2023

CHEMISTRY — HONOURS

Paper : CC-11

(Physical Chemistry - 4)

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) Find out the average amplitude of oscillation $<x>$ of a harmonic oscillator in its ground state

$$\left(given\ \psi_0 = \left(\frac{a}{\pi}\right)^{\frac{1}{4}} e^{-\frac{ax^2}{2}} \right).$$

(b) What approximation method do we choose to solve a many-electron problem and why is it necessary?

(c) "The angular momentum operators $\widehat{L}_x, \widehat{L}_y$ and $\widehat{L}_z$ commute with each other."— Comment on the statement.

(d) How do cannonical and grand cannonical ensembles differ? Which type of systems do they describe?

(e) Name one paramagnetic salt that is generally used in the adiabatic demagnetization process.

(f) How would you define partition function of a system in a phase space?

(g) Why Trapezoidal rule is called so?

(h) "Though Newton-Raphson method converges rapidly, it requires more computing time."— Comment of the statement.

(i) Write down the potential energy $V(r)$ operator of a central force problem like Hydrogen atom.

(j) Can Maxwell-Boltzmann statistics to be applied to a system of real gas?— Explain.

(k) Why can not temperature below 1 Kelvin be obtained using liquid Helium?

(l) Write the expression of the Hamiltonian operator of the Helium atom in atomic unit.

2. (a) Find out the normalising factor of the wave function (ψ_1) of a harmonic oscillator at $v = 1$ level. Also show that ψ_0 and ψ_1 of a harmonic oscillator are orthogonal.

[Given : $\psi_0(x) = \left(\dfrac{\alpha}{\pi}\right)^{\frac{1}{4}} e^{\frac{-\alpha x^2}{2}}$; $\psi_1(x) = A.x.e^{\frac{-\alpha x^2}{2}}$, where A is the normalization constant.

Integration $\int\limits_0^\alpha x^{2n} e^{-\alpha x^2} dx = \dfrac{(2n)!}{2^{2n+1}.n!}\left(\dfrac{\pi}{\alpha^{2n+1}}\right)^{\frac{1}{2}}$, $\alpha > 0$ where n is a positive integer].

(b) Calculate the $\langle p_x^2 \rangle$ for harmonic oscillator in its ground state. 3+2

3. (a) Express the $\widehat{L^2}$ and $\widehat{L_y}$ in spherical polar coordinate and show whether they are simultaneously accurately measurable or not.

(b) Using the expression of $\widehat{L^2}$, find out the kinetic energy of a rigid rotator having the wave function

$Y_1^1(\theta, \phi) = \left(\dfrac{3}{8\pi}\right)^{\frac{1}{2}} \sin\theta e^{i\phi}$. 3+2

4. (a) Find out the probability density of finding the 1s electron of Hydrogen atom (with wave function

$\dfrac{1}{\sqrt{\pi}}\left(\dfrac{1}{a_0}\right)^{\frac{3}{2}} e^{-\frac{r}{a_0}}$) at the nucleus and at the first Bohr orbit a_0.

(b) Find out the probability of finding the 1s electron in the first Bohr orbit and at a distance of 1×10^{-4} a_0 from the nucleus. Comment on the result. 2+3

5. (a) Considering a trial wavefunction for the particle in a box (PIB) problem to be $\phi = x(L - x)$.

With appropriate boundary conditions, the Hamiltonian being $\hat{H} = -\dfrac{\hbar^2}{2m}\dfrac{\partial^2}{\partial x^2}$, the box being 1-D, find the expected ground state energy expression, where 'L' is the length of the 1-D box.

(b) What are the properties to be considered when we choose the trial wave function for a one-dimensional (PIB) box? 3+2

6. (a) State the Born-Oppenheimer approximation as used in LCAO method.

(b) State limitations of the LCAO-MO and V_B treatments of Hydrogen (3 each). 2+3

7. Show that the two maxima of $r^2\psi_{2s}(r)$ against r occur at $(3\pm\sqrt{5})a_0$. Find the nodal point for the radial distribution for ψ_{2s} wavefunction.

Given : $\psi_{2S} = \sqrt{\dfrac{1}{32\pi}} \cdot \left(\dfrac{1}{a_0}\right)^{\frac{3}{2}} \cdot \left(2-\dfrac{r}{a_0}\right)e^{-\frac{r}{2a_0}}$. 　　　　5

8. (a) Calculate the value of ln5! with and without Sterling's approximation. Comment on the result.

