GS-2023 (Chemistry) X

Full Name :

_____

Roll No. :

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TATA INSTITUTE OF FUNDAMENTAL RESEARCH

Written Test in **CHEMISTRY**

December 11th, 2022

Duration: Three hours (3 hours)

Please read all instructions carefully before you attempt the questions.

1. Write your FULL NAME and ROLL NUMBER (see hall ticket) in block letters, both on this page and on your answer sheet (at the end of this booklet).
2. This is a multiple-choice question paper with **ONE** section having a total of 40 questions. Each correct answer will get you 3 marks. Every wrong answer will get you -1 mark. Marks are not awarded or deducted when a question is not attempted. It is better not to answer a question if you are not sure.
3. Indicate your answers on the ANSWER SHEET by filling completely in the appropriate boxes. Do not mark more than one box for any question; this will be treated as an incorrect answer.
4. We advise you to first mark the correct answers in the QUESTION SHEET, and later transfer them to the ANSWER SHEET only when you are sure of your choice.
5. Rough work may be done on the back of the QUESTION SHEET. If needed, you may ask for extra rough sheets from an invigilator.
6. In answering the questions, please choose the option that best describes the solution to the problem.
7. **Use of calculators is permitted in this subject test.**

SOME USEFUL DATA

Avogadro number = 6.02×10^{23} mol^{-1}
RT/F = 0.0257 V at 25°C
Faraday constant = 96500 C/mol
Boltzmann constant $k_B = 1.38\times10^{-23}$ J K^{-1}
Mass of an electron = 9.109×10^{-31} kg

e = 1.6×10^{-19} C
h = 6.626×10^{-34} J s
c = 3×10^{8} m s^{-1}
R = 8.314 J K^{-1} mol^{-1}

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1. If A and B are two operators that do not commute, which amongst the following is the correct statement (here [A, B] = AB – BA is the commutator and {A, B} = AB + BA is the anticommutator):

   A) A and B can be measured simultaneously with zero error.

   B) exp(A) exp(B) = exp(A + B)

   C) exp(A) exp(B) = exp(A + B + ½ [A, B] + 1/12 [A, [A,B]] - 1/12 [B, [A, B]] + …)

   D) exp(A) exp(B) = exp(A + B + ½ {A, B} + 1/12 {A, {A,B}} - 1/12 {B, {A, B}} + …)

2. Consider the bound states of the following three potentials:

   (1) $V(x) = x^2$: harmonic potential
   (2) $V(x) = x^4$: quartic potential
   (3) $V(x) = (1-\exp(-a\,(x-x0)))^2$: morse potential

   If $\Delta E(n) = E(n+1) - E(n)$ is the difference between the $(n+1)^{th}$ and n^{th} bound states of a potential, which of the following statements is true:

   A) $\Delta E(n)$ is constant for all three potentials

   B) $\Delta E(n)$ is constant for potential (1), but monotonically decreases for potentials (2) and (3)

   C) $\Delta E(n)$ is constant for potential (1), monotonically increasing for potential (2), and monotonically decreasing for potential (3)

   D) Insufficient information provided

3. Based on Crystal Field Stabilization Energy, predict the order of binding constants for the following divalent metal ion to ethylenediaminetetra-acetic acid

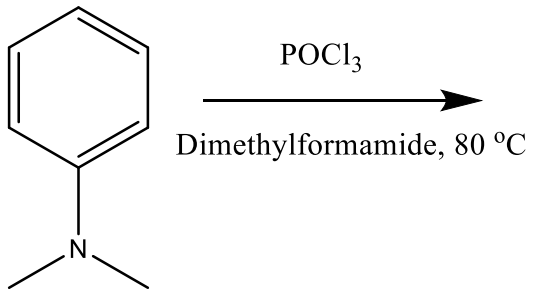
   A) Mn(II) < Fe(II) < Co(II) < Ni(II) < Zn (II) < Cu(II)

B) Mn(II) < Fe(II) < Co(II) < Ni(II) < Cu(II) < Zn(II)

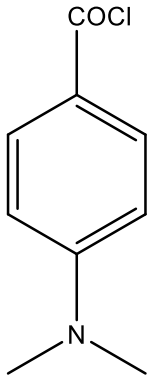
C) Mn(II) < Fe(II) < Co(II) < Zn (II) < Ni(II) < Cu (II)

D) Mn(II) < Cu(II) < Co(II) < Zn (II) < Ni(II) < Fe(II)

