## PUMDET-2023

## Subject : CHEMISTRY

## (Booklet Number)

Duration: 90 Minutes
No. of Questions : $\mathbf{5 0}$
Full Marks : 100

## INSTRUCTIONS

1. All questions are of objective type having four answer options for each. Only one option is correct. Correct answer will carry full marks 2. In case of incorrect answer or any combination of more than one answer, $1 / 2$ mark will be deducted.
2. Questions must be answered on OMR sheet by darkening the appropriate bubble marked $\mathrm{A}, \mathrm{B}, \mathrm{C}$ or D .
3. Use only Black/Blue ink ball point pen to mark the answer by complete filling up of the respective bubbles.
4. Mark the answers only in the space provided. Do not make any stray mark on the OMR.
5. Write question booklet number and your roll number carefully in the specified locations of the OMR Sheet. Also fill appropriate bubbles.
6. Write your name (in block letter), name of the examination centre and put your signature (as is appeared in Admit Card) in appropriate boxes in the OMR Sheet.
7. The OMR Sheet is liable to become invalid if there is any mistake in filling the correct bubbles for question booklet number/roll number or if there is any discrepancy in the name/signature of the candidate, name of the examination centre. The OMR Sheet may also become invalid due to folding or putting stray marks on it or any damage to it. The consequence of such invalidation due to incorrect marking or careless handling by the candidate will be sole responsibility of candidate.
8. Candidates are not allowed to carry any written or printed material, calculator, pen, docupen, log table, wristwatch, any communication device like mobile phones, bluetooth devices etc. inside the examination hall. Any candidate found with such prohibited items will be reported against and his/her candidature will be summarily cancelled.
9. Rough work must be done on the question booklet itself. Additional blank pages are given in the question booklet for rough work.
10. Hand over the OMR Sheet to the invigilator before leaving the Examination Hall.
11. Candidates are allowed to take the Question Booklet after examination is over.

Signature of the Candidate : $\qquad$
(as in Admit Card)
Signature of the Invigilator : $\qquad$

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SPACE FOR ROUGH WORK

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## CHEMISTRY

1. By how much will the potential of half-cell $\mathrm{Cu}^{2+} \mid \mathrm{Cu}$ change if the solution is diluted to 100 times at 298 K ?
(A) Increases by 59 mV
(B) Decreases by 59 mV
(C) Increases by 29.5 mV
(D) Decreases by 29.5 mV
2. In an irreversible process taking place at constant $T$ and $P$ in which $P-V$ work is being done, the change in Gibbs free energy (dG) and change in internal energy (dU) satisfies the criteria.
(A) $\mathrm{dG}_{\mathrm{T}, \mathrm{P}}<0, \mathrm{dU}_{\mathrm{S}, \mathrm{V}}<0$
(B) $\mathrm{dG}_{\mathrm{T}, \mathrm{P}}<0, \mathrm{dU}_{\mathrm{S}, \mathrm{V}}>0$
(C) $\mathrm{dG}_{\mathrm{T}, \mathrm{P}}<0, \mathrm{dU}_{\mathrm{S}, \mathrm{T}}<0$
(D) $\mathrm{dG}_{\mathrm{T}, \mathrm{P}}<0, \mathrm{dU}_{\mathrm{S}, \mathrm{P}}<0$
3. The value of $\Delta_{\mathrm{r}} \mathrm{G}-\Delta_{\mathrm{r}} \mathrm{G}^{0}$ of the reaction

$$
\mathrm{N}_{2}(\mathrm{~g}, 0.2 \text { bar })+2 \mathrm{O}_{2}(\mathrm{~g}, 0.2 \text { bar }) \rightarrow 2 \mathrm{NO}_{2}(\mathrm{~g}, 0.2 \text { bar })
$$