   (b) For a system having three energy levels 0, ϵ and 2ϵ, where $\epsilon = 4.267\times10^{-14}$ erg, find out the probability function $\left(\dfrac{1}{z}\right)$ at 300 K, 400 K and 800 K. Interpret the results. (where $z =$ partition function) 　　　　2½+2½

9. (a) Calculate the thermodynamic probabilities of arranging 6 classical particles among three energy levels having configurations (6,0,0), (5,1,0), (4,1,1), (3,2,1), (2,2,2) and (4,2,0). Show clearly which configuration will be the most dominating configuration.

   (b) Could you guess the above answer without doing any calculation? Explain. 　　　　3+2

10. (a) For a system the available energy levels are 0, ϵ, 2ϵ and 3ϵ, where $\epsilon = 4.14\times10^{-21}$ erg and the degeneracy of the levels are 1,1,3,5 respectively. Find out the molecular partition function at 300 K.

    (b) At what altitude, the atmospheric pressure gets reduced to its $\dfrac{1}{4}$ th? [Assume average value of temp = 250 K and the average molar mass = 0.029 kg mol^{-1}] 　　　　3+2

11. (a) One mole of an ideal gas is allowed to expand at 300 K from 1 lit to 5 lit. Find out the magnitude of the Boltzmann constant k.

    (b) In an experiment, the ratios of the number of molecules in the excited levels with respect to the ground level are given below :

$\epsilon_i - \epsilon_0$	$5\cdot52\times10^{-21}$ J	$1\cdot104\times10^{-20}$ J	$1\cdot104\times10^{-19}$ J
$n_i - n_0$	$0\cdot368$	$0\cdot135$	$2\cdot06\times10^{-9}$

Calculate the temperature of the system applying Boltzmann distribution law. 　　　　2½+2½

12. (a) Evaluate $I = \displaystyle\int_0^1 \dfrac{1}{1+x}dx$ correct to three decimal places, using $h = 0.5$ using both Trapezoidal and Simpson rules.

    (b) Comment on the accuracy of these two rules. (Given the exact value of the integral = 0.693147) 　　　　3+2

Please Turn Over

13. Determine the constants 'a' and 'b' by the method of least squares such that $y = a.e^{bx}$ fits the following sets of data : 5

| x	2	4	6	8	10
y	4·077	11·084	30·128	81·897	222·62

2023

CHEMISTRY — HONOURS

Paper : CC-12

### (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** questions from the rest (**question nos. 2** to **12**).

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

   (a) Explain why anthracene is more reactive than naphthalene towards Diels-Alder reaction.

   (b) What happens when pyridine is treated with sodamide ($NaNH_2$) in toluene and then quenched with water?

   (c) Draw the most stable conformation of *cis*- 1,4,-ditertiarybutylcyclohexane.

   (d) Give one example of [1, 5] sigmatropic rearrangement.

   (e) Write down the structure of one D-aldohexose that could be oxidised to *meso*- aldaric acid by nitric acid.

   (f) Draw the structure of the following tripeptide : Ala–Gly–Phe.

   (g) Name one aldohexose and one ketohexose which give the same osazone as D-mannose.

   (h) Why 1,4-disubstituted cyclohexanes are always achiral irrespective of the conformations and the nature of the substituents?

   (i) How do anomers differ from epimers?

   (j) Draw the preferred conformation of 1-methyl-1-phenylcyclohexane. (Structure only)

   (k) Write down the structure of Boc derivative of alanine.

   (l) Write down the reagent used in Sanger's method for N-terminal analysis of peptides.

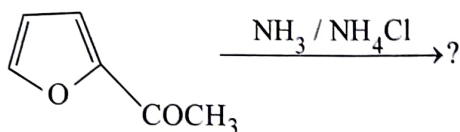   (m) Identify the product with stereochemistry of the following pericyclic reaction :
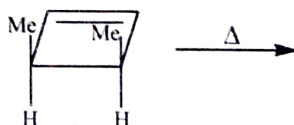
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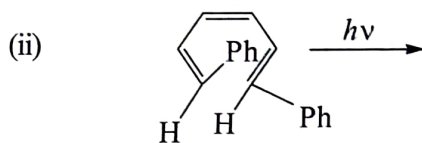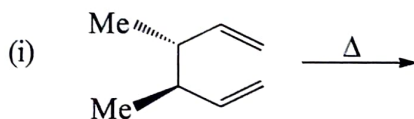
2. (a) Carry out the following transformation :

