SUBJECT: Chemistry

COURSE UNIT:CHE 4412   Time :Two (02) hours

Answer **three (03)** questions only.

Speed of light (c)	$=2.997 \times 10^8$ m s^{-1}
Universal gas constant (R)	$=8.314510$ J K^{-1} mol^{-1}
Faraday constant (F)	$=9.648530 \times 10^4$ C mol^{-1}
Planck constant (h)	$=6.626 \times 10^{-34}$ J s
Boltzmann constant (k$_B$)	$=1.386 \times 10^{-23}$ J K^{-1}
Charge of the electron (e)	$= -1.602 \times 10^{-19}$ C
Vacuum permittivity (ε_0)	$=8.854 \times 10^{-12}$ J^{-1} C^2 m^{-1}
1 eV	$=1.602 \times 10^{-19}$ J

01.   Answer **all** parts.

(a) Partition function contains all the information needed to calculate the thermodynamic
      properties of a system of independent particles.
      Use the partition function, z, given below to answer the following questions

$$z = \left(2e^{-\beta \epsilon} + 1\right)$$

(i) Write down the information you can gather from the above partition function.

(05 marks)

(ii) Calculate the fraction of molecules occupy in each energy level.

(05 marks)

(iii) Show that

(I) $E = -N \dfrac{d}{d\beta} \ln Z = \dfrac{2N\epsilon e^{-\beta \epsilon}}{2e^{-\beta \epsilon}+1}$

(20 marks)

(II) $S = k\beta E + Nk \ln z = Nk \left[\dfrac{2\beta \epsilon e^{-\beta \epsilon}}{2e^{-\beta \epsilon}+1} + \ln\left(2e^{-\beta \epsilon} + 1\right)\right]$

$$\left[Hint: S = k \ln W \text{ and } \ln W = N \ln N - \sum_i n_i \ln n_i\right]$$

(20 marks)

(III) $\dfrac{C_v}{Nk} = 2\epsilon^2 \beta^2 \dfrac{e^{\beta \epsilon}}{(2+e^{\beta \epsilon})^2}$

(10 marks)

(b)   Gibbs free energy difference can be used to predict spontaneity of a process.

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(i) Show that $G - G(0) = -nRT \ln\left(\frac{q_m}{N_A}\right)$

(10 marks)

(ii) Calculate the equilibrium constant of the reaction $I_2(g) \rightleftharpoons 2I(g)$ at 1000 K from the following data for I_2.

[Vibrational wavenumber, $\bar{v} = 214.36\ cm^{-1}$, rotational constant, $B = 0.0373\ cm^{-1}$, bond dissociation energy, $D_e = 1.5422\ eV$. The ground state of I atoms is $2_{P_{3/2}}$, implying 4-fold degeneracy.]

$$\left[Hint: G - G(0) = -kT \ln Q + kTV\left(\frac{\partial \ln Q}{\partial V}\right)_T, \quad p = kT\left(\frac{\partial \ln Q}{\partial V}\right)_T\right]$$

(30 marks)

02.   Answer all parts.

(a) (i) Derive an expression for $\Delta_{mix}S$ for an ideal binary mixture.

(10 marks)

(ii) Giving necessary assumption(s), calculate $\Delta_{mix}G$, $\Delta_{mix}S$, and $\Delta_{mix}H$ when 1.00 mol of hexane is mixed with 2.00 moles of heptane.

(10 marks)

(iii) If you are provided with the same amounts of hexane and heptane as in part (ii), how would you mix them in order to achieve maximum value for ΔS?

(15 marks)

(b)(i) Define the word 'partial molar volume' and write down the mathematical expression for it.

(15 marks)

(ii) The partial molar volume of species 'A', in a binary mixture (A+B) at constant T and p is given by
$$\overline{V_A} = V_A^o - 0.2x_B^2$$
Where V_A^o is the molar volume of pure species A and x_B the molar fraction of species B. If the molar volume of pure species B is V_B^o, derive an expression for $\overline{V_B}$.

(15 marks)

(iii) Draw a sketch showing $\overline{V_A}, \overline{V_B}$ and x_B.
(Note: Assume that V_A^o and V_B^o are equal to 5.0 and 8.0 cm^3 respectively.)

