# Ph.D. (CHEMISTRY) Programme - 2016 

## Note :

(i) This paper has two parts.
(ii) Part A is based on Research Methodology and las ten questions of 5 marks each.
(iii) Part B is Chemistry based and las twenty five questions of 2 marks each.
(iv) All questions are compulsory.

## Part A <br> (Research Methodology)

1. Briefly explain the primary and secondary data in research methodology.
2. Differentiate between precision and accuracy with the help of an example.
3. As a research schalar how would you effectively utilize internet for your research ?
4. What are significant figures ? Explain with examples.
5. What should be kept in mind while selecting a research problem ?
6. Briefly discuss the steps involved in a scientific research.
7. Explain the role of softwares in chemical research.
8. Describe the applications of spectroscopy in chemical research.
9. Name any five journals relevant to chemical research.
10. What are the different ways of graphical representation of research data ?

## Part B

(Chemistry)
The questions from 11-35 have only one correct answer. Write the correct option in your answer sheet.
11. Reaction of 1-hexene with NBS in presence of light gives :
(1) 3-bromo-1-hexene
(2) 1-bromo-2-hexene
(3) 6-bromo-1-hexene
(4) 1-bromo-4-hexene
12. The Cannizzaro reaction of benzaldehyde involves:
(1) intramolecular shift of proton
(2) intermolecular shift of hydride
(3) intermolecular shift of proton
(4) intramolecular shift of hydride
13. The reaction of $m$-bromoanisole with $\mathrm{NaNH}_{2}$ in liquid ammonia yields :
(1) $o$-aminoanisole
(2) $m$-aminoanisole
(3) $p$-aminoanisole
(4) 1, 3-diaminobenzene
14. The UV spectrum of acetone shows absorption maximum at 279 nm besides other bands. This absorption maximum is because of which of the following transition ?
(1) $n-\sigma^{*}$
(2) $\pi-\pi^{*}$
(3) $n-\pi^{*}$
(4) $\sigma-\sigma^{*}$
15. Predict the product of the following reaction from the choices given :

(1)

(2)

(3)

(4)

16. Choose the correct product of the following reaction from the options given :

(1)

(2)

(3)

(4)

17. Gilman reagents may be synthesized by the treatment of the corresponding alkyllithium compound with :
(1) copper (II) iodide in diethyl ether
(2) copper (I) chloride in diethyl ether
(3) copper (I) iodide in diethyl ether
(4) copper (II) chloride in diethyl ether
18. Choose the correct order of decreasing nucleophilicity of the following in an aqueous solution from the options given :
(1) $\mathrm{PhO}^{-}>\mathrm{CH}_{3} \mathrm{OH}>\mathrm{OH}^{-}>\mathrm{CH}_{3} \mathrm{COO}^{-}>\mathrm{CH}_{3} \mathrm{~S}^{-}$
(2) $\mathrm{CH}_{3} \mathrm{~S}^{-}>\mathrm{CH}_{3} \mathrm{COO}^{-}>\mathrm{OH}^{-}>\mathrm{CH}_{3} \mathrm{OH}>\mathrm{PhO}^{-}$
(3) $\mathrm{CH}_{3} \mathrm{~S}^{-}>\mathrm{OH}^{-}>\mathrm{PhO}^{-}>\mathrm{CH}_{3} \mathrm{COO}^{-}>\mathrm{CH}_{3} \mathrm{OH}$
(4) $\mathrm{OH}^{-}>\mathrm{CH}_{3} \mathrm{OH}>\mathrm{CH}_{3} \mathrm{~S}^{-}>\mathrm{CH}_{3} \mathrm{COO}^{-}>\mathrm{PhO}^{-}$
19. Which of the following is an essential fatty acid ?
(1) Oleic acid
(2) linolenic acid
(3) palmitoleic acid
(4) stearic acid
20. The +1 oxidation state is more stable than the +3 oxidation state for which Group 13 element?
(1) Al
(2) In
(3) Ga
(4) Tl
21. The average atomic mass of Cl is 35.453 . About $75 \%$ of all Cl atoms are ${ }^{35} \mathrm{Cl}$. If there is only one other common isotope, it is likely to be :
(1) ${ }^{36} \mathrm{Cl}$
(2) ${ }^{37} \mathrm{Cl}$
(3) ${ }^{38} \mathrm{Cl}$
(4) ${ }^{34} \mathrm{Cl}$
22. The Pauli exclusion principle :
(1) states that $m_{s}$ quantum number must have values of $-1 / 2$ or $+1 / 2$
(2) states that all electrons in an orbital have the same set of four quantum numbers.
(3) states that electrons have wavelike behavior.
(4) limits the number of electrons that can occupy an orbital to 2 .
23. Effective nuclear charge is:
(1) the total charge of the nucleus.
(2) the charge on the nucleus experienced by an electron when the shielding effect of other electrons is accounted for.
(3) the amount of energy required to remove an electron from the valence shell when the atom is in gaseous state.
(4) the energy released when a proton is added to the nucleus.
24. The correct statement among the following is:
(1) $\mathrm{N}_{2}$ has higher bond order than $\mathrm{N}_{2}{ }^{+}$and hence, has larger bond length compared to $\mathrm{N}_{2}{ }^{+}$.
(2) $\mathrm{N}_{2}$ has higher bond order than $\mathrm{N}_{2}{ }^{+}$and hence, has higher dissociation energy compared to $\mathrm{N}_{2}{ }^{+}$.
(3) $\mathrm{N}_{2}+$ has higher bond order than $\mathrm{N}_{2}$ and hence, has larger bond length compared to $\mathrm{N}_{2}$.
(4) $\mathrm{N}_{2}$ has lower bond order than $\mathrm{N}_{2}{ }^{+}$and hence, has lower dissociation energy compared to that of $\mathrm{N}_{2}{ }^{+}$energy.
25. Mossbauer spectrum of a metal complex gives information about :
(a) oxidation state and spin state of metal.
(b) types of ligands coordinated to metal.
(c) nuclear spin state of metal.
(d) geometry of metal.

