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1 (Sem–4/AR) CHE 04 (A)

2026

CHEMISTRY

(Major/Minor–1)

Paper : CHE0400404

(Magnetic Resonance Spectroscopy and Analytical Techniques)

Full Marks : 45

Time : 2 hours

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

1. Answer the following questions as directed : 1×5=5

(a) The crystal system with lowest symmetry has its unit cell parameters as follows– $a \neq b \neq c$; $\alpha \neq \beta \neq \gamma \neq 90°$.

Name the crystal system—

(b) Define base peak in mass spectroscopy.

(c) Choose the wrong answer—

NMR specta are shown by nucleus with-

(i) Even mass number and odd atomic number

(ii) Odd mass number and odd atomic number

(iii) Odd mass number and even atomic number

(iv) Even mass number and even atomic number

(d) What is the typical g–value for a free electron ?

(e) What is the role of salt bridge in galvanic cell ?

2. Answer ***any five*** questions : 2×5=10

(a) Define chemical shift. Write *any two* factors that effect chemical shift.

(b) Which of the following species are ESR active— NO, CH_3, H_2O, O_2

(c) Show, how McLafferty rearrangement takes place in pentanal and identify the species with $m/z = 44$.

(d) Write a short note on asymmetric effect and relaxation time.

(e) With a suitable diagram discuss the expected high resolution spectrum of methanol and their relative peak intensities.

(f) State the principle of chromatography and write the expression for R_F factor in chromatography.

(g) Calculate the Miller of crystal planes which cut through the crystal axes at —

(i) 6a, 3b, 3c

(ii) 2a, -3b, -3c

(h) How anisotropic effect causes shielding and deshielding of protons while studying chemical shift in NMR spectroscopy ?

(i) Discuss the variation of κ and $\wedge_{eqv}$ of electrolytic solution(s) with dilution.

(j) Write *two* reasons for using TMS as reference in non–aqueous solvents in ^1H NMR spectroscopy.

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3. Answer ***any four*** questions : 5×4=20

(a) State how many ^1H NMR signals will be shown by $(CH_3)_2 CHCH_2Cl$. Draw a schematic diagram to show all signals. Indicate the ratio between the peak areas. Show the spin-spin coupling that occurs citing reasons. 1+1+1+2=5

(b) *(i)* What is nitrogen rule in mass spectroscopy ? 1

(ii) An organic compound forms a molecular peak at $m/e = 114$. The other prominent peaks appears at m/e – 85,72 (NR ion), 57,41 and 29. Confirm the compound by writing the various fragmentation modes. 4

(c) *(i)* What is the $E°$ value for calomel electrode when measured w.r.t. standard hydrogen electrode ? 1

(ii) In calomel electrode, the electrode is reversible w.r.t which ion ? 1

(iii) Draw a suitable diagram representing calomel electrode. Write the half cell reactions for the electrode, when it acts as anode and cathode. 3

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(d) State the principle of chromatography. What is thin layer chromatography (TLC) ? In what way TLC is superior to paper chromatography ?

(e) What is Gel Permission Chromatography (GPC) ? Discuss the mechanism of GPC working. What types of detectors are basically used in GPC ?

(f) *(i)* What effect does the isotopic substitution of deuterium for hydrogen have on ^1H NMR spectra ? 1

(ii) Deuterated acetone (CD_3COCD_3) in often used as a solvent for ^1H NMR. In fact, samples usually contain some residual CD_3COCD_2H ; predict the ^1H NMR spectrum of this molecule assuming no coupling between CD_3 and CD_2H groups. 3

(iii) What is value for 1 for deuterium ? 1

(g) *(i)* What particle is used to bombered samples in mass spectroscopy ? 1

(ii) Write the basic principle underlying mass spectroscopy. 2

(iii) What is the most abundant peak in the mass spectrum of toluene, explain ? 2

(h) (i) Draw a suitable diagram and discuss the conditions when it will act as concentration cell with transference and without transference : 2

(ii) Calculate the EMF of the following cell — 3

$$Pt; Co^{2+}(2.0M), Co^{3+}(0.010M)$$

$$\| Cr^{3+}(0.50M), Cr_2O_7^{2-}(4.0M), H^+(1.5M); Pt$$

given, $E°Co^{3+} \mid Co^{2+} = 1.82V$

$E°Cr_2O_7^{2-} \mid Cr^{3+} = 1.33V$

4. Answer ***any one*** question : 10×1=10

(a) (i) State the Bragg's law and derive Bragg's equation. 4

(ii) X–rays of wavelength 0.15 *nm* are used in X–ray diffraction experiment. First order diffraction is observed when the angle of incidence is 10·2°. Calculate interplaner distance in the crystal used. 3

(iii) Sketch 100 planes of a cubic lattice. 1

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(iv) A crystal plane has interrupts on the three axes of crystal in the ratio $\frac{1}{2} : \frac{2}{3} : \alpha$. What are the Miller indices of the plane ? 2

(b) (i) A free electron is placed in a magnetic field of strength 1·3T. Calculate the resonance frequency if $g_e = 2.0023$ and $\beta_e = 9.274 \times 10^{-24} JT^{-1}$. 2

(ii) Consider the two ^1H NMR signals shown by CH_3OH. Explain which protons will show resonance at downfield compared to the other if the energy of the radiation is kept constant and the magnetic field is swept. Discuss whether the position of the signals will change or not if the magnetic field in kept constant and radiation is swept. 5

(iii) Predict the high resolution NMR spectra of CH_3CH_2Cl and CH_3CHDCl. 3

(c) (i) What is potentiometry ? Write the principle for potentiometric titration. 2

(ii) Discuss the variation of P^H *vs* volume of base adoled in a potentiometric titration of a strong acid against a strong base. How will determine end point with the help of above curve? 3

(iii) How potentiometric titration is advantageous over visual indicator titration? 2

(iv) Define Zeta potential. Draw a suitable diagram showing electrical double layer in colloidal substances. 3

(d) (i) An organic compound $C_{10}H_{14}$ gives the following NMR data –

Singlet $\delta = 7.12, 5H$; doublet, $\delta = 2.45, 2H$; multiplate $\delta = 1.86$, 1 H and doublet $\delta = 0.86, 6H$.

Predict the structure of the compound. 5

(ii) Find the intensity distribution in the lines of the ESR spectrum of CD_3. 2

(iii) What causes hyperfine splitting if Zeeman states in ESR? 1

(iv) Predict the fragmentation pattern of ethyl amine and acetophenone in mass spectroscopy. 2

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