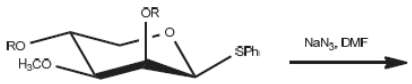
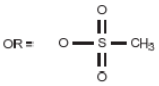
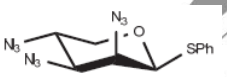
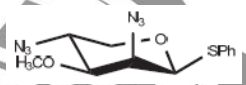
TIFR M.Sc. CHEMISTRY ENTRANCE - 2015

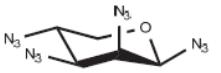
1. Predict the product for the following sugar functionalization reaction :

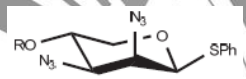




(a) 

(b) 

(c) 

(d) 

2. Which of the following cannot act as a chelating agent?

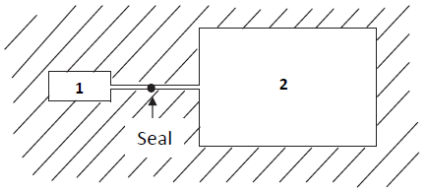
(a) $HC(CH_2CH_2NH_2)_3$

(b) $CH_3NHCH_2CH_2CH_3$

(c) $N(CH_2CH_2NH_2)_3$

(d) $H_2NCH_2CH_2CH_2NH_2$

3. In the following setup, two chambers 1 and 2 are enclosed by a thermally insulated material. Chamber 1 contains an ideal gas at 100 atm. Chamber 2 is completely evacuated. The two chambers are separated by a breakable seal. Before the seal is broken, the temperature of the chamber 1 is $T_{1,\ initial}$. Then the seal is broken, and the gas is allowed to rush to chamber 2. The volume of chamber 2 is 100 times the volume of chamber 1. When the pressure in the two chambers becomes equal, their respective temperature is $T_{1,final}$ and $T_{2,final}$. Which of the following statements is true?



(a) $T_{1,final} = T_{2,final} = T_{1,initial}$

(b) $T_{2,\text{final}} = T_{1,\text{final}} < T_{1,\text{initial}}$

(c) $T_{2,\text{final}} < T_{2,\text{final}}, T_{1,\text{final}} = T_{1,\text{initial}}$

(d) Only a very small drop in temperature is expected. So $T_{1,\text{initial}}, T_{2,\text{initial}}$ will be approximately equal to $T_{1,\text{initial}}$.

4. Consider the trigonometric function $\frac{\cos A - \sin A + 1}{\cos A + \sin A - 1}$. It can be simplified as

(a) $\frac{1+\sec A - \tan A}{1-\sec A + \tan A}$ (b) $\text{cosec}A + \cot A$ (c) $\frac{1}{(\text{cosec}A - \cot A)}$ (d) All of these

5. The combustion of ethane (C_2H_6) is represented by the following reaction :

$$2C_2H_6(g) + 7O_2(g) \rightarrow 4CO_2(g) + 6H_2O(l)$$

Which of the following is TRUE for the above reaction?

(a) The rate of consumption of thane is seven times faster than the rate of consumption of oxygen.

(b) Water is formed at a rate equal to two-thirds the rate of formation of CO_2

(c) The rate of consumption of oxygen equals the rate of formation of water

(d) CO_2 is formed twice as fast as thane is consumed

6. Consider the following reaction : $Au + O_2 + 3F_2 \rightarrow [O_2]^+ + [AuF_6]^-$

Which statements is correct about the redox changes in this reaction?

