## INSTRUCTIONS

1. This question-cum-answer booklet has $\mathbf{4 0}$ pages and has 44 questions. Please ensure that the copy of the question-cum-answer booklet you have received contains all the questions.
2. Write your Registration Number, Name and the name of the Test Centre in the appropriate space provided on the right side.
3. Write the answers to the objective questions against each Question No. in the Answer Table for Objective Questions, provided on Page No. 7. Do not write anything else on this page.
4. Each objective question has $\mathbf{4}$ choices for its answer: (A), (B), (C) and (D). Only ONE of them is the correct answer. There will be negative marking for wrong answers to objective questions. The following marking scheme for objective questions shall be used:
(a) For each correct answer, you will be awarded 3 (Three) marks.
(b) For each wrong answer, you will be awarded -1 (Negative one) mark.
(c) Multiple answers to a question will be treated as a wrong answer.
(d) For each un-attempted question, you will be awarded 0 (Zero) mark.
(e) Negative marks for objective part will be carried over to total marks.
5. Answer the subjective question only in the space provided after each question.
6. Do not write more than one answer for the same question. In case you attempt a subjective question more than once, please cancel the answer(s) you consider wrong. Otherwise, the answer appearing last only will be evaluated.
7. All answers must be written in blue/black/blueblack ink only. Sketch pen, pencil or ink of any other colour should not be used.
8. All rough work should be done in the space provided and scored out finally.
9. No supplementary sheets will be provided to the candidates.
10. Clip board, log tables, slide rule, calculator, cellular phone and electronic gadgets in any form are NOT allowed.
11. The question-cum-answer booklet must be returned in its entirety to the Invigilator before leaving the examination hall. Do not remove any page from this booklet.

READ INSTRUCTIONS ON THE
SIDE OF THIS PAGE CAREFULLY

| REGISTRATION NUMBER |  |  |  |  |  |  |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- |
|  |  |  |  |  |  |  |

Name:

Test Centre:

Do not write your Registration Number or Name anywhere else in this question-cum-answer booklet.

I have read all the instructions and shall abide by them.

Signature of the Candidate

I have verified the information filled by the Candidate above.

Signature of the Invigilator

## IMPORTANT NOTE FOR CANDIDATES

- Questions 1-30 (objective questions) carry three marks each and questions 31 (subjective questions) carry fifteen marks each.
- Write the answers to the objective questions in the Answer Table for Objective Questions provided on page 7 only.
Q. 1 Molecular shape of $\mathrm{SOCl}_{2}$ is
(A) square planar
(B) trigonal pyramidal
(C) triangular planar
(D) T-shaped
Q. 2 Number of three-centre two-electron (3c-2e) bonds present in diborane is
(A) 2
(B) 4
(C) 6
(D) 8
Q. 3 The lattice energy of LiF calculated from Born-Landé equation is $-1000 \mathrm{~kJ} \mathrm{~mol}^{-1}$. Assume that for both LiF and MgO the Madelung constants, interionic distances and Born exponents have the same value. The lattice energy of MgO in $\mathrm{kJ} \mathrm{mol}^{-1}$ is
(A) -4000
(B) -2000
(C) 2000
(D) 4000
Q. 4 The compound formed by dissolving elemental gold in aqua regia is
(A) AuCl
(B) $\mathrm{AuNO}_{3}$
(C) $\mathrm{H}\left[\mathrm{AuCl}_{4}\right]$
(D) $\mathrm{H}\left[\mathrm{Au}\left(\mathrm{NO}_{3}\right)_{4}\right]$
Q. 5 Number of moles of ions produced by complete dissociation of one mole of Mohr's salt in water is
(A) 3
(B) 4
(C) 5
(D) 6
Q. 6 The tetrachloro complexes of $\mathrm{Ni}(\mathrm{II})$ and $\mathrm{Pd}(\mathrm{II})$ respectively, are (atomic numbers of Ni and Pd are 28 and 46 respectively)
(A) diamagnetic and diamagnetic
(B) paramagnetic and paramagnetic
(C) diamagnetic and paramagnetic
(D) paramagnetic and diamagnetic
Q. 7 The total number of steps involved and number of beta particles emitted in the spontaneous decay of ${ }_{92}^{238} \mathrm{U} \rightarrow{ }_{82}^{208} \mathrm{~Pb}$ respectively, are
(A) 8 and 6
(B) 14 and 6
(C) 6 and 8
(D) 14 and 8
Q. 8 A filter paper moistened with ammoniacal sodium nitroprusside solution turns violet on contact with a drop of alkaline $\mathrm{Na}_{2} \mathrm{~S}$ solution. The violet color is due to the formation of
(A) $\left[\mathrm{Fe}(\mathrm{SCN})_{5}(\mathrm{NO})\right]^{1-}$
(B) $\left[\mathrm{Fe}(\mathrm{SCN})_{5}(\mathrm{NO})\right]^{2-}$
(C) $\left[\mathrm{Fe}(\mathrm{CN})_{5}(\mathrm{NOS})\right]^{3-}$
(D) $\left[\mathrm{Fe}(\mathrm{CN})_{5}(\mathrm{NOS})\right]^{4-}$
Q. 9 The species/compounds that are aromatic among the following are