4. Predict the product of the following reaction.



A)



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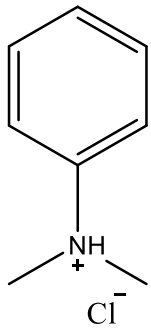

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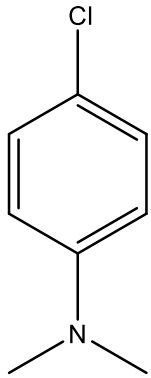
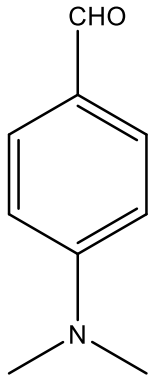


D)



5. Predict the order of basicity.

A)

$$CH_3^- > R\text{-}C{\equiv}C^- > OH^- > NH_3$$

B)

$$CH_3^- < R\text{-}C{\equiv}C^- < OH^- > NH_3$$

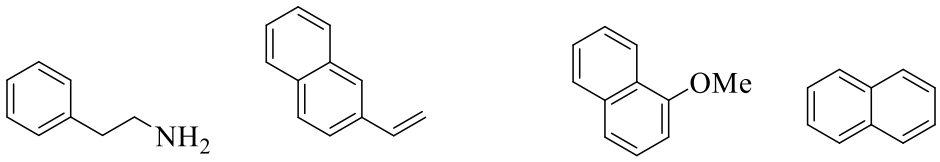
C)

$$CH_3^- < R\text{-}C{\equiv}C^- < OH^- < NH_3$$

D)

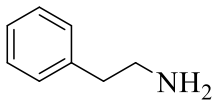
$$CH_3^- < R\text{-}C{\equiv}C^- > OH^- < NH_3$$

6. A mixture of four compounds is separated on a silica thin layer chromatography plate.



Which molecule will have the lowest retention factor?

A)



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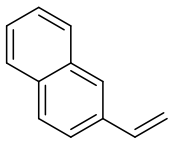
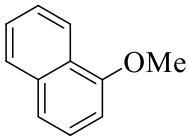
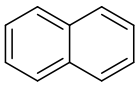


C)



D)



7. Estimate the minimum uncertainty in the speed of an electron in a hydrogen atom given that the atomic diameter is 1 Å.

   A) 540 nm/s

   B) 520 m/s

   C) 580 km/s

   D) 500 Å/s

8. Consider a quantum particle trapped in a 1-d box (potential energy zero inside the box and infinity outside) of length L. What can be said about the probability of finding the particle, P_c, at the center of the box in the n=1 and n=2 states for this system if the box length is doubled.

A) P_c decreases for n=1 but is unchanged for n=2

B) P_c decreases for both states

C) P_c is unchanged for n=1 but decreases for n=2

D) P_c is unchanged for both states

9. Consider a solid lattice formed out of identical atoms. Each atom is constrained to its equilibrium position x_e by a harmonic potential of the form $V = 0.5k(x - x_e)^2$; where k is the spring constant. If this system is heated, then the atomic positions will fluctuate about their equilibrium positions. Which of the following is true for the relation between the root mean square deviations (RMSD) of atomic fluctuations and temperature (T):

A) $RMSD \propto T^{3/2}$

B) $RMSD \propto T^{1/2}$

C) $RMSD \propto T^{2/3}$

D) $RMSD \propto T$

10. The vector triple product of any three vectors in 3 dimensions: $(\boldsymbol{b} \times \boldsymbol{a}) \times \boldsymbol{c}$ is always equal to

A) $(\boldsymbol{b} \cdot \boldsymbol{c})\boldsymbol{a} - (\boldsymbol{a} \cdot \boldsymbol{c})\boldsymbol{b}$

B) $(\boldsymbol{b} \cdot \boldsymbol{c})\boldsymbol{a} - (\boldsymbol{b} \cdot \boldsymbol{a})\boldsymbol{c}$

C) $(\boldsymbol{c} \cdot \boldsymbol{a})\boldsymbol{b} - (\boldsymbol{b} \cdot \boldsymbol{c})\boldsymbol{a}$

D) $(\boldsymbol{b} \cdot \boldsymbol{a})\boldsymbol{c} - (\boldsymbol{a} \cdot \boldsymbol{c})\boldsymbol{b}$

11. A = $\begin{pmatrix} 1 & 2 \\ 3 & 4 \end{pmatrix}$ and B = $\begin{pmatrix} 1 & 3 \\ 2 & 4 \end{pmatrix}$. If |A| represents the determinant of matrix A and |B| represents the determinant of matrix B, which of the following statements is most appropriate:

A) |A| ≠ |B| as A and B are different.