(a) Au is oxidized; O is oxidized; F is reduced

(b) Au is reduced; O is oxidized; F is reduced

(c) Au is oxidized; O does not undergo a redox change; F is reduced

(d) Au is reduced; O is oxidized; F does not undergo a redox change

7. Formation of **Z** from **X** is theoretically expected to obey the following kinetic scheme.

$$X \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Y \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Z$$

An experimentalist wants to verify the above scheme, but can observe and measure the concentration of only **X** or **Z**. Is it possible that under certain conditions, the measurements of $[\mathbf{X}]$ or $[\mathbf{Z}]$ as function of time would lead the experimenter to conclude that the kinetic scheme is as given below, and that the species **Y** is absent?

$$X \underset{k_{-obs}}{\overset{k_{obs}}{\rightleftharpoons}} Z$$

(a) No, that is not possible

(b) Yes, if $k_{-1} \gg k_1$ and $k_{-2} \gg k_2$

(c) Yes, if $\frac{k_1}{k_{-1}} = \frac{k_2}{k_{-2}}$

(d) Yes, if $[\mathbf{Y}]$ attains a steady-state concentration during the experiment

8. NaCl, KCl, NaBr and KBr crystallize in FCC lattices. Their anion and cation touch along the edge of the unit cell. The dimensions of their unit cells are 562.8 pm, 627.7 pm and 658.6 pm, respectively. From these data, what can you say about the size of the ionic radii (within an error of about 5%)?

(a) Ionic radii of the cations depend on the nature of the anions

(b) Ionic radii of the cations depend on the nature of the anions

(c) Both (a) and (b)

(d) Ionic radii are independent of the ions

9. Indicate which of the following is/are "acceptable" wave functions(s) in quantum mechanics in the range $-\infty < x < +\infty$

i. $\psi = x$

ii. $\psi = x^2$

iii. $\psi = \sin x$

iv. $\psi = \exp(-x)$

v. $\psi = \exp(-x^2)$

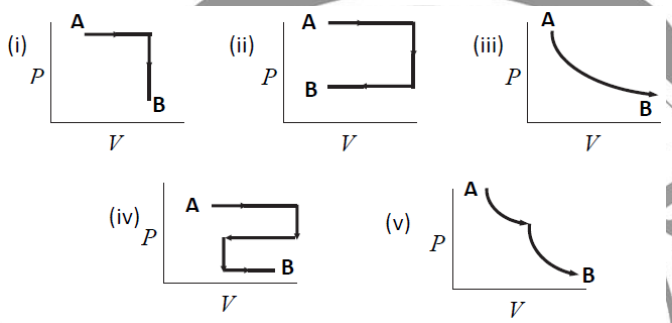
(a) iii and v (b) iv only (c) iv and v (d) i and iii

10. For a harmonic oscillator in its ground state i.e. $v = 0$ state, the energy is given by $E = \frac{1}{2}hv$ where v is the vibrational frequency. This is due to its

(a) Kinetic energy (b) Potential energy

(c) Sum of kinetic and potential energy (d) Heat of formation

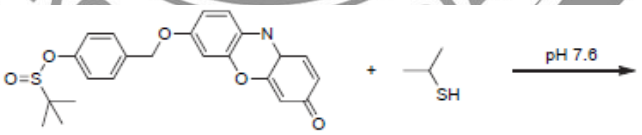
11. The state of a certain amount of a gas, not necessarily ideal, is changed from A to B in various hypothetical paths, as shown below. The total amount of the gas remains constant. Which of the following paths are physically realizable?

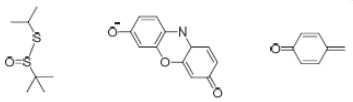


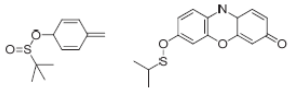
(a) All of them (b) Only (i), (ii) and (iii)

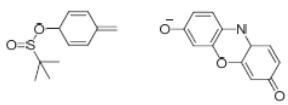
(c) Only (iii) and (v) (d) Only (i) and (iii)

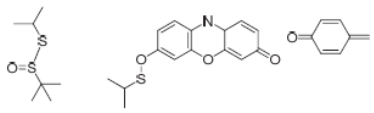
12. Thiols are important molecular species present in cells and can mediate cell signaling processes. A procedure for detecting thiols has been recently reported based on the following reaction. Predict the structures of reaction products.