at 300 K is (given $\log 0.2=-0.699$ )
(A) $\quad 4015.2 \mathrm{~J} \mathrm{~mol}^{-1}$
(B) $-6030.2 \mathrm{~J} \mathrm{~mol}^{-1}$
(C) $8030.4 \mathrm{~J} \mathrm{~mol}^{-1}$
(D) $-2015.1 \mathrm{~J} \mathrm{~mol}^{-1}$
4. Under the same reaction condition of $A \rightarrow B$, initial concentration of $1.386 \mathrm{~mol} \mathrm{dm}^{-3}$ of a substance becomes half in 40 seconds and 20 seconds through first order and zero order kinetics respectively. Ratio $k_{1} / k_{0}$ of the rate constants for first order $\left(k_{1}\right)$ and zero order $\left(\mathrm{k}_{0}\right)$ of the reaction is
(A) $0.5 \mathrm{~mol}^{-1} \mathrm{dm}^{3}$
(B) $1.0 \mathrm{~mol}^{-1} \mathrm{dm}^{3}$
(C) $1.5 \mathrm{~mol}^{-1} \mathrm{dm}^{3}$
(D) $2.0 \mathrm{~mol}^{-1} \mathrm{dm}^{3}$

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5. An aqueous solution of a drug of 0.10 millimolar shows a percentage transmission of 50 in a 1 cm . cell at 250 nm . The molar absorptivity in $\mathrm{L} \mathrm{mol}^{-1} \mathrm{~cm}^{-1}$ is
(A) 2020
(B) 3100
(C) 3010
(D) 6990
6. Given that, $\mathrm{E}_{\mathrm{Fe}^{2+} / \mathrm{Fe}}=-0.44 \mathrm{~V}$ and $\mathrm{E}_{\mathrm{Fe}^{3+} / \mathrm{Fe}^{2+}}=0.77 \mathrm{~V}$ at $298 \mathrm{~K} . \mathrm{E}^{0} \mathrm{Fe}^{3+/ \mathrm{Fe}}$ is
(A) -0.036 V
(B) 0.036 V
(C) 0.33 V
(D) 1.21 V
7. For the equilibrium $\mathrm{NH}_{2} \mathrm{COONH}_{4}(\mathrm{~s}) \rightleftharpoons 2 \mathrm{NH}_{3}(\mathrm{~g})+\mathrm{CO}_{2}(\mathrm{~g})$
$\mathrm{p}_{\mathrm{CO}_{2}}=1$ bar at $100^{\circ} \mathrm{C}$. Hence equilibrium constant $\left(\mathrm{K}_{\mathrm{p}}\right)$ is
(Assume the reaction vessel initially was evacuated)
(A) 1
(B) 2
(C) 3
(D) 4
8. For an enzyme catalysed reaction obeying Michaelis-Menton equation, the slope and intercept of the plot of $\frac{1}{\mathrm{r}_{0}}$ against $\frac{1}{[\mathrm{~s}]_{0}}$ are $3.5 \times 10^{2} \mathrm{~s}$ and $5 \times 10^{4} \mathrm{~mol}^{-1} \mathrm{~L}$ s respectively, where $\mathrm{r}_{0}$ and $[\mathrm{s}]_{0}$ are the initial rate and initial substrate concentration. The Michaelis constant $\left(\mathrm{K}_{\mathrm{M}}\right)$ is
(A) $142.8 \mathrm{~m} \mathrm{~mol} \mathrm{~L}^{-1}$
(B) $17.5 \mathrm{~m} \mathrm{~mol} \mathrm{~L}^{-1}$
(C) $7.0 \mathrm{~m} \mathrm{~mol} \mathrm{~L}^{-1}$
(D) $3.5 \mathrm{~m} \mathrm{~mol} \mathrm{~L}^{-1}$

