



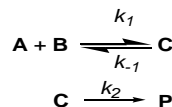
15) State *true* or *false* for the following statements (i) The rate law of overall reaction for a hypothetical process  $A+B \rightarrow \text{Products}$  must be always; rate =  $k [A][B]$ ; (ii) Homogeneous reaction rate have the dimensions of concentration divided by time; (iii) The activation energy is positive for all reactions. [1+1+1=3]

16) The rate of formation of C in the reaction  $A + 2 B \rightarrow 4 C + 3 D$  is  $10.0 \text{ mol dm}^{-3} \text{ s}^{-1}$ . Find the rate of formation of D and rates of consumption of A & B. [1+1+1=3]

17) A reaction  $3 A \rightarrow P$  has a second-order rate law with rate constant  $0.5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . Calculate the time required for the concentration of A to change from  $0.200 \text{ mol dm}^{-3}$  to  $0.01 \text{ mol dm}^{-3}$ . [3]

18) The Arrhenius parameters for a reaction  $\log(A/s^{-1}) = 10$  and  $E_a = 100 \text{ kJ mol}^{-1}$ . (i) What is the rate constant of the reaction at  $25^\circ\text{C}$ ? (ii) Find the temperature (in K) at which the rate constant of the reaction of the above process will be tripled than that of the rate constant at  $25^\circ\text{C}$ ? [2+2=4]

19) A hypothetical overall process  $A + B \rightarrow P$  proceeds through the following mechanism. Write the final rate equation for the formation of P using steady state approximation to the appropriate species. [3]



20) The fundamental ( $0 \rightarrow 1$ ) and first overtone ( $0 \rightarrow 2$ ) vibrational bands of HCl are observed at  $2885 \text{ cm}^{-1}$  and  $5664 \text{ cm}^{-1}$  respectively. Calculate the anharmonicity constant. [4]

21) In atmospheric chemistry, the OH radical is an important gas phase species. The radical  $^{16}\text{OH}$  has an OH stretching vibration observed at  $3546 \text{ cm}^{-1}$ . Calculate the wavenumber (in  $\text{cm}^{-1}$ ) that you expect for the OH stretch of the radical  $^{18}\text{OH}$  ( $^{16}\text{O} = 15.9994 \text{ amu}$ ,  $^{18}\text{O} = 17.999160 \text{ amu}$ ,  $\text{H} = 1.00784 \text{ amu}$ ). Assume the bond vibration is harmonic and the force constant remains unchanged on isotope substitution. [3]

22) An aqueous solution of methylene blue (dye) has absorption maximum at  $660 \text{ nm}$  with molar absorption coefficient of  $1.08 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ . The absorption of  $50 \text{ mg dm}^{-3}$  of methylene blue solution is 0.5 when it is measured in a cell of path length  $1 \text{ cm}$ . A methylene blue solution of unknown concentration absorbs to the same extent when it is measured in a cell of path length  $2 \text{ mm}$ . Calculate the concentration (in  $\text{mg dm}^{-3}$ ) of methylene blue in this solution? [3]

23) A solution mixture consisting of two absorbing dyes A & B. The light intensity is dropped to 20 % at  $\lambda_1$  and to 10 % at  $\lambda_2$  of its initial value, when measured in a cell of path length  $2 \text{ cm}$ . Given that  $\epsilon_A(\lambda_1) = 22 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ,  $\epsilon_A(\lambda_2) = 25 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ,  $\epsilon_B(\lambda_1) = 10 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ,  $\epsilon_B(\lambda_2) = 15 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ . Calculate the ratio of concentrations of A and B present in the mixture. [3]

24) The IR spectrum of the Haber-Bosch process ( $\text{N}_2 + 3 \text{ H}_2 \rightarrow 2 \text{ NH}_3$ ) at time  $t = 0 \text{ sec}$  and also upon completion of the reaction was recorded. How many vibration bands one can expect in the **initial** and **final** IR spectrum? [2+2=4]

25) Which of the following complexes in each series has the minimum  $\Delta_o$  value? (i)  $[\text{Cr}(\text{NH}_3)_6]^{3+}$ ,  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ ,  $[\text{CrCl}_6]^{3-}$ ,  $[\text{Cr}(\text{CN})_6]^{3-}$ ; (ii)  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ ,  $[\text{Fe}(\text{CN})_6]^{4-}$ ,  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ . [2]

26) Against each of the following metal ion d-electronic configuration, write the extent of tetragonal distortion possible in octahedral complexes of corresponding metal ions as NIL / weak /strong: (i)  $d^3$  in strong field; (ii)  $d^4$  in weak field (iii)  $d^5$  in strong field; (iv)  $d^8$  in weak field. [4]

27) Enthalpy of hydration of  $\text{Cr}^{2+}$  is  $-460 \text{ kcal/mol}$ , whereas the predicted enthalpy in the absence of CFSE is  $-435 \text{ kcal/mol}$ . What is the value of crystal field splitting ( $\Delta_o$ ) for  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$  expressed in  $\text{cm}^{-1}$ ? [2]

28) The UV visible spectrum of  $[\text{VCl}_6]^{2-}$  gives a broad peak for the d-d transition with a maximum at  $15,400 \text{ cm}^{-1}$ . Calculate the CFSE (in  $\text{kJ/mol}$ ). [3]

29) Predict the hybridization of following complexes with the number of unpaired electrons in brackets. (i)  $[\text{Fe}(\text{CN})_6]^{4-}$  (0), (ii)  $[\text{Ni}(\text{dmg})_2]$  (0), (iii)  $[\text{Ni}(\text{CN})_4]^{2-}$  (0), (iv)  $[\text{Mn}(\text{NO}_2)_6]^{3-}$  (2). [4]

