WEST BENGAL STATE UNIVERSITY

B.Sc. Honours 6th Semester Examination, 2022

CEMACOR14T-CHEMISTRY (CC14)

PHYSICAL CHEMISTRY-IV

Time Allotted: 2 Hours   Full Marks: 40

The figures in the margin indicate full marks.
Candidates should answer in their own words and adhere to the word limit as practicable.
All symbols are of usual significance.

**Answer any *three* questions taking *one* from each unit**

UNIT-I

1. (a) Terms having their usual meanings, show that for a diatomic molecule the quantum number (J_{max}) of the rotational energy level with maximum population of molecules is given by the expression.   **3**

$$J_{max} = \sqrt{(k\mathrm{T}/2\mathrm{B}hc)} - \frac{1}{2}$$

(b) Given that the spacing of lines in the microwave spectrum of $^{35}Cl\,^{19}F$ is constant at $1.033\ \mathrm{cm}^{-1}$, calculate the moment of inertia and bond length of the molecule $(m\,(^{35}Cl) = 34.9688\,u, m\,(^{19}F) = 18.9984\,u)$.   **3**

(c) What do you mean by Rayleigh, Stokes and anti-Stokes lines in a Raman spectrum? How do the characteristics of a Raman spectrum depend on (i) the nature of substance and (ii) the wave length of the radiation?   **4**

(d) Vibrational wave number of HCl, DCl, D_2 and HD at their $v = 0$ vibrational states are 2885, 1990, 2990 and $3627\,\mathrm{cm}^{-1}$ respectively. Calculate the energy change (in $kJ\,mol^{-1}$) associated with the following reaction and indicate whether the reaction is exothermic or endothermic.   **4**

$$HCl + D_2 = DCI + HD$$
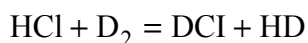
2. (a) In a roto-vibrational spectra, a Q-band is usually absent, Why? What is the line spacing between the 1st P and R line of the roto-vibrational spectra? What will be the relative intensities of these two lines for $^1H^{19}F$ at 20ºC with bond distance $2.9\times10^{-9}m$?   **1+1+4**

(b) What is the nomenclature of the Raman lines obtained at higher wavelength than the incident frequency? The intensity of such lines are more than that of the lower wavelength lines. Justify / criticize the statement. In rotational Raman spectra the line spacing between the 1st lines of the O and S bands is given as 154Å. What is the value of the rotational constant (B)?   **1+2+2**

(c) Write the expression for the nuclear magneton and hence derive its SI unit. Calculate the magnetic field needed to satisfy the resonance condition for unshielded proton in a 150MHz radiofrequency field.　3

UNIT-II

3. (a) State and explain Stark-Einstein law of photochemical equivalence. Is this law always valid for very high intensity LASER radiation? Give reasons for your answer.　4

(b) Why are low temperature and viscous medium suitable for high intensity phosphorescence?　2

(c) Rate of formation of CO due to photodecomposition of propionaldehyde with radiation of wavelength 3025 Å is 2.05×10^{-9} mol. s^{-1}. If the intensity of the incident radiation is 1500 erg s^{-1}, find the quantum yield.　3

(d) What do you mean by 'photosensitized reactions'? Give example of one such reaction that is useful to living system.　$1\frac{1}{2}+1\frac{1}{2}$ $=3$

4. (a) A dye solution (0.01 g/cc) absorbs 40% of blue light in a cell of thickness 1 cm. What would be the concentration to ensure 90% absorption in the same cell?　3

(b) Plot I_a (Intensity of absorbed light) vs. Concentration of the solution and explain the nature of the curve.　3

(c) Define Einstein. At 500 nm the energy absorbed by a sample is 60 W. How many photons does the sample absorb in 1 min?　1+2

(d) Explain pre-dissociation with a properly labelled potential energy diagram.　3

UNIT-III

5. (a) "Unimolecular process are always not first order" — Justify the statement using Lindemann mechanism.　2

(b) Explain the following:　2+2
   (i) Adsorption is accompanied by decrease in enthalpy and entropy of system.
   (ii) Easily liquefiable gases are adsorbed to a large extent.

(c) Show that when a diatomic gas gets adsorbed as atoms on the surface of solid, the Langmuir adsorption isotherm becomes　3

$$\theta = \frac{\sqrt{K_P}}{1 + \sqrt{K_p}}$$

where the symbols have their usual meanings.

(d) What will be the pressure inside a soap bubble of radius 0.1 mm kept in air? [Given surface tension of soap water is 150 dynes/cm and atmospheric pressure is 76 mm of Hg].　3

(e) At 0ºC and at a pressure of 1 atm only 0.20 fraction of the surface of a finely divided nonporous solid was covered by CO. Find out ΔG° of the adsorption process at 0ºC.　2

6. (a) Electroosmosis is a consequence of existence of electrical double layer at the solid-liquid interface — Justify.   2

(b) "Adsorption of a gas on solid is exothermic" — Justify or criticize.   2

(c) Define with an example, a lyophilic colloid. How many such a colloid help in stabilizing a lyophobic colloid like a *gold sol*? Explain what do you mean by the term 'gold number'.   3

(d) Why do electrolytes increase the surface tension of a liquid? Explain, with the help of Gibbs adsorption isotherm.   2

(e) Find the change in surface energy when two identical Hg droplets of diameter 2 mm merged isothermally to form one drop [Surface tension of Hg is 490 dynes cm^{-1} at that temperature]   3

(f) For a soap solution $\gamma = \gamma_0 - bc$. Derive the corresponding equation of state of the adsorbed film by assuming Gibbs adsorption isotherm.   2

N.B. : *Students have to complete submission of their Answer Scripts through E-mail / Whatsapp to their own respective colleges on the same day / date of examination within 1 hour after end of exam. University / College authorities will not be held responsible for wrong submission (at in proper address). Students are strongly advised not to submit multiple copies of the same answer script.*

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