(10 marks)

(c)   Wood and Delanty measured the solubility of He in N-methylacetamide (NMA) at 1atm and temperatures 35 and 70 ^{0}C. The results fit the equation

$$\ln x = -\frac{1152.5}{T} - 6.0579$$

Where $x = molar\ fracion\ and\ T = temperature\ in\ K.$

Assuming an ideal solution, calculate ΔG^0 and ΔH^0 for 1 mole of

$$He\ (gas) \rightarrow He(dilute\ solution\ in\ NMA) \quad at\ 310\ K.$$
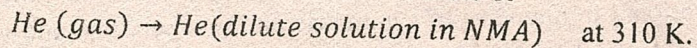
$$\left[Note: \left(\frac{\partial \left(\frac{\Delta G^\theta}{T} \right)}{\partial \left(\frac{1}{T} \right)} \right)_p = \Delta H^\theta \right]$$

(25 marks)

03.   Answer all parts.

Average rate constant derived using simple collision theory for the reaction between fluorine (F) and hydrogen (H_2) that follows the reaction, $F + H_2 \longrightarrow HF + H$, is

$$k(T) = \pi b_{max}^2\, v_r\, \exp\left(-\frac{\varepsilon^*}{k_B T} \right), \text{ where } \pi b_{max}^2, \quad v_r \text{ and } \varepsilon^* \text{ are collision cross section,}$$

relative velocity and threshold energy, respectively. All the molecules are considered to be hard spheres.

(a)   Explain the shortcoming of simple collision theory that is addressed by the modified simple collision theory.

(10 marks)

(b)   Average rate constant derived from activated complex theory can be expressed as

$$k(T) = K \exp\left(-\frac{\varepsilon^*}{k_B T} \right),$$

where K is a constant that depends only on the temperature for a given reaction. Give the expression for the K for the above given reaction assuming that linear activated complex is formed.

(10 marks)

(c)   Derive the terms in the expression of K assuming that the reaction forms a linear activated complex.

(50 marks)

(d) Calculate the K value and hence the rate constant for hard-sphere collisions at 25 ^{0}C.

Relative molecular mass of F and H_2 are 19 and 2, respectively. Moment of inertia of transition state molecule and H_2 molecule are 1.24 x 10^{-46} m^2 kg and 4.56 x 10^{-48} m^2 kg. Vibrational frequencies of symmetric and two bending, and vibrational frequency of H_2 molecule are 1.2×10^{14} s^{-1}, 1.2×10^{13} s^{-1}, and 1.3×10^{14} s^{-1}.

(30 marks)

04. Answer **all** parts.

(a) A population of 1,000,000 particles has two accessible energy states where $\Delta\varepsilon = 4.14 \times 10^{-21}$ J.

(i) Calculate the population of the levels for T=10 K, 300 K and 3000 K

(26 marks)

(ii) What will be the populations as $T \rightarrow \infty$?

(08 marks)

(b) A property used to assess the ability of medicinal compounds to transfer between phases (i.e., aqueous to hydrophobic as involved in partitioning from outside to inside of cells) is the oil/water partition coefficient. The coefficient models the following equilibrium.

$$Solute(oil, T, p, X_{solute}^{oil}) \rightleftharpoons Solute(oil, T, p, X_{solute}^{oil})$$
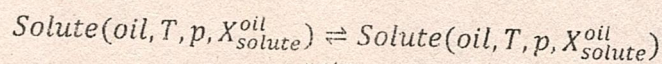
The partition coefficient is $K_{oil}^{water}(T) = \frac{X_{solute}^{water}}{X_{solute}^{oil}}$.

The partitioning process between water and oil of a particular compound involves $\Delta S^0 = -50$ cal $(mol$ $K)^{-1}$ and $\Delta H^0 = 0$ at 300 K.

(i) Calculate $\Delta\mu^0$ at 300 K.

(10 marks)

(ii) Calculate the partition coefficient at 300 K.

(10 marks)

(iii) Estimate the partition coefficient at 320 K. State any assumptions you make.

(13 marks)

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(c) The equilibrium constant between activated complex and reactants is related to the corresponding change in Gibbs free energy of the reaction $A + B \rightleftharpoons AB^{\ddagger}$ according to

$$- RT \ln K^{\pm \prime} = \Delta G^{\ddagger},$$

where rate constant, $k(T) = \dfrac{k_B T}{h} K^{\pm}$. Show that the Arrhenius constant can be derived to be

$$A = \exp(1) \frac{k_B T}{h} \exp\left(\frac{\Delta S^{\ddagger}}{R} \right)$$

(33 marks)

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