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9. From the kinetic study of a reaction, it is observed that the slope of the plot of $\sqrt{ }$ Rate versus concentration of reactant is 2.0 (where concentration is expressed in $\mathrm{mol} \mathrm{L}^{-1}$ and time in second). The numerical values of rate constant and order of the reaction are
(A) 4.0 and 2
(B) $\sqrt{ } 2$ and 0
(C) 2 and 1
(D) 2 and $\frac{1}{2}$
10. A system at 300 K consists of $10^{24}$ atoms. Assuming that there is no interatomic energy in the system, its total internal energy will be
(A) 3.10 kJ
(B) 4.56 kJ
(C) 6.21 kJ
(D) 9.36 kJ
11. For an adiabatic reversible expansion of an ideal gas, it appears that $\mathrm{P} \propto \mathrm{T}^{3}$. The ratio $\mathrm{C}_{\mathrm{P}} / \mathrm{C}_{\mathrm{V}}$ (i.e. $\gamma$ ) for the gas is
(A) $3 / 2$
(B) $5 / 3$
(C) $7 / 5$
(D) $9 / 7$
12. The dimension of A that appears in Maxwell's speed distribution equation $P(c)=A c^{2} \exp \left(-\frac{m c^{2}}{2 k_{B} T}\right)$ is
(A) $\mathrm{ML}^{-1} \mathrm{~T}^{-1}$
(B) $\mathrm{ML}^{2} \mathrm{~T}^{-2}$
(C) $\quad \mathrm{M}^{0} \mathrm{~L}^{-3} \mathrm{~T}^{3}$
(D) $\quad \mathrm{M}^{0} \mathrm{~L}^{-2} \mathrm{~T}^{2}$
13. For $\Psi=\mathrm{A} \exp \left(-\frac{x^{2}}{\mathrm{a}^{2}}\right),(-\infty \leq x \leq \infty)$ the expectation value of $\mathrm{p}_{x}$ is
(A) -a
(B) +a
(C) 0
(D) undefined

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14. The molar conductivity at infinite dilution for $\mathrm{Na}_{2} \mathrm{SO}_{4}, \mathrm{~K}_{2} \mathrm{SO}_{4}, \mathrm{KCl}, \mathrm{HCl}$ and HCOONa at 300 K are $260,308,150,426$ and $105 \mathrm{~S} \mathrm{~cm}^{2} \mathrm{~mol}^{-1}$ respectively. Hence $\Lambda_{\mathrm{m}}^{0}$ for formic acid in the same unit and at the same temperature is
(A) 381
(B) 405
(C) 429
(D) 531
15. The crystal $\mathrm{Ca}_{\mathrm{x}} \mathrm{Ti}_{\mathrm{y}} \mathrm{O}_{\mathrm{z}}$, has Ca at the corners, Ti at the body centres and O at the face centres of a cubic unit cell. Find $x, y, z$ and the number of atoms contributed by a 200-plane placed within the crystal.
(A) 1, 1, 3 and 3
(B) 1, 1, 3 and 1
(C) 4, 1, 6 and 1
(D) 2, 1, 3 and 1.5
16. Which two quantities are same ?
(A) The transport no. of $\mathrm{H}^{+}$in 0.1 N HCl and $\mathrm{HNO}_{3}$
(B) The transport no. of $\mathrm{H}^{+}$in infinitely dilute HCl and $\mathrm{HNO}_{3}$
(C) The mobility of $\mathrm{H}^{+}$in 0.1 N HCl and $\mathrm{HNO}_{3}$
(D) The mobility of $\mathrm{H}^{+}$in infinitely dilute HCl and $\mathrm{HNO}_{3}$
17. A sparingly soluble salt $M_{2} X$ ionizes as $M_{2} X \rightleftharpoons 2 M^{+}+X^{2-}$, then $K_{a}$ (activity solubility product)
(A) $\mathrm{K}_{\mathrm{a}}=\mathrm{S}^{2} \gamma_{ \pm}{ }^{2}$
(B) $\mathrm{K}_{\mathrm{a}}=4 \mathrm{~S}^{3} \gamma_{ \pm}{ }^{3}$
(C) $\mathrm{K}_{\mathrm{a}}=4 \mathrm{~S}^{3} \gamma_{ \pm}{ }^{2}$
(D) $\mathrm{K}_{\mathrm{a}}=\mathrm{S}^{3} \boldsymbol{\gamma}_{ \pm}{ }^{3}$

