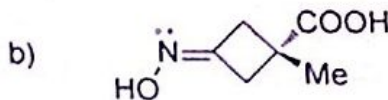
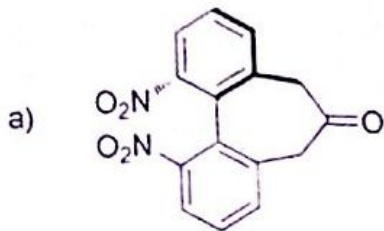


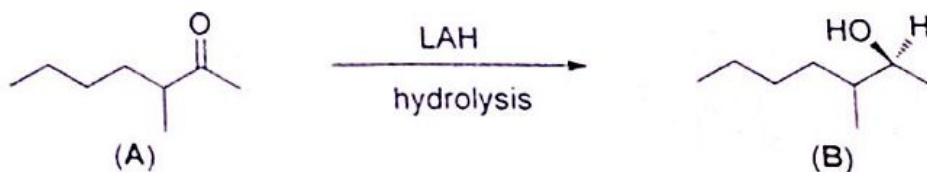
PART A (24 marks)

1. Assign absolute configuration to the compounds given below.

(1×2=2 marks)

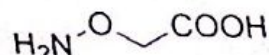
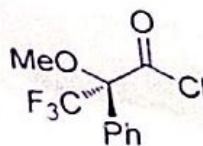
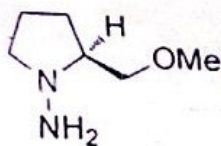
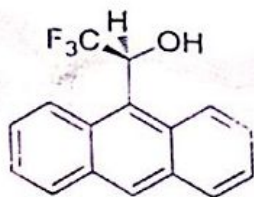


2. a) What is the absolute configuration of the starting ketone (A) for the following reaction? Using Cram's rule, illustrate the product formation in Newman representation. (2+0.5=2.5 marks)

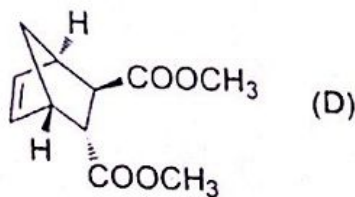


b) Identify the face (Re/Si) of delivery of hydride to the carbonyl that would yield B.

3. Which one of the following reagents can bring about the chiral resolution of a racemic mixture of 2-butanol. Write the reaction involved and represent schematically the procedure that will be adopted for getting enantiopure compounds. (2 marks)



4. Compound (C) can exist in two diastereomeric forms. It reacts with cyclopentadiene to give a product (D) whose structure is given below. (1+1.5=2.5 marks)



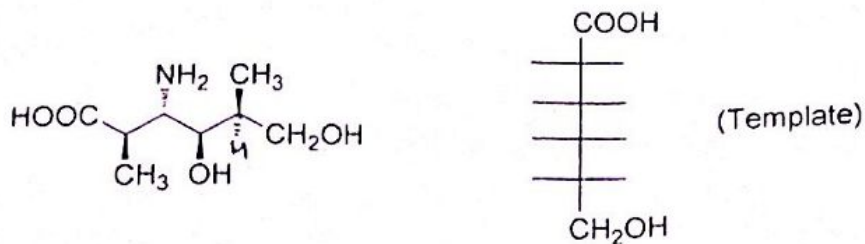
a) Which diastereomer of C yields D?

b) Write the IUPAC name of D indicating its absolute configuration at all stereocentres.

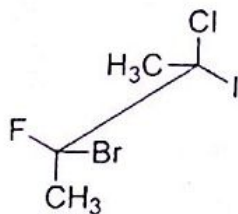
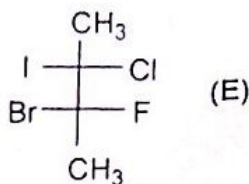
5. The specific rotation of (S)-2-bromobutane is +23.1°. If a 1.0 M solution of (S)-2-bromobutane is mixed with an equal volume of 1.0 M solution of racemic 2-bromobutane, what is the observed rotation α of the resulting solution? The measurements are done in a 10.0 cm polarimeter cell (Atomic wt. of Br = 80).

