TIFR M.Sc. CHEMISTRY ENTRANCE - 2017

1. All natural amino acids, except one, react with cold nitrous acid and produce nitrogen gas. Which one of the following is that odd amino acid?

(a) Tryptophan (b) Glycine (c) Proline (d) Histidine

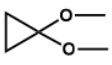
2. Predict the multiplicities for hydrogens on Cl, C3, and C4 of butanone associated with the spin-spin coupling in its ^{1}H NMR spectrum.

(a) H's on C1: Singlet; H's on C3: Doublet ; H's on C4: Triplet
(b) H's on C1: Singlet; H's on C3: Triplet; H's on C4: Quartet
(c) H's on C1: Singlet; H's on C3: Quartet; H's on C4: Triplet
(d) H's on C1: Triplet; H's on C3: Doublet; H's on C4: Triplet

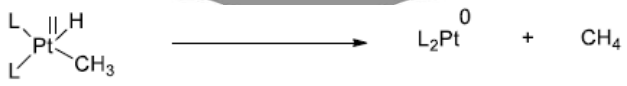
3. If standard potential of the reaction $2H_2O(l) = O_2(g, 1bar) + 4H^+(aq) + 4e^-$ is $E^0 = -1.23\,V$. At $25°C$ and $pH = 7$, what is the oxidation potential of pure water according to this reaction?

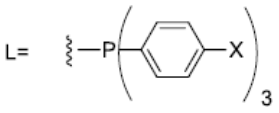
(a) $0.410\,V$ (b) $-2.620\,V$ (c) $-0.817\,V$ (d) $-0.410\,V$

4. An organic compound has the following spectroscopic properties: Mass Spectrometry: m/z 102 (very small), 87 and 43 are the largest ions; ^{1}H NMR : δ 1.4 and 3.9 ppm (both singlets, intensity ratio 3:2); ^{13}C NMR : δ 108, 64 and 25 ppm; Infrared spectroscopy: several strong absorptions in the 1000 to 1300 cm^{-1} region. Which of the following is the most likely formula of this compound?

(a)  (b)  (c)  (d) 

5. Predict the relative rates for the following reductive elimination for $X = H, Cl, CH_3, OCH_3$

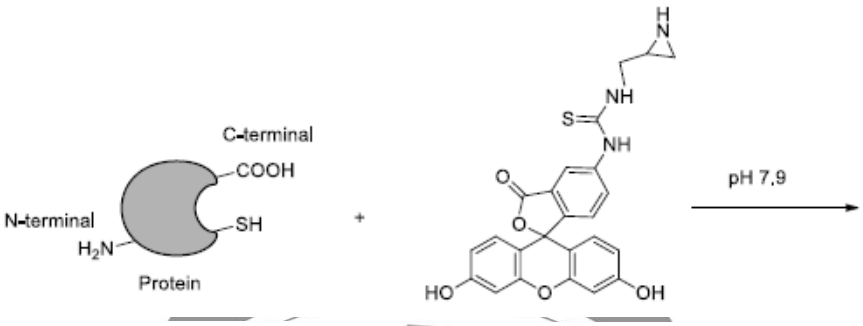


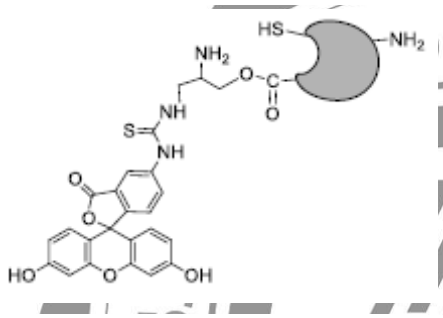


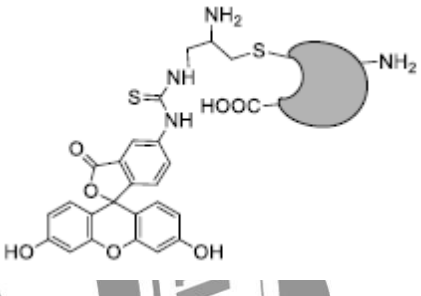
(a) $Cl > H > CH_3 > OCH_3$ (b) $H > Cl > OCH_3 > CH_3$