(a) 

(b) 

(c) 

(d) 

13. If the peak in the mass spectrum of C_2F_6 at mass number 138 is 100 units tall, what will be heights of the peak at mass numbers 139 and 140.

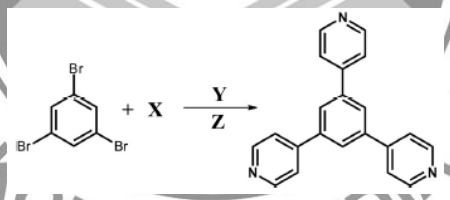
(Isotopic abundances : ^{12}C, 98.8%, ^{13}C, 1.11%, ^{19}F, 100%)

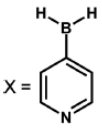
(a) 2.24 and 0.0126 (b) 1.12 and 0.0126 (c) 50 and 25 (d) 2.24 and 0.025

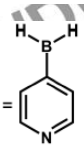
14. According to the Nernst equation, the potential of an electrode changes by 59.2 mV whenever the ratio of the oxidized and the reduced species changes by a factor of 10 at $25°C$. What would be the corresponding change in the electrode potential if the experiment is carried out at $30°C$?

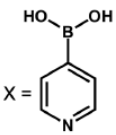
(a) 59.0 mV (b) 71.0 mV (c) 60.2nV (d) None of these

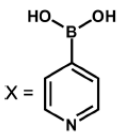
15. Degenerate C-C coupling reactions are very important for synthesizing supramolecular organic structures. Name the reagents **X**, **Y** and **Z** that would be necessary to make the C_3 symmetric product?



(a)  Y = $Pd(PPh_3)_3$ Z = Na_2CO_3

(b)  Y = $NiCl_2(PPh_3)_2$ Z = Na_2CO_3

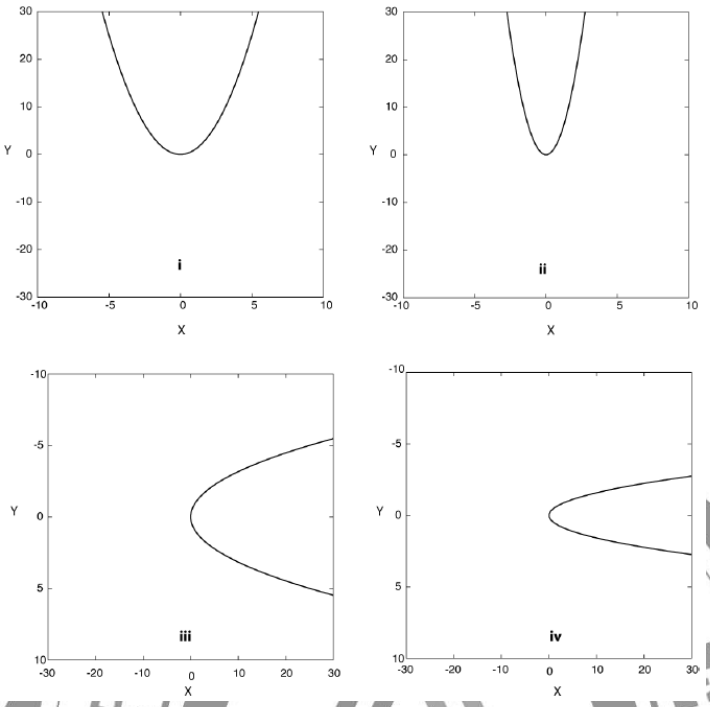
(c)  Y = $Pd(PPh_3)_4$ Z = Na_2CO_3

(d)  Y = $Pd(PPh_3)_4$ Z = HCl

16. What is the point group of $Fe_2(CO)_9$?

(a) C_{3h} (b) D_{3h} (c) C_{3v} (d) D_{3d}

17. Which of the following is the curve $x = y^2$.



(a) i (b) ii (c) iii (d) iv

18. For a particle undergoing quantum tunneling through a barrier, which of the following is NOT true :

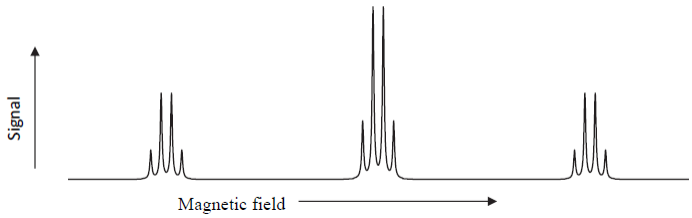
(a) The amplitude the particle wave function after passing the barrier decreases with an increase in tunneling distance.

