TIFR M.Sc. CHEMISTRY ENTRANCE - 2010

1. What is $\left[H^{+}\right]$ in 1.0 L solution that contains 0.2 M of NH_4Cl?

(a) 1.1×10^{-5} M

(b) 1.9×10^{-3} M

(c) 1.8×10^{-5} M

(d) Not solvable with the information given

2. It is not easy to locate H atoms in the structure of proteins obtained by X-rays diffraction due to which the following reasons:

(a) H atoms are transparent to the X-rays

(b) H-bonding interaction present in protein structure

(c) interaction of H with solvent molecules

(d) Very low levels of scattering of X-rays by H

3. Glucose and galactose (found in the human body) are related to each other as :

(a) Enantiomers (b) Anomers (c) Epimers (d) L-sugars

4. Consider the formation of MgO(s). Assume that ΔH_r° and ΔS_r° are independent of temperature.

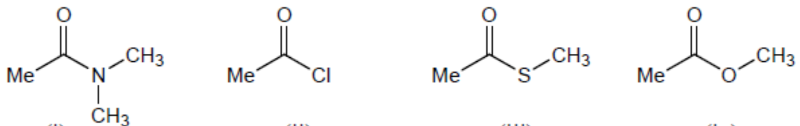
$$Mg(s)+\frac{1}{2}O_2(g)\rightarrow MgO(s)$$
$$\Delta H_r^\circ=-602\ kJ/mol$$
$$\Delta S_r^\circ=-108\ J/K\ mol$$

Calculate ΔG_r° for the formation of MgO(s) at $0^\circ C$ and is the reaction spontaneous or non-spontaneous at $0^\circ C$?

(a) $-573\ kJ/mol$, non-spontaneous (b) $-573\ kJ/mol$, spontaneous

(c) 632 kJ/mol, non-spontaneous (d) $-632\ kJ/mol$, spontaneous

5. Rank the following molecules in order if electrophillicity (from most to least electrophilic):



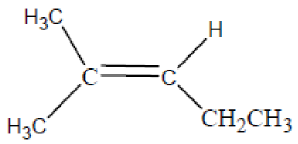
(i) (ii) (iii) (iv)

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

6. Which of the following transitions is the highest energy transition in any given organic molecule?

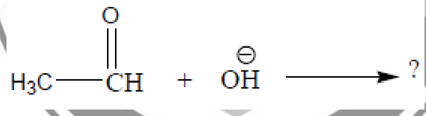
(a) n to σ^* (b) n to π^* (c) σ to σ^* (d) π to π^*

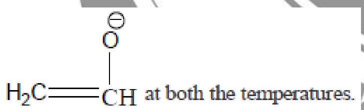
7. How many absorption lines will the following naturally occurring compound have in its proton-decoupled ^{13}C NMR spectrum?

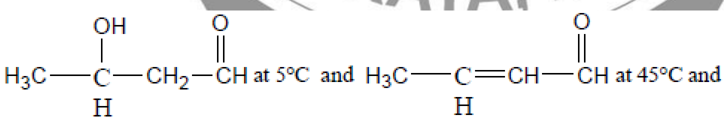


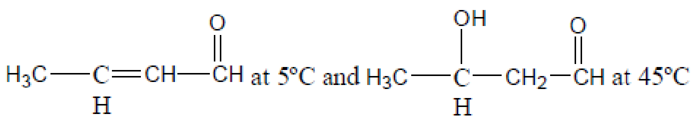
(a) 3 (b) 4 (c) 5 (d) 6

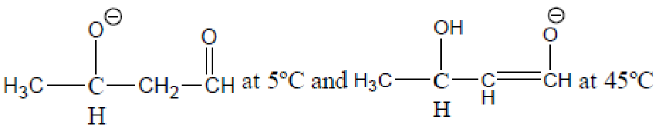
8. What would be the final major product of the following chemical reaction if it is carried out twice, once at $5°C$ and the second time at $45°C$?



(a) 

(b) 

(c) 

(d) 

9. 0.1 M solution of a compound transmits 10% of the incident light. Another solution of the same compound transmits 1% of the incident light of the same wavelength in the same container. Calculate concentration of the solution.

(a) 0.02 M (b) 0.20 M (c) 0.21 M (d) 0.11 M

10. A polypeptide chain has six-SH groups. Any two SH groups can combine to give a disulphide (-S-S-) bond. If such combinations are allowed to take place randomly, how many different protein structures can be formed?

