BITS PILANI,INTERNATIONAL ACADEMIC CITY ,DUBAI
I YEAR FIRST SEMESTER,2007-2008
COMPREHENSIVE EXAMINATION

Course Title :Chemistry- I **Course No:CHEM UC141**
Date: 6.01.2008 **Total Marks:120**
Time: 3 hours **Weightage: 40%**

1. **Answer all questions sequentially.**
2. **Answer PART A , B , C and D in separate answer sheets.**
3. **Show stepwise calculation indicating the units wherever its required**
4. **Useful data : h = 6.626 x 10^{-34} J.sec , c = 3 x 10^{10} cm/s, m_e = 9.110 x 10^{-31} Kg,**
   1 eV = 1.602 X 10^{-19} C, R_H = 109677 cm^{-1} ,R = 8.314 J/K/mol,
   R = 0.0821 litre atmK^{-1} mol^{-1},F = 96500 C, 1a.m.u = 1.66 x 10^{-27} kg.
   Atomic mass of C= 6, F = 9, H =1
5. **Question paper contains 3 pages .**

PART – A

1. (i) A lamp emits blue light of wavelength 350 nm.How many photons does it emit per second if its power is 2.00 W ?
(ii) Clearly indicate the difference between degenerate and non degenerate states with respect to the rotational motion of a particle.
(iii) Draw the energy levels of a simple harmonic oscillator. **[5+3+2M]**

2. (i) Give one example each for a charge transfer donor and acceptor .
(ii) Mention any 2 applications of CD spectra.
(iii)Summarize the thermodynamic criteria of spontaneity for an exothermic reaction.
(iv) Calculate the equilibrium constant for the reaction

$\frac{3}{2} O_{2\,(g)} \rightleftharpoons O_{3\,(g)}$ at 25°C, given that $\Delta_r G^{\theta}$ = 163.43 $kJmol^{-1}$. **[2+2+3+3M]**

3. (i) Calculate the osmotic pressure in mm of mercury at 20°C of a solution of naphthalene ($C_{10}H_8$) in benzene containing 12g of naphthalene per litre of solution.
(ii) Write the expression for the chemical potential of a solute in a solution .
(iii) When 2g of a non-volatile hydrocarbon is dissolved in 100g of benzene, the vapour pressure of benzene at 20°C is lowered from 74.66 mm to 74.01 mm . Calculate the molecular mass of the hydrocarbon. **[4+2+4M]**

PART-B

1. (i) Calculate the wave number for the longest wavelength transition in the Balmer series of hydrogen atom.
(ii) Write the selection rule for electronic transitions in hydrogenic atoms.
(iii) Illustrate H-bonding with a suitable example.Which of the following pairs is expected to show hydrogen bonding?
(a) CH_3CH_2OH and CH_3OCH_3 (b) CH_3NH_2 and CH_3SH. **[3+2+2+3M]**

2. (i) Write the equation that gives energies of Linear rotor molecules.
(ii) Write the source and wavelength region of IR spectroscopy.
(iii) Suppose C=O group in a peptide bond can be regarded as isolated from the rest of the molecule. Given the force constant of the bond in a carbonyl group is 908 N/m. Calculate the vibrational frequency of $^{13}C=O^{16}$. **[3+3+4M]**

3. (i) Write Steady state approximation and list the factors affecting the rate of a reaction.
(ii) The value of rate constant for the decomposition of nitrogen pentoxide,
$N_2O_5 \rightarrow N_2O_4 + \frac{1}{2}O_2$ is 3.46×10^{-5} at 25° C and 4.87×10^{-3} at 65° C
Calculate the energy of activation for the reaction .
(iii) For a reaction, $4NH_3(g) + 5O_2(g) \rightarrow 4NO_2(g) + 6H_2O(g)$.
If the rate expression in terms of disappearance of NH_3 is $-\Delta[NH_3]/\Delta t$, write the expression in terms of concentrations of O_2 and H_2O.
[2+2+3+3M]

PART-C

1. (i) Draw the MO diagram of CF molecule . Calculate its bond order and predict the magnetic behaviour.
(ii) Mention any three differences between VB theory MO theory
(iii)Arrange the following molecules in the decending order of their covalent character and give reason
NaCl, RbCl, LiCl, CsCl,KCl **[4+3+3M]**