(2 marks)

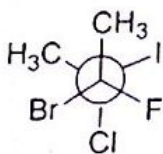
6. Convert the following structures into Fischer Projection in the template provided. (1 mark)



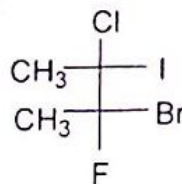
7. Shown below is a Fischer Projection of a compound **E**. Classify each structure below (a-d) by its stereochemical relationship to **E**. Note that conformational differences are unimportant in this question. (2 marks)



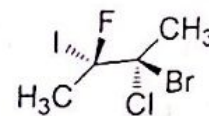
(a)



(b)

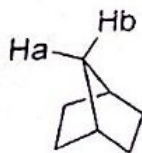


(c)

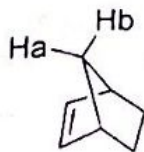


(d)

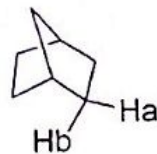
8. Indicate if the hydrogens marked Ha and Hb are homotopic, enantiotopic, or diastereotopic in the following compounds (e-h). (2 marks)



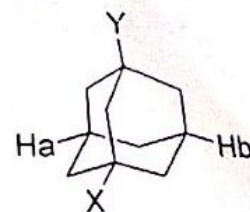
(e)



(f)



(g)



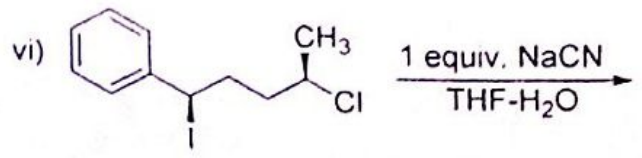
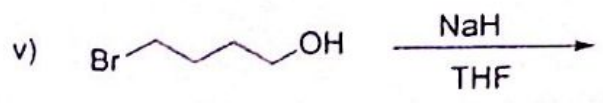
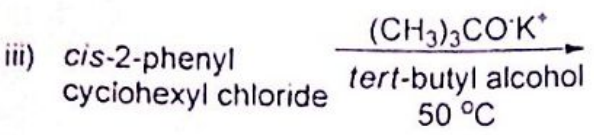
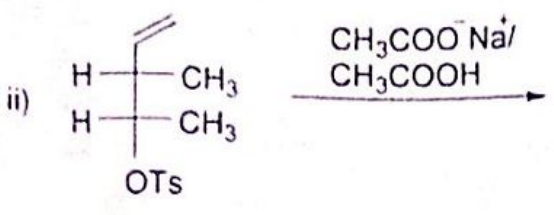
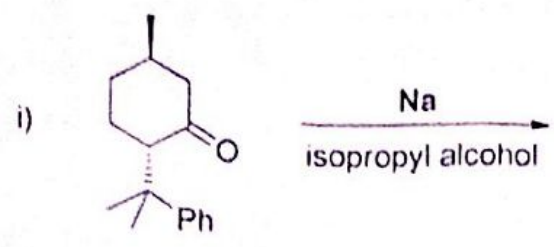
(h)

9. a) Write the correct stereochemical structure of the major product for the following reactions. (1×6=6 marks)

b) Which one of the two reactions (ii) & (iii) will show kinetic hydrogen isotopic effect? Explain your answer with the help of a suitable mechanism. (1 mark)

c) Draw a labeled energy profile diagram for reaction (iv). (1 mark)

150
139129



PART B (9 marks)

10. Fill in the blanks

(1×9=9 marks)

