

[2]

4. $A+B \rightleftharpoons AB$ is a rapid exchanging system.

How can the equilibrium constant (K) of the above reaction be determined from NMR measurement ? (A, B and AB are all NMR active species) 4

OR

^{19}F NMR of TiF_4 dissolved in EtOH affords a spectrum featuring two triplets with equal integration at dry ice temperature, which on warming to a temperature 0°C coalesce to a singlet. Upon addition of ethanolic solution of Na_2TiF_6 to the former mixture in equimolar proportion, NMR spectrum features a quintet and a doublet with an integration ratio of 1 : 4. Elucidate the structure of the Ti complex formed in different stages as stated above.

[For ^{48}Ti , $I = 0$] 4

UNIT - I - 3121b

5. “ PFCl_4 retains its molecular symmetry in crystalline state where as PPhCl_4 does not.” Explain the statement of the basis of NQR spectral study, 2
6. Enumerate the reasons for appearance of multiline Mössbauer spectrum. Why Mössbauer spectra can only be measured in the solid state ? $3+1\frac{1}{2}$

[3]

7. Predict giving reason, the number of possible resonance line (s) be observed in NQR spectrum of CH_3I molecule. Calculate the energy of each level generated due to quadrupole interaction in the molecule as function of eQq .

[For ^{127}I ; $I = \frac{5}{2}$] 2+3

8. What is Isomer Shift (IS) ? 1

UNIT - I - 3122

9. a) What makes a molecule Raman active ? using classical theory, explain the occurrence of Stokes and anti-stokes Raman scattering. 3
- b) The equilibrium vibration frequency of I_2 is 215 cm^{-1} and the anharmonicity constant is 0.003. Calculate the intensity of the ‘hot band’ relative to that of the fundamental at 300 K. 2
- c) How will you prove the occurrence of linkage isomerism in $[\text{Ru}(\text{dmsO})_6]^{2+}$ (dmsO = dimethylsulfoxide) with the help of IR spectroscopy ? 2
- d) The symmetrical stretching mode of CO_2 is infrared inactive but Raman active. Explain. 2
- e) Taking ν_{CO} as a probe, how will you monitor the oxidative addition reaction in Vaska compound ? $1\frac{1}{2}$

[Turn over