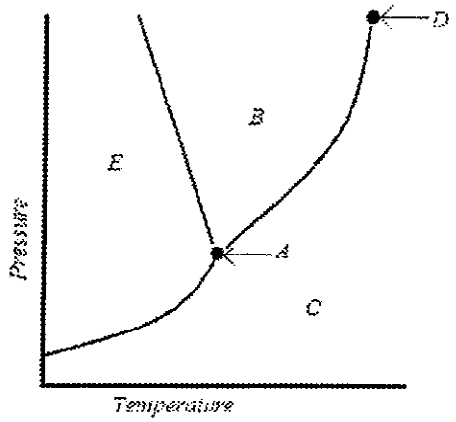
2. (i) Sketch the pH curve for the titration of CH_3COOH Vs NaOH and explain how pka can be calculated from the graph
(ii) What is meant by common ion effect ? Explain with an example.
(iii) If the molar concentration of OH^- is 1×10^{-4} mol dm^{-3}, calculate the pH of the solution.
[4+3+3M]

3. (i) The standard electrode potentials of $Fe^{3+}/Fe = -0.04V$ and $Fe^{2+}/Fe = -0.44V$. Calculate E° for Fe^{3+}/Fe^{2+}.
(ii) Explain any two applications of standard electrode potential with an example
(iii)The emf of the following cell is −1.426 V. Write the half cell reactions and predict whether the reaction is spontaneous or not

$Zn_{(s)} / ZnSO_{4(aq)} \parallel Hg_2SO_{4(aq)} / Hg_{(s)}$ **[4+3+3M]**

Part-D

1.(i) Draw the phase diagram for water (not to scale) in your answer booklet and label all the points A to E.



(ii)Use the phase diagram of water to predict the state of a sample of water under the following sets of conditions: (a) 1 atm 200 °C (b) 100 atm 200 °C (c) 218 atm 375 °C.

(iii)Tetrachloromethane $CC\ell_4$ which is now known to be carcinogenic was once used as a dry cleaning solvent. The enthalpy of vaporization of $CC\ell_4$ is 33.05 kJ/mol and its vapour pressure at 57.8 °C is 0.5 atm. Estimate the normal boiling point of tetrachloromethane.

[3+3+4M]

2.(i) A sample consisting of 2.0 mol helium is expanded isothermally at 22 °C from 22.8 dm^3 to 31.7 dm^3 (i) reversibly, (ii) against a constant external pressure equal to the final pressure of the gas. For the two processes calculate *q, w, ΔU, and ΔH.*

(ii) How does entropy differ from enthalpy? **[6+4M]**

3. (i) Calculate the change in molar entropy, when 60 dm^3 of carbon dioxide expand isothermally from 1.5 dm^3 to 4.5 dm^3 (1 mol of a gas occupies 24 dm^3 at RTP).

(ii)Calculate the standard enthalpy of hydrogenation of benzene from its enthalpy of combustion and the enthalpy of combustion of cyclohexane. Given that the standard enthalpy of combustion of cyclohexane is -3920 kJ/mol and the standard enthalpy of combustion of benzene is -3268 kJ/mol. The standard enthalpy of formation of water ($\Delta_c H^\circ$) is -285.83 kJ/mol.

[4+6M]

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BITS PILANI,DUBAI INTERNATIONAL ACADEMIC CITY,DUBAI
I YEAR FIRST SEMESTER 2007-2008

TEST- 2 (open book)

Course Title :Chemistry-I
Date: 6.12.2007
Time: 50 min

Course No:CHEM UC141
Total Marks: 60
Weightage: 20%

1. Answer all questions
2. Show stepwise calculation indicating the units wherever it is required

1.(i) Why are pure rotational spectra studied only in the gaseous states of atoms and Molecules ?
(ii) Sketch and name the IR active and Raman active modes of carbondioxide molecule.
(iii)In the near IR spectrum of CO there is an intense band at 2144 cm^{-1} .Calculate (a) the fundamental frequency of CO (b) the force constant (c) the zero point energy in J / mole. [m(C) =12.00 u ,m(O) =16u]

[4+5+6M]

2.(i) Calculate q, W and ΔU for the following isothermal process:
1.5 mol of an ideal gas at 2 atm and 25°C expands to 3 times of its original volume against the external pressure of 1 atm.
(ii)Calculate the standard enthalpy change (ΔH°)and standard internal energy change (ΔU°) for the reaction:

$$OF_2(g)+H_2O(g) \rightarrow O_2(g) + 2HF(g)$$

Given that the standard enthalpies of formation ΔH°_f of $OF_2(g)$,$H_2O(g)$ and HF(g) as +23.0, - 241.8, - 268.6 kJ mol^{-1} respectively.