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18. Number of radial nodes in 7 g orbital will be
(A) 1
(B) 2
(C) 6
(D) 7
19. Which one of the following electronic transitions corresponds to the lowest energy band in the absorption spectrum of $\mathrm{Ni}(\mathrm{en})_{3}{ }^{2+}$ ?
(A) ${ }^{3} \mathrm{~T}_{2 \mathrm{~g}} \leftarrow{ }^{3} \mathrm{~A}_{2 \mathrm{~g}}$
(B) ${ }^{3} \mathrm{~T}_{1 \mathrm{~g}} \leftarrow{ }^{3} \mathrm{~A}_{2 \mathrm{~g}}$
(C) ${ }^{4} \mathrm{~T}_{1 \mathrm{~g}} \leftarrow{ }^{4} \mathrm{~A}_{2 \mathrm{~g}}$
(D) ${ }^{4} \mathrm{~A}_{2 g} \leftarrow{ }^{4} \mathrm{~T}_{2 g}$
20. For which of the following molecules, the IR active stretching vibrations will be Raman active?
(A) cis- $\mathrm{N}_{2} \mathrm{~F}_{2}$
(B) trans- $\mathrm{N}_{2} \mathrm{~F}_{2}$
(C) $\mathrm{H}_{2} \mathrm{O}$
(D) Pyridine N -oxide
21. Which of the following is expected to be inert among the following ?
(A) $\mathrm{Cu}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}{ }^{2+}$
(B) $\mathrm{Ni}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}{ }^{2+}$
(C) $\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}{ }^{3+}$
(D) $\mathrm{CoF}_{6}{ }^{3-}$
22. The self-indicating silica gel (impregnated with cobalt chloride) turns pink on absorbing moisture and becomes blue on heating. The pink and blue colours are respectively due to
(A) $\mathrm{Co}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}{ }^{2+}$ and $\mathrm{CoCl}_{4}{ }^{2-}$
(B) $\mathrm{Co}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}{ }^{2+}$ and $\mathrm{Co}_{2} \mathrm{O}_{3}$
(C) $\mathrm{Co}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}{ }^{2+}$ and $\mathrm{Co}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}{ }^{3+}$
(D) $\mathrm{Co}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}{ }^{3+}$ and $\mathrm{CoCl}_{4}{ }^{2-}$

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23. At what $\mathrm{pH}, \mathrm{Fe}(\mathrm{OH})_{3}$ starts to precipitate from a solution of $10^{-5}(\mathrm{M}) \mathrm{Fe}(\mathrm{III})$ ? Solubility Product of $\mathrm{Fe}(\mathrm{OH})_{3}$ is $10^{-38}$.
(A) 3
(B) 11
(C) 5
(D) 9
24. The correct order of the spectrochemical series of the species $\mathrm{NO}_{2}^{-}, \mathrm{NH}_{3}$, en, $\mathrm{F}^{-}$ $(\mathrm{en}=$ ethylenediamine $)$ is
(A) $\mathrm{NO}_{2}^{-}>\mathrm{NH}_{3}>$ en $>\mathrm{F}^{-}$
(B) $\quad$ en $>\mathrm{NO}_{2}^{-}>\mathrm{NH}_{3}>\mathrm{F}^{-}$
(C) en $>\mathrm{NH}_{3}>\mathrm{NO}_{2}^{-}>\mathrm{F}^{-}$
(D) $\mathrm{NO}_{2}^{-}>$en $>\mathrm{NH}_{3}>\mathrm{F}^{-}$
25. The complex that undergoes oxidative addition reaction in presence of $\mathrm{H}_{2}$ is
(A) $\quad\left[\mathrm{Ru}(\text { bipy })_{2}(\mathrm{CO})\left(\mathrm{H}_{2} \mathrm{O}\right)\right]^{2+}$
(B) $\quad\left[\mathrm{Mn}(\mathrm{CO})_{5}\left(\mathrm{CH}_{3}\right)\right]$
(C) $\quad\left[\operatorname{Ir}(\mathrm{CO}) \mathrm{Cl}\left(\mathrm{PPh}_{3}\right)_{2}\right]$
(D) $\left[\mathrm{Cr}(\mathrm{CO})_{4}\left(\mathrm{PPh}_{3}\right)\left(\mathrm{PBu}_{3}\right)\right]$
26. Number of d-d transitions observed in the visible region in $\mathrm{Cu}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}{ }^{2+}$ ion is
(A) 2
(B) 3
(C) 1
(D) 4
27. The total number of the microstates of the term symbol, ${ }^{3} \mathrm{~F}$ is
(A) 3
(B) 21
(C) 9
(D) 6
28. The ground spin state (s) of $\mathrm{C}_{2}{ }^{2-}$ ion is
(A) 1
(B) $\frac{1}{2}$
(C) 0
(D) 2