The correct option is :
(1)
(a) and (c)
(2) (b) and (c)
(3) (a), (b) and (d)
(4)
(b) and (d)
26. The structures of $\mathrm{XeF}_{2}$ and $\mathrm{XeO}_{2} \mathrm{~F}_{2}$, respectively are :
(1) bent, tetrahedral
(2) linear, square planar
(3) linear, see-saw
(4) bent, see-saw
27. Which one of the following is not an example of an acid buffer ?
(1) $\mathrm{HNO}_{2} / \mathrm{NO}_{2}^{-}$
(2) $\mathrm{HClO}_{2} / \mathrm{ClO}_{2}^{-}$
(3) $\mathrm{CH}_{3} \mathrm{COOH} / \mathrm{CH}_{3} \mathrm{COO}^{-}$
(4) $\mathrm{H}_{2} \mathrm{PO}_{4}^{-} / \mathrm{HPO}_{4}^{2-}$
28. The ${ }^{1} \mathrm{H}-\mathrm{NMR}$ spectrum of ethyl ethanoate shows :
(1) two singlets and one doublet.
(2) one singlet, one triplet and one quartet.
(3) two triplets and one quartet.
(4) one singlet, one doublet and one triplet.
29. According to the variation theorem :
(1) all arbitrary wave functions will give the true value of the ground state energy.
(2) a trial wave function would give energy equal to or more than the ground state energy.
(3) the exact wave function would give energy greater than the ground state energy.
(4) the Hamiltonian can be suitably modified to determine the energy of the ground state.
30. For a linear polyatomic molecule having four atoms, the number of translational degrees of freedom would be :
(1) three
(2) $\operatorname{six}$
(3) nine
(4) twelve
31. Maxwell relations in thermodynamics provide means for the determination of certain thermodynamic variables which cannot be determined in terms of easily measurable thermodynamic variables. Which of the following expressions does not represent a Maxwell relation?
(1) $\left(\frac{\partial S}{\partial P}\right)_{T}=-\left(\frac{\partial V}{\partial T}\right)_{P}$
(2) $\left(\frac{\partial P}{\partial T}\right)_{S}=-\left(\frac{\partial V}{\partial S}\right)_{P}$
(3) $\left(\frac{\partial T}{\partial V}\right)_{S}=-\left(\frac{\partial P}{\partial S}\right)_{V}$
(4) $\left(\frac{\partial S}{\partial V}\right)_{T}=\left(\frac{\partial P}{\partial T}\right)_{V}$
32. The magnetic susceptibility versus temperature curve for solid material shows a gradual increase with an increase in temperature. At a certain characteristic temperature, it acquires paramagnetic behaviour. The magnetic nature of the material and the characteristic temperature, respectively are :
(1) Ferromagnetic and Curie temperature
(2) Ferrimagnetic and Curie temperature
(3) Ferromagnetic and Neel temperature
(4) Antiferromagnetic and Neel temperature
33. In the UV spectrum of acetone, the $\pi \rightarrow \stackrel{*}{\pi}$ and $n \rightarrow \stackrel{*}{\pi}$ electronic transitions, respectively are expected to be :
(1) weak and weak
(2) weak and strong
(3) strong and weak
(4) strong and strong
34. Which of the following is not true about the Lindemann's hypothesis for unimolecular reactions ?
(1) The activated molecules obtained from collision may undergo either decomposition or deactivation.
(2) There is a time lag between the activation and decomposition of the molecules.
(3) The rate of decomposition is much faster than the rate of deactivation of the activated molecules.
(4) A stationary concentration of the activated molecules gets built up with time.
35. Using Hückel's approximation for $\pi$-electrons in organic molecules, the energy levels for butadiene and ethylene are as under :
Butadiene : $\alpha+1.618 \beta ; \alpha+0.618 \beta ; \alpha-0.618 \beta ; \alpha-1.618 \beta$
Ethylene : $\alpha+\beta ; \alpha-\beta$
Using these, the resonance stabilisation energy for butadiene can be computed to be :
(1) $0.472 \alpha$
(2) $0.472 \beta$
(3) $1.472 \alpha$
(4) $1.472 \beta$