Phenanthrene →
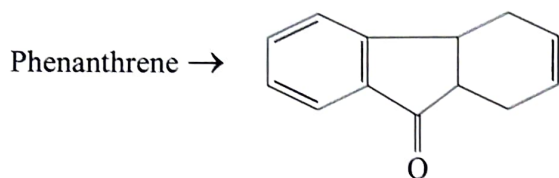
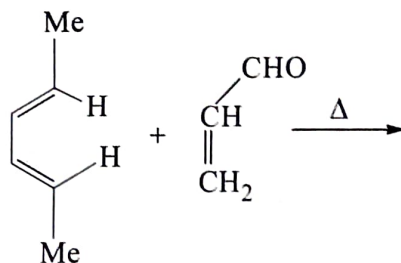(b) Predict the product with mechanism :   3+2

$$\xrightarrow{\text{NH}_3 / \text{NH}_4\text{Cl}} ?$$

3. (a) Predict the products with stereochemistry of the following reactions :

(i)

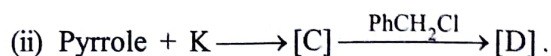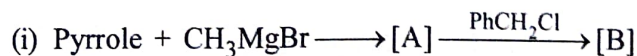 $\xrightarrow{\Delta}$

(ii)

      $\xrightarrow{hv}$

(b) Predict the major product of the following reaction from FMO consideration :

1½+1½+2

4. (a) Pyridine N-oxide is more reactive towards both electrophiles and nucleophiles. Explain.

(b) Complete the following sequence of reactions :

(i) Pyrrole + $CH_3MgBr \longrightarrow [A] \xrightarrow{\text{PhCH}_2\text{Cl}} [B]$

(ii) Pyrrole + $K \longrightarrow [C] \xrightarrow{\text{PhCH}_2\text{Cl}} [D]$.   3+2

5. (a) When D-glucose is treated with aqueous $Ca(OH)_2$ and the solution is allowed to stand for several days, a mixture of products results including D-mannose, D-fructose and D-glucose. Account for the mechanism of the reaction.

(b) Why is sucrose called a non-reducing sugar? Explain with structure.   3+2

6. (a) When *trans*-4-tertiarybutylcyclohexylamine is treated with nitrous acid (HNO_2), the corresponding alcohol with retention of configuration is obtained; but in case of *cis*- isomer, cyclohexene is obtained. Explain with mechanism.

   (b) *trans*-1,2-diaxial cyclohexanehalohydrins undergo epoxidation several times faster than the diequatorial isomer. Explain.   3+2

7. (a) In thermal ring opening of *trans*-3,4-dimethylcyclobutane, two isomeric products are expected to be formed by the allowed conrotatory mode of rotation. However, only one product is obtained. Explain this observation.

   (b) Account for the fact that in cycloaddition reaction of cyclopentadiene with maleic anhydride, the less stable *endo*-adduct predominantes. Explain by orbital interaction.   3+2

8. (a) How can you determine N-terminal amino acid of a peptide chain by Edman method? What advantage does it offer over Sanger's method?

   (b) How would you synthesise (±)-methionine using Strecker's method?   3+2

9. (a) Compare the rates of chromic acid oxidation of the following compounds with explanation.

and
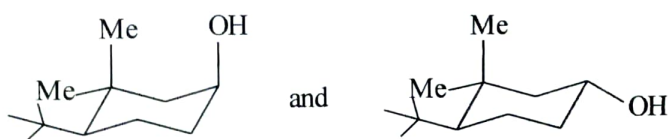
   (b) Predict the products of the following with suitable mechanism :   3+2

10. (a) Using solid phase peptide synthesis, prepare the dipeptide Ala – Gly.

    (b) How can lysine (pI = 9.7) be separated from alanine (pI = 6.0) by electrophoresis?   3+2

11. (a) Explain the course of the following reaction mechanistically :

