

**B.S. ABDUR RAHMAN UNIVERSITY**  
**Vandalur, Chennai - 600048**



**Department of chemistry**

**Ph.D Entrance Exam**

**16.06.2016**

NAME :

Application No :

Address :

Phone no:



## TABLE OF INFORMATION

Electron rest mass	$m_e = 9.11 \cdot 10^{31} \text{ kg}$
Proton rest mass	$m_p = 1.672 \cdot 10^{27} \text{ kg}$
Neutron rest mass	$m_n = 1.67510^{27} \text{ kg}$
Magnitude of the electron charge $e =$	$1.60 \cdot 10^{19} \text{ C}$
Bohr radius	$a_0 = 5.29 \cdot 10^{11} \text{ m}$
Avogadro number	$N = 6.02 \cdot 10^{23} \text{ per mol}$
Universal gas constant	$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ $= 0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1}$ $= 0.08314 \text{ L bar mol}^{-1} \text{ K}^{-1}$
Boltzmann constant	$k = 1.38 \cdot 10^{23} \text{ J/K}$
Planck constant	$h = 6.63 \cdot 10^{34} \text{ J s}$ $= h/2\pi = 1.0510^{34} \text{ J s}$
Speed of light	$c = 3.00 \cdot 10^8 \text{ m/s} = 3.0010^{10} \text{ cm/s}$
1 bar pressure	$1 \text{ bar} = 1.000 \text{ N m}^{-2}$ $= 1.00010^5 \text{ Pa}$ $= 0.987 \text{ atm}$
1 atmosphere pressure	$1 \text{ atm} = 1.01310^5 \text{ N m}^{-2}$ $= 1.01310^5 \text{ Pa}$ $= 1.013 \text{ bar}$
Faraday constant	$= 9.65 \cdot 10^4 \text{ C/mol}$
1 atomic mass unit (amu)	$1 \text{ amu} = 1.66 \cdot 10^{27} \text{ kg}$
1 electron volt (eV)	$1 \text{ eV} = 1.602 \cdot 10^{19} \text{ J}$
Angstrom	$1 \text{ \AA} = 10^{10} \text{ m} = 10^1 \text{ nm}$
Volume of 1 mol of ideal gas at 0 °C, 1 atmosphere	$= 22.4 \text{ L}$

1. Which element has the highest first ionization energy?

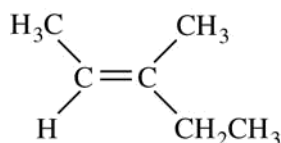
- (A) As
- (B) Ge
- (C) Ga
- (D) Rb
- (E) Sr

2. Which of the following is the most acceptable Lewis electron dot structure for carbon monoxide?

- (A)  $\text{C}=\text{O}$
- (B)  $\cdot\ddot{\text{C}}=\ddot{\text{O}}\cdot$
- (C)  $\cdot\text{C}\equiv\text{O}\cdot$
- (D)  $\text{C}\equiv\text{O}$
- (E)  $\cdot\ddot{\text{C}}\equiv\ddot{\text{O}}\cdot$

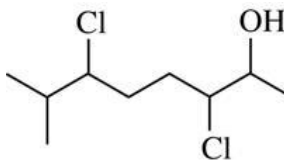
3. What is the correct IUPAC name for the compound shown above?

- (A) *trans*-3-methyl-3-pentene
- (B) *cis*-2-ethyl-2-butene
- (C) (*E*)-3-methyl-2-pentene
- (D) (*Z*)-3-methyl-2-pentene
- (E) (*Z*)-2-ethyl-2-butene



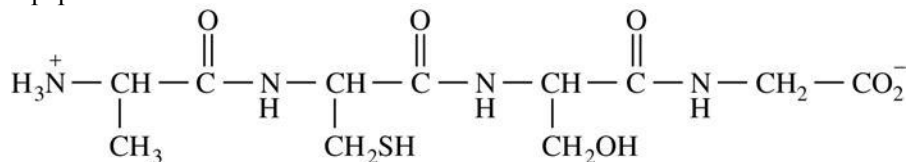
4. What is the total number of stereoisomers possible for the compound shown above?