(a) 12 (b) 15 (c) 30 (d) 36

11. Consider the following reaction carried out in presence of catalyst, C :

$$aA + bB \rightarrow dD + eE$$

The rate law for this reaction is, $\text{rate} = k[A]^q[B]^r[C]^s$

Which of the following statement is false?

(a) The exponents q, r and s are often integers

(b) The overall reaction order is $q + r + s$.

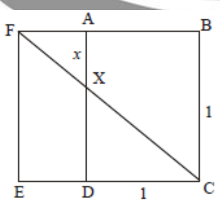
(c) The exponents q and r are always equal to the coefficients a and b, respectively.

(d) The exponents must be determined experimentally.

12. The crystal lattice structure of sodium, vanadium and molybdenum is BCC (Body centered cubic). Which of the following metallic mixtures are most likely to form a solid solution?

(a) V and Mo (b) V and Na (c) Mo and Na (d) Na, V, Mo

13. FBCE is a rectangle. ABCD is a square in it with length of each side being of unit length. If AX has length of x units then the length of FA is given by



(a) $2(1-x)$ (b) $\frac{x}{1-x}$ (c) $\frac{1}{4x^2}$ (d) $\frac{2x^2}{(1-x)}$

14. At $1000°K$ for the following two equilibria, the representative K_p values are given :

(i) $CaCO_3 \leftrightarrow CaO + CO_2$ $\quad K_p = 4.0 \times 10^{-2}$ atm

(ii) $C + CO_2 \leftrightarrow 2CO$ $\quad K_p = 2.0$ atm

Solid Carbon (C), CaO, $CaCO_3$ are mixed and allowed to attain equilibrium at $1000°K$. What is the pressure of CO achieved at equilibrium?

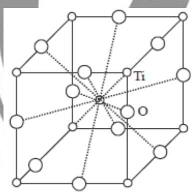
(a) 0.56 atm (b) 0.08 atm (c) 2.8 atm (d) 0.28 atm

15. Assume that a carnot engine is working in reverse in a refrigerator, with perfect thermodynamic efficiency. Calculate the amount of work needed (i) to freeze 100 g of water at $0°C$, the temperature of the surrounding being $25°C$; (ii) to withdraw the same amount of heat from a body at 10^{-5} K, the surrounding being at 1 K.
$(\Delta H_{melt} = 0.01\,kJ/mol)$

(a) (i) 601 kJ; (ii) 601 kJ (b) (i) 33.4 kJ; (ii) 33.4 kJ

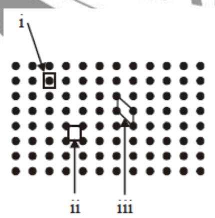
(c) (i) 3.06 kJ; (ii) 33.4 kJ (d) (i) 3.06 kJ; (ii) 33.4×10^5 kJ

16. What is the empirical formula for the following unit cell:



(a) $CaTi_{12}O_8$ (b) $CaTi_8O_{12}$ (c) $CaTiO_3$ (d) $CaTi_2O_3$

17. Which of the parallelogram in the figure below are viable unit cells?



(a) i (b) ii (c) iii (d) all of the above

18. The following reaction is at equilibrium in a cylinder fitted with a movable plunger.

$$N_2O_4(g) \leftrightarrow NO_2(g)$$

If the volume is decreased at constant temperature by moving the plunger, will the concentration of $NO_2(g)$ be higher or lower than the original concentration when the equilibrium is reestablished?

(a) The concentration of NO_2 will decrease, as Le Chatelier principle predicts that the equilibrium must shift so as to oppose/minimize/relieve the total pressure.

(b) The concentration of NO_2 will increase.

(c) The concentration of NO_2 will decrease. If the volume is decreased, the equilibrium must shift to produce fewer molecules. Thus the equilibrium must shift to produce fewer molecules. Thus the equilibrium must shift to the left.

(d) The change in the concentration of NO_2 is not certain. Le Chatelier principle predicts that the equilibrium must shift to the left to minimize the total pressure. However, the volume has decreased, so the number of NO_2 molecules must also decrease, making it difficult to say whether the concentration of NO_2 would decrease or increase.

19. To a green solution of $Ni(H_2O)_6^{2+}$, a small quantity of ammonia was added, which turned the solution blue through formation of $Ni(HO_3)_6^{2+}$. The value of the equilibrium constant K for this reactions is $\sim 10^9$. To this blue solution, the same number of moles of a chelating ligand ethylenediamine (en) were added, turning the solution violet through formation of $Ni(en)_3^{2+}$. The value of K for this reaction is also $\sim 10^9$. Using these same quantities, what would happens if en was added first, then ammonia was added?

