

**TDC Odd Semester Exam., 2020
held in July, 2021**

CHEMISTRY

(Honours)

(5th Semester)

Course No. : CHMH-503

(Physical Chemistry—V)

Full Marks : 35

Pass Marks : 12

Time : 2 hours

*The figures in the margin indicate full marks
for the questions*

Answer **five** questions, taking **one** from each Unit

UNIT—I

1. (a) State the third law of thermodynamics.
Explain its importance. 1+3=4
- (b) How can you test the validity of third
law of thermodynamics? 2

- (c) Choose the correct option :

A chemical reaction proceeds with increase in both the enthalpy (H) and entropy (S). It will be spontaneous, if—

(i) $H < T S$

(ii) $H > T S$

(iii) $H = T S$

(iv) None of the above 1

2. (a) State and explain Nernst heat theorem.
Show how it leads to third law of thermodynamics. 2+2=4
- (b) What is residual entropy? “Residual entropy of ice at 0 K is 3.3 JK^{-1} but that of hydrogen is 6.2 JK^{-1} .” Explain. 1+2=3

UNIT—II

3. (a) Mention some of the differences between the photochemical and thermochemical reactions. 3
- (b) What is chemiluminescence? Give examples of it. 2
- (c) Explain the primary and secondary processes in photochemical reactions. 2

(3)

4. (a) When a substance A was exposed to light, 0.002 mole of it reacted in 20 minutes and 4 seconds. At the same time, A absorbed 2.0×10^6 photons of light per second. Calculate the quantum yield of the reaction. (Avogadro's number $N = 6.023 \times 10^{23}$) 2
- (b) Draw a neat Jablonski diagram, showing various photochemical reactions and explain them. 3
- (c) Enumerate the causes for high- and low-quantum yield in photochemical reactions. 2

UNIT—III

5. (a) What are selection rules for vibrational and rotational spectra? 2
- (b) Derive an expression for the rotational energy of a diatomic molecule taking it as a rigid rotator. 3
- (c) What type of molecules gives rotational spectra? Which of the following molecules will show rotational spectra? 1+1=2
- H_2, O_2, CO, HCl

(4)

6. (a) Show that for a rigid diatomic rotator, the moment of inertia is given by $I = r^2$. 2
- (b) The pure rotational (microwave) spectrum of gaseous HCl consists of a series of equally spaced lines separated by 20.80 cm^{-1} . Calculate the internuclear distance, i.e., bond length of the molecule. The atomic masses are—
- $^1H = 1.673 \times 10^{-27} \text{ kg}$
 $^{35}Cl = 58.06 \times 10^{-27} \text{ kg}$ 3
- (c) Mention the different types of electromagnetic radiations along with frequency ranges. 2

UNIT—IV

7. (a) Using a harmonic oscillator model, show that the frequency of a photon absorbed by a diatomic molecule is equal to that of its vibration. 3
- (b) Explain Born-Oppenheimer approximation in relation to electronic spectra of molecule. 2

(5)

- (c) How many modes of vibrations are possible for a linear and a non-linear molecule? 2
8. (a) Show diagrammatically the electronic transition for carbonyl (>C=O) group in the electronic spectra. 3
- (b) What are meant by shielding and deshielding of protons? 2
- (c) Why is tetramethylsilane used as a reference in NMR spectroscopy? 2

UNIT—V

9. (a) Classify liquid crystals on the basis of their molecular structure. 2
- (b) Draw vapour pressure temperature curve for a substance undergoing mesomorphic change. Explain it in detail. $1\frac{1}{2}+1\frac{1}{2}=3$
- (c) State the differences between electron and ion-conducting polymers. 2
10. (a) What is critical micelle concentration? Draw the phase diagram for an ionic surfactant and mention the Kraff temperature. $1+2=3$

(6)

- (b) Define liquid-glass transition and glass transition temperature. Show how glass transition temperature can be measured by differential scanning calorimetry, giving heat capacity versus temperature curve. $2+2=4$