- (A) 3
- (B) 4
- (C) 6
- (D) 8
- (E) 16



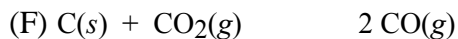
5. The total number of peptide bonds in the structure shown above is

- (A) 1
- (B) 2
- (C) 3
- (D) 4
- (E) 5



6. A 0.10 L solution of  $\text{Cl}^- (aq)$  is titrated with  $1.0 \times 10^{-3} \text{ M Ag}^+ (aq)$ . The end point is reached when 0.025 L of the  $\text{Ag}^+$  solution has been added. What was the concentration of  $\text{Cl}^-$  in the original solution

- (A)  $1.0 \times 10^{-4} \text{ M}$
- (B)  $2.5 \times 10^{-4} \text{ M}$
- (C)  $4.0 \times 10^{-4} \text{ M}$
- (D)  $8.0 \times 10^{-4} \text{ M}$
- (E)  $1.0 \times 10^{-3} \text{ M}$



7.  $\Delta H$  for the reaction shown above is greater than zero. Assuming  $\Delta H$  is independent of temperature, which of the following statements about the percent yield of  $\text{CO}(g)$  is true?
- (A) It increases as the amount of  $\text{C}(s)$  increases.  
 (B) It increases as the temperature increases.  
 (C) It decreases as the temperature increases.  
 (D) It doubles when the initial partial pressure of  $\text{CO}_2$  is doubled.  
 (E) It increases when the total pressure of the reaction system increases.

[A]	[B]	Initial Rate
0.50 M	0.50 M	$10 \text{ M s}^{-1}$
0.50 M	1.00 M	$20 \text{ M s}^{-1}$
0.25 M	0.50 M	$5 \text{ M s}^{-1}$
1.00 M	1.00 M	$40 \text{ M s}^{-1}$

8. The initial rates given above were determined for the reaction  $\text{A} + 2 \text{B} \rightarrow \text{AB}_2$ . What is the overall rate law for this reaction?

- (A)  $\text{Rate} = k[\text{A}]^2[\text{B}]^2$   
 (B)  $\text{Rate} = k[\text{A}]^2[\text{B}]$   
 (C)  $\text{Rate} = k[\text{A}][\text{B}]^2$   
 (D)  $\text{Rate} = k[\text{A}][\text{B}]$   
 (E)  $\text{Rate} = k$

9. Assuming that air is approximately 80 percent nitrogen and 20 percent oxygen by volume, which of the following is closest to the density of air at  $0^\circ\text{C}$  and 1 atmosphere?

- (A) 0.01 g/L  
 (B) 0.1 g/L  
 (C) 1 g/L  
 (D) 10 g/L  
 (E) 100 g/L



10. How many bonds are there in acetylene, shown above?

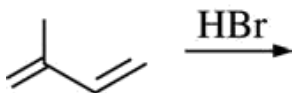
- (A) 1  
 (B) 2  
 (C) 3  
 (D) 4  
 (E) 5

- $\text{CHF}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$
- $\text{CH}_3\text{CF}_2\text{CH}_2\text{CO}_2\text{H}$
- $\text{CH}_3\text{CH}_2\text{CF}_2\text{CO}_2\text{H}$
- $\text{CH}_3\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$

11. In which of the following are the carboxylic acids shown above listed in order of decreasing acidity, from most acidic to least acidic?

- (A)  $1 > 2 > 3 > 4$   
 (B)  $1 > 4 > 3 > 2$

- (C) 3 > 2 > 1 > 4  
 (D) 3 > 4 > 1 > 2  
 (E) 4 > 1 > 2 > 3



12. Which of the following is a 1,4-addition product of the reaction shown above?

- (A)
- (B)
- (C)
- (D)
- (E)

13. Which of the following is a weak Brønsted-Lowry acid?

- (A) HCl  
 (B) HNO<sub>3</sub>  
 (C) H<sub>2</sub>SO<sub>4</sub>  
 (D) H<sub>2</sub>S  
 (E) HClO<sub>4</sub>

14. Which of the following correctly lists the species in order of increasing radius from smallest to largest?

- (A) K<sup>+</sup> < Ar < Cl  
 (B) Ar < Cl < K<sup>+</sup>  
 (C) K<sup>+</sup> < Cl < Ar  
 (D) Cl < Ar < K<sup>+</sup>  
 (E) Ar < K<sup>+</sup> < Cl

15. The half-life of <sup>14</sup>C is 5,730 years. All of the following are true for the method of carbon dating expect

- (A) <sup>14</sup>C undergoes *β*-decay to produce <sup>14</sup>N.  
 (B) The <sup>14</sup>C content of an organism decreases after it dies.  
 (C) The <sup>14</sup>C/<sup>12</sup>C ratio is the same in living terrestrial organisms as in the atmosphere.

(D) The  $^{14}\text{C}/^{12}\text{C}$  ratio can be used to date a sample from a dead organism.

(E) Carbon dating is equally useful for

Samples that are millions of years old as for samples that are about 10,000 years old.