B) |A| = |B| as the rows and columns in A and B have been interchanged.

C) |A| = |B| as they have the same numbers.

D) Both statements b and c.

12. You are given a string of length L. What is the area of the largest rectangle you can construct with it?

A) L

B) $L^2/4$

C) $L^2/2$

D) $L^2/16$

13. You are monitoring an isomerization reaction like a protein folding reaction. You find that the rate constant (k) of the reaction does not vary with temperature. Assuming Arrhenius kinetics of the type $k = k_o e^{-\frac{-\Delta G^*}{RT}}$, where $\Delta G^* = \Delta H^* - T\Delta S^*$. Here the activation enthalpy (ΔH^*), the activation entropy (ΔS^*) and k_o are all independent of temperature. What can you conclude about the reaction?

A) That $\Delta H^* \approx 0$

B) That $\Delta S^* \approx 0$

C) That ΔG^* is independent of temperature

D) That $\Delta G^* < 0$.

14. For an endothermic chemical reaction which of the following statement is correct:

A) With increasing temperature forward rate increases and backward rate decreases

B) With increasing temperature backward rate increases and forward rate decreases

C) With increasing temperature, both forward and backward rate increases

D) With increasing temperature, forward rate increases and backward rate stays unaffected

15. Consider a process of separating isotopes of helium ^{3}He from ^{4}He using a process of gas effusion-based separation. Given that one starts the separation process from a mixture with natural abundance of ^{3}He = 0.000134% and ^{4}He = 99.999866%, how many effusion steps are needed to get ^{3}He with a purity of at least 99%?

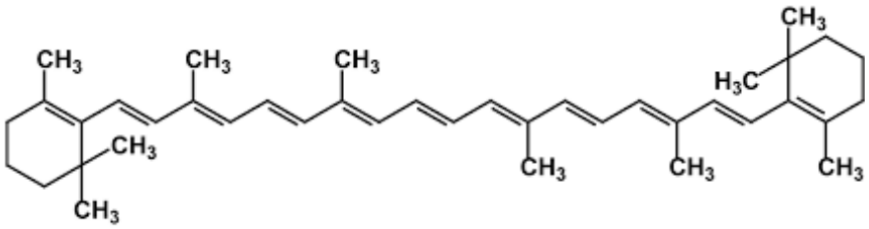
A) 100 steps

B) 94 steps

C) 941 steps

D) 35 steps

16. Consider the following molecule:



Assuming that the delocalised pi-electron system can be described by the particle in 1-D box model, estimate the wavelength region where the lowest energy electronic transition is expected to appear? (Note that the C-C single bond length is 1.54 Angstrom and C-C double bond length is 1.35 Angstrom)

A) 200 – 300 nm

B) 1200 – 1400 nm

C) 3000 – 3200 nm

D) 500 – 600 nm

17. Consider the following equation where c is a real number :

$$f(x) = x^3 - 2x^2 + 6x + c = 0$$

What is the maximum number of real roots this equation can have?

A) 1

B) 0

C) 3

D) 2

18. The value of change in enthalpy (ΔH) at 298 K and one bar for the reaction described by

$$2H_2(g)+O_2(g) \rightarrow 2H_2O\ (l)$$

is -572 kJ. What is change in internal energy (ΔU) for this reaction (assume ideal behavior):

A) -106 kJ

B) -565 kJ

C) -7702 kJ

D) -233 kJ

19. Calculate the number of ways of dividing 10 distinguishable objects into three groups containing 2,5 and 3 objects:

A) 5598

B) 8100

C) 678

D) 2520

20. Molar entropy change upon melting of ice at 1 atm at 273 K

A) Would be 0

B) Would depend on latent heat of melting

C) Would be independent of temperature

D) Would be independent of pressure

21. In gas chromatography, what is the basis of the separation of the mixture of molecules on a solid stationary phase,

A) molecular weight of the molecules

B) size of the molecules

C) polarity of the molecules

D) polarity and molecular weight of the molecules

22. The low-resolution mass spectrum of 2-chlorohexane exhibits a group of signals associated with the intact molecule at m/z 120, 121, 122 and 123. What isotopes are responsible for the signal at m/z 122?