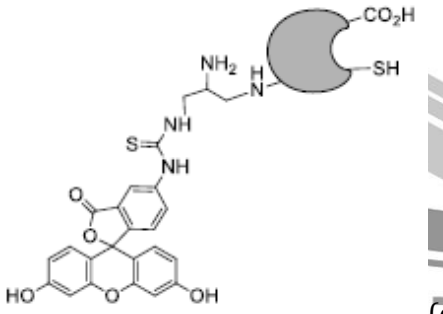
(c) $OCH_3 > CH_3 > H > Cl$ (d) $CH_3 > H > Cl > OCH_3$

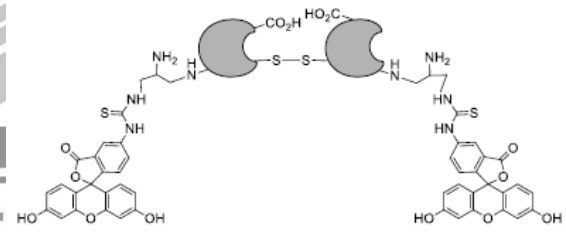
6. A bio-conjugation reaction can be used to modify a specific residue on a protein to attach therapeutics and diagnostic agents. Predict the major product of the following bio-conjugation reaction with Fluorescein.



(a) 

(b) 

(c) 

(d) 

7. For a hydrogen atom, which of the following orbital(s) have the lowest energy:

(a) 4s (b) 4p

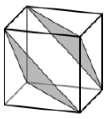
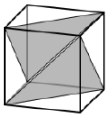
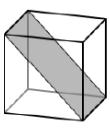
(c) 4d (d) All of the above have same energy

8. An electron tunnels through a square barrier of width d and height h. Ig h is fixed and d is is normally distributed, then the electron transfer probability distribution is:

(a) a normal distribution (b) a delta function

(c) a log normal distribution (d) a poisson distribution

9. In a cubic unit cell, identify the Miller plane (111)

(a)  (b)  (c)  (d) None of these

10. Zinc solid has hcp (hexagonal close packed) structure. In a unit cell of Zinc solid, the Zinc atoms occupy

(a) 74% of volume of unit cell. (b) 80% of volume of unit cell.

(c) 68% of volume of unit cell. (d) 90% of volume of unit cell.

11. The acidity of molecules is usually measured by a parameter called the pK_a. Metal ions $\left(M^{n+}\right)$ solubilized in water solvated aqua complexes commonly denoted by $\left[M\left(H_2O\right)_m\right]^{n+}$ or M_{aq}^{n+}. It is known that the pK_a of coordinated water in such metal-aqua complexes will be different format that of bulk water. For the following set of metal-aqua complexes: $Ca_{aq}^{2+}, Fe_{aq}^{2+}, Mn_{aq}^{2+}, Fe_{aq}^{3+}$; arrange the complexes with decreasing value of expected pK_a of the coordinated water molecule:

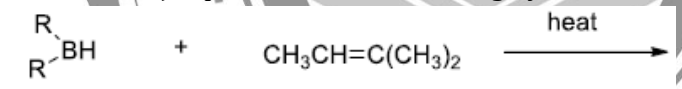
(a) $Fe_{aq}^{2+} > Mn_{aq}^{2+} > Ca_{aq}^{2+} > Fe_{aq}^{3+}$ (b) $Ca_{aq}^{2+} > Mn_{aq}^{2+} > Fe_{aq}^{2+} > Fe_{aq}^{3+}$

(c) $Fe_{aq}^{2+} > Fe_{aq}^{3+} > Mn_{aq}^{2+} > Ca_{aq}^{2+}$ (d) $Mn_{aq}^{2+} > Ca_{aq}^{2+} > Fe_{aq}^{2+} > Fe_{aq}^{3+}$