(α-D-Glucopyranose)   (β-D-Glucopyranose)
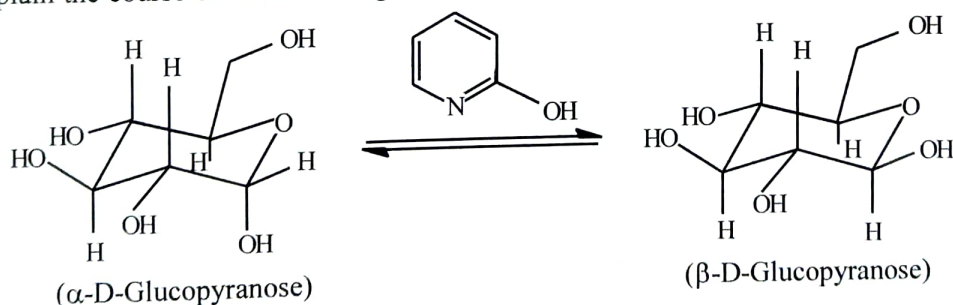
    (b) Identify the compounds [E] to [H] in the following sequence of reactions :   3+2
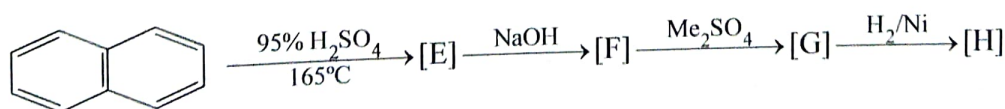
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12. (a) Explain the formation of different isomeric heterocyclic products obtained from reaction of ethyl acetoacetate and α-chloroacetone in the presence of
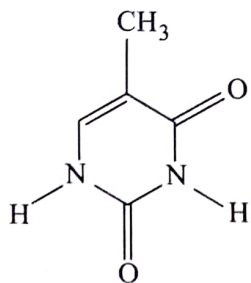
(i) aqueous NaOH.

(ii) NaI / EtOH / NaOEt followed by heating with oxalic acid at 100°C-150°C

(b)

(i) Name the base as shown above.

(ii) Name its complementary base present in DNA. (Structure not needed)   3+2

2023

CHEMISTRY — HONOURS

Paper : DSE-A-1 and DSE-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 : DSE-A-1

(Molecular Modelling and Drug Design)

Full Marks : 50

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

1. Answer *any ten* questions : 1×10

   (a) What are the internal coordinates of a molecule?

   (b) What are non-covalent interactions?

   (c) Write an expression to estimate the bond-angle distortion energy identifying the parameters used in the expression.

   (d) What are local and global minima of a molecule?

   (e) Write an expression for Coulomb interaction energy between two point charges, identifying the parameters used in the expression.

   (f) What is the significance of 'time step' in a Molecular Dynamics simulation?

   (g) While running a molecular dynamics simulation, what are most commonly stored in the computer?

   (h) What is a ligand?

   (i) In a Molecular Dynamics simulation how the kinetic energy of a molecule is calculated?

   (j) What is the criterion for selection of a successful step in Monte Carlo method?

   (k) What is meant by 'stable conformation' of a molecule?

2. What is a potential energy surface? For a molecule containing N atoms comment on the dimensionality of its potential energy surface. What does the slope at a particular point on the surface signify? 2+1+2

3. Write a short note on Steepest Descent method for energy minimization. 5

4. What is a scoring function? How are they used in molecular docking? 2+3

Please Turn Over

Paper : DSE-A-2

(Applications of Computers in Chemistry)

Full Marks : 50

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

1×10

1. Answer *any ten* questions :

   (a) Give appropriate statement(s) in Fortran for evaluating value of 11 divided by 2.

   (b) Translate the following algebraic expression to Fortran :

   $$\left(3 + \frac{a}{b}\right)^{m-1}$$

   (c) Distinguish between a function subprogram and a subroutine subprogram (at least 2 points of difference).

   (d) Translate the following Fortran expression to algebraic form :

   $$\text{ABS(SQRT(X} - \text{Y**3)} - \text{Z**3/COS(A + B))}$$

   (e) Atomic masses of the following elements are typed into cells given in parenthesis: Hydrogen (B2), Phosphorus (C2), Oxygen (D2). The molar mass of phosphoric acid is to be calculated in D5. What formula is to be typed in cell D5?

   (f) In the following Excel spreadsheet:

	A	B	C	D
1	1	5	4	?

   Cell C1 has been generated using formula = B1 – A1. The cell C1 has been copied and simply pasted in cell D1. Find out the value in cell D1.

   (g) For a set of data points (x, y), typed in column A and B in a spreadsheet, mention two methods using inbuilt Excel function to find the slope and intercept of the best fit line.

   (h) Give syntax for the library function MMULT in Excel. What does it perform?

   (i) What Excel function will calculate Fischer F value at 95% probability?

   (j) What are Type-I and Type-II error in Hypothesis testing?

