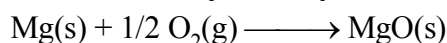


## TIFR-2010 CHEMISTRY

1. What is  $[H^+]$  in 1.0 L solution that contains 0.2 M of  $NH_4Cl$ ?  
 (a)  $1.1 \times 10^{-5} M$  (b)  $1.9 \times 10^{-3} M$   
 (c)  $1.8 \times 10^{-5} M$  (d) Not solvable with the information given
2. It is not easy to locate H atoms in the structure of proteins obtained by X-ray diffraction due to which of the following reasons:  
 (a) H atoms are transparent to the X-rays (b) H-bonding interaction present in protein structures  
 (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  $\Delta H_r^\circ$  and  $\Delta S_r^\circ$  are independent of temperature.

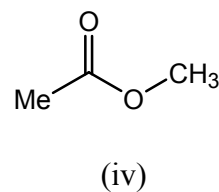
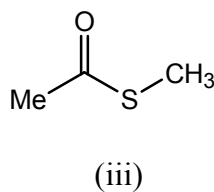
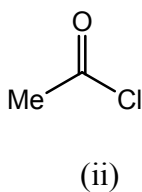
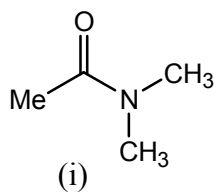


$$\Delta H_r^\circ = -602 \text{ kJ/mol}$$

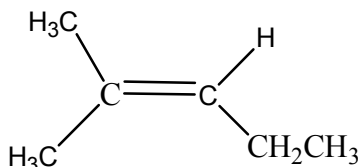
$$\Delta S_r^\circ = -108 \text{ J/Kmol}$$

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

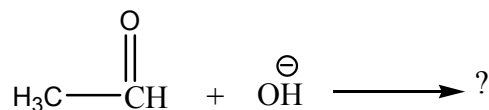
- (a)  $-573 \text{ kJ/mol}$ , non-spontaneous (b)  $-573 \text{ kJ/mol}$ , spontaneous  
 (c)  $632 \text{ kJ/mol}$ , non-spontaneous (d)  $-632 \text{ kJ/mol}$ , spontaneous
5. Rank the following molecules in order of electrophilicity (from most to least electrophilic):



- (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  $\sigma^*$  (b) n to  $\pi^*$  (c)  $\sigma$  to  $\sigma^*$  (d)  $\pi$  to  $\pi^*$
7. How many absorption lines will the following naturally occurring compound have in its proton-decoupled  $^{13}C$  NMR spectrum?

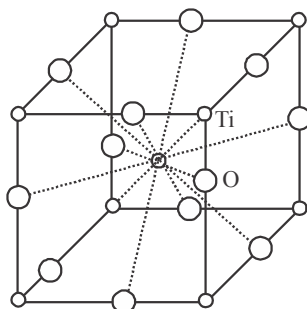


- (a) 3 (b) 4 (c) 5 (d) 6
8. What would be the final major product of the following chemical reaction if it is carried out twice, once at  $5^\circ C$  and the second time at  $45^\circ C$ ?

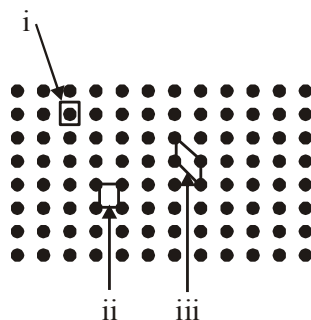




14. At 1000°K for the following two equilibria, the representative  $K_p$  values are given :
- (i)  $\text{CaCO}_3 \leftrightarrow \text{CaO} + \text{CO}_2$   $K_p = 4.0 \times 10^{-2}$  atm  
(ii)  $\text{C} + \text{CO}_2 \leftrightarrow 2 \text{CO}$   $K_p = 2.0$  atm
- Solid Carbon (C), CaO,  $\text{CaCO}_3$  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. ( $\Delta H_{\text{melt}} = 0.01$  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)  $33.4 \times 10^5$  kJ
16. What is the empirical formula for the following unit cell:

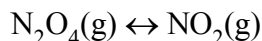


- (a)  $\text{CaTi}_{12}\text{O}_8$  (b)  $\text{CaTi}_8\text{O}_{12}$  (c)  $\text{CaTiO}_3$  (d)  $\text{CaTi}_2\text{O}_3$
17. Which of the parallelogram in the figure below are viable unit cells?