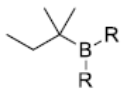
12. Solid inorganic materials are commonly classified as conductors, semi-conductors or insulators as determined by their bandgap. Carbon has many allotropes such as diamond, graphite, carbon nanotubes and graphene with distinct bandgaps. Considering the properties of diamond, what should its bandgap:

(a) 7.0 eV (b) 1.0 eV (c) 0.01 eV (d) 0 eV

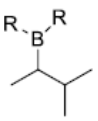
13. Predict the major product of the following hydroboration reaction:



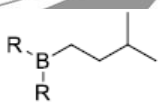
R =



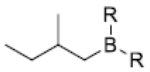
(a)



(b)



(c)



(d)

14. Given an operator A and a set of vectors X which obey the following relationship

$$AX = \lambda X,$$

where λ is the set of scalars. If A commutes with B and $B \neq A$, which of the following is correct:

(a) X are eigenvectors of A only if the λ are all distinct (no two eigenvalues are equal)

(b) X are eigenvectors of B

(c) X are eigenvectors of B with set of eigenvalues λ

(d) X need not be eigenvectors of A

15. Given the molecular formula of the hexa-coordinated complexes

(I) $Co\,Cl_3(NH_3)_6$

(II) $Co\,Cl_3(NH_3)_5$

(III) $Co\,Cl_3(NH_3)_4$

If the number of coordinated NH_3 molecules in (I), (II), and (III) respectively are 6, 5 and 4 then the oxidation state of Co in (I), (II) and (III) are respectively:

(a) $+6,+5,+4$ (b) $+3,+2,+1$ (c) $0,+1,+2$ (d) $+3,+3,+3$

16. An aqueous solution contains 0.300 mole L^{-1} of KH_2PO_4 and 0.015 mole L^{-1} of KH_2PO_4. Which of the following statements is true about this solution? $[Data: For\ H_3PO_4, pK_1 = 2.16, pK_2 = 7.21, pK_3 = 12.32]$

(a) It can act as a buffer solution around $pH = 2$

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

(c) Its pH will approximately equal to 6.9

(d) Both b and c.

17. What is the value of the continued fraction given below?

$$1+\cfrac{2000}{2+\cfrac{2000}{2+\cfrac{2000}{2+...}}}$$

(a) 1999 (b) $\sqrt{2000}$ (c) $\sqrt{2001}$ (d) None of them

18. For angular momentum vector operator $\vec{L}$, which of the following relation is true:

(a) $\vec{L}\times\vec{L} = i\hbar\vec{L}^2$ (b) $\vec{L}\times\vec{L} = i\hbar\vec{L}$ (c) $\vec{L}\times\vec{L} = -i\hbar\vec{L}^2$ (d) $\vec{L}\times\vec{L} = 0$

19. The complex showing a spin-only magnetic moment od 2.82 B.M. is

(a) $\left[Ni(CO)_4\right]$ (b) $\left[NiCl_4\right]^{2-}$ (c) $\left[Ni(NH_3)_4\right]^{2+}$ (d) $\left[Ni(CN)_4\right]^{2-}$

20. What are the products of the following reaction?

$$LiAlH_4 + Et_3NHCl \xrightarrow{\text{Toluene}}$$

(a) $H_2 + Et_3N + LiCl + AlH_3$ (b) $LiH + Et_3N + HCl + 0.5\ Al_2H_6$

(c) $LiCl + H_3Al:NEt_3 + H_2$ (d) $LiCl + NEt_3 + H_2 + 0.5\ Al_2H_6$

21. Isotopic substitution an often-used procedure in assigning vibrational spectroscopic features but the difference in isotopic of the vibrating atoms has to be sufficiently large to make the vibrational shift observable. In a double isotopic replacement experiment, a

proline with a $^{13}C=^{18}O$ carbonyl group is inserted in the middle of the polypeptide using molecular recombinant techniques. Given that in the naturally found proline the $^{12}C=^{16}O$ group exhibits a narrow vibrational feature at 1, 711 cm^{-1}, what is the shift of the carbonyl stretching vibration for the $^{13}C=^{18}O$ proline isotopomer.