(a) The violet solution would turn blue.

(b) The violet solution would stay violet.

(c) There will be an equimolar mixture of $Ni(NH_3)_6^{2+}$, giving the solution a colour which is an intermediate between blue and violet.

(d) The question cannot be answered without knowing the concentrations and the volumes of all the reactants.

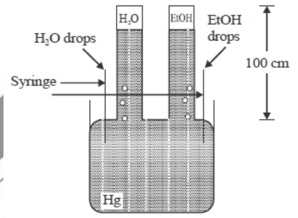
20. In a mass spectrum of bromine molecule shows three peaks due to the species Br_2^+ with the mass numbers 158, 160 and 162. Which isotopes of bromine occur in nature?

(a) ^{79}Br and ^{80}Br

(c) ^{79}Br and ^{81}Br

(b) ^{80}Br and ^{81}Br (d) ^{79}Br, ^{80}Br and ^{81}Br

21. Two 120-cm long test tubes are filled with mercury and then placed in a mercury reservoir in an inverted position, as shown below. The height of the test tubes above the mercury pool is 100 cm. Syringes are used to bring drops of H_2O and ethanol to the top of columns of Hg, as shown below. Drops are added till a small amount after the addition? The experiment is done at normal temperature and pressure.



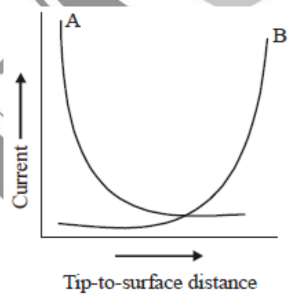
(a) Both column heights will be the same

(b) The column below H_2O is shorter.

(c) The column below EtOH is shorter.

(d) The column that has more number of drops will be shorter

22. Scanning tunneling microscopy depends upon the flow of electricity (current) between a surface and an atomically-sharp probe tip. Two plots of current vs. Tip-to-surface distance are shown below. Which one is correct?



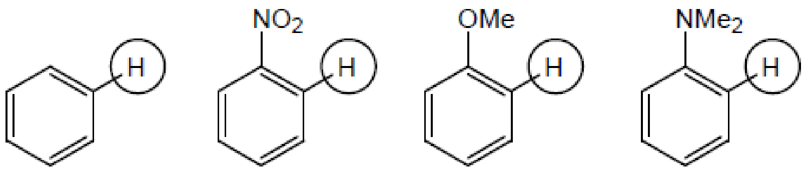
(a) A

(b) B

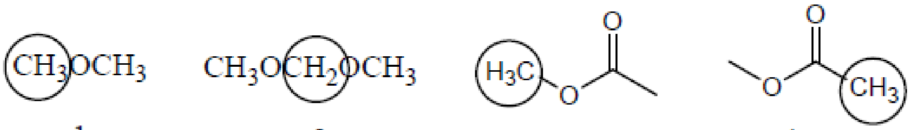
(c) If the tip is more conducting than the surface, then the answer is A. Otherwise, the answer is B.

(d) Insufficient information is given to answer the question.

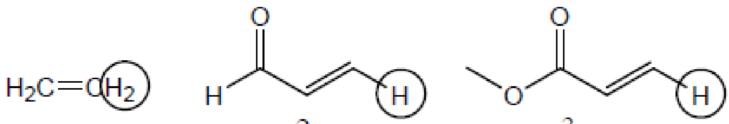
23. For each of compounds below, choose the one in which the indicate hydrogen is farthest upfield in a proton NMR spectrum :

(A) 

1 2 3 4

(B) 

1 2 3 4

(C) 

1 2 3

(a) A3 or A4, B4, C1 (b) A1, B2, C3 (c) A2, B3, C2 (d) A4, B1, C1

24. Consider the following two infinite series:

$$A=\sum_{n=0}^{n=\infty}(-1)^{n}\frac{x^{2n+1}}{(2n+1)!}\qquad B=\sum_{n=0}^{n=\infty}(-1)^{n}\frac{x^{2n}}{(2n)!},\ \text{where x is real}$$

What is the value of A^2+B^2?

(a) 0

(b) $+\infty$

(c) 1

(d) Its value cannot be defines, as the series A and B are divergent.

25. Four separate solutions are present in separate containers: HCL, NaOH, CH_3COOH, and CH_3COOK. What possible pars can be used to make a buffer solution?