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29. Which of the following statements regarding Haemoglobin $(\mathrm{Hb})$ and Myoglobin $(\mathrm{Mb})$ is incorrect?
(A) The active sites of both $\mathrm{Hb}_{4}$ and Mb contain the heme group in which $\mathrm{Fe}^{\mathrm{II}}$ is equatorially coordinated by four pyrrole nitrogen atoms of porphyrin.
(B) $\mathrm{Fe}^{\mathrm{II}}$ in deoxy- $\mathrm{Hb}_{4}$ and deoxy- Mb is present in low spin configuration.
(C) Oxygenation of $\mathrm{Hb}_{4}$ is autocatalytic due to cooperative interaction but such effects are absent in Mb due to its monomeric nature.
(D) The successive oxygen binding constants of $\mathrm{Hb}_{4}$ gradually increases.
30. On the basis of 18 electron rule, identify the first-row transition metal for

$$
\left[\left(\eta^{4}-\mathrm{C}_{8} \mathrm{H}_{8}\right) \mathrm{M}(\mathrm{CO})_{3}\right] \text { and }\left[\mathrm{M}(\mathrm{CO})_{3} \mathrm{PPh}_{3}\right]^{-}
$$

(A) Mn and Fe
(B) Mn and Co
(C) Fe and Co
(D) Fe and Ni
31. The elements $\mathrm{A}, \mathrm{B}, \mathrm{C}$ and D have electronegativities 3.8, 3.3, 2.8 and 1.3 respectively. The correct order of increasing covalent character for the compounds $\mathrm{AB}, \mathrm{AD}, \mathrm{BD}$ and AC will be
(A) $\mathrm{AC}<\mathrm{AB}<\mathrm{BD}<\mathrm{AD}$
(B) $\mathrm{AD}<\mathrm{BD}<\mathrm{AC}<\mathrm{AB}$
(C) $\mathrm{AB}<\mathrm{AC}<\mathrm{BD}<\mathrm{AD}$
(D) $\mathrm{BD}<\mathrm{AD}<\mathrm{AC}<\mathrm{AB}$
32. Total number of isomers for $\mathrm{Ma}_{2} \mathrm{~b}_{2} \mathrm{~cd}(\mathrm{a}, \mathrm{b}, \mathrm{c}, \mathrm{d}$ represents monodentate ligands) are
(A) 10
(B) 6
(C) 8
(D) 4
33. The number of unpaired electron(s) present in $\left[\mathrm{CoF}_{6}\right]^{3-}$ is
(A) zero
(B) two
(C) four
(D) one

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34. The allylic hydrogen of limonene which is most readily deprotonated, is

(A) $\mathrm{H}_{\mathrm{A}}$
(B) $\mathrm{H}_{\mathrm{B}}$
(C) $\mathrm{H}_{\mathrm{C}}$
(D) $\mathrm{H}_{\mathrm{D}}$
35. Correct order of stability of the following carbocations is