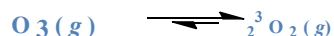
16. The energy required for various transitions follow the order.

a)  $\sigma \rightarrow \sigma^* > n \rightarrow \sigma^* > \pi \rightarrow \pi^* > n \rightarrow \pi^*$

b)  $\sigma \rightarrow \sigma^* > \pi \rightarrow \pi^* > n \rightarrow \sigma^* > n \rightarrow \pi^*$

c)  $\pi \rightarrow \pi^* > n \rightarrow \pi^* > \sigma \rightarrow \sigma^* > n \rightarrow \sigma^*$

d)  $n \rightarrow \pi^* > \sigma \rightarrow \sigma^* > n \rightarrow \sigma^* > \pi \rightarrow \pi^*$



17. For the reaction shown above at 298 K,  $G = 163$  kJ/mol. What is the value of the equilibrium constant,  $K_P$ , for this reaction?

(A)  $K_P > 1.0$

(B)  $K_P = 1.0$

(C)  $0.0 < K_P < 1.0$

(D)  $K_P = 0.0$

(E)  $K_P < 0.0$

18. In an isolated hydrogen atom, the  $2p_x$  orbital has the same principal quantum number,  $n$ , as which of the following orbitals?

I.  $2s$

II.  $2p_z$

III.  $3p_x$

(A) I only

(B) II only

(C) III only

(D) I and II only

(E) II and III only

19. Which of the following is NOT an allotrope of carbon?

(A) Diamond

(B) Graphite

(C)  $\text{C}_{60}$

(D)  $\text{C}_{70}$

(E)  $\text{C}_2$

20. Of the following covalent bonds, which has the greatest bond dissociation energy?

(A)  $\text{C}=\text{C}$

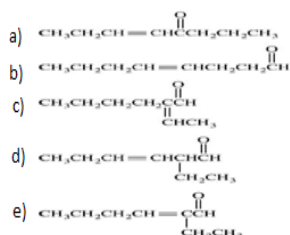
(B)  $\text{O}=\text{O}$

(C)  $\text{C}=\text{Si}$

(D)  $\text{Si}=\text{Si}$

(E)  $\text{C}=\text{O}$

21. Assuming complete dissociation, which of the following is NOT true about a 1.00 M  $\text{Mg}(\text{NO}_3)_2$  solution? (Molar masses:  $\text{Mg} = 24.30 \text{ g}$ ;  $\text{NO}_3 = 62.01 \text{ g}$ ;  $\text{Mg}(\text{NO}_3)_2 = 148.31 \text{ g}$ )
- (A) The concentration of nitrate ions is  $2.0 \text{ mol L}^{-1}$ .
- (B) The total concentration of ions is  $3.0 \text{ mol L}^{-1}$ .
- (C) The total mass of solute in 1.00 L of this solution is 148 g.
- (D) There are 2.43 g of  $\text{Mg}^{2+}$  in 100 mL of this solution.
- (E) There are 6.20 g of  $\text{NO}_3$  in 100 mL of this solution
22. A 499 mg sample of  $\text{CuSO}_4 \cdot n\text{H}_2\text{O}$  is heated to drive off the waters of hydration and then reweighed to give a final mass of 319 mg. Given that the sample contains 2.0 mmol of Cu, what is the average number of waters of hydration,  $n$ , in  $\text{CuSO}_4 \cdot n\text{H}_2\text{O}$  ?
- (A) 2.0  
 (B) 5.0  
 (C) 10.  
 (D) 18  
 (E) 20.
23. Which of the following is the aldol condensation product of butanal ( $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$ ) ?



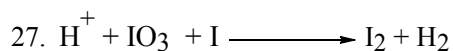
24. When 1.0 kJ of heat is added to 5.0 L of an ideal gas, the gas expands against a constant external pressure of 1.0 bar to a final volume of 8.0 L. What is the change in internal energy,  $\text{DU}$ , for the gas? (1.0 L bar = 0.10 kJ)
- (A) 0.30 kJ  
 (B) 0.70 kJ  
 (C) 1.0 kJ  
 (D) 1.3 kJ  
 (E) 1.8 kJ
25. Which of the following must be true for adiabatic processes?
- (A)  $C_V = C_P$   
 (B)  $\text{DH} = 0$   
 (C)  $\text{DU} = 0$   
 (D)  $\text{DS} = 0$   
 (E)  $q = 0$



26. At 37 C, the dissociation constant,  $K_w$ , of water is  $2.5 \times 10^{-14}$  ( $pK_w = 13.6$ ).

What is the pH of a  $1.0 \times 10^{-5}$  M NaOH solution at 37 C ?