30)  $[\text{Cu}(\text{NH}_3)_6]^{2+}$  has four Cu-N bonds of length  $2.07 \text{ \AA}$  and two Cu-N bonds of  $2.62 \text{ \AA}$ . Write the d-orbital electronic configurations of  $\text{Cu}^{2+}$  in the complex according to crystal field theory, in the increasing order of energy (with correct labeling and electron occupancy of each d orbital) separating with = or < symbol wherever appropriate. [3]

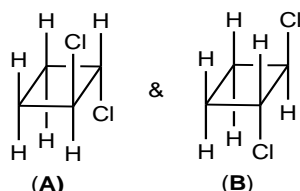
31) Predict if the following complexes will show tetragonal distortion? (Write YES/NO).  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ ,  $[\text{Co}(\text{NH}_3)_6]^{2+}$ ,  $[\text{Cr}(\text{NH}_3)_6]^{3+}$ . [3]

32) Calculate effective atomic number (EAN) for the following complexes. (i)  $[\text{Pt}(\text{NH}_3)_6]^{4+}$ , (ii)  $[\text{Fe}(\text{CN})_6]^{3-}$ , (iii)  $[\text{Cr}(\text{NH}_3)_6]^{3+}$ . [3]

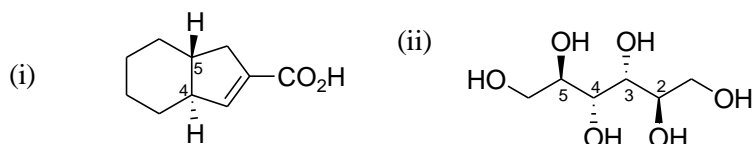
33) Which one among the following cationic complexes has the highest spin only magnetic moment value:  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ ,  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ ,  $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$ ? Also calculate the value in BM for that complex. [1+1=2]

34) Predict the structure and magnetic behavior (paramagnetic/diamagnetic) of the following complexes: (i)  $[\text{PtCl}_4]^{2-}$ , (ii)  $[\text{Ni}(\text{CO})_4]$ . [2+2=4]

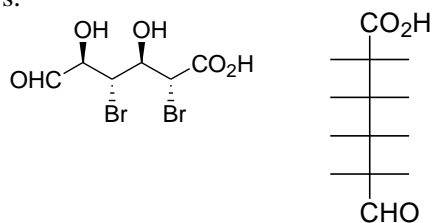
35) Label the given pair of molecules as identical/ enantiomers/diastereoisomers. [2]



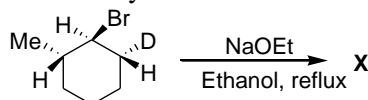
36) Assign R/S descriptors for the numbered chiral centers of the following molecules: [2+4=6]



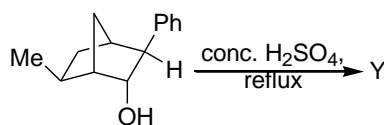
37) Convert the following molecule in correct Fischer projection formula using the skeleton structure given and assign the R/S descriptors for the chiral centers. [1+1=2]



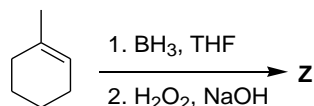
38) The bromo compound shown below on treatment with NaOEt in refluxing ethanol gives predominantly product X. Write down the structure of X with correct stereochemistry. [3]



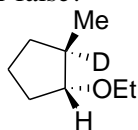
39) Write down the major product Y for the following reaction. [3]



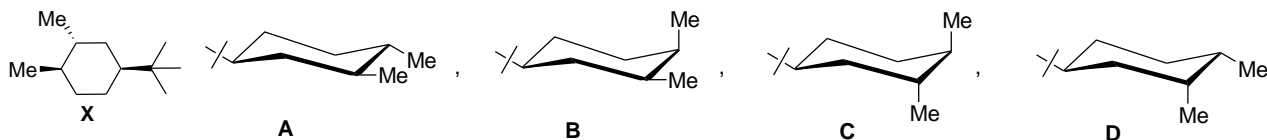
40) Write down the structure of the major product Z for the following reaction with suitable stereochemistry. [2]



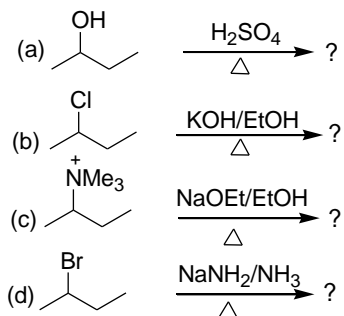
41) Oxymercuration-demercuration of 1-methylcyclopentene using  $\text{Hg}(\text{OAc})_2/\text{EtOH}$  and then reduction with  $\text{NaBD}_4$  gives the following stereoisomer as the only product. Is it true or false? [2]



42) Identify the most stable conformation of the compound (X) in gas phase from the given ones (A, B, C, D). [1]



43) Identify the elimination reaction from the list below (a, b, c, d) will give 1-butene as the major product. [2]



44) Identify the nucleophiles among the given ones which will exclusively give a substitution product and no elimination product upon reaction with secondary alkyl bromides at 50 °C in DMF:  $^-OEt$ ,  $^-CN$ ,  $^-OH$ ,  $^-AcO$ ,  $^-OTs$ ,  $^-SMe$ . [3]

45) In E2 elimination with potassium tert-butoxide, the Hoffman product formation arises due to the formation of the most stable carbocation and then removal of the less hindered  $\beta$ -hydrogen. Is this statement true or false? [1]

**End**