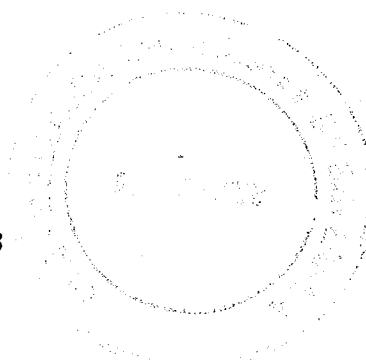




Uva Wellassa University, Sri Lanka
BTech. Science and Technology
End Semester Examination – December 2008

CHE 381-2 Advanced Physical Chemistry



Answer for **three (03) questions only**. All questions carry equal marks
 Total number of questions: Six (06)
 All symbols carry standard meanings
Time: Two hours

Universal gas constant $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

Boltzmann gas constant $k = 1.38 \times 10^{-23} \text{ J K}^{-1}$

Velocity of light, $c = 2.99 \times 10^{10} \text{ cm s}^{-1}$

Planck constant, $h = 6.626 \times 10^{-34} \text{ J s}$ and $h/2\pi = 1.054 \times 10^{-34} \text{ J s}$

Question 1 (100 marks)

- (a) Explain briefly steady state and non-steady state diffusion. How they differ from self-diffusion (20 marks).
- (b) Write Fick's equations of diffusion and identify all terms therein (10 marks).
- (c) Aluminum is to be diffused into a silicon single crystal. At what temperature will the diffusion constant (D) be $5 \times 10^{-11} \text{ cm}^2/\text{s}$? (Given: $E_a = 315 \text{ kJ/mole}$ and $D_0 = 1.70 \text{ cm}^2/\text{s}$) (30 marks).
- (d) It is desired to diffuse In (indium) into pure silicon such that the In concentration at a depth of $3 \times 10^{-4} \text{ cm}$ from the surface will be one-half of the surface concentration. How long should the silicon be in contact with In at 1600K in order to accomplish this diffusion? ($D = 8 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$) (40 marks).

Question 2 (100 marks)

- (a) Maxwell distribution of speeds of an ideal gas is given by following equation:

$$f(v) = 4\pi(M/2\pi RT)^{3/2} v^2 e^{-Mv^2/2RT}$$

State meaning of following expressions (answer in one sentence) (20 marks)

(i) $f(v)$ (ii) $f(v) dv$ (iii) $\int_0^\infty v f(v) dv$

- (b) What is collision frequency (z), collision cross section (σ) and mean free path (λ) and collision density (Z)? Write equations for each parameter (20 marks).

Question 2 cont.

(c) Carbon monoxide (molecular weight 28) is considered as a hard sphere of diameter 180 pm. At 298 K it exhibits 100 kPa of pressure. Calculate the following (40 marks):

- (i) Collision cross section (ii). Average speed of CO molecules
(ii) Collision frequency (iv). Collision density

(d) At constant volume $Z \propto \sqrt{T}$. For CO, what is the percentage increase of collision density when the temperature is raised by 10 K at constant volume? (20 marks)

Question 3 (100 marks)

(a) State briefly the assumptions made in collision theory (20 marks).

(b) According to collision theory the collision rates in CH₄ (A) and OH (B) gases are given by following equation: $Z_{AB} = \sigma_{AB} \left(\frac{8kT}{\pi\mu}\right)^{1/2} N_A N_B$. Define all symbols (10 marks).

(c) Consider following reaction in gas phase: OH + CH₄ → H₂O + CH₃ at 298 K. All molecules are considered as hard spheres. Hard sphere diameters of OH and CH₄ are 3.2 Å and 3.8 Å respectively. Calculate following:

- (i) Collision cross section of the two molecules (10 marks)
(ii) Reduced mass of OH and CH₄ molecules (10 marks)
(iii) Rate constant according the equation given in section (b) (20 marks)

(d) The experimental rate constant for the reaction given in section (c) is 1.4×10^{12} cm³ mol⁻¹ s⁻¹. Explain why your answer is different from the value obtained under part (iii) of section (c). Calculate steric factor of the reaction (30 marks).