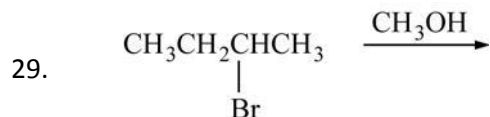
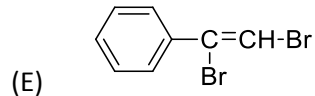
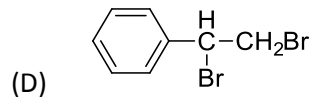
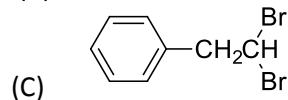
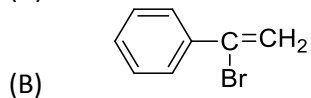
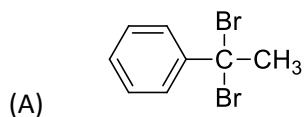
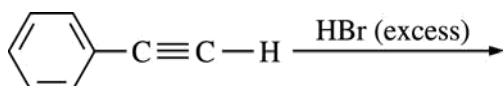
- (A) 4.6
- (B) 5.0
- (C) 8.6
- (D) 9.0
- (E) 13.6



The reaction shown above is not balanced. If the reaction is balanced using the smallest whole number coefficients possible, the coefficient for I will be

- (A) 1
- (B) 2
- (C) 3
- (D) 5
- (E) 10

28. Which of the following is the major product of the reaction shown below?



The reaction of 2-bromobutane with methanol, as shown above, yields which of the following as the major product?



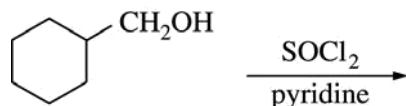
- (B)  $\text{CH}_3\text{CH}_2\underset{\text{OCH}_3}{\text{CH}}\text{CH}_3$
- (C)  $\text{CH}_3\text{CH}_2\underset{\text{OCH}_3}{\overset{\text{OCH}_3}{\text{C}}}\text{CH}_3$
- (D)  $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2$
- (E)  $\text{CH}_3\text{C}\equiv\text{CCH}_3$

30.  $\int y_1(x) y_2(x) dx = 0$  If two wavefunctions  $y_1(x)$  and  $y_2(x)$  satisfy the condition given above, the two wavefunctions are

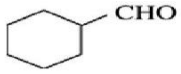
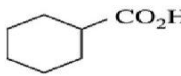
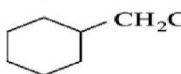
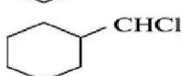
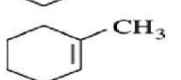
- (A) orthogonal  
 (B) degenerate  
 (C) normalized  
 (D) continuous  
 (E) symmetrical

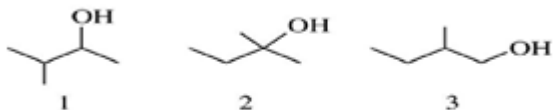
31. Which of the following statements is true about a pure substance above its critical point?

- (A) One fluid phase is present.  
 (B) Solid, liquid, and gas are in equilibrium.  
 (C) Only liquid and gas are in equilibrium.  
 (D) A liquid forms.  
 (E) A solid form.



32. Which of the following is the major organic product of the reaction shown above?

- (A)  A cyclohexane ring with a  $\text{CHO}$  group attached to one of the carbons.
- (B)  A cyclohexane ring with a  $\text{CO}_2\text{H}$  group attached to one of the carbons.
- (C)  A cyclohexane ring with a  $\text{CH}_2\text{Cl}$  group attached to one of the carbons.
- (D)  A cyclohexane ring with a  $\text{CHCl}_2$  group attached to one of the carbons.
- (E)  A cyclohexane ring with a double bond between two adjacent carbons and a  $\text{CH}_3$  group attached to one of the double-bonded carbons.



33.

In which of the following are the compounds shown above listed in order of increasing reactivity to acid-catalyzed dehydration?

- (A)  $1 < 2 < 3$
- (B)  $1 < 3 < 2$
- (C)  $2 < 3 < 1$
- (D)  $3 < 1 < 2$
- (E)  $3 < 2 < 1$

34. At standard temperature and pressure, all of the following compounds exist in the gas state EXCEPT

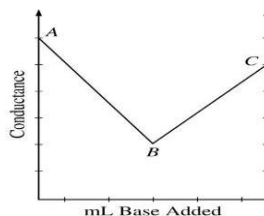
- (A) HCl
- (B) HBr
- (C) NH<sub>3</sub>
- (D) BH<sub>3</sub>
- (E) LiH

35. The electron configuration of Co in [Co(NH<sub>3</sub>)<sub>6</sub>]Cl<sub>3</sub> is

- (A) [Ar] 4s<sup>2</sup>3d<sup>7</sup>
- (B) [Ar] 4s<sup>2</sup>3d<sup>4</sup>
- (C) [Ar] 3d<sup>9</sup>
- (D) [Ar] 3d<sup>7</sup>
- (E) [Ar] 3d<sup>6</sup>

36. A 0.600 g sample of a pure, weak diprotic acid gives end points at 20.0 mL and 40.0 mL when it is titrated with 0.100 M NaOH. What is the molar mass of the weak acid?