Assume:

(A) The force constant for different isotopes can be considered identical.

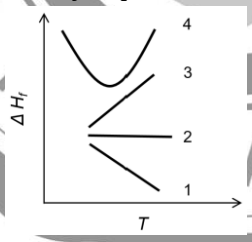
(B) The isotopic changes in the carbonyl group will have little effect on the vibrations of other atoms in proline.

(a) 80 cm^{-1} (b) 165 cm^{-1} (c) 85 cm^{-1} (d) 42.5 cm^{-1}

22. A compound with molecular formula $C_5H_{12}O_2$, has strong infrared absorption at 3300 to 3400 cm^{-1}. The ^1H NMR spectrum showed three singlets at δ 0.90, δ 3.45 and δ 3.20 ppm; with relative areas 3:2:1. Addition of D_2O to the sample eliminates the lower field signal. The ^{13}C NMR spectrum shows three signals all higher than δ 100 ppm. Which of the following compounds best fits this data?

(a) 1,5-pentanediol (b) 1,3-dimethoxypropane
(c) 2,2-dimethyl-1,3-propanediol (d) 2,4-pentanediol

23. The heat of formation (ΔH_f) for the reaction $2Cu(s)+O_2(g)\rightarrow 2CuO(s)$ is measured and plotted as a function of temperature (T). Of the 4 possible graphs shown below, which one would most likely represent the observed trend?



(a) 1 (b) 2 (c) 3 (d) 4

24. During isothermal expansion of an ideal gas which of the following happen:

(i) Temperature does not change

(ii) process is spontaneous

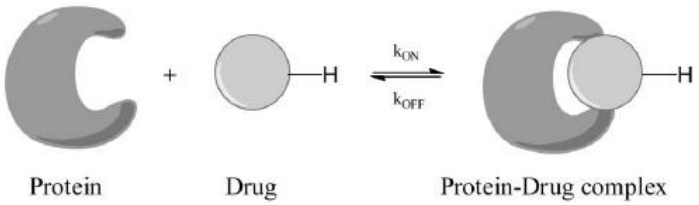
(iii) The energy of the system does not change

(iv) Entropy increases

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

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

25.



NMR spectroscopy can be used to assay for drug binding to certain protein targets. One of the primary objectives of any binding assay is the quantification of the free and the bound forms of a drug molecule at a certain concentration of the protein target. Let us assume that the fully bound drug exhibits a ^1H chemical shift of δ_A while that of the free form resonates at δ_B for the same proton (see figure above). If the exchange timescale (i.e. proportional to $k_{OFF}ask_{ON}$ is diffusion limited) between the free form of the drug and its bound form is in microseconds, which of the following statements cannot be true assuming that the drug is only 50% bound with its protein target?

(a) The NMR linewidth of the observed transition(s) will be different from the free form of the drug.

(b) There will be two resonances obtained in the NMR spectrum of the Protein-Drug complex: one of the free form while other for the bound form.

(c) We will see a single resonance at a position δ_{eff} which is in between δ_A and δ_B

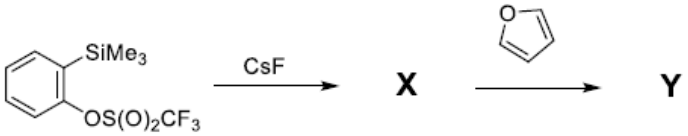
(d) Varying the concentration of the drug molecule while observing the NMR signatures will provide an estimate of the binding constant.

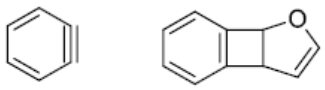
26. What is the value of $i\log_{10} i^2$, where $i=\sqrt{-1}$?

