2023

CHEMISTRY — HONOURS

Paper : CC-5

(Physical Chemistry - 2)

Full Marks : 50

The figures in the margin indicate full marks.

Candidates are required to give their answers in their own words as far as practicable.

Answer ***question no.*** **1** and ***any eight*** questions from the rest.

1. Answer ***any ten*** questions : 1×10

(a) Why does C_P exceed C_V for an ideal gas? Give a molecular explanation.

(b) In a given change of state, 44 J of work are destroyed and the internal energy increases by 170 J. If the temperature of the system rises by 10 K, what is the heat capacity of the system?

(c) What is the connection between Hess's law and the fact that enthalpy is a state function?

(d) Plot the value of $(\mu - \mu_0)/RT$ for an ideal gas as a function of pressure.

(e) At 298 K, calculate the value of ΔA for an isothermal expansion of one mole of an ideal gas from 10 L to 40 L.

(f) Suggest a physical interpretation of the dependence of the Gibbs energy on the temperature.

(g) Ice is melted at 273 K and 1 atm.— State which of ΔU, ΔH, ΔS, ΔS_{univ}, ΔA and ΔG must be zero for the process.

(h) Define ionic mobility and mention its unit.

(i) Define standard electrode potential.

(j) Define equivalent conductance of an electrolyte solution (without using its relation with specific conductance). What is its C.G.S. unit?

(k) 'Joule's Experiment is an isenthalpic process.'— Comment on the statement.

(l) Why is a dilute solution of ammonium acetate itself a buffer?

2. (a) Evaluate the value of $\left(\frac{\partial C_V}{\partial V}\right)_T$ for a van der Waals gas.

(b) The coefficient of thermal expansion α of copper at 298 K is 5.00×10^{-5} K^{-1} and its isothermal compressibility β is 7.85×10^{-7} atm^{-1}. Given that the density of copper is 8.92 gm cm^{-3} at 298 K. Calculate the value of $\bar{C}_P - \bar{C}_V$ for copper. [Given molar mass of Cu = 63.54 gm mol^{-1}] 2+3

3. (a) Derive the equation that shows temperature dependence of enthalpy change of a reaction.

(b) Distinguish between 'Bond energy' and 'Bond dissociation energy'. 3+2

4. (a) Show that for any reversible cycle (not necessarily a Carnot Cycle), $\oint \frac{dq_{rev}}{T} = 0$.

(b) One mole of CO is transformed from 298 K and 5 atm. to 398 K and 2 atm. If $\bar{C}_P / R = (3.1916 + 0.9241 \times 10^{-3}T - 1.410 \times 10^{-7}T^2)$, calculate ΔS assuming the gas to be ideal. 3+2

5. (a) Show that for a gas obeying equation $P\bar{V} = RT(1 + bP)$, where 'b' is constant, the following relations held good : (i) $\left(\frac{\partial U}{\partial V}\right)_T = bP^2$ (ii) $\mu_{J,T} = 0$. Comment on the value of $\mu_{J,T}$.

(b) Comment on the validity of the relation, $\Delta H = q$, for the process in which pressure is not constant throughout, but the initial and the final pressures are same. 3+2

6. (a) Using Maxwell's relation, show that

$$Tds = C_V dT + T\left(\frac{\partial P}{\partial T}\right)_V dV$$

$$= C_P dT - T\left(\frac{\partial V}{\partial T}\right)_P dP$$

(b) Show that for a multi-component open system, where G is a function of pressure, temperature and composition of different components, $\left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j\neq i}} = \left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_{j\neq i}}$. 3+2

7. (a) A gas 'A' isomerizes to 'B' according to the reaction, $A \rightarrow B$ and forms an ideal gas mixture with equilibrium constant, K_P. Starting with 1 mole of pure 'A' at 1 atm., the gas is allowed to isomerise at constant T and P until it reaches equilibrium.

(i) Express the free energy change (ΔG) as a function of x, where x is the number of moles of 'B' at any time during the course of reaction.

(ii) Show the equilibrium, $\Delta G^\circ = \mu_B^\circ - \mu_A^\circ$

$$= -RT \ln K_P$$

$$= -RT \ln \frac{x_e}{1 - x_e},$$

where x_e is the number of moles of 'B' at equilibrium.