(a) HCl and CH_3COOK (b) NaOH and CH_3COOH

(c) CH_3COOH and CH_3COOK (d) All of the above

26. It is well known that the structure of ethylene $(CH_2 = CH_2)$ is planar. Hence, what would be the structure of allene $(CH_2 = C = CH_2)$ and cumulene $(CH_2 = C = C = CH_2)$?

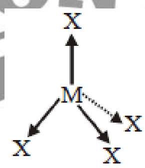
(a) Both will be planar

(b) Both will be staggered

(c) Allene will be planar, and cumulene will be staggered

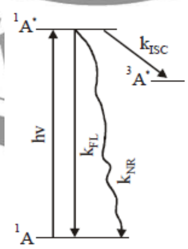
(d) Allene will be staggered, and cumulene will be planar

27. In the T_d molecule MX_4, the A_1 vibrational mode corresponds to all the M-X bonds stretching the same distance simultaneously. With which spectroscopic technique is this vibrational mode observable?



(a) IR (b) Raman (c) Neither (d) Both

28. An organic molecule A on photoexcitation goes to $^1A*$. Its various decay channels are shown below. You measure the concentration of $^3A*$ as a function of time using a fast-response spectrometer, in order to determine the intersystem crossing rate constant k_{ISC}. Assume that the lifetime of $^3A*$ is very long compared to the other kinetic processes shown there. Which of the following statements would be true for this experiment?



(a) The decay of $^1A*$ will be multi-exponential

(b) The formation of $^3A*$ will be single exponential.

(c) Plotting the concentration of $[^3A*]$ as a function of time, and fitting it to a single exponential will not give k_{ISC}.

(d) Both (b) and (c) above.

29. Consider the four sulphates $FeSO_4, MnSO_4, ZnSO_4$. Four separate capsules of these materials have been made containing 0.1 mole of the substance and are suspended separately by a thread. Then a strong magnet is brought close to each capsule. Order these sulphates according to the strength of the response that the magnet will produce on these capsules.

(a) $MnSO_4 > FeSO_4 > CoSO_4 > ZnSO_4$ (b) $FeSO_4 > MnSO_4 > CoSO_4 > ZnSO_4$

(c) $ZnSO_4 > CoSO_4 > FeSO_4 > MnSO_4$ (d) $CoSO_4 > FeSO_4 > MnSO_4 > ZnSO_4$

30. $N_2O_5(g)$ and $NO(g)$ react to form NO_2 according to the stoichiometric equation

$$N_2O_5(g) + NO(g) \rightarrow 3NO_2(g) \qquad (R1)$$

at a given temperature and pressure. A possible mechanism for this overall reaction is:

$N_2O_5 \xrightarrow{k_1} NO_2 + NO_3$ (M1)

$NO_2 + NO_3 \xrightarrow{k_2} N_2O_5$ (M2)

$NO_3 + NO \xrightarrow{k_3} 2NO_2$ (M3)

where NO_3 is an unstable intermediate. What would be the rate expression of the disappearance of NlO_5 in terms of the concentrations of the stable species and the rate constants given above?

(a) The mechanism given above is not correct since the resultant of the reaction $M1 + M2 + M3$ is not the original reaction R1.

(b) $-\frac{d}{dt}[N_2O_5] = k_1[N_2O_5]\left(1 - \frac{k_2[NO_2]}{k_2[NO_2] + k_3[NO]}\right)$

(c) $-\frac{d}{dt}[N_2O_5] = k_{eff}[N_2O_5][NO]$, where k_{eff} is some function of k_1, k_2 and k_3.

(d) $\frac{d}{dt}[N_2O_5] = k_1[N_2O_5]\left(1 + \frac{k_2[NO_2]}{k_2[NO_2] + k_3[NO]}\right)$

31. For a cell constructed with a $Cu(s)|Cu^{2+}(aq)$ anode and $Ag^{+}|Ag(s)$ cathode at $25.0°C$, under non-standard conditions: $\left[CU^{2+}\right]=0.300\,M$ and $\left[Ag^{+}\right]=0.0500\,M.$

(a) 0.44 V (b) 0.41 V (c) 0.40 V (d) 0.34 V

32. Photo-exciation promotes an electron from the HOMO (highest occupied molecular orbital) to the LUMO (lowest unoccupied molecular orbital) of a molecule. Between a molecule in its ground state and its excited state, which would be the stronger oxidant and the stronger reductant?

(a) The molecule in its ground state would be a stronger oxidant and also a stronger reductant.

(b) The molecule in its excited state would be stronger oxidant and also a stronger reductant.

(c) The molecule in its ground would be a stronger reductant, and in the excited state, a stronger reductant.