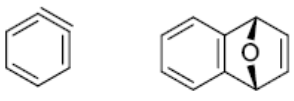
(a) Real and positive number (b) Real and negative number

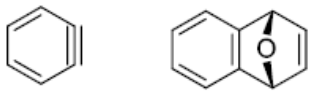
(c) Complex number (d) Purely imaginary

27. What are X and Y in the following reaction?

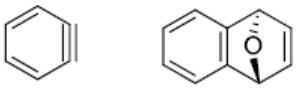


(a) 

(b) 



(c) **X** **Y**



(d) **X** **Y**

28. At $25°C$, if the pK_a value for a weak acid is smaller than is aqueous solution pH by 2, what is the fraction of the acid in dissociated form?

(a) 1.10% (b) 99.01%

(c) 0.99% (d) More information is needed

29. Cyclooctatetraene is

(a) aromatic, because it is planner ad it follows Hückel's rule

(b) antiaromatic, because it is not planner and it does not follow Hückel's rule

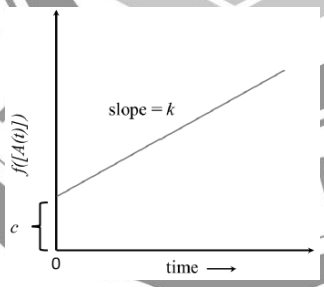
(c) antiaromatic, because it is planner and it does not follow Hückel's rule

(d) nonaromatic, because it is not planar and it does not follow Hückel's rule

30. In an experiment measuring the weight of the object, 100 repeats were performed by one student. He found the mean weight of 332 grams with standard error of the mean as 5 grams. A lazier student only performs 10 measurements on the same object. Which of the following values will her result be closest to?

(a) 330 ± 50 grams (b) 400 ± 15 grams (c) 330 ± 15 grams (d) 330 ± 5 grams

31. The graph below plots the progress of a dimerization reaction involving species A. It depicts a straight line with slope k (the rate constant). What is the value of the intercept, c in the graph?



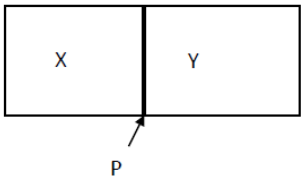
(a) $\left[A(0)\right]$ (b) $\left[A(0)\right]^2$ (c) $\left[A(0)\right]^{-1}$ (d) $k \times \left[A(0)\right]^2$

32. Two compartments X and Y are separated by an impermeable partition P. In the compartment X, the following reaction is going on in a solvent S, while the compartment Y contains only the solvent S:

$$A_2 + B_2 \leftrightarrow 2AB$$

Contents of both the compartments are continuously and vigorously stirred. After the reaction in the compartment X has reached equilibrium, the concentrations of A_2, B_2 and AB are measured and the equilibrium constant calculated. Then the partition

is quickly removed. After waiting for a very long time, all the concentrations are measured again, and the new value of the equilibrium calculated. What is the most appropriate statement you can make about the result of this experiment? Assume that the chemicals are behaving ideally and the temperature is kept constant.



(a) The concentrations of all the chemicals and the equilibrium constant will be less than their values before the partition was removed.

(b) After removing the partition, the concentrations of A_2 and B_2 will increase, and that of AB will decrease.

(c) After removing the partition, the concentrations of A_2 and B_2 will decrease and that of AB will increase.

(d) After removing the partition, the concentrations of all the chemicals will decrease.

33. Assume that the temperature (T) dependence of ΔG for a chemical reaction can be represented by an equation of the form

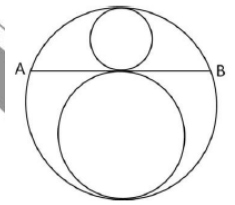
$$\Delta G = x + yT + zT^2$$

What is the expression for the heat capacity change at constant pressure, ΔC_p ?