(b) Nitrogen trioxide dissociates according to the equation $N_2O_3(g) \rightleftharpoons NO_2(g) + NO(g)$.

At 298 K and 1 atm. total pressure, the degree of dissociation is 0.30. Calculate ΔG^o for this reaction at 298 K. 3+2

8. (a) Discuss the relaxation effect and electrophoretic effect in the light of the Debye-Hückel theory.

(b) At 291 K, the mobility at infinite dilution of the ammonium ion is 6.6×10^{-4} cm^2 V^{-1}S^{-1}, while that of the chlorate ion is 5.7×10^{-4} cm^2 V^{-1}S^{-1}. Calculate Λ^o_{eq} of ammonium chlorate and the transport number of the two ions. 3+2

9. (a) Consider the hydrolysis of a salt (BCl) formed from a strong acid and weak base. Show that,

$$[H_3O^+]^3 K_b + [H_3O^+]^2 K_w - (K_b + C)K_w\left[H_3\overset{+}{O}\right] - K_w^2 = 0,$$

where C is the concentration of the salt in water, K_b is the dissociation constant of the weak base.

Simplifying the above expression, show that; $pH = \frac{1}{2}pK_w - \frac{1}{2}pK_b - \frac{1}{2}\log C$.

(b) Calculate the ionic strength of a solution obtained by mixing aqueous solution of 25 ml of 0.02 M K_2SO_4 and 0.02 M urea. 3+2

10. (a) How can you determine the degree of hydrolysis and the hydrolytic constant from the conductance measurement of the solution of a salt from a weak acid? (e.g., aniline hydrochloride)

(b) $\Delta_f G^\circ_{298}$ values for $K^+(aq)$, $Cl^-(aq)$ and KCl(s) are -283.3 KJ mol^{-1}, -131.2 KJ mol^{-1} and -409.2 KJ mol^{-1}, respectively. Find K_{sp} for KCl in water at 25°C. 3+2

11. (a) How can you determine the ionic product of water (K_w) from e.m.f. measurement?

(b) Calculate the E.M.F. of the electrode-concentration cell :

$$Hg - Zn(C_1)|\ Zn^{2+}(aq)\ |Hg - Zn(C_2) \text{ at } 25°C,$$

if the concentrations of the zinc amalgam are :

$C_1 = 2$ gm of Zn/100 gm of Hg and $C_2 = 1$ gm of Zn/100 gm of Hg. 3+2

12. (a) Show that pressure of an ideal gas is a state function.

(b) Calculate the entropy change when,

(i) one mole of He and one mole of H_2 are mixed at constant temperature (298 K).

(ii) one mole of He is mixed with one mole of He at constant temperature (298 K). 2+3

13. (a) Derive the equations showing the temperature dependence of G and G/T at a constant pressure.

(b) One mole of oxygen expands adiabatically against a constant external pressure of 1 atm. until the pressure balances. The initial temperature and volume are 473 K and 20 L respectively. Calculate the final temperature and the work done. 3+2

2023

CHEMISTRY — HONOURS

Paper : CC-6

(Inorganic Chemistry)

Full Marks : 50

The figures in the margin indicate full marks.

Candidates are required to give their answers in their own words as far as practicable.

Question no. **1** is compulsory and answer ***any eight*** questions from the rest.

1. Answer ***any ten*** questions : 1×10

(a) Arrange the following in order of their increasing size :
H^-, F^-, Cl^- and Br^-.

(b) Between white phosphorus and red phosphorus, which one is less reactive?

(c) Draw the VSEPR structure of PH_4^+.

(d) Give an example of clathrate compound.

(e) Cite an example of coordination isomer.

(f) Give the products of the reaction : $BF_3 + EtOH \rightarrow$?

(g) In which estimation $S_2O_8^{2-}$ is used as an oxidizing agent?

(h) Write the formula of pentaammine(dinitrogen)ruthenium(III)chloride.

(i) Write one example of innermetallic complex.

(j) Find the most stable dihalide : $SnCl_2$, $GeCl_2$, $PbCl_2$.

(k) Give an example of paramagnetic nitrogen oxide.

(l) What is Wij's solution?

2. (a) How does the structure of graphite account for its use as (i) lubricant (ii) electrodes?

(b) Write down a chemical reaction to establish the basic properties of halogens. 3+2

3. (a) Calculate the electronegativity of chlorine in the Mulliken's scale. Hence, find out the electronegativity in the Pauling's scale. EA of Cl = 4.0 eV/atom, I.E. of Cl = 13 eV/atom.