[7+8M]

3.(i)Specify diagrmatically the possible electronic transitions of acetophenone ($C_6H_5COCH_3$) .Compare and comment that with benzene (C_6H_6) molecule.
(ii) The molar heat capacity at constant pressure of solid calcium is expressed by $Cp = 5.20+ 2.30x10^{-3}T - 6.8x10^4 T^{-2}$. Calculate the increase in entropy in J when the substance is heated from 27 °C to 127 °C at constant pressure.
(iii) What are the differences between CT spectra and CD spectra?

[5+5+5M]

4. (i)Draw the MO diagram of CN molecule and calculate its bond order .
(ii)Of the following species ,which has the shortest bond length ? Explain
NO, NO^+, NO^{2+}, NO^-
(iii)Describe the factors which favour polarization and covalency.

[6+4+5M]

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BITS PILANI,INTERNATIONAL ACADEMIC CITY ,DUBAI
I YEAR FIRST SEMESTER,2007-2008

TEST- 1 (Closed book)

Course Title :Chemistry-I **Course No:CHEM UC141**
Date:21.10.2007 **Total Marks:75**
Time: 50 min **Weightage:25%**

1.Answer all questions
2.Show stepwise calculation indicating the units wherever it is required
3.Useful data : h =6.626 x 10^{-34} J sec,c = 3 x 10^{8} m/sec, m_e = 9.11 x 10^{-31} Kg.
1 eV = 1.602 x 10^{-19}J , a_o = 52.9 pm , R_H = 109677 cm^{-1}
4.Question paper has 2 pages

1.(i)Give the boundary conditions for a particle travelling on a circular path of radius r.

(ii)Consider a particle of mass 9.1 x 10^{-31} Kg in a certain one dimensional box of length 3.0 nm .Calculate the energy in eV to excite it from the level with n=2 to the next higher level.

(iii)Calculate the minimum energy needed to start rotating HCl molecule in a plane. The masses of H and Cl atoms are 1.673 x 10^{-27} Kg and 5.807 x 10^{-26} Kg respectively. The equilibrium bond length is 127.4 pm.

(4+8+7M)

2. (i) A lamp emits radiation of wavelength 720nm. What would be the surface temperature of the lamp?

(ii)When a certain metal was irradiated with light of frequency 1.8 x 10^{16} Hz, the photoelectrons emitted had twice the K.E. as did photoelectrons emitted when the same metal was irradiated with light of frequency 1.2 x 10^{16} Hz. Calculate the threshold frequency of the metal.

(iii)In atomic & molecular spectra , the radiation is emitted or absorbed at a series of discrete frequency-why?

(6+8+5M)

3.(i)The frequency of one of the lines in Balmer series of the spectrum of atomic hydrogen is 4.7415x 10^{14} Hz. Identify the quantum number of the upper state in the transition .

(ii)Calculate the C-H stretching vibrational frequency in cm^{-1} from the following data Force constant = 500Nm^{-1} m_C=20x10^{-27}Kg m_H = 1.6x10^{-27}Kg

(iii)Give the equation to calculate the permitted energies of hydrogenic atom. Explain the role of n and Z in the expression.

(6+8+5M)

4. (i) How many orbitals are there in a shell with n = 5 ? When n=5 give the possible values of l and m_l .

(ii) When ultraviolet radiation of wavelength 60.4 nm from a helium lamp is directed on to a sample of Xenon, electrons are ejected with a speed of 1.79×10^6 m s^{-1}. Calculate the ionization energy of xenon.

(iii)Calculate the probability of finding an electron found between a shell of radius a_0 and a shell of radius 3.0 pm greater. $\psi = \frac{1}{\sqrt{\pi a_o^3}} e^{-r/a_o}$

(6+6+6M)

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