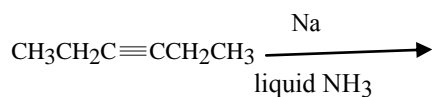
- (A) 120 g
- (B) 150 g
- (C) 180 g
- (D) 300 g
- (E) 450 g



37. The figure shown above is a plot of conductance data obtained during the titration of HCl with a standard solution of NaOH. Which of the following statements about the results is NOT true?

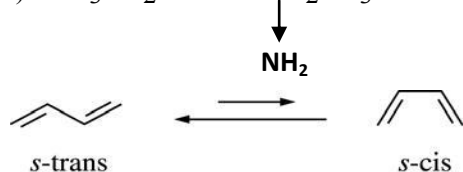
- (A) Point *B* is the end point of the titration.
- (B) slope *AB* > slope *BC*
- (C) The measured conductance increases after point *B* because the overall concentration of ions increases.
- (D) Na<sup>+</sup> must have a higher equivalent conductance than H<sub>3</sub>O<sup>+</sup>.
- (E) Segment *BC* represents the conductance due to ions from NaCl and NaOH in solution.

38. The molecular geometry of  $\text{IF}_5$  is
- (A) square pyramidal
  - (B) trigonal planar
  - (C) bent
  - (D) linear
  - (E) octahedral
39. At a given temperature, the vapor pressure of  $\text{SiF}_4$  is significantly higher than that of  $\text{SF}_4$ . The major physical basis for the difference in vapor pressure is that  $\text{SiF}_4$  and  $\text{SF}_4$  have different
- (A) dipole moments
  - (B) molar masses
  - (C) ionization energies
  - (D) electron affinities
  - (E) magnetic susceptibilities
40. Which of the protons indicated will be observed as a doublet in the  $^1\text{H}$  NMR spectrum of the molecule shown above?
- (A) *a*
  - (B) *b*
  - (C) *c*
  - (D) *d*
  - (E) *e*

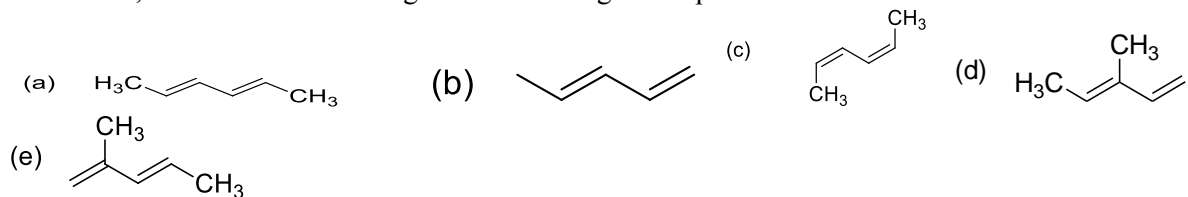


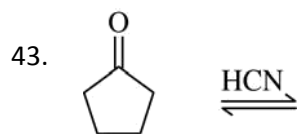
41. Which of the following is the major product of the reaction shown above?

- (A)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{C}\equiv\text{CNa}$
- (B)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$
- (C) *cis*- $\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}_3$
- (D) *trans*- $\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}_3$
- (E)  $\text{CH}_3\text{CH}_2\text{CH}=\text{CCH}_2\text{CH}_3$

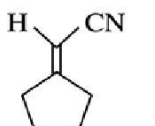
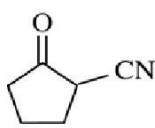
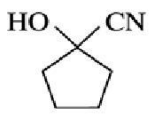
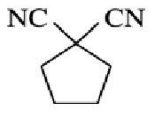



42. Acyclic conjugated dienes may exist in two conformations, as shown above. Based on differences in steric strain, which of the following dienes has the greatest preference for the *s-trans* conformation?





Which of the following substances is in equilibrium with cyclopentanone and HCN shown above?

- (A) 
- (B) 
- (C) 
- (D) 
- (E) 

44. All of the following elements have at least one isotope that is not radioactive EXCEPT..

- (A) O  
 (B) Pb  
 (C) Sn  
 (D) No  
 (E) He

45. Based on the molecular orbital model, which of the following is the number of unpaired electrons and the bond order for the superoxide ion,  $O_2^-$  ?