(b) Show that BH_3 can behave as both electron acceptor and donor in the adduct $OC.BH_3$. 3+2

4. (a) Explain the greater oxidizing power of selenate and tellurate than that of sulfate.

(b) Aqueous solution of Be^{2+} salt is acidic in nature. Explain. 3+2

5. (a) Justify the ionization energy values of the following elements :

Element	I_1 (eV)	I_2 (eV)
Ga	5.99	20.51
Ge	7.89	15.93
As	9.81	18.63

(b) A mixture of $FeSO_4$ and $(NH_4)_2SO_4$ (1:1 mole ratio) in aqueous solution gives the test for Fe^{2+} while a mixture of $CuSO_4$ and NH_4OH (excess) does not give the test for Cu^{2+}. Justify. 3+2

6. (a) 'C' shows highest catenation property among C, Si and Ge.— Justify with suitable compounds.

(b) How trace amount of Al^{3+} can be detected using chelating ligand? Provide the structure and colour of the chelate. 3+2

7. (a) Complete the following reactions :

(i) $NaNH_2 + N_2O \longrightarrow$

(ii) $KBrF_4 \xrightarrow{\Delta}$

(iii) $XeF_6 + H_2O \longrightarrow$

(b) What happens when NO_2 gas is cooled? Mention the visual change, if any. 3+2

8. (a) What are phosphazenes? P-N bond distances in $P_3N_3F_6$ are shorter than those in $P_3N_3Cl_6$. — Explain.

(b) $F-\widehat{Xe}-O$ angle in $XeOF_4$ is nearly 90°. — Justify. 3+2

9. (a) Using VSEPR theory, justify the expected trend of $O-\widehat{N}-O$ bond angles in NO_2^+, NO_2 and NO_2^-.

(b) What abnormal properties of liquid Helium are observed when it is cooled below 2K? 3+2

10. (a) Compare the basicities of tri-metaphosphoric acid and tri-polyphosphoric acid from their structures.

(b) Write down the structure of an optically active purely inorganic complex. 3+2

11. (a) Write down the postulates of Werner's theory with suitable examples.

(b) There are no stable sulfur analogues of CO and NO. — Explain. 3+2

12. (a) Reducing property of hydrides increases in going from top to bottom in any group. Justify your answer with suitable reactions.

(b) Atomic size of niobium ($Z = 41$) and tantalum ($Z = 73$) are almost identical. — Justify. 3+2

13. (a) Compare the hydrolysis products of Me_3SiCl and Me_3CCl with proper reason.

(b) Mercury is liquid at room temperature. Explain. 3+2

2023

CHEMISTRY — HONOURS

Paper : CC-7

(Organic Chemistry)

Full Marks : 50

The figures in the margin indicate full marks.

Candidates are required to give their answers in their own words as far as practicable.

Answer ***question no.*** **1** (Compulsory) and ***any eight*** (8) questions from the rest (from ***question no.*** **2** to ***question no.*** **12**).

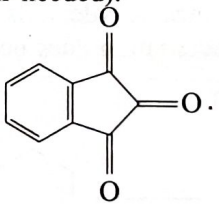
1. Answer ***any ten*** questions : 1×10

(a) Nitrobenzene is commonly used as a solvent in Friedel-Crafts reaction. Explain why.

(b) Convert ethanal into ethylethanoate in one step (no mechanism needed).

(c) $C_5H_{11}CH_2CH_2OH \xleftarrow{\underline{B}} C_5H_{11}-CH=CH_2 \xrightarrow{\underline{A}} C_5H_{11}CH(OH)CH_3$

Indicate the reagents **A** and **B**. (No mechanism needed).

(d) Write down the structure of stable hydrate of  .

(e) Define ylide with an example.

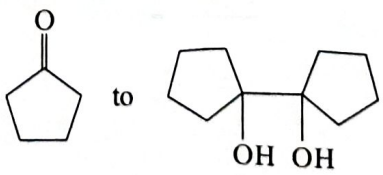
(f) Draw the structural formula of the alkene which on ozonolysis yields only 2-butanone.