- (a) The transfer of dioxygen from hemoglobin to myoglobin depends upon factors such as and
- (b) In Monsanto process, the catalyst, is useful for industrial production of from
- (c) Polysilanes show a strong electronic absorption in the UV region due to
- (d) The number of M-M bond(s) in $[\eta^5\text{-C}_5\text{H}_5](\text{CO})_2\text{Cr}_2$ is
- (e) From the metal-carbonyls listed below, will NOT undergo oxidative addition of methyl iodide.
 $\text{Ir}(\text{PPh}_3)_2(\text{CO})\text{Cl}$, $[\text{RhI}_2(\text{CO})_2]^-$, $\eta^5\text{-Cp}_2\text{Ti}(\text{Me})\text{Cl}$
- (f) $(\text{H}_3\text{Si})_2\text{O}$ is basic than $(\text{H}_3\text{C})_2\text{O}$.

1.0536

0.05223

PART C (17 marks)

- 11. Liquid water can be superheated to 120°C at 1.01325 bar. Calculate the changes (per mole) in entropy, enthalpy, and Gibbs energy for the process of superheated water at 120°C and 1.01325 bar changing to steam at the same temperature and pressure. The enthalpy of vaporization is 40.58 kJ mol at 100°C and 1.01325 bar. Given: $C_{p,m}(\text{H}_2\text{O}, l) = 75.3 \text{ J K}^{-1} \text{ mol}^{-1}$ and $C_{p,m}(\text{H}_2\text{O}, g) = (36 + 0.013T) \text{ J K}^{-1} \text{ mol}^{-1}$, where T is in Kelvins. (5 marks)
- 12. The relative humidity of an air-water mixture is defined as the ratio of the partial pressure of water vapor (H_2O) in the mixture to the equilibrium vapor pressure of water at a given temperature, usually reported as a percentage. $\text{CuSO}_4 \cdot \text{H}_2\text{O}(s) \rightleftharpoons \text{CuSO}_4(s) + \text{H}_2\text{O}(g)$ describes the decomposition of the hydrated form of cupric sulfate. What is the equilibrium partial pressure of $\text{H}_2\text{O}(g)$ over a mixture of $\text{CuSO}_4 \cdot \text{H}_2\text{O}(s)$ and $\text{CuSO}_4(s)$ at 298 K kept in a closed chamber.



What is the relative humidity in this closed chamber at 373 K? You may assume the standard constant pressure heat capacities to not change over this temperature range. The equilibrium vapor pressure of water at 373 K is 0.023 bar. Use the thermodynamic values given below for 298 K. (6 marks)

	$\Delta H_f^0 / \text{kJ mol}^{-1}$	$\Delta G_f^0 / \text{kJ mol}^{-1}$
$\text{CuSO}_4 (\text{s})$	-771.36	-661.80
$\text{CuSO}_4 \cdot \text{H}_2\text{O} (\text{s})$	-1085.83	-918.11
$\text{H}_2\text{O} (\text{g})$	-241.82	-228.57

13. Short answers

- The undistorted bond length of $^{14}\text{N}^{16}\text{O}$ molecule is 115 pm. The lowest energy transition in the microwave region occurs at _____ meV. (2 marks)
- The number of degenerate states for the 3D particle in a cubic box for $(n_x = 2, n_y = 1, n_z = 1)$ is _____. The energy of this state is _____. (2 marks)
- Comment on the statement: Since the value of the radial wavefunction for the 1s orbital is largest at the nucleus, it is most likely to find the electron at the nucleus when it is in the 1s state. (1 mark)
- Comment on the statement: The variation principle states that you can never find a solution lower than the ground-state energy whatever trial function you choose. (1 mark)

Useful information

$$h = 6.626 \times 10^{-34} \text{ J}\cdot\text{s}; m_e = 9.1 \times 10^{-31} \text{ kg}, \epsilon_0 = 8.854 \times 10^{-12} \text{ F}\cdot\text{m}^{-1}, m_p = 1.67 \times 10^{-27} \text{ kg},$$

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$