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

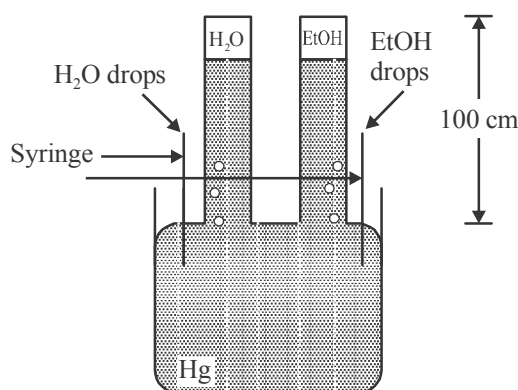
18. The following reaction is at equilibrium in a cylinder fitted with a movable plunger.



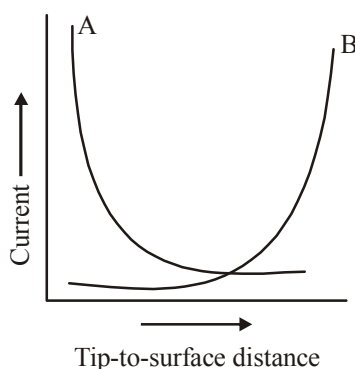
If the volume is decreased at constant temperature by moving the plunger, will the concentration of  $\text{NO}_2(\text{g})$  be higher or lower than the original concentration when the equilibrium is reestablished?

- (a) The concentration of  $\text{NO}_2$  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  $\text{NO}_2$  will increase.
- (c) The concentration of  $\text{NO}_2$  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  $\text{NO}_2$  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  $\text{NO}_2$  molecules must also decrease, making it difficult to say whether the concentration of  $\text{NO}_2$  would decrease or increase.

19. To a green solution of  $\text{Ni}(\text{H}_2\text{O})_6^{2+}$ , a small quantity of ammonia was added, which turned the solution blue through formation of  $\text{Ni}(\text{NH}_3)_6^{2+}$ . 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  $\text{Ni}(\text{en})_3^{2+}$ . 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 ?
- The violet solution would turn blue.
  - The violet solution would stay violet.
  - There will be an equimolar mixture of  $\text{Ni}(\text{NH}_3)_6^{2+}$ , giving the solution a colour which is an intermediate between blue and violet.
  - 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  $\text{Br}_2^+$  with the mass numbers 158, 160 and 162. Which isotopes of bromine occur in nature?
- $^{79}\text{Br}$  and  $^{80}\text{Br}$
  - $^{80}\text{Br}$  and  $^{81}\text{Br}$
  - $^{79}\text{Br}$  and  $^{81}\text{Br}$
  - $^{79}\text{Br}$ ,  $^{80}\text{Br}$  and  $^{81}\text{Br}$
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  $\text{H}_2\text{O}$  and ethanol to the top of columns of Hg, as shown below. Drops are added till a small amount of water or alcohol is seen at the top of the Hg column. What will happen to the heights of the Hg columns after the addition? The experiment is done at normal temperature and pressure.