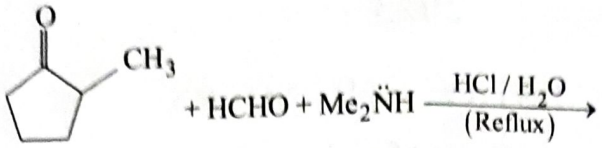
(g) Mention the major product formed when benzene reacts with 1-chlorobutane under Friedel-Crafts alkylation conditions.

(h) Draw the structure of the major product formed when N, N-dimethylaniline reacts with N-phenyl-N-methylformamide and $POCl_3$ followed by hydrolysis. (No mechanism needed).

(i) Explain briefly why β-hydroxy esters can be prepared by the Reformatsky reaction but not by Grignard reaction.

(j) Draw the structural formula of the product formed when salicylaldehyde is condensed with anhydrous acetic anhydride in presence of sodium acetate followed by hydrolysis. (No mechanism needed).

(k) Convert (reagents only) : 

(l) 

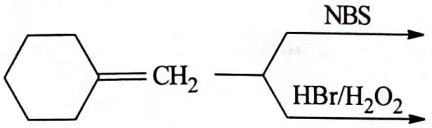
Indicate the major product only in the above reaction (No mechanism needed).

2. (a) Explain why acetone is formed when $H_2C = C = CH_2$ is subjected to acid catalysed hydration and not the alternative product. Give mechanism.

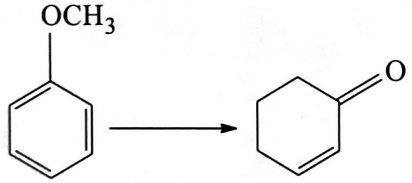
(b) Benzaldehyde undergoes Cannizzaro reaction whereas N, N-dimethylbenzaldehyde does not. Justify. 3+2

3. (a) Compound **C** (C_8H_{12}) produces butanedial ($O=\overset{H}{\overset{|}{C}}-CH_2CH_2-\overset{H}{\overset{|}{C}}=O$) as the only product when treated with O_3 followed by reductive work up with Zn/H_2O. Identify **C** with structural formula while justifying your answer.

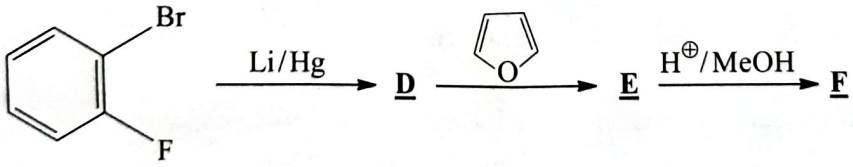
(b) Write the structure of the major products in the following reactions with explanation : 3+2



4. (a) *para*-Dimethylaminobenzaldehyde fails to undergo benzoin condensation but when mixed with benzaldehyde, the condensation does occur. Explain.

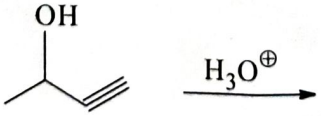
(b) Convert : 

3+2

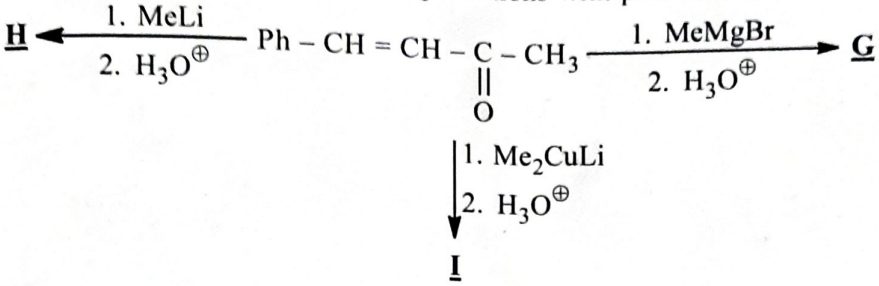
5. (a) 

Identify **D**, **E**, and **F**. Suggest a mechanism for the formation of **F** from **E**.

(b) Give the product of the following reaction with plausible mechanism : 3+2



6. (a) Give the products of the following reactions with plausible mechanism :



(b) Acetanilide undergoes nitration with $Ac_2O - HNO_3$ predominantly at the *ortho* position. Explain the observation with plausible mechanism. 3+2

7. (a) Which of the following two compounds will undergo nucleophilic substitution reaction at a faster rate and why?

