$+ 2H$^+$ +2e$^-$→lactate$^-$ $\qquad$ $E^{0'}= -0.185V$
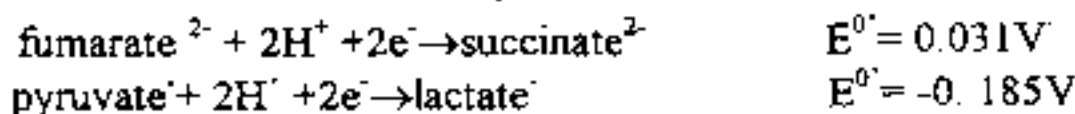
The $E^{0'}$ values relate to ph7.   The temperature coefficient $\partial E^\circ/\partial T$ for this cell

is 2.18×10^{-5} VK^{-1}

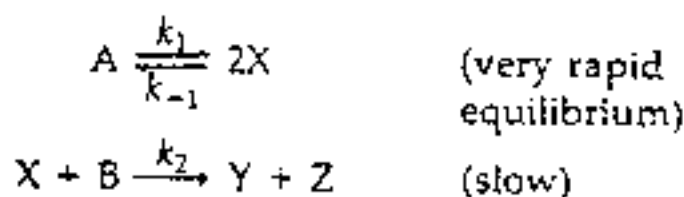b. Calculate $\Delta G^\circ, \Delta H^\circ$, and ΔS° at 25 0 ℃.

(20%)

7. Derive the following relationship for the half-life $t_{1/2}$ of a reaction of order n, with

all reactants having an initial concentration a_0:

$$t_{1/2} = \frac{2^{n-1}-1}{ka_0^{n-1}(n-1)}$$

(10%)

8. A reaction A + 2B = 2Y + 2Z occurs according to the mechanism

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2X \qquad \text{(very rapid equilibrium)}$$

$$X + B \xrightarrow{k_2} Y + Z \qquad \text{(slow)}$$

Obtain an expression for the rate of formation of the product Y. (10%)

9. How many lattice points belong to a unit cell of

a. a face-centered lattice;

b. a body-centered lattice?

Please sketch and calculate.　　　　(10%)