(d) The molecule in its ground state would be a stronger reductant, and in the excited state, a stronger oxidant.

33. The stretching frequency of the $O-H$ is about $3600\,cm^{-1}$. Compared to that, the stretching frequencies of $O-D$ and $S-H$ bonds are very similar and appear at about $2500\,cm^{-1}$. What can you conclude from these data?

(a) The electronic structure of $O-D$ and $O-H$ are same, and that $S-H$ is different.

(b) The force constant of the bonds $O-D$ and $O-H$ is same.

(c) $S-H$ is a weaker bond than $O-H$ or $O-D$ bond.

(d) All of the above.

34. Read the following two statements carefully:

1. The change in total angular momentum that occurs when a diatomic molecule (i.e. a rigid rotor) changes rotational level from $J=2$ to $J=3$ is the same as the change in total angular momentum that occurs when an electron on a H atom changes from a d to an f orbital, i.e. from $l=2$ to $l=3$.

2. The change in energy that occurs when a diatomic molecule (i.e. a rigid rotor) changes level from $J=2$ to $J=3$ is the same as the change in energy that occurs when an electron on a H atom changes from a d to an f orbital, i.e. from $l=2$ to $l=3$.

Based on the above, which of the following is the correct statement:

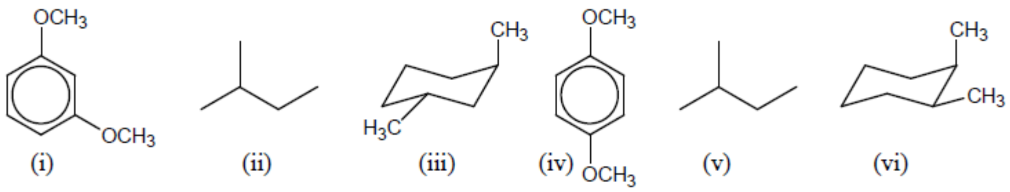
(a) Both statements 1 and 2 are true

(b) Both statements 1 and 2 are false

(c) Statement 1 is true, statement 2 is false

(d) Statement 1 is false, and statement 2 is true

35. At room temperature, which of the molecules are expected to give five NMR lines in the proton-decoupled ^{13}C NMR spectrum?



(a) Only 1 and 3 (b) Only 2 and 6 (c) Only 3 and 6 (d) All of the above

36. Do you expect that the minimum energy necessary to eject a 3s electron from phosphorus in a photoelectron spectroscopy experiment for the process.

$$[Ne]3s^2 3p^3 \rightarrow [Ne]3s^1 3p^3 + e^-,$$

Be larger than, smaller than, or the same as the 4th ionization energy (IE_4) of phosphorus?

(a) Smaller

(b) Larger

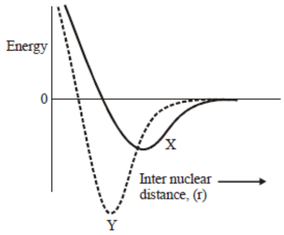
(c) The same

(d) cannot be answered from the given information

37. An average human DNA molecule has 5×10^8 base pairs, with four different kinds of bases. If the DNA sequence was completely random, what would be the residual entropy associated with this typical DNA molecule?

(a) 9.57×10^{-15} JK^{-1} (b) 4.15×10^{-15} JK^{-1} (c) 6.90×10^{-15} JK^{-1} (d) 1.38×10^{-14} JK^{-1}

38. Consider the two diatomic molecules CN and CN^-, and the potential energy diagram shown below.



which of the following is the correct statement?

(a) Bond order of CN is 2.5 and the curve Y corresponds to CN.

(b) Bond order of CN is 3 and the curve X corresponds to CN.

(c) Bond order of CN^- is 3 and the curve Y corresponds to CN^-.

(d) Bond order of CN^- is 2.5 and the curve X corresponds to CN^-.

39. Consider the following two matrices:

$$A = \begin{pmatrix} 7 & 0 & 0 \\ 0 & 1 & -i \\ 0 & i & -1 \end{pmatrix} \text{ and } B = \begin{pmatrix} 1 & 0 & 3 \\ 0 & 2i & 0 \\ i & 0 & -5i \end{pmatrix}$$

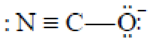
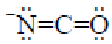
(a) 0

(b) The trace will be a real number, less than 0

(c) The trace will be a real number, greater than 0

(d) The trace will be a complex number

40. In valence-bond calculations, contributions of various resonance structures are used to calculate the total energy of a molecule. Given below are four resonance structures of the cyanate ion. Which one contributes least to the total energy.

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