2013/02

M.SC. CHEMISTRY
Second Semester
Physical Chemistry

(MSC-08)

Duration: 3Hrs. **Full Marks: 70**

(PART-B: Descriptive)

Duration: 2 hrs. 40 mins. **Marks: 50**

1. Answer the following questions (any six): **2×6= 12**

i) What is the inter planar distance (in Å) for a (100) plane in cubic structure with the lattice parameter of 4 Å?

ii) What is the maximum efficiency of an engine operating between 100°C and 30°C?

iii) Calculate the collision number, Z_{AB} for the reaction between H_2 and I_2 at 700 K and 1 atm pressure. Given that, $n_{H2}=n_{I2} \approx 10^{19}$ molecules per cm^{-3}; σ_{H2}= 2.2 Å, σ_{I2} = 4.6 Å.

iv) The rotational constant of gaseous HCl is 10.23 cm^{-1}. Calculate the rotational partition function of HCl at 200 K.

v) Mo forms body-centred cubic crystals with density 10.3 g cm^{-3}. Calculate the edge length of the unit cube.

vi) What do you mean by conjugate flows? Explain with the help of Onsager's reciprocal relations.

vii) Show that, $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$

viii) What do you mean by turnover frequency? How is it related to catalytic efficiency of an enzyme?

2. Answer the following questions (any five): 3×5= 15

i) Discuss the property of electrical conductivity of a semiconductor.

ii) Show that reflections of X-rays from the planes of a cube are given by;

$\sin^2\theta_{hkl} = K(h^2+k^2+l^2)$

where, K is a constant, θ is the incident angle and hkl are the Miller indices.

iii) Discuss autocatalysis reactions with the help of Lotka-Volterra mechanism.

iv) Derive the expression for Gibbs-Helmholtz equation.

v) One mole of an ideal gas at 26 °C expands adiabatically against a constant pressure of 1 atm from a volume of 10 dm^3 to a volume of 20 dm^3. Calculate q, w, ΔU and ΔH. Assume that $C_V = 3/2R$.

vi) Discuss entropy production in coupled phenomena.

vii) The fundamental vibrational frequency of F_2 is 2.676×10^{13} Hz. Calculate the vibrational partition function of F_2 at 27 °C.

3. Answer the following questions (any two): 4×2=8

(i) The heat capacity C_P (in $JK^{-1}mol^{-1}$) of a substance is given by the following equations:

$C_{P(S)} = 16.74 \times 10^{-5}$ (0< T< 50K)
$C_{P(S)} = 20.72$ (50< T< 150K)
$C_{P(l)} = 25.22$ (150< T< 400K)

At the melting point (150 K), $\Delta H_f = 1255.2$ J mol^{-1}. Calculate the absolute entropy of the substance in the liquid state at 350 K.

ii) Discuss the kinetics of the reaction between H_2 and Br_2 and derive the expression for the rate constant of the reaction.

iii) Derive the relationship between entropy and the molecular partition function.

4. Answer the following questions (any two): 3×5= 15

i) What do you mean by fugacity? For a real gas how it shows the departure from ideal behaviour? Explain. What is the expression for fugacity at low pressure?

ii) Write short notes on (a) Schottky Defects and (b) Frenkel Defects.

iii) What are first and second explosion limits in a branched chain reaction? Discuss the kinetics of H_2-O_2 reaction.

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REV-00
MSC /08/12 2013/02

M.SC. CHEMISTRY
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(The figures in the margin indicate full marks for the questions)

Duration: 20 minutes **Marks – 20**

(PART A- Objective)

1. Select the correct answer: **1x20= 20**
(put '√' mark on the appropriate answer)

i) What is the atomic term symbol for He atom with electronic configuration $1s^2$:
(a) $^1P_0$
(b) $^2S_{1/2}$
(c) $^1S_0$
(d) $^1S_1$

ii) An aqueous mixed solution of NaCl and HCl is exactly neutralised by an aqueous NaOH solution. The number of components in the final mixture is:
(a) 1
(b) 2
(c) 3
(d) 4

iii) Which of the following statement is true for a cyclic process:
(a) $\oint dq = 0$
(b) $\oint dw = 0$
(c) Work can be completely converted into heat
(d) Heat can be completely converted into work

iv) From the following, identify the correct ionic strengths for 0.01 molal solution of NaCl:
(a) 0.01 mol kg^{-1}
(b) 0.02 mol kg^{-1}
(c) 0.001 mol kg^{-1}
(d) 0.025 mol kg^{-1}