A) ^{12}C, ^{35}Cl, ^{1}H

B) ^{12}C, ^{35}Cl, ^{2}H

C) ^{12}C, ^{37}Cl, ^{1}H

D) ^{13}C, ^{37}Cl, ^{1}H

23. Dissolving $CoCl_2$ in water produces a pale pink solution due to the formation of $[Co(H_2O)_6]^{+2}$. On adding HCl it forms $[Co(Cl)_4]^{-2}$. Which of the following statements is false

A) Both the complexes have spin allowed transitions.

B) Only $[Co(Cl)_4]^{-2}$ has Laporte allowed transitions.

C) Both the complexes have Laporte allowed transitions.

D) Only $[Co(H_2O)_6]^{+2}$ has Laporte allowed transitions.

24. If standard potential of the reaction $2H_2O(l) = O_2(g, 1bar) + 4H^+(aq) + 4e^-$ is $E^0 = -1.23$ V. At ambient condition, i.e. at 25°C and pH =7, what is the oxidation potential of pure water according to this reaction?

A) -0.41 V

B) -2.62 V

C) -0.817 V

D) -1.41 V

25. What is the value of $i \log_{10} i^2$, where $i = \sqrt{-1}$

A) Real number

B) Complex number

C) Cannot be calculated

D) None of the above

26. The acidity of molecules is usually measured by a parameter called the pKa. The pKa of regular bulk water is 15.7. Arrange the pK_a of water in decreasing trend of acidity for the following water solubilized aqua complexes: Ca^{2+}, Fe^{2+}, Mn^{2+}, Fe^{3+}

A) $Fe^{2+} > Mn^{2+} > Ca^{2+} > Fe^{3+}$

B) $Fe^{3+} > Fe^{2+} > Mn^{2+} > Ca^{2+}$

C) $Fe^{2+} > Mn^{2+} > Ca^{2+} > Fe^{3+}$

D) $Mn^{2+} > Ca^{2+} > Fe^{2+} > Fe^{3+}$

27. To the naked eye, oceans are always blue. With this premise, we compare a pool of regular water versus that of heavy water (D_2O). Why will the pool of heavy water always look more transparent than regular water? Is it due to:

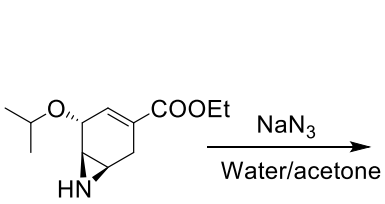
A) Rayleigh Scattering

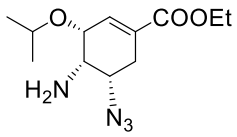
B) Kinetic Isotope effects

C) Absorption

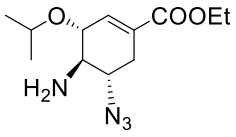
D) Marine life cannot be sustained in D_2O

28. Predict the major product in the following transformation.

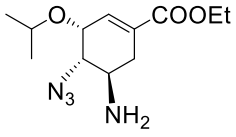




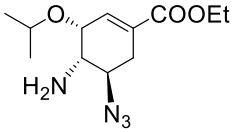
A



B



C



D

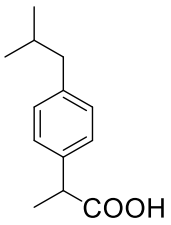
A) A

B) B

C) C

D) D

29. Ibuprofen is an anti-inflammatory agent taken orally to suppress inflammation. It penetrates the tissues through passive diffusion.



Ibuprofen

Pka = 4.5

pH in Mouth saliva = 7.3
pH in Stomach = 2.5
pH of intestine = 7.5

Where would ibuprofen be absorbed preferentially?