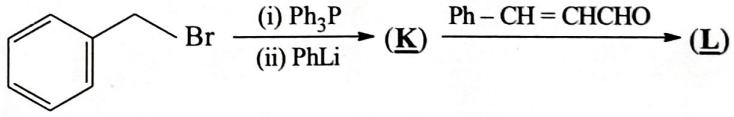
(i) 2, 6 - Dimethyl - 4 - nitrochlorobenzene

(ii) 3, 5 - Dimethyl - 4 - nitrochlorobenzene

(b) Predict the product of the following reaction with mechanism.

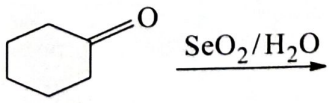
$$PhCHO + CH_3COCH_2CH_3 \xrightarrow{H_3O^{\oplus}} \underline{J}$$ 3+2

8. (a) Identify the products (**K**) and (**L**) in the following reactions with plausible mechanism in each case :



(b) Chloral ($Cl_3C–\overset{\overset{O}{\|}}{C}–H$) does not undergo Cannizzaro reaction though it has no α-hydrogen atom. Explain. 3+2

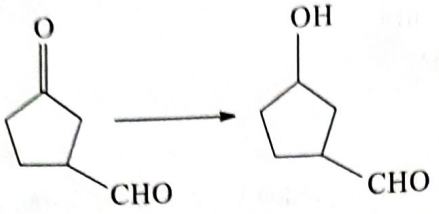
9. (a) Give the product and mechanism of the following reaction ;



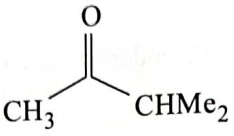
(b) Convert : $CH_3CH_2C \equiv C - H \longrightarrow CH_3CH_2CH_2CHO$ (No mechanism needed). 3+2

10. (a) CF_3CHO reacts rapidly with ethanol to form the corresponding hemiacetal. However, it gives acetal very slowly in the presence of anhydrous acid. Explain for the observation with reaction mechanism.

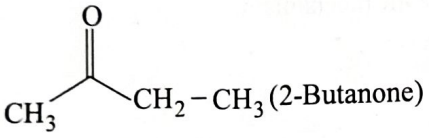
(b) How can you accomplish the following transformations?

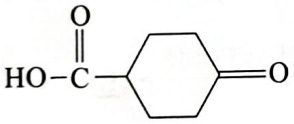
(i) 

(No mechanism needed)

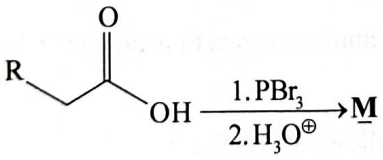
(ii) $CH_3CHO \longrightarrow$  (No mechanism needed) 3+2

11. (a) Show how diethyl malonate can be used to prepare the following molecules :

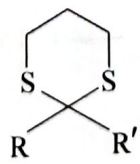
(i)  (2-Butanone)

(ii) 

(b) Predict the product(s) of the following reaction with plausible mechanism : 3+2



12. (a) 1,3-Dithiane (**N**) is cleaved to the corresponding carbonyl compound in presence of $HgCl_2/CdCO_3$ but not with acid or alkali. Explain.

 (**N**)

(b) Give the mechanism for the reduction of a ketone with $LiAlH_4$ followed by acid treatment. Explain the role of $Li^{\oplus}$ ion regarding this reduction. 3+2

2023

CHEMISTRY — HONOURS

Paper : SEC-A-1 and SEC-A-2

The figures in the margin indicate full marks.

Candidates are required to give their answers in their own words as far as practicable.

Paper : SEC-A-1

(Mathematics and Statistics for Chemists)

Full Marks : 80

Answer ***question no.*** **1** (compulsory) and ***any twelve*** questions from the rest.

1. Answer the following questions : 1×20

(a) If $\frac{\partial^2 z}{\partial x \partial y} = \frac{\partial^2 z}{\partial y \partial x}$ for a function $z = f(x, y)$, what does the equality signify?

(b) What are the mathematical criteria for $P = f(V)$ to show a minimum at a point V_1?

(c) One cannot evaluate the limit $\lim_{x \to 0} \frac{\sin x}{x}$ as the value seems to be $\frac{0}{0}$. Is it true?

