RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College affiliated to University of Calcutta)

B.A./B.Sc. SIXTH SEMESTER EXAMINATION, JUNE 2022

THIRD YEAR [BATCH 2019-22]

Date : 13/06/2022 **CHEMISTRY (HONOURS)**

Time : 11 am – 1 pm **Paper : XIII [CC13]** Full Marks : 50

[Attempt **any one** from **each unit**]

Unit –I

[1×10]

1. a) The CsCl structure is observed in alkali halides only when the radius of the cation is sufficiently large to keep its eight nearest neighbor anions from touching. Calculate the minimum value of r_+/r_- needed to prevent this contact. [3]

   b) Copper forms cubic crystals. When an x-ray powder pattern of crystalline copper is taken using x-rays from a Cu target (λ = 154.04 pm), reflections are found at 21.65°, 25.21°, 37.06°, 44.96°, 47.58°, and other larger angles. What type of lattice is formed? What is the length of the side at this temp.? [2+2]

   c) A thorough analysis of X-ray crystallographic data of NaCl crystal shows that both Na and Cl ions have separately occupy the FCC lattice points leading to have a compact interleaved FCC structure consisting two different ions. Show the (100), (110) and (111) planes in the unit cell of NaCl crystal. (3 different unit cells) [3]

2. a) Mn crystallizes in the same type of cubic unit cell as does Cu, but with an a value 5% larger. Calculate the density of Mn, if the density of Cu is 8920 kg m^{-3} and the atomic wts are 0.0636 and 0.0546 kg $mole^{-1}$, for Cu and Mn, respectively. [3]

   b) A crystal plane cuts the x, y and z axis at P, Q and R points with p, q and r values. Given that the unit distances along X, Y and Z axis are a, b and c, respectively, designate the PQR plane in terms of Miller indices. (Geometric description) [3]

   c) (i) Calculate the percent void space in crystalline polonium metal, if it has SCC lattice.
   (ii) Show the (100) plane for this crystal lattice. Whether the description of this plane is changed or not, if the center of the unit cell is occupied? Explain. [2+2]

Unit –II

[1×10]

3. a) Ozone decomposes to O_2 (g) with a qunatum yield of 1.0 when it is irradiated with radiation of wavelength 300 nm. If ozone is irradiated with a power of 100 W, how long will it take for 0.020 mol of O_3 (g) to decompose? [3]
   b) How does the molar absorption coefficient of a substance at λ_{max} in general change with temperature? Explain with reason. [2]
   c) Consider a molecular system with two electrons occupying two different spatial orbitals. Taking into account both spin and spatial states write down all the possible electronic states of the system that are permitted by the Pauli's exclusion principle. [3]

d) A Chemiluminescent reaction is often used to create the precondition for LASER. Explain. [2]

4. a) With the aid of a potential energy diagram for a diatomic molecule show how an electronic transition may lead to bond breaking. [3]

b) Explain (with the help of a schematic diagram depicting the relevant transitions) why the fluorescent emission wavelength is generally independent of the excitation wavelength. [2]

c) The quantum yield for the photodissociation of ICN(g) into I(g) and CN(g) by a 306 nm pump pulse is 1.00. If the radiant energy of the pump pulse is 1.55×10^{-4} J, determine the number of CN(g) radicals created per pulse if only 0.100 % of the incident light is absorbed by the ICN(g) sample. [3]

d) With the aid of a qualitative plot show how absorbance changes with solute concentration in a range of wavelength where the solvent absorbs as well. [2]

Unit –III

[1×18]

5. a) In between Stokes' and anti-Stokes', which one is more intense and which one is red-shifted? Explain with proper transition diagram. [3]

b) (i) The ground and the excited vibration states are at the constant energy gaps for the harmonic oscillator, but decrease with v (vibrational quantum no) for anharmonic oscillator. Using this idea, find out the v_{max}. [Start from energy expression]

(ii) Also show that the zero point energy for anharmonic oscillator is different from that of harmonic one. [3+2]

c) Rotational absorption lines from $^{1}H^{35}Cl$ gas were found at the following wavenumbers: 83.32, 104.13, 124.73, 145.37 cm^{-1}, etc. Calculate the moment of inertia and the bond length of the molecule. Predict the position of the corresponding first line in $^{2}H^{35}Cl$. [5]

d) Which of the following molecules are pure IR and microwave active? [2]

HCl, CH_4, $^{1}H^{2}D$, CH_3Cl

e) The asymmetric stretching of CO_2 is both IR and Raman inactive. True or false, explain. [3]

6. a) Make a table for hot band, 1st overtone and 2nd overtone, specifying the Δv, $\Delta\varepsilon$ and the intensities. [Only the expressions] [3]

b) For $^{14}N_2$, $\Delta\varepsilon$ values for the transitions $v = 1 \leftarrow 0$, $2 \leftarrow 0$ and $3 \leftarrow 0$ are, respectively, 2345.15, 4661.40, 6983.73 cm^{-1}. Calculate $\tilde{\nu}$ and x_e. [Assume only x direction] [3]

c) The geometric structure of a molecule of type AB_2 can be either symmetric linear or asymmetric non-linear. What type(s) of spectroscopy is involved in the determination of the geometric structure of the molecule? Explain with necessary rules involved. [5]

d) (i) Justify that vibrational transitions in HCl are generally observed from v = 0 to v = 1 at room temperature (27°C) i.e. v = 0 is normally more populated than higher levels. [Given that the fundamental vibrational frequency is $8.66 \times 10^{13}\ S^{-1}$]

(ii) What is the approximation used here? [3+1]

e) With the help of a qualitative picture involving ground and excited vibrational as well as the rotational levels of a hypothetical molecule, explain the appearance of P, Q and R lines. Find the corresponding energies also. [3]

Unit –IV

[1×12]

7. a) Derive the expression for spreading coefficient of a liquid A over another B. At what condition would this spreading be spontaneous? [3]

b) A narrow tube is inserted in water, water rises by l mm, if you add some detergent to the water how would the height of water column in the tube would change? If you continue adding the detergent would the the liquid level continue to change forever (the tube could be as high as you wish)? [3]

c) Derive an expression which shows how the vapor pressure on the liquid surface changes with surface tension for a liquid solution which curves concavely at the surface (like water). [4]

d) What will be the pressure inside an air bubble of 0.1 mm radius situated just below the surface of water. (surface tension : 72 dyn cm^{-1} , atmospheric pressure : 1.013×10^6 dyn cm^{-2}) [2]

8. a) The stability of a colloid is kinetic, not thermodynamic in nature. Explain. [3]

b) Show in a qualitative diagram how (i) surface tension and (ii) conductance changes as a surface active agent is added from very low value to above its CMC. [3]

c) Find out how much work you need to do to disperse a spherical drop of liquid weighing 0.04 g into 1500 microglobules of radius 0.02 each. (density of liquid = 0.8 g cm^{-3} and surface tension 72 dyn cm^{-1}) [4]

c) Extent of adsorption decreases with increase in temperature. Explain. [2]

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