$P$

Q

R

S
(A) R and S
(B) P and Q
(C) Q and S
(D) P and S
Q. 10 The major product obtained in the reaction below is

(A)

(B)

(C)

(D)

Q. 11 The rates of acetolysis for the following norbornyl derivatives are in the order

P

Q

R
(A) R $>$ Q $>$ P
(B) Q $>$ R $>$ P
(C) P $>$ R $>$ Q
(D) R $>$ P $>$ Q
Q. 12 The Haworth projection for $\alpha$-anomer of D-glucose is
(A)

(B)

(C)

(D)

Q. 13 The complementary DNA sequence of the given DNA $5^{\prime}$-G-A-A-T-T-C-3' is
(A) $5^{\prime}$-C-T-T-A-A-G-3'
(B) $5^{\prime}$ '-C-U-U-A-A-G-3'
(C) 3'-C-T-T-A-A-G-5'
(D) $3^{\prime}$-G-A-A-T-T-C-5'
Q. 14 The order of nucleophilicity of the following anions in a $\mathrm{S}_{\mathrm{N}} 2$ reaction is

P

Q


(A) Q $>$ R $>$ S $>$ P
(B) Q $>$ P $>$ R $>$ S
(C) Q $>$ R $>$ P $>$ S
(D) P $>$ S $>$ R $>$ Q
Q. 15 The pair of conformation that has maximum energy difference is
(A)
 and

(B)

(C)

(D)

Q. 16 The major mono-sulfonation product of $\alpha$-tetralone is
(A)

(B)

(C)

(D)

Q. 17 Electrophilic nitrations of the following compounds follow the trend




(A) S $>$ R $>$ P $>$ Q
(B) R $>$ S $>$ P $>$ Q
(C) R $>$ P $>$ S $>$ Q
(D) P $>$ S $>$ R $>$ Q
Q. 18 The compounds those would not respond to tests of both nitrogen and sulfur with sodium fusion extracts are

I

II

III

IV
(A) I and III
(B) III and IV
(C) I and IV
(D) II and IV
Q. 19 The correct epimeric pair of the following is

P

Q

R

S
(A) P and Q
(B) R and Q
(C) Q and S
(D) R and S
Q. $20 \alpha$-Farnesene shown below is a