v) One of the assumptions made in conventional activated complex theory is:
(a) equilibrium is maintained between the reactants and the activated complex
(b) equilibrium is maintained between the products and the activated complex
(c) equilibrium is maintained between the reactants and products
(d) equilibrium is maintained between the reactants, products and the activated complex

vi) How many atoms are there in an element packed in a fcc structure:
(a) 1
(b) 2
(c) 4
(d) 8

vii) $\left(\frac{\partial G}{\partial p}\right)_T$ = ?
(a) S
(b) V
(c) –S
(d) –V

viii) For water, $\Delta H_{vap} = 41 kJ\ mol^{-1}$. The molar entropy of vaporisation at 1 atm pressure is:
(a) $410\ J\ K^{-1}\ mol^{-1}$
(b) $110\ J\ K^{-1}\ mol^{-1}$
(c) $41\ J\ K^{-1}\ mol^{-1}$
(d) $11\ J\ K^{-1}\ mol^{-1}$

ix) The rotational partition function for hydrogen molecule is:
(a) $\sum_{J=0}^{\infty}(2J+1)\exp[-J(J+1)C]$
(b) $\sum_{J=0}^{\infty}J(J+1)\exp[-J(J+1)C]$
(c) $\sum_{J=0}^{\infty}J(2J+1)\exp[-J(J+1)C]$
(d) $\sum_{J=0}^{\infty}(J+1)\exp[-J(J+1)C]$

x) When an ideal gas is expanded adiabatically and irreversibly from volume V_1 to V_2, which one is correct?
(a) ΔS (system) = 0 and ΔS (surrounding) = +ve
(b) ΔS (system) = +ve and ΔS (surrounding) = 0
(c) ΔS (system) = 0 and ΔS (surrounding) = 0
(d) ΔS (system) = +ve and ΔS (surrounding) = –ve

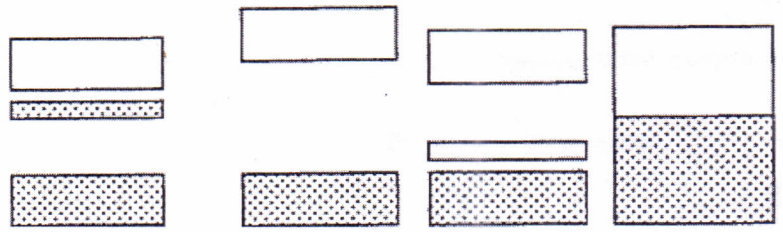
xi) If ΔG^o is zero for a reaction, then which one of the following is correct?
(a) ΔH = 0
(b) ΔS = 0
(c) Equilibrium constant is 1
(d) Rate constant is one

xii) $\left(\frac{\partial H}{\partial T}\right)_P$ =?
(a) C_p
(b) C_v
(c) G
(d) A

xiii) For the reaction, $CH_3COOC_2H_5 + OH^-$, which of the following relation is correct?
(a) $Z_AZ_B = 4$
(b) $Z_AZ_B = 0$
(c) $Z_AZ_B = -1$
(d) $Z_AZ_B = -2$

xiv) The packing fraction of a simple cubic crystal is close to:
(a) 94%
(b) 76%
(c) 52%
(d) 68%

xv) The band structure of an n-type semiconductor is:



(a) (b) (c) (d)

xvi) If, A= reactant, P= product and I= intermediate of the following reaction: A → I →P, then according to steady state approximation:
(a) $\frac{d[A]}{dt} = 0$
(b) $\frac{d[I]}{dt} = 0$
(c) $\frac{d[P]}{dt} = 0$
(d) $-\frac{d[A]}{dt} = 0$

xvii) As the substrate concentration increases, the reaction rate of an enzyme catalysed reaction changes-
(a) from 1st order to 2nd order
(b) from 1st order to zero order
(c) from zero order to 1st order
(d) from 2nd order to 1st order

xviii) In an fcc crystal, the ratio of octahedral voids: tetrahedral voids is:
(a) 2:1
(b) 1:2
(c) 1:1
(d) 3:1

xix) The lowest value of radius ratio in a bcc arrangement is:
(a) 0.414
(b) 0.732
(c) 0.225
(d) 0.635

(xx) For an isothermal process, which of the following relation is correct?
(a) $\Delta U=0, \Delta H\neq 0$
(b) $\Delta U\neq 0, \Delta H=0$
(c) $\Delta U= 0, \Delta H=0$
(d) $\Delta U\neq 0, \Delta H\neq 0$

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