I


II


III


IV
(A) I $>$ II $>$ III $>$ IV
(B) I $>$ III $>$ II $>$ IV
(C) III $>$ I $>$ II $>$ IV
(D) III $>$ I $>$ IV $>$ II
36. Among the following molecules, the molecule which does not exist in different conformations is
(A) ammonia
(B) hydrogen peroxide
(C) hydroxylamine
(D) methanol
37. Which of the following statements is NOT CORRECT ?
(A) A molecule with $\mathrm{D}_{2}$ point group is chiral.
(B) All epimers are diastereomers.
(C) A molecule cannot have both enantiotopic and diastereotopic ligands.
(D) A molecule may be optically inactive although it contains chirality centres.

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38. The most stable conformer for the trans and the cis-isomers of 1,3-ditert-butylcyclohexane are respectively
(A) Twist - boat; chair
(B) Chair; twist - boat
(C) Chair for both
(D) Twist - boat for both
39. The number of different types (non-equivalent) of hydrogen atoms in cis-1,2-dimethyl cyclopropane is
(A) $\quad$ six
(B) four
(C) three
(D) two
40. Among the following molecules, the molecule that records two doublets with coupling constant of about 16 Hz in the ${ }^{1} \mathrm{H}-$ NMR spectrum is
(A) $(\underline{Z})-1,2$-dichloroethene
(B) (E) - 1, 2 - dibromoethene
(C) (E) - 1- bromo - $2-$ chloroethene
(D) (Z) - 1- bromo-2-chloroethene
41. The correct order of $\mathrm{C}-\mathrm{H}$ stretching frequency in IR spectroscopy



iii

iv
(A) iv $<$ i $<$ ii $<$ iii
(B) i $<$ ii $<$ iv $<$ iii
(C) i $<$ iv $<$ ii $<$ iii
(D) i $<$ ii $<$ iii $<$ iv
42. The final product(s) in the following sequence of reactions is (are)

2 - Butyne $\xrightarrow[\text { (ii) } \mathrm{Br}_{2} / \mathrm{CCl}_{4}]{\text { (i) } \mathrm{H}_{2} / \text { Lindlar's catalyst }} \operatorname{Product(s)~}$
(A) racemic-2,3-dibromobutane
(B) meso-2,3-dibromobutane
(C) racemic - and meso - 2, 3- dibromobutane
(D) 2, 2, 3, 3 - tetrabromobutane

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43. Major product in the following reaction will be


(A)

(B)

(C)

(D)

44. The major product of the following reaction is

(A)

(B)

(C)

(D)


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45. Among the following molecules, the molecule which responds to iodoform test and forms benzoic acid on strong oxidation is
(A)

(B)

(C)

(D)

46. 




Structure of X and Y are -
(A)

and

(B)


(C)
 and $\quad \mathbf{C H}_{3} \mathbf{O H}$
(D)

and


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47. Identify the major product in the following reaction.

(A)

(B)

(C)

(D)

48. An electric current is passed through an aqueous solution (buffered at pH 6.0 ) of alanine, glutamic acid and arginine. The isoelectric points of alanine, glutamic acid and arginine are 6.0, 3.2 and 10.7 respectively. The correct statement among the following is
(A) Glutamic acid is present as an anion in this solution.
(B) Arginine is present as an anion in this solution.
(C) Alanine is present as an anion in this solution.
(D) Alanine migrates to cathode in this solution.

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49. Which of the given options represents $\alpha-\mathrm{D}$-glucopyranose ?
(A)

(B)

(C)

(D)

50. Which of the following statement(s) is/are CORRECT ?
(I) Sucrose exhibits mutarotation.
(II) Naturally occurring cysteine has S configuration.
(III) Thymine is not an RNA base.
(IV) D-Glucose and D-galactose yield the same osazone.
(A) (I) only
(B) (III) only
(C) (II) and (III)
(D) (II) and (IV)

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