(A) diterpene having two isoprene units
(B) triterpene having three isoprene units
(C) triterpene having four isoprene units
(D) sesquiterpene having three isoprene units
Q. 21 For the equilibrium $\mathrm{N}_{2}+3 \mathrm{H}_{2} \rightleftharpoons 2 \mathrm{NH}_{3}$, the equilibrium constant, $K_{p}$ is expressed as
(A) $3^{3} K_{p}=\frac{p_{N H_{3}}}{p_{N_{2}}^{2}}$
(B) $3^{3} K_{p}=\frac{p_{N H_{3}}^{2}}{p_{N_{2}} p_{H_{2}}^{3}}$
(C) $3^{3} K_{p}=\frac{p_{N H_{3}}^{2}}{p_{N_{2}}^{4}}$
(D) $3^{3 / 2} K_{p}^{1 / 2}=\frac{p_{N H_{3}}^{2}}{p_{N_{2}}^{4}}$
Q. 22 The average speed of $\mathrm{H}_{2}, \mathrm{~N}_{2}$ and $\mathrm{O}_{2}$ gas molecules is in the order
(A) $\mathrm{H}_{2}>\mathrm{N}_{2}>\mathrm{O}_{2}$
(B) $\mathrm{O}_{2}>\mathrm{N}_{2}>\mathrm{H}_{2}$
(C) $\mathrm{H}_{2}>\mathrm{O}_{2}>\mathrm{N}_{2}$
(D) $\mathrm{N}_{2}>\mathrm{O}_{2}>\mathrm{H}_{2}$
Q. 23 The enthalpy of vaporization ( $\Delta_{\text {vap }} H$ ) is zero at
(A) Boyle temperature
(B) critical temperature
(C) inversion temperature
(D) boiling temperature
Q. 24 The half-life of any zero-order reaction is
(A) independent of concentration
(B) proportional to inverse of concentration
(C) proportional to concentration
(D) proportional to square of the concentration
Q. 25 The molality of $\left(\mathrm{NH}_{4}\right)_{2} \mathrm{SO}_{4}$ solution that has the same ionic strength as $1 \mathrm{~mol} \mathrm{~kg}^{-1}$ solution of KCl is
(A) $1 / 3 \mathrm{~mol} \mathrm{~kg}^{-1}$
(B) $1 / 2 \mathrm{~mol} \mathrm{~kg}^{-1}$
(C) $2 / 5 \mathrm{~mol} \mathrm{~kg}^{-1}$
(D) $3 / 5 \mathrm{~mol} \mathrm{~kg}^{-1}$
Q. 26 The standard enthalpy of formation $\left(\Delta_{f} H_{300}^{0}\right)$ at 1 bar and 300 K for the formation of $\mathrm{CF}_{2} \mathrm{ClCF}_{2} \mathrm{Cl}(\mathrm{g})$ from its constituent elements in the standard state is $-900 \mathrm{~kJ} \mathrm{~mol}^{-1}$. Given $\mathrm{R}=8.3 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}$, the standard internal energy of formation ( $\Delta_{f} U_{300}^{0}$ ) at the same pressure and temperature is
(A) $-905 \mathrm{~kJ} \mathrm{~mol}^{-1}$
(B) $-895 \mathrm{~kJ} \mathrm{~mol}^{-1}$
(C) $895 \mathrm{~kJ} \mathrm{~mol}^{-1}$
(D) $905 \mathrm{~kJ} \mathrm{~mol}^{-1}$
Q. 27 The percent transmittance of a solution having absorbance (optical density) 1.0 is
(A) 1
(B) 10
(C) 50
(D) 99
Q. 28 The matrix which transforms $\binom{x}{y}$ to $\binom{-y}{-x}$ is
(A) $\left(\begin{array}{ll}-1 & -1\end{array}\right)$
(B) $\binom{-1}{-1}$
(C) $\left(\begin{array}{cc}-1 & 0 \\ 0 & -1\end{array}\right)$
(D) $\left(\begin{array}{cc}0 & -1 \\ -1 & 0\end{array}\right)$
Q. 29 A concentration cell with two hydrogen electrodes at two different pressures is depicted

$$
\begin{gathered}
H_{2}(g)(P t) \\
p_{H_{2}}=p_{1}
\end{gathered}|\operatorname{HCl}(a q)| \begin{gathered}
H_{2}(g)(P t) \\
p_{H_{2}}=p_{2}
\end{gathered}
$$