	<u>Unpaired Electrons</u>	<u>Bond Order</u>
(A)	1	0.5
(B)	1	1.5
(C)	1	2.5
(D)	2	1
(E)	2	2

46. For a system at thermal equilibrium, which of the following is the Boltzmann distribution expression for the probability,  $p_i$ , that a single molecule is in the  $i$ th energy state with energy  $e_i$  ?

- (A)  $p_i e_i / kT$

(B)  $p_i = 1 e^{-\epsilon_i / kT}$

(C)  $p_i = \frac{e^{-\epsilon_i / kT}}{\sum_{i=0} e^{-\epsilon_i / kT}}$

(D)  $p_i = e^{-\epsilon_i / kT} N_i$

(E)  $p_i = \frac{e^{-\epsilon_i / kT}}{\sum_{i=0} e^{-\epsilon_i / kT}}$

47. Sodium acetate spontaneously crystallizes out of a supersaturated solution on standing or on the addition of a seed crystal. Which of the following is true for the thermodynamic quantities of this system for this process?

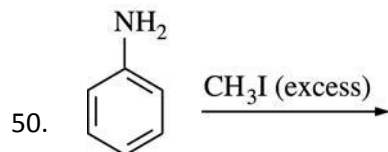
- (A)  $\Delta S < 0$ ,  $\Delta H < 0$
- (B)  $\Delta S < 0$ ,  $\Delta G > 0$
- (C)  $\Delta S > 0$ ,  $\Delta H > 0$
- (D)  $\Delta S > 0$ ,  $\Delta G < 0$
- (E)  $\Delta G < 0$ ,  $\Delta H > 0$

48. If ideal gas behavior is assumed, for which of the following reactions does  $\Delta H$  equal  $\Delta U$ ?

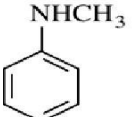
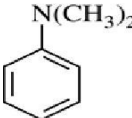
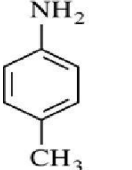
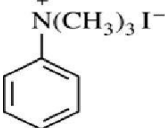
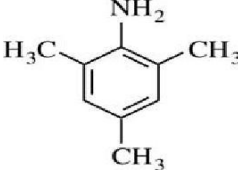
- (A)  $\text{N}_2\text{O}_4(\text{g}) \rightarrow 2 \text{NO}_2(\text{g})$
- (B)  $\text{CH}_4(\text{g}) + 2 \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l})$
- (C)  $\text{SO}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{SO}_3(\text{g})$
- (E)  $\text{Br}_2(\text{l}) + 3 \text{Cl}_2(\text{g}) \rightarrow 2 \text{BrCl}_3(\text{g})$
- (F)  $\text{Cl}_2(\text{g}) + \text{F}_2(\text{g}) \rightarrow 2 \text{ClF}(\text{g})$

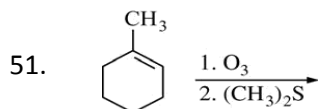
49.  $\text{PbF}_2(\text{s})$ , which is slightly soluble in water, is dissolved in water to form a saturated solution in equilibrium with solid  $\text{PbF}_2$ . Which of the following will cause additional  $\text{PbF}_2(\text{s})$  to dissolve?

- (G) Adding  $\text{HNO}_3$
- (H) Adding  $\text{Pb}(\text{NO}_3)_2$
- (I) Adding a seed crystal
- (J) Adding solid  $\text{PbF}_2$
- (K) Evaporating some of the water to decrease the volume of solution



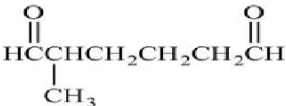
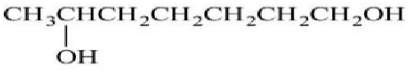
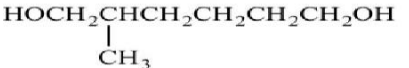


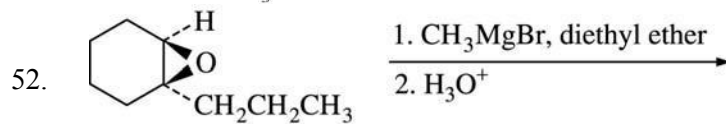
Which of the following is the major product of the reaction shown above?