(b) The probability of finding the particle after passing the barrier decreases with increase in tunneling barrier height.

(c) The energy of the particle after crossing the barrier decrease with increase in tunneling distance.

(d) The change in the phase of the particle wave function upon transmission is proportional to the tunneling distance.

19. A magnetic resonance spectrum, recorded using a radiation of frequency 100 MHz, is shown below. What can you say about the nature of this spectrum?



(a) It is a continuous-wave NMR spectrum

(b) It is Fourier transform NMR spectrum

(c) It is an ESR spectrum

(d) None of the above

20. An electron can transfer from state D to state A with a rate k_{DA}. The intrinsic)in the absence of any charge transfer between states D and A) lifetimes of charge transfer states D and A are τ_D and τ_A, respectively. Assuming that initially the electrons is in state D, under what conditions would k_{DA} be completely determined in terms of the overall rate at which the electron leaves the combined $D + A$ system.

(a) $k_{DA} \gg \frac{1}{\tau_D}$ and $k_{DA} \gg \frac{1}{\tau_A}$ (b) $k_{DA} \gg \frac{1}{\tau_D}$ and $k_{DA} \ll \frac{1}{\tau_A}$

(c) $k_{DA} \ll \frac{1}{\tau_D}$ and $k_{DA} \gg \frac{1}{\tau_A}$ (d) $k_{DA} \ll \frac{1}{\tau_D}$ and $k_{DA} \ll \frac{1}{\tau_A}$

21. A common characteristic of conducting polymers, such as polypyrrole and polythiophene, which make them conduct electricity is

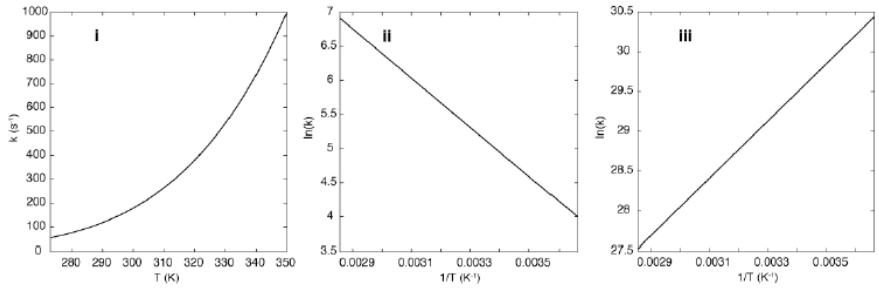
(a) The presence of stereogenic centres of the same configuration

(b) A monodisperse distribution in molecular weight

(c) Conjugation throughout the polymer chain

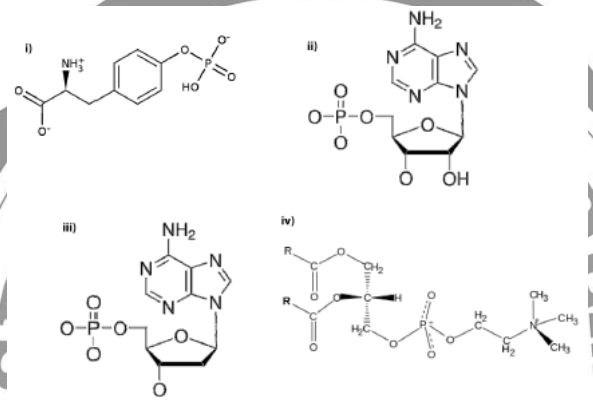
(d) A very low glass transition temperature