The potential $\left(\mathrm{E}_{\text {cell }}\right)$ of the cell is
(A) $\frac{R T}{F} \ln \frac{p_{2}}{p_{1}}$
(B) $\frac{R T}{F} \ln \frac{p_{1}}{p_{2}}$
(C) $\frac{R T}{2 F} \ln \frac{p_{2}}{p_{1}}$
(D) $\frac{R T}{2 F} \ln \frac{p_{1}}{p_{2}}$
Q. 30 An aqueous solution containing $1 \mathrm{~g} \mathrm{~L}^{-1}$ of a polymer exerts osmotic pressure of 4 torr at 300 K . Given $\mathrm{R}=0.082 \mathrm{~L} \mathrm{~atm}$, the molar mass $\left(\mathrm{g} \mathrm{mol}^{-1}\right)$ of the polymer is
(A) 4500
(B) 4564
(C) 4674
(D) 4800

Write the Code of your chosen answer only in the 'Answer' column against each Question Number. Do not write anything else on this page.

| Question <br> Number | Answer | Do not write <br> in this column | Question <br> Number | Answer | Do not write <br> in this column |
| :---: | :--- | :---: | :---: | :---: | :---: |
| 01 |  |  | 16 |  |  |
| 02 |  |  | 17 |  |  |
| 03 |  |  | 18 |  |  |
| 04 |  |  | 19 |  |  |
| 05 |  |  | 20 |  |  |
| 06 |  |  | 21 |  |  |
| 07 |  |  | 22 |  |  |
| 08 |  |  | 23 |  |  |
| 09 |  |  | 24 |  |  |
| 10 |  |  | 25 |  |  |
| 11 |  |  | 26 |  |  |
| 12 |  |  | 28 |  |  |
| 13 |  |  | 29 |  |  |
| 14 |  |  | 30 |  |  |
| 15 |  |  |  |  |  |

FOR EVALUATION ONLY

| Number of Correct Answers |  | Marks | $(+)$ |
| :--- | :--- | :--- | :--- |
| Number of Incorrect Answers |  | Marks | $(-)$ |
| Total Marks in Question 1-30 |  | $(\quad)$ |  |

(a) Identify the most acidic compound from the following: $\mathrm{CH}_{3}-\mathrm{CH}_{3}, \mathrm{CH}_{2}=\mathrm{CH}_{2}$ and $\mathrm{CH} \equiv \mathrm{CH}$, and justify your answer. Draw overlap of the orbitals to show bonding in the most acidic compound using the concept of hybridization.
(b) Write a balanced chemical equation to represent acid-base reaction of orthoboric acid in water.
Addition of ethylene glycol to aqueous orthoboric acid enhances its acidity. Explain the above statement using appropriate chemical equation.
Q. 32
(a) Draw the unit cell structure of NaCl . Calculate the limiting radius ratio of any ionic solid having NaCl like structure.
(b) Give molecular formula and structure of the compound formed by reaction of $\mathrm{Be}(\mathrm{OH})_{2}$ with acetic acid.
(a) The spin-only magnetic moments of $\mathrm{K}_{3}\left[\mathrm{Fe}(\text { oxalate })_{3}\right]$ and $\left.\mathrm{K}_{3}[\mathrm{Ru} \text { (oxalate) })_{3}\right]$ are $5.91 \mu_{\mathrm{B}}$ and $1.73 \mu_{\mathrm{B}}$, respectively. Write down their ligand field electronic configurations. Justify your answer. Atomic numbers of Fe and Ru are 26 and 44 respectively.
(b) Draw the structures of $\mathrm{NO}_{2}^{+}, \mathrm{NO}_{2}$ and $\mathrm{NO}_{2}{ }^{-}$. Arrange them in the increasing order of $\mathrm{O}-\mathrm{N}-\mathrm{O}$ bond angles.
(a) Show with labels the splitting of $d$-orbitals in an octahedral ligand field. Calculate the CFSE of (i) high spin $d^{6}$ and (ii) low spin $d^{6}$ metal ions in octahedral field.
(b) Schematically represent orbital overlaps in metal carbonyls. Show the correct signs of the lobes.
(a) A coordination compound is composed of one $\mathrm{Co}(\mathrm{III})$, one chloride, one sulfate and four molecules of ammonia. The aqueous solution of the compound gives no precipitate when combined with aqueous $\mathrm{BaCl}_{2}$, while a white precipitate is formed with aqueous $\mathrm{AgNO}_{3}$ solution. Draw its structure and explain the observations with chemical equations.
(b) Draw the structures of dimethylglyoxime $\left(\mathrm{DMGH}_{2}\right)$ and its $\mathrm{Ni}(\mathrm{II})$ complex formed in aqueous ammonia.
Q. 36
(a) Write the structures of $\mathbf{E}, \mathbf{F}$ and $\mathbf{G}$ in the following scheme of reactions