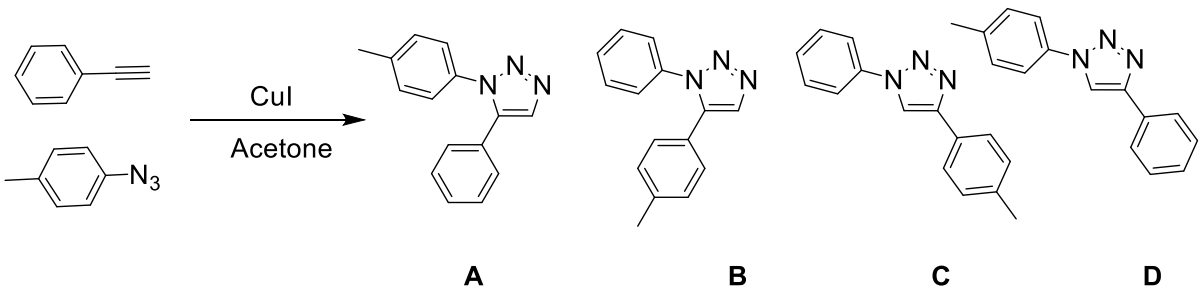
A) Mouth

B) Stomach

C) Intestine

D) Mouth and intestine

30. Predict the correct product of the following reaction?



A) A

B) B

C) C

D) D

31. Which of the following operators is Hermitian ?

A) -d/dx

B) $e^{-i\pi/2}\ d/dx$

C) d/dx

D) x + d/dx

32. In the 1D particle-in-a-box problem, which of the following is NOT true for the wavefunction?

A) The wavefunction is an eigenfunction of kinetic energy operator

B) The wavefunction is an eigenfunction of momentum operator

C) The number of nodes increases as one goes to higher energy states

D) The probability density close to the walls increases as we go to higher excited states

33. Which of the following is NOT a linear operator?

A) d/dx

B) $\int dx$

C) $(\ )^2$

D) d^2/dx^2

34. For a given first-order reaction, if 63.5% of the material is reacted in 100 s, what is the half-life of the reaction?

A) 69 s

B) 91 s

C) 154 s

D) 32 s

35. The mass spectrum of a non-polar organic compound shows M^+, M^++2 and M^++4 peaks at the ratio of 9:6:1. The compound could be

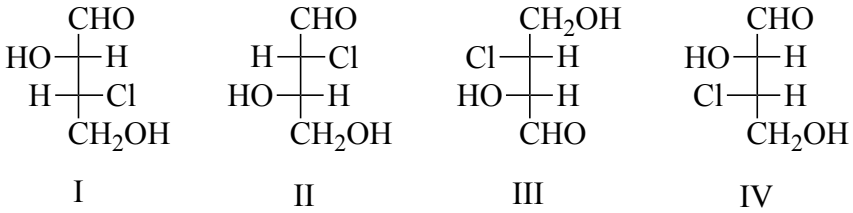
(A) 1, 3 - Dichlorobenzene

(B) 1, 4 - Dibromobenzene

(C) 1, 4 - Dichlorobenzene

(D) 1, 1 - Difluoroethylene

36. Identify the pair of enantiomers.



I II III IV

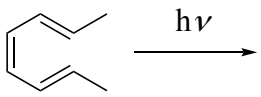
A) I & II

B) III & IV

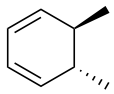
C) I & IV

D) II & III

37. Predict the product



A)



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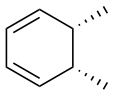

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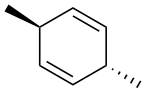
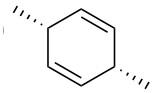
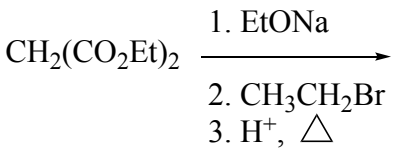


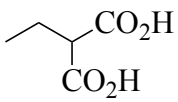
D)



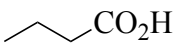
38. Predict the product



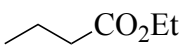
A)



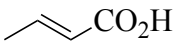
B)



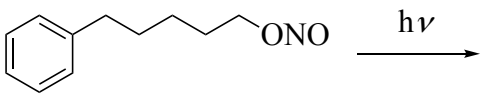
C)



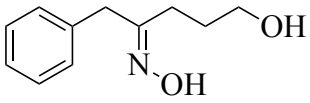
D)



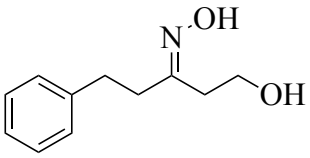
39. Predict the product



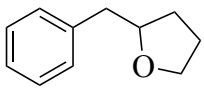
A)



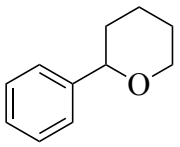
B)



C)



D)



40. If $A = \begin{pmatrix} 1 & -2 \\ 1 & 4 \end{pmatrix}$, find the smallest eigenvalue of A^{10}

A) 10

B) 59049

C) 1024

D) 0.999