22. Which of the following plots represent(s) the Arrhenius rate equation, $k = Ae^{-Ea/RT}$ with $A = 3 \times 10^7 s^{-1}$ and $E_a = 3 \times 10^4 J/mol.$



(a) (i) (b) (ii) (c) (iii) (d) (i) and (ii)

23. Which of the following monomers do you expect to find in a RNA molecule?



(a) (i) (b) (ii) (c) (iii) (d) (iv)

24. How many normal modes does the CO_2 molecule have? What if the C and the O atoms were constrained to move in one dimension?

(a) 4 normal modes for free CO_2 and 4 for constrained CO_2

(b) 3 normal modes for free CO_2 and 2 for constrained CO_2

(c) 3 normal modes for free CO_2 and 3 for constrained CO_2

(d) 4 normal modes for free CO_2 and 2 for constrained CO_2

25. Two containers X and Y have equal fixed number of particles. Container X is maintained at constant temperature while container Y is maintained at constant temperature and pressure. What statistical ensemble will you use to best describe the properties of particles in the two containers?

(a) Canonical ensemble for both X and Y

(b) Microcanonical ensemble of X and canonical for Y

(c) Canonical ensemble for X and grand canonical ensemble for Y

(d) Microcanonical ensemble for both X and Y

26. An aqueous solution contains 0.300 mole L^{-1} of KH_2PO_4 and 0.0150 mole L^{-1} of K_2HPO_4. Which of the following statement(s) is/are true about this solution?

(a) It can act as a buffer solution around $pH \approx 7.0$

(b) It can act as a buffer solution around $pH = 12$

(c) Its pH will approximately equal to 6.9

(d) Both (a) and (c)

27. A catalyst :

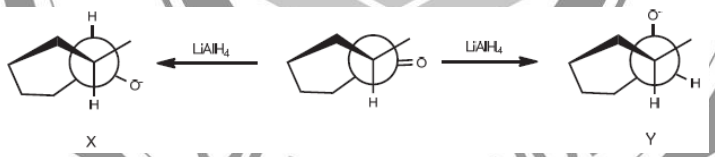
(a) Participates in the reaction

(b) Does not affect a reaction energy path

(c) Always decreases the rate for a reaction

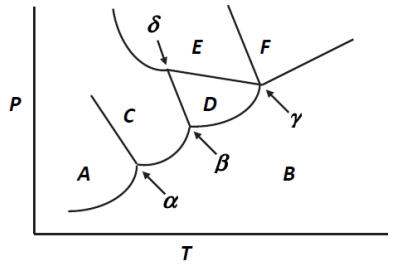
(d) Always increase the activation energy for a reaction

28. What would be the likely ratio of products X and Y for the following reaction on 2-methyl-cyclohexanone if we consider that torsional effects play a significant role in the reaction outcome?



(a) $X:Y = 80:20$ (b) $X:Y = 50:50$ (c) $X:Y = 20:80$ (d) $X:Y = 1:99$

29. A pure substance can exist in several different phases A, b, C,..... Its partial phase diagram shown below.



Which of the following statements is correct about the above diagram?

(a) The diagram is correct in all respects

(b) The diagram is wrong as it has more than one triple point

(c) A phase diagram cannot have an island, such as D

(d) The point γ cannot be present in any phase diagram

30. Free water pKa is 15.7 at $25°C$. Based on the free water pKa benchmark, arrange the acidity of the "bound" water molecules in increasing order within the following metal aqua complexes:

$\left[Mn(H_2O)_6\right]^{2+}, \left[Cu(H_2O)_5\right]^{2+}, \left[Ca(H_2O)_8\right]^{2+}, \left[Sr(H_2O)_8\right]^{2+}$

(a) $Ca^{2+} < Mn^{2+} < Cu^{2+} < Sr^{2+}$ (b) $Mn^{2+} < Cu^{2+} < Sr^{2+} < Ca^{2+}$