(b) Identify the structures of $\mathbf{H}$ and $\mathbf{I}$ in the following synthetic transformation

Q. 37
(a) Complete the following reaction sequence with appropriate structures of $\mathbf{J}, \mathbf{K}$ and $\mathbf{L}$.

(b) Identify the structures of $\mathbf{M}$ and $\mathbf{N}$ in the following synthetic transformation

Q. 38
(a) In the following reaction scheme, write the structures of $\mathbf{O}, \mathbf{P}$ and $\mathbf{Q}$.

(b) Given below are structures of some natural products. Identify them as vitamin $\mathrm{A}, \mathrm{B}_{6}$, C, and D and classify them according to their classes (isoprenoid, alkaloid, carbohydrate and steroid).




Q. 39
(a) Write the appropriate structures for $\mathbf{R}, \mathbf{S}$ and $\mathbf{T}$ in the following scheme.

(b) Choose the correct stereoisomer between $\mathbf{U}$ and $\mathbf{V}$ that would furnish $\mathbf{W}$ on controlled hydrolysis. Write the stable conformation of $\mathbf{W}$.

Q. 40 The mechanism of isomerization of cyclobutene $(C B)$ to 1,3-butadiene $(B D)$ is as follows.
$C B+C B \xrightarrow{k_{1}} C B^{*}+C B$
$C B^{*}+C B \xrightarrow{k_{-1}} C B+C B$
$C B^{*} \xrightarrow{k_{2}} B D$
(a) Show that the rate law is $\frac{d[D B]}{d t}=\frac{k_{2} \cdot k_{1} \cdot[C B]^{2}}{k_{-1} \cdot[C B]+k_{2}}$.
(b) The apparent first-order rate constant, $k_{\text {app }}=\frac{k_{2} \cdot k_{1} \cdot[C B]}{k_{-1} \cdot[C B]+k_{2}}$. At the $C B$ concentration of $1 \times 10^{-5} \mathrm{~mol} \mathrm{dm}^{-3}$, the value of $k_{\text {app }}$ reaches $50 \%$ of its limiting value obtained at very high concentrations of $C B$. Evaluate the ratio $\frac{k_{2}}{k_{-1}}$.
Q. 41 (a) The molar conductance of $0.012 \mathrm{~mol} \mathrm{dm}^{-3}$ aqueous solution of chloroacetic acid $100 \Omega^{-1} \mathrm{~cm}^{2} \mathrm{~mol}^{-1}$. The ion conductance of chloroacetate and $\mathrm{H}^{+}$ions are $50 \Omega^{-1} \mathrm{~cm}^{2} \mathrm{~mol}^{-1}$ and $350 \Omega^{-1} \mathrm{~cm}^{2} \mathrm{~mol}^{-1}$, respectively.
Calculate (i) degree of dissociation and $\mathrm{pK}_{\mathrm{a}}$ of chloroacetic acid, and (ii) $\mathrm{H}^{+}$ion concentration in the solution.
(b) Sketch the conductivity versus concentration of base curves for the titration of aqueous solutions of acetic acid (i) with NaOH , and (ii) with $\mathrm{NH}_{4} \mathrm{OH}$.