Please Turn Over

(k) How will the nature of normal distribution change if we increase standard deviation keeping the mean constant?

(l) Consider the following spreadsheet :

1.	A	B	C
2.	x	$f(x)$	$f'(x)$
3.	0	12	
4.	5	15	
5.	10	16	

Find the derivative $f'(x)$ at $x = 5$ by using a suitable formula for differentiation.

2. (a) Give appropriate statement to open an output file 'OUTPUT.DAT'. Also give the write statement in the Fortran program.

(b) A first-order reaction proceeds with rate constant k_1. Reading the value of k_1, write a Fortran program to find out the time of completion of 80% of the reaction. 2+3

3. (a) Write a program using DO LOOP to find the sum of first 10 positive integers.

(b) Find the output of the following program :

```
INTEGER  A(10)
DO  I = 1,10,2
A(I) = 2*I - 3
A(I + 1) = I**2 - 5
END DO
WRITE  (*,*)  (A(I),I = 1,10)
END
```
2+3

4. Read the following matrices A and B from the input file :

$$A = \begin{pmatrix} 1.0 & 2.5 & 3.2 \\ 3.1 & -2.4 & 1.9 \end{pmatrix} \quad B = \begin{pmatrix} 3.0 & 2.1 \\ 1.0 & -1.2 \\ 1.2 & 0.9 \end{pmatrix}$$

Write a Fortran program to multiply the above two matrices and write the product matrix $AB = C$ to an output file. 5

5. (a) Write a program to identify the largest 5 numbers read into an one-dimensional array.

(b) Write a program which calculates the sum of the following series : $\dfrac{1}{2} + \dfrac{2}{3} + \dfrac{3}{4} + ... + \dfrac{99}{100}$.

3+2

6. (a) For titrating 10 ml of a 0.1(N) solution with a 0.1(N) titrant, the following volume of titrant were obtained by the analyst :

   Analyst A :   9.8,   9.91,   9.85,   10.08,   10.25 (ml)

   Analyst B : 10.09, 10.12, 10.10, 10.12, 10.08 (ml)

   Calculate the mean and standard deviation for the above two sets of results and hence comment on the accuracy and precision of the results.

   (b) How can we represent the above calculation in Excel spreadsheet?   3+2

7. (a) Consider a fourth order polynomial of the form $ax^4 + bx^3 + cx^2 + dx + e = 0$, where a, b, c, d, e are known quantities. Describe a step by step Excel procedure to find out the maxima or minima of the function using GOALSEEK.

   (b) Mention the syntax of the LINEST function and its corresponding arguments.   3+2

8. The following table shows the value of the acceleration due to gravity 'g' obtained through experiment.

 | $g(m/s^2)$ | 9.68 | 9.85 | 9.73 | 9.76 | 9.74 |
   |---|---|---|---|---|---|

   (a) Is the mean of the values significantly different statistically from a hypothesised value of $g = 9.81$ m/s²?

   (b) Test the hypothesis at the $\alpha = 0.05$ level of significance given t_{crit} with $\alpha = 0.05$ and $\gamma = 4$ is 2.776.
                                                                                         3+2

9. In thermodynamics, it is known that the entropy change of a system that is heated at constant pressure from temperature T_1 to temperature T_2 is given by $\Delta S = \int_{T_1}^{T_2} \left(C_P/T \right) dT$, where C_p is the constant-pressure molar heat capacity and T is the temperature on the Kelvin scale. Calculate ΔS for the heating of 1.00 mol of solid zinc from 20.0 K to 100.0 K by carrying out a five-point integration using Trapezoidal Rule. The C_p values corresponding to different temperatures are given below. Determine the different Excel quantities using calculator.

T (Kelvin)	C_p (J/mol/K)
20	1.7
40	8.171
60	13.6
80	16.87
100	19.15

   5

10. The water-gas reaction shown below has an equilibrium constant value of 0.106 at 700 K. The reaction was started using 0.150(M) each of hydrogen and carbon dioxide, respectively. Make a rough sketch of an Excel Spreadsheet and describe step by step how you would find the equilibrium composition of all chemical species using SOLVER.

$$H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$$
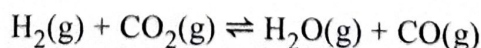
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Please Turn Over

11 (a) For the titration of weak mono-protic acid HA with a strong base MOH, deduce the following explicit expression for the titration curve :

$$\frac{V_b}{V_a} = \frac{C_a\left(\dfrac{[A^-]}{[HA]+[A^-]}\right) - \left([H^+]-[OH^-]\right)}{C_b + \left([H^+] - \dfrac{K_W}{[H^+]}\right)},$$

where,

C_a is the concentrations of acid HA

C_b is the concentrations of base MOH

V_a and V_b are the volumes of the acid and base respectively.