(c) $Sr^{2+} < Ca^{2+} < Mn^{2+} < Cu^{2+}$ (d) All have same acidities

31. The number of peptide bonds in a protein consisting of a linear chain of 128 amino acids is

(a) 127 (b) 128 (c) 129 (d) None of these

32. Which of the following statement(s) is/are true?

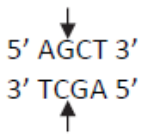
(i) The state function $\psi(x,t)$ is always equal to function of time multiplied by a function the coordinates

(ii) If f_1 and f_2 are eigenfunctions of an operator B, then $c_1f_1 + c_2f_2$ must always be an eidgenfunction of B, where c_1 and c_2 are constants

(iii) The operator L^2 commutes with $L_x + L_y$

(a) i and ii (b) i and iii (c) ii and iii (d) Only iii

33. The restriction enzyme AluI recognizes four DNA base pairs and cuts right in the middle as shown below:



What fragments of DNA do you expect to recover from the reaction mixture if the following DNA sequence

5′ CGACTAGCTACTGAGCTAAA 3′

3′ GCTGATCGATGACTCGATTT 5′

is partially digested with AluI. Partially digested means that the reaction is not allowed to proceed to completion, say only to 50%.

(i) 5′ GACTAG 3′ and 5′ CTACTGAGCTAAA 3′

3′ GCTGATC 5′ and 3′ GATGACTCGATTT 5′

(ii) 5′ CGACTAGCTACTGAG 3′ and 5′ CTAAA 3′

3′ GCTGATCGATGACTC 5′ and 3′ GATTT 5′

(iii) 5′ CGACTAG 3′ and 5′ CTACTGAG 3′ and 5′ CTAAA 3′

3′ GCTGATC 5′ 3′ GATGACTC 5′ 3′ GATTT 5′

(iv) 5′ CGACTAGCTACTGAGCTAAA 3′

3′ GCTGATCGATGACTCGATTT 5′

(a) Only i and ii (b) Only i and iii (c) Only iii and iv (d) i, ii, iii and iv

34. Which of the following statement are true?

(i) For a harmonic oscillator potential, the spacing between adjacent energy levels remain constant with increasing the quantum number.

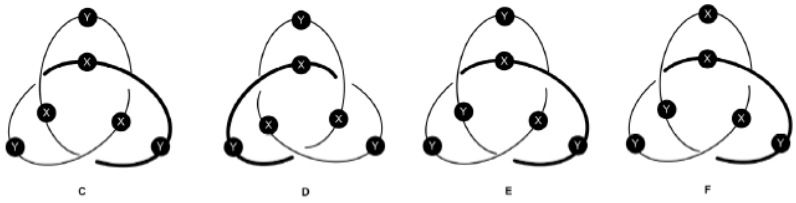
(ii) For a Morse oscillator potential, the spacing between adjacent energy levels increases with increasing the vibrational quantum number.

(iii) Harmonic oscillators are be used to explain the bond dissociation.

(iv) Morse oscillators cane be used to explain the vibration of molecules.

(a) i, ii and iii only (b) i and iv only (c) i, ii and iv only (d) i, ii, iii and iv

35. Molecular knots have been observed in DNA and proteins. Although synthetically challenging, a few purely organic molecular knots have also been reported in the literature. One such elusive knot is the trefoil knot. An organic trefoil knot was prepared by reacting two structurally distinct components X and y. the reaction mixture contained four products as shown in the figure below:



Which spectra will afford distinguishable spectral features for (1) C and D ? and (2) E and F?