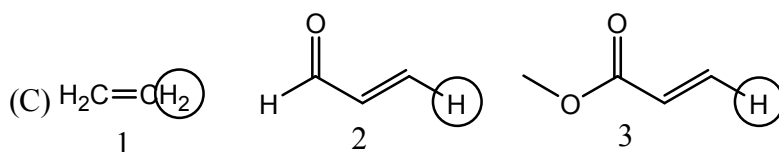
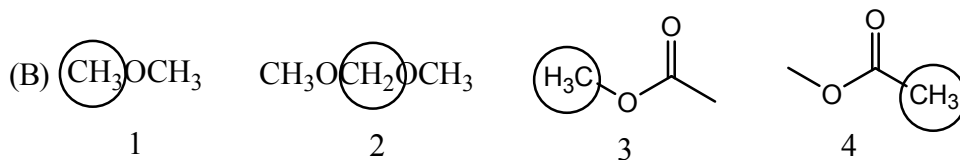
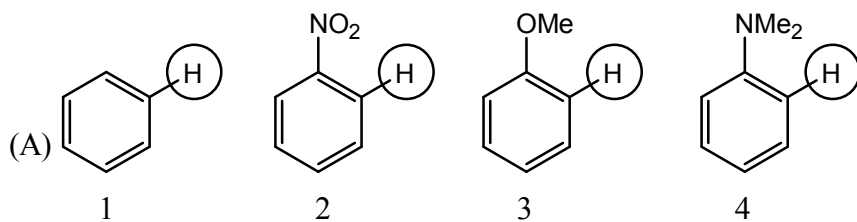


- Both column heights will be the same
  - The column below  $\text{H}_2\text{O}$  is shorter.
  - The column below EtOH is shorter.
  - The column that has more number of drops will be shorter.
22. Scanning tunneling microscopy depends upon the flow of electricity (current) between a surface and an atomically-sharp probe tip. Two plots of current vs. Tip-to-surface distance are shown below. Which one is correct?



- A
- B
- If the tip is more conducting than the surface, then the answer is A. Otherwise, the answer is B.
- Insufficient information is given to answer the question.

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



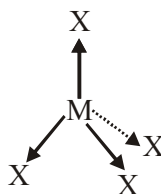
- (a) A3 or A4, B4, C1    (b) A1, B2, C3                      (c) A2, B3, C2                      (d) A4, B1, C1

24. Consider the following two infinite series:

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

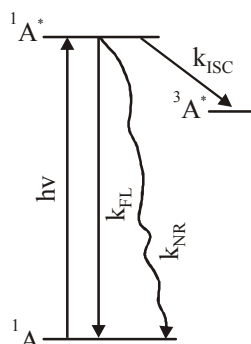
What is the value of  $A^2 + B^2$  ?

- (a) 0                      (b)  $+\infty$                       (c) 1  
 (d) Its value cannot be defined, as the series A and B are divergent.
25. Four separate solutions are present in separate containers: HCl, NaOH,  $\text{CH}_3\text{COOH}$ , and  $\text{CH}_3\text{COOK}$ . What possible pairs can be used to make a buffer solution?
- (a) HCl and  $\text{CH}_3\text{COOK}$                       (b) NaOH and  $\text{CH}_3\text{COOH}$   
 (c)  $\text{CH}_3\text{COOH}$  and  $\text{CH}_3\text{COOK}$                       (d) All of the above
26. It is well known that the structure of ethylene ( $\text{CH}_2 = \text{CH}_2$ ) is planar. Hence, what would be the structure of allene ( $\text{CH}_2 = \text{C} = \text{CH}_2$ ) and cumulene ( $\text{CH}_2 = \text{C} = \text{C} = \text{CH}_2$ )?
- (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  $\text{MX}_4$ , 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?

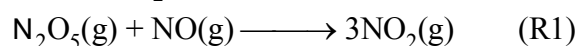


- (a) IR                      (b) Raman                      (c) Neither                      (d) Both

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



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



where  $NO_3$  is an unstable intermediate. What would be the rate expression of the disappearance of  $N_2O_5$  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) 
$$\frac{d}{dt}[N_2O_5] = k_1[N_2O_5] \left( 1 + \frac{k_2[NO_2]}{k_2[NO_2] + k_3[NO]} \right)$$