- (A) 
- (B) 
- (C) 
- (D) 
- (E) 

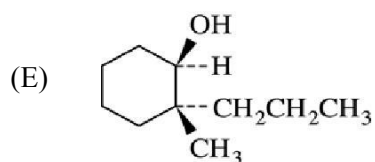
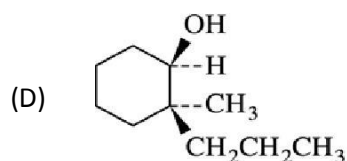
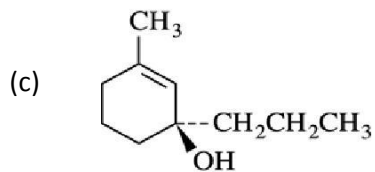
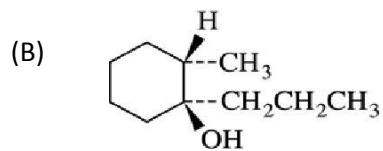
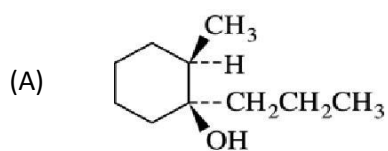


Which of the following is the product of the reaction shown above?

- (A) 
- (B) 
- (C) 
- (D) 
- (E) 



Which of the following is the major product of the reaction shown above?



53. If for  $\text{Ni}(\text{OH})_2$  the  $K_{sp}$  is  $8.0 \times 10^{-18}$ , then the expression used to calculate the molar solubility  $S$  of  $\text{Ni}(\text{OH})_2$  is

(A)  $S^3 = 2.0 \times 10^{-18}$

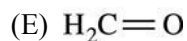
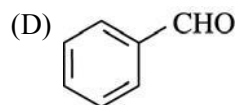
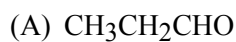
(B)  $S^3 = 4.0 \times 10^{-18}$

(C)  $S^3 = 8.0 \times 10^{-18}$

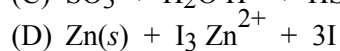
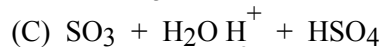
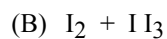
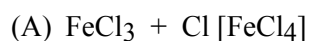
(D)  $S^3 = 5.0 \times 10^{-19}$

(E)  $S^3 = 1.5 \times 10^{-19}$

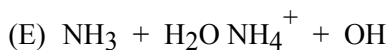
54. Which of the following compounds will react with  $(\text{CH}_3)_2\text{NH}$  to form an enamine?



55. All of the following reactions are examples of the Lewis definition of acid-base behavior EXCEPT



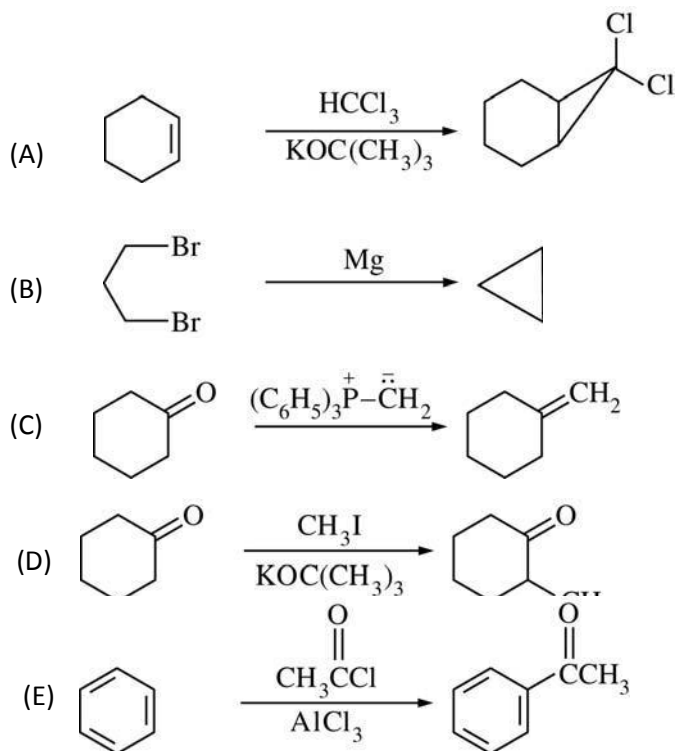




56. Of the following, which is the weakest oxidizing agent?

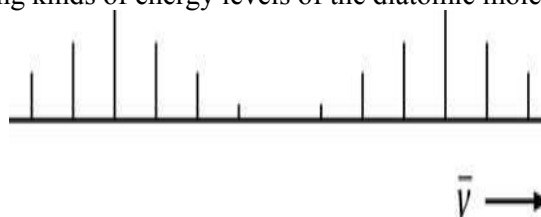
- (A)  $\text{MnO}_4^- (aq)$
- (B)  $\text{H}_2\text{O}_2 (aq)$
- (C)  $\text{I}_2 (s)$
- (D)  $\text{H}^+ (aq)$
- (E)  $\text{Mg} (s)$

57. Which of the following reactions proceeds via a carbene (or carbenoid) intermediate?



58. A high-resolution infrared absorption spectrum of a heteronuclear diatomic molecule is shown above. Information about which of the following kinds of energy levels of the diatomic molecule can be obtained from this spectrum?