(a) x/T (b) $-y$

(c) $-2zT$ (d) Insufficient information

34. If the outer circle radius is 'Z', in the diagram given below, then what is the line segment AB? The ratio of inner circles' diameters is 2.



(a) $\frac{4\sqrt{2}}{3}Z$ (b) close to 2 Z (c) $\frac{\sqrt{5}}{\sqrt{2}}Z$ (d) $\frac{2\sqrt{5}}{3}Z$

35. A kid has been playing with an inflated balloon, suddenly, a reaction happens inside the balloon. This causes the inside surface of the balloon to become sticky, so that some of the air molecules inside which collide against the surface get stuck to it. As a result, immediately after the reaction, the balloon will

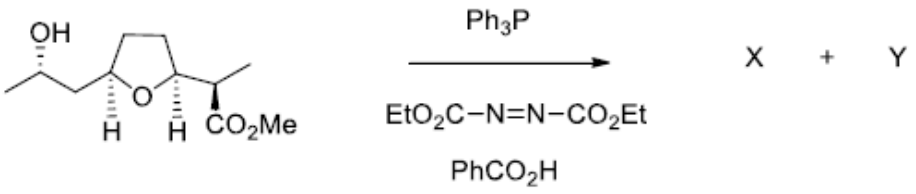
(a) Inflate

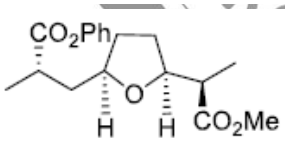
(b) Deflate
(c) Remain unaltered
(d) Will change its shape without changing its volume

36. The non-bonded interactions between two molecules consist of electrostatic (EI) and van der Waals (vdW) forces. Which of the following is a correct description of the distance dependence intermolecular interactions between two molecules?
(a) At large distances, El interactions decay faster than the vdW interactions
(b) At large distances, vdW interactions decrease faster than the el interactions
(c) Which force drops faster depends on the net charge of the molecules
(d) Both interactions have same distance dependence

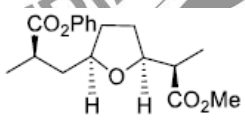
37. "Doping" and "Alloying" are two common terms used to describe the presence of two different elements in one material. Which one of the following statements is false?
(a) Doping is the process of intentionally introducing impurities into an semiconductor in order to change its electrical properties.
(b) Doping means making one solid solution.
(c) Alloying is a homogeneous mixture of two or more elements, at least one of which is a metal.
(d) In an alloy, the combined mixture has different properties from those of its component elements.

38. What major products are obtained in the following Mitsunobu reaction?

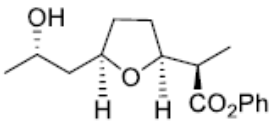


(a) 

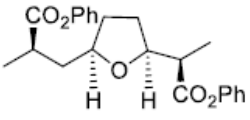
and $Ph_3P=O$

(b) 

and $Ph_3P=O$

(c) 

and $Ph_3P=O$

(d) 

and $Ph_3P=O$

39. A particle in a 1-D box of length L has eigenstates $\psi_n(x)$ with energies E_n. Consider two initial states of the particle at time $t=0$: $case(1)\ \psi(x,t=0)=\psi_n$ (arbitrary n), and $case(2)\ \psi(x,t=0)=\psi_n+\psi_n$ (arbitrary n and m; $n\neq m$). The probability to find the particle at a specific position within the box:
(a) Varies with time for case 1 but not for case 2

(b) Is time dependent for both cases

(c) Is time independent for both cases

(d) Varies with time for case 2 but for case 1

40. In a rotational microwave spectrum of $C^{12}O^{16}$ lines were equally spaced by $3.863\ cm^{-1}$. In a rotational Raman spectrum of N_2 (normal isotope) the lines were equally spaced $8.04\ cm^{-1}$. Assuming that the force constant for the two molecules in inversely proportional to their bond lengths, the ratio of the vibrational frequency of CO to that of N_2 will be:

(a) 0.8368 (b) 0.9952 (c) 1.0258 (d) 1.2198