Q. 42 A solution of a free particle Schrödinger equation $\frac{-h^{2}}{8 \pi^{2} m} \frac{d^{2} \psi(x)}{d x^{2}}=E \psi(x)$ is $\psi(x)=e^{i k x}=\cos k x+i \sin k x$
(a) Derive expressions for energy ' $E$ ' and momentum ' $p$ ' of the particle.
(b) Using the above relations, show that the wavelength $(\lambda)$ is $\frac{h}{p}$.
Q. 43 (a) Sketch the temperature-composition phase diagram at 1 atm pressure for the ethanol-water system.
(i) Label all the areas in the diagram.
(ii) Indicate the temperature at which the composition of the vapor is same as that of the liquid. What is this mixture known as?
(iii) What is the degree of freedom at the corresponding composition?
(b) Estimate the pressure necessary to melt ice at $-10^{\circ} \mathrm{C}$ if the molar volume of liquid water is 18.01 mL and molar volume of ice is 19.64 mL . The entropy change for the melting process is $16.3 \mathrm{~J} \mathrm{~K}^{-1}$. Assume that the molar volumes and entropy change remain constant in this temperature range. [ $100 \mathrm{~J}=1 \mathrm{~L}$ bar]
Q. 44 (a) (i) Show that for $n$ moles of a van der Waals gas, $\left(\frac{\partial U}{\partial V}\right)_{T}=\frac{n^{2} a}{V^{2}}$.
(ii) Can a gas that obeys the equation of state $p(V-n b)=n R T$ be liquefied? Explain.
(b) Consider ideal mixing of 2 moles of toluene and 2 moles of benzene at 1 atm and 300 K . Calculate the values of $\Delta_{\text {mix }} \mathrm{V}, \Delta_{\text {mix }} \mathrm{U}, \Delta_{\text {mix }} \mathrm{H}, \Delta_{\text {mix }} \mathrm{G}$, and $\Delta_{\text {mix }} \mathrm{S}$ for the process. ( $\ln 2=0.69$ )

| 2012 CY |  |
| :---: | :---: |
| Objective Part |  |
| (Question Number 1 - 30) |  |$|$| Total Marks |
| :---: |


| Subjective Part |  |  |  |  |  |
| :---: | :---: | :--- | :---: | :---: | :---: |
| Question <br> Number | Marks |  | Question <br> Number | Marks |  |
| 31 |  |  | 38 |  |  |
| 32 |  |  | 39 |  |  |
| 33 |  |  | 40 |  |  |
| 34 |  |  | 41 |  |  |
| 35 |  |  | 42 |  |  |
| 36 |  |  | 43 |  |  |
| 37 |  |  | 44 |  |  |
| Total Marks in Subjective Part |  |  |  |  |  |


| Total (Objective Part) | $:$ |  |
| :--- | :--- | :--- |
| Total (Subjective Part) | $:$ |  |
| Grand Total | $:$ |  |
| Total Marks (in words) | $:$ |  |
| Signature of Examiner(s) | $:$ |  |
| Signature of Head Examiner(s) | $:$ |  |
| Signature of Scrutinizer | $:$ |  |
| Signature of Chief Scrutinizer | $:$ |  |
| Signature of Coordinating <br> Head Examiner | $:$ |  |