(a) Circular Dichroism Spectra for C and D; ^{1}H -NMR for E and F

(b) ^{1}H -NMR and ^{13}C -NMR Spectra for C and D; Circular Dichroism for E and F

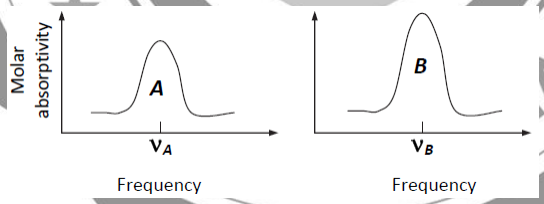
(c) Absorbance and Emission Spectra for C and D; Circular Dichroism for E and F

(d) Infra-Red Spectra for C and D; Circular dichroism for E and F

36. The molar absorption coefficient of sea water in the visible region is $6.2\times10^{-5}M^{-1}cm^{-1}$. What will be depth from the sea surface at which intensity of light becomes one-tenth of that at the surface?

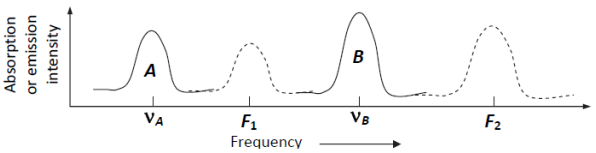
(a) 2.9 m (b) 0.9 m (c) 1.1 m (d) 8.0 m

37. The electronic absorption spectra or two species A and B are shown below:

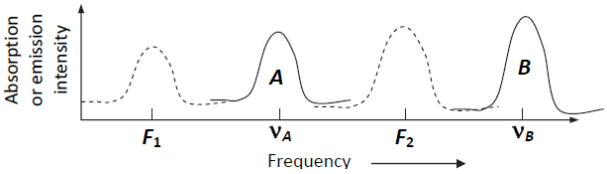


In a solution, these two species are dissolved, and they are moving freely, using a tunable laser, when the solution is excited at ν_A, a single fluorescence band is seen around frequency F_1. When the laser frequency is changed to ν_B, two fluorescence bands are seen around frequencies F_1 and F_2. Which of the following figures can qualitatively describe the correct relative positions of the frequencies ν_A, ν_B, F_1 and F_2 ? The continuous line shows absorption and the dashed line shows fluorescence emission spectra?

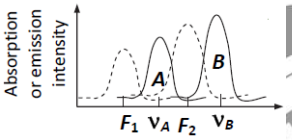
(a)



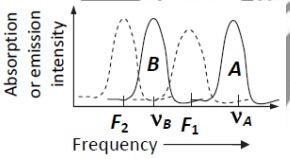
(b)



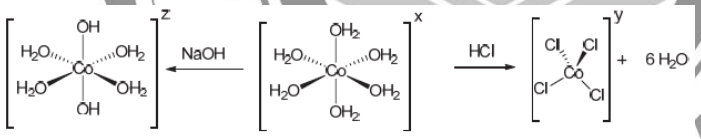
(c)



(d)



38. For Co in oxidation state II, predict the overall charges of the coordination complexes shown in the reactions below:



(a) $z=+2; x=-2; y=+2$ (b) $z=0; x=+2; y=-2$

(c) $z=0; x=+2; y=+2$ (d) $z=-2; x=+2; y=-2$

39. If $\psi(x,t)$ can be expressed as a product of two functions f(t)g(x), where f(t) has the form $\exp\left[-(iEt/h)\right]$ then it can be shown that the probability of finding the particle between x and $(x+dx)$

(a) Equal to 1

(b) Is independent of time

(c) Can be obtained by solving Time Dependent Schrodinger Equation

(d) Can be obtained by solving Time Independent Schrodinger Equation

40. Which of the following statements is TRUE regarding the electrical conductivity of HCl in aqueous solution, HCl as a gas and HCl in benzene?

(a) All three conduct electricity because HCl is a strong acid

(b) HCl in aqueous solution only conducts electricity because it is ionized but not HCl gas and HCl in benzene

(c) HCl in benzene is not conducting because benzene is a non-polar solvent and but HCl gas and HCl in aqueous solution conduct electricity

(d) HCl in aqueous solution and HCl in benzene are conducting because they are solutions but not HCl gas