(b) Describe the step by step Excel procedure to generate the pH-metric titration curve using SOLVER function.   3+2

12. Why do we use t-test in chemical analysis? For the two-sample t-test whose standard deviations are not significantly different, state null and alternate hypothesis. Write down the mathematical expression for calculating t-statistics. What Excel function will you use to determine t-statistics? Write down the syntax of the function and explain the arguments.   5

13. (a) How will you use Excel to calculate the area under the curve between $x = 46$ and $x = 51$ for normally distributed data with mean = 50 and standard deviation = 4?

46   51

x ⟶
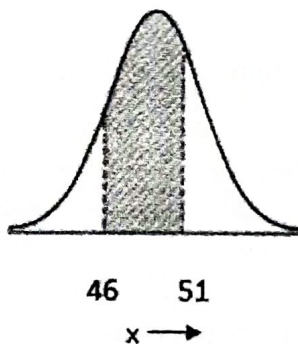
(b) What is the difference between population standard deviation and sample standard deviation? Give mathematical formula for them.   3+2

2023

CHEMISTRY — HONOURS

Paper : DSE-B-1 and DSE-B-2

(Inorganic Materials of Industrial Importance)

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.

Paper : DSE-B-1

(Inorganic Materials of Industrial Importance)

Full Marks : 50

Answer **question no. 1** (compulsory) and **any eight** questions from the rest (**question nos. 2 to 13**).

1. Answer the following questions (**any ten**) :
   1×10
   (a) What is the role of linseed oil in varnish?
   (b) What makes steel stainless?
   (c) Mention one role of plasticizer added to a paint.
   (d) State any one application of Monel metal.
   (e) Give an example of a super+*+*+*/conducting oxide.
   (f) What is muriate of potash?
   (g) Which type of cement is used in underwater constructions?
   (h) Name the principal constituent of white paint.
   (i) Cite one example each of a primary and a secondary explosive.
   (j) Which common element is present in brass and bronze?
   (k) What is the composition of clay?
   (l) Mention any one industrial application of heterogeneous catalysis.

2. (a) Which compound(s) is (are) used to give—
      (i) amber colour,   (ii) blue colour,   (iii) purple colour to glass?
   (b) Compare the properties of solid and liquid propellants.
   3+2

Please Turn Over

3. (a) What are carbon nanotubes? State any one application of carbon nanotubes.

   (b) What is vehicle? 3+2

4. (a) State the composition and properties of borosilicate glass.

   (b) Explain the process— 'Carburizing'. 3+2

5. (a) The following equation shows reaction products of the molecular explosive PETN ($C_5H_8N_4O_{12}$).

$$C_5H_8N_4O_{12} \rightarrow 4CO_2 + 4H_2O + 2N_2 + C$$

   Calculate the oxygen balance for PETN.

   (b) What is meant by 'Acid pickling'? State its use. 3+2

6. (a) Write down with equations the working principle of Pb–acid battery.

   (b) What are the differences between glass and ceramics? 3+2

7. (a) How is calcium ammonium nitrate manufactured? Construct the flow chart diagram for the above manufacturing process.

   (b) Discuss the chemical changes that occur during the setting of cement. 3+2

8. (a) What is the basic difference between an emulsion paint and an ordinary paint? Give the approximate formulation of an ordinary paint.

   (b) What are the active materials used in the fabrication of solar cells? 3+2

9. (a) What are fillers? Cite an example. Write down the functions of fillers in a paint.

   (b) Distinguish between drying oils and semi-drying oils. 3+2

10. (a) Explain the two commonly used techniques for metal spraying. Why is sand blasting done on the metal surface prior to spraying?

    (b) What is the function of gypsum in cement? 3+2

11. (a) Differentiate between ferrous and non-ferrous alloys with examples.

    (b) Explain the role of a phase transfer catalyst with the help of a suitable example. 3+2

12. (a) What is glazing? State two advantages of glazed ceramics.

    (b) Write down one advantage and one disadvantage of Ni-Cd batteries. 3+2

13. (a) What are the objectives of electroplating? Mention the difference between electroplating and electroless plating.

    (b) What is an eco-friendly paint? 3+2