(d) Justify that $x = 0$ is the only point of inflection for the function $f(x) = x^3$.

(e) How det (***AB***) is related to the individual determinants det(***A***) and det(***B***)?

(f) What do you mean by a diagonal matrix and an identity matrix?

(g) A single 6-sided die is rolled. What is the probability of rolling a **2** or a **5**?

(h) Correct the statement : For independent events, probability is additive, not multiplicative.

(i) Put proper suffixes to complete the following relation :

$$\left(\frac{\partial x}{\partial y}\right)\left(\frac{\partial y}{\partial z}\right)\left(\frac{\partial z}{\partial x}\right) = -1$$

(j) Explain why $f(x) = \ln(x)$ has no Maclaurine expansion.

(k) An odd function $f(x)$ can be expanded in the Fourier series as $f(x) = \sum b_n \sin nx$. Give the integral expression of b_n.

(l) A square matrix A is called orthogonal if

(i) $A = A^2$ (ii) $A' = A^{-1}$ (iii) $A \cdot A^{-1} = I$

Choose the correct answer.

Paper : SEC-A-2

(Analytical Clinical Biochemistry)

Full Marks : 80

Answer ***question no.*** **1** (compulsory) and ***any twelve*** questions from the rest.

1. Answer ***any twenty*** questions : 1×20

(a) Name the sugar present in the chemical structure of nucleic acid (structure not needed).

(b) If the amino acid glycine has pK_a= 2.34 and pK_b= 9.6, then what is its pI?

(c) Name a chemical which prevents clotting of blood.

(d) How many hydrogen bonds are present between G and C in a DNA?

(e) What is called as the active site of an enzyme?

(f) Mention any two types of secondary structures of protein.

(g) What is a prosthetic group?

(h) Write down the name of a sulphur containing amino acid (no structure needed).

(i) Name an amino acid which has no chiral centre (name only).

(j) Give an example of a conjugated protein.

(k) Which sugar is commonly called an 'invert sugar'?

(l) What is formed when two amino acids are joined by a peptide bond?

(m) Name the class of enzymes that causes cleavage of bonds.

(n) Name a compound which is found in all living cells and play a key role in energy transformation.

(o) Name a physical agent and a chemical agent that causes denaturation of proteins.

(p) Give an example of anticoagulating agent of blood.

(q) Name one base present in DNA.

(r) Name the most abundant animal sterol.

(s) Name the metabolic waste product resulting from the breakdown of creatinine.

(t) What is metabolism?

(u) Draw the chemical structure of glycine.

(v) What type of reaction is done by the enzyme isomerase?

(w) What is coagulation of blood?

(x) In which cellular organelle does the TCA cycle take place?

2. (a) What is TCA cycle? Why is it called amphibolic in nature?
   (b) Oxaloacetate plays a catalytic role in TCA cycle. Justify. 3+2

3. (a) Define glycolysis. Write down the regulatory steps of glycolysis.
   (b) Glycolysis proceeds even in the absence of oxygen. Why? 3+2

4. (a) What is the secondary structure of a protein?
   (b) State the essential characteristics of α-helix structure of a protein. 3+2

5. (a) Illustrate with examples the competitive and non-competitive inhibition of enzymes.
   (b) What is meant by allosteric regulation of enzymes? 3+2

6. (a) Name any six components present in normal urine.
   (b) What is renaturation of proteins? 3+2

7. (a) What is cholesterol? Mention the important biological function of cholesterol.
   (b) What is artherosclerosis? 3+2

8. Describe with a labelled diagram, various features of Watson and Crick model of DNA. 5

9. (a) What are liposomes? Mention one biological function of it.
   (b) Differentiate between fats and oils. 3+2

10. (a) How will you collect blood sample from a human being?
    (b) How will you preserve a blood sample after collecting from a patient? 3+2

11. (a) Write any three procedures (in brief) to denature a protein.
    (b) Write a brief note on the denaturation of proteins. 3+2

12. (a) What are pernicious anaemia and hemolytic anaemia?
    (b) State the major complications of uncontrolled diabetes mellitus (*any two*). 3+2

13. (a) Mention three different types and functions of white blood cells.
    (b) Name two hormones that play important roles in regulation of sugar in blood. 3+2

14. Briefly explain the alcoholic fermentation and show the chemical reactions (writing of chemical structures not needed) involved. 5