(C=12, O=16, H=1)

Question 4 (100 marks)

(a) State selection rules of vibration transitions of energy. Which of the following molecules may show infrared activity? (20 marks):

- (i) H₂O (ii) CO₂ (iii) CH₃Cl (iv) N₂

(b) In vibrational spectroscopy define fundamental and overtone frequencies (20 marks)

(c) The force constant for ²³Na ³⁵Cl molecule is $k = 117$ N m⁻¹. Calculate fundamental vibrational frequency in cm⁻¹ (30 marks)

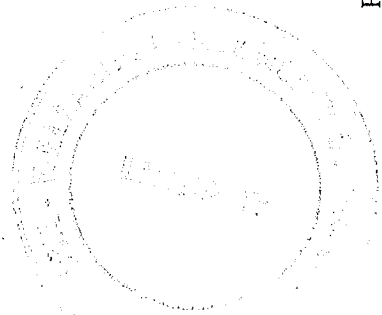
(d) Now consider both isotopes ²³Na³⁵Cl and ²³Na³⁷Cl. Will the observed fundamental frequency differ? Why? Predict fundamental frequency for ²³Na³⁷Cl. Show all work (30 marks)

Question 5 (100 Marks)

- (a) Draw energy level diagrams for harmonic and anharmonic oscillators. State a major difference in these diagrams (20 marks).
- (b) The energy levels for anharmonic oscillator is given by the following equation: $\bar{E}_v = \tilde{\nu} \left(v + \frac{1}{2} \right) - \tilde{\nu} \tilde{x} \left(v + \frac{1}{2} \right)^2$ where $\tilde{x} = \frac{hc\tilde{\nu}}{4D}$. Define all terms (10 marks).
- (c) Use the relationship shown in section (b) to calculate anharmonicity of $^1\text{H}^{19}\text{F}$. Following data were given for HF. $\tilde{\nu}$ 4138 cm^{-1} and D 566.2 kJ mol^{-1} (30 marks)
- (d) Use the equation shown in section (b) to identify the energy terms correspond to harmonic and anharmonic oscillators. Calculate the value of vibrational quantum number for which the anharmonic correction term exceeds 25% (40 marks)?

Question 6 (100 marks)

- (a) Consider rotational properties for each of molecules given below. For each answer the question "can we observe pure rotational transitions for this molecule using absorption of microwave light?"
- (i) H_2O (ii) NH_3 (iii) CH_4 (iv) CO_2
- Categorize the class of rotor of these molecules (20 marks).
- (b) The wave number of the $J = 0 \rightarrow 1$ rotational transition of $^1\text{H}^{81}\text{Br}$ considered as a rigid rotator is 16.93 cm^{-1} . What is (i) the moment of inertia of the molecule (ii) the bond length (40 marks)?
- (c) State selection rules for Raman active vibrations. Explain Raleigh, Stokes and anti-Stokes line in a Raman spectrum (30 marks)
- (d) State Franck-Condon Principle (10 marks).



Useful Equations

$$\bullet D = D_0 e^{-E_a/RT}$$

$$\bullet \frac{C}{C_0} = \frac{\chi}{2\sqrt{Dt}}$$

$$\bullet J = -D \frac{\partial C}{\partial x}$$

$$\bullet \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}$$

$$\bullet \bar{C}_{rel} = \sqrt{2} \bar{C}$$

$$\bullet z = \sigma \bar{C}_{rel} N$$

$$\bullet z = \sqrt{2} N \sigma \bar{C} = \sqrt{2} \frac{P}{kT} \sigma_0 \bar{C}$$

$$\bullet \lambda = \frac{kT}{\sqrt{2} \sigma P}$$

$$\bullet F(J) = BJ (J + 1)$$

$$\bullet S(v, J) = (v + \frac{1}{2})\bar{v} + BJ (J + 1)$$