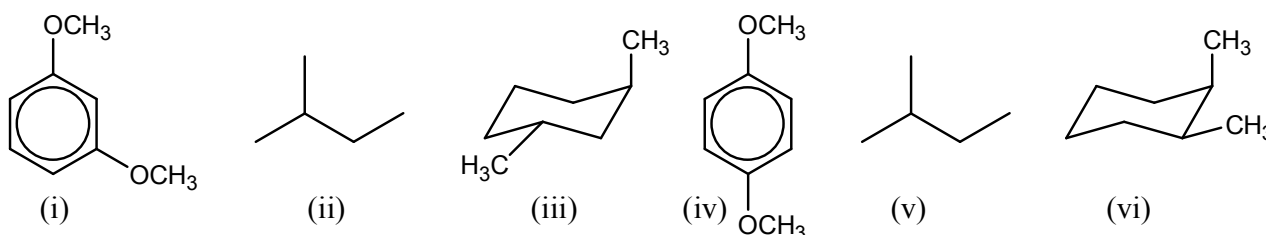
31. For a cell constructed with a  $\text{Cu(s)} \mid \text{Cu}^{2+}(\text{aq})$  anode and  $\text{Ag}^+ \mid \text{Ag(s)}$  cathode at  $25.0^\circ\text{C}$ , Calculate the cell potential at  $25.0^\circ\text{C}$  under non-standard conditions:  $[\text{Cu}^{2+}] = 0.300 \text{ M}$  and  $[\text{Ag}^+] = 0.0500 \text{ M}$ .
- (a) 0.44 V                    (b) 0.41 V                    (c) 0.40 V                    (d) 0.34 V
32. Photo-excitation 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 oxidant, 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  $3600 \text{ cm}^{-1}$ . Compared to that, the stretching frequencies of O–D and S–H bonds are very similar and appear at about  $2500 \text{ cm}^{-1}$ . 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:

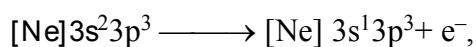
- The change in total angular momentum that occurs when a diatomic molecule (i.e. a rigid rotor) changes rotational level from  $J = 2$  to  $J = 3$  is the same as the change in total angular momentum that occurs when an electron on a H atom changes from a d to an f orbital, i.e. from  $l = 2$  to  $l = 3$ .
- The change in energy 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 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  $^{13}\text{C}$  NMR spectrum?



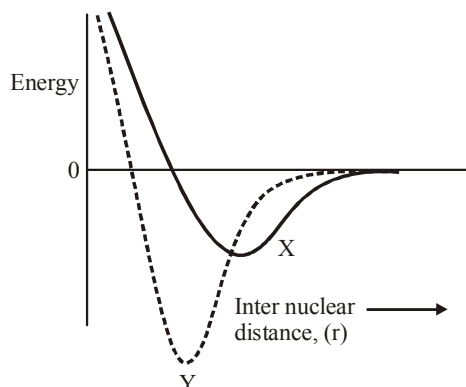
- (a) Only 1 and 3                    (b) Only 2 and 6                    (c) Only 3 and 6                    (d) All of the above
36. Do you expect that the minimum energy necessary to eject a  $3s$  electron from phosphorus in a photoelectron spectroscopy experiment for the process.



be larger than, smaller than, or the same as the 4th ionization energy ( $\text{IE}_4$ ) of phosphorus?

- (a) Smaller                    (b) Larger  
 (c) The same                    (d) cannot be answered from the given information

37. An average human DNA molecule has  $5 \times 10^8$  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)  $9.57 \times 10^{-15} \text{ JK}^{-1}$  (b)  $4.15 \times 10^{-15} \text{ JK}^{-1}$  (c)  $6.90 \times 10^{-15} \text{ JK}^{-1}$  (d)  $1.38 \times 10^{-14} \text{ JK}^{-1}$
38. Consider the two diatomic molecules CN and  $\text{CN}^-$ , 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  $\text{CN}^-$  is 3 and the curve Y corresponds to  $\text{CN}^-$ .  
 (d) Bond order of  $\text{CN}^-$  is 2.5 and the curve X corresponds to  $\text{CN}^-$ .
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)  $\text{:N} \equiv \text{C} - \ddot{\text{O}}^-$       (b)  ${}^2-\text{:}\ddot{\text{N}} - \text{C} \equiv \ddot{\text{O}}^+$       (c)  ${}^-\ddot{\text{N}} = \text{C} = \ddot{\text{O}}$       (d)  $\ddot{\text{N}} - \ddot{\text{C}} - \ddot{\text{O}}^-$