- I. Electronic
- II. Vibrational
- III. Rotational



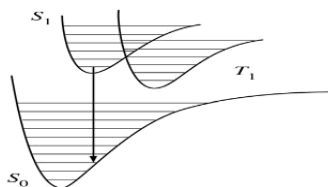
- (A) I only
- (B) II only
- (C) III only
- (D) II and III only
- (E) I, II, and III

59. All of the following are true about lasers EXCEPT:

- (A) The light does not diverge significantly.
- (B) The light is emitted only in pulses.
- (C) The light waves are in phase.
- (D) The light is essentially all the same wavelength.
- (E) The light is essentially all the same frequency.

60. Consider the ground electronic state  $S_0$ , the excited singlet state  $S_1$ , and the triplet state  $T_1$  of a molecule, shown above. The  $S_1 \rightarrow S_0$  transition corresponds to

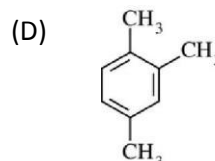
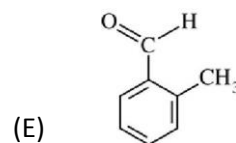
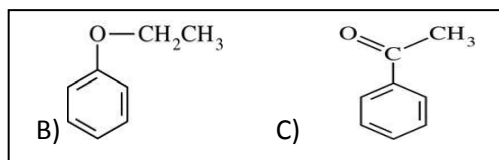
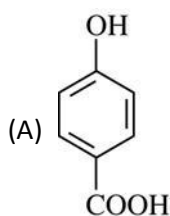
- (A) a forbidden transition
- (B) fluorescence
- (C) phosphorescence
- (D) photoionization
- (E) vibrational relaxation



61. The experimental technique most suited for the determination of the three-dimensional structure of a crystalline solid is

- (A) UV-visible spectroscopy
- (B) X-ray diffraction
- (C) measurement of colligative properties
- (D) polarimetry
- (E) Fourier transform mass spectrometry

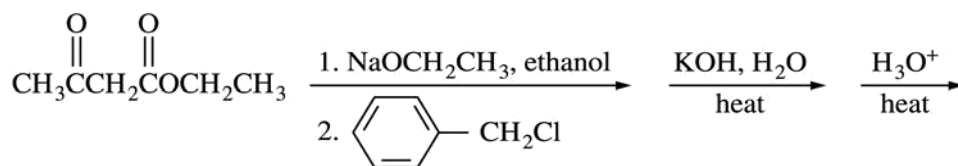
62. In a particular TLC separation, the stationary phase is a C<sub>2</sub> plate (= CH<sub>2</sub>CH<sub>3</sub>), and the mobile phase is 60% methanol: 40% water (v:v). Of the following compounds, which will likely travel the greatest distance during the analysis?



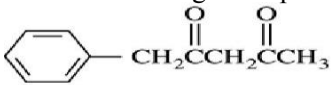
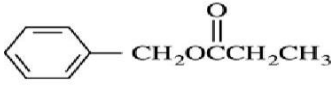

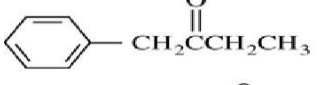

63. Graphite reacts with potassium to produce a compound with the empirical formula  $KC_8$ . Of the following, which is the best description of this compound's structure?

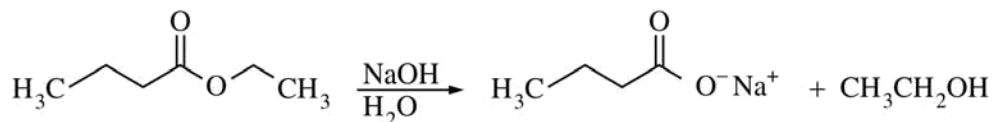
- (A)  $K^+$  ions close-packed with polyhedral  $C_8$  ions
- (B) K ions close-packed with polyhedral  $C_8^{+}$  ions
- (C)  $K^+$  ions packed with  $C_{22}$  ions
- (D) Negatively charged hexagonal carbon layers with intercalated  $K^+$  ions between the
- (E) An expanded diamond lattice with  $K^+$  ions in the tetrahedral holes

64. Which of the following statements about sulfur dioxide is true?
- (A) It forms an S S bonded dimer in condensed phases.
  - (B) It is the anhydride of sulfuric acid, H<sub>2</sub>SO<sub>4</sub>.
  - (C) It plays an important physiological role in the transmission of nerve impulses.
  - (D) Its O S O angle is 180.
  - (E) It is a product of the combustion of fossil fuels that contain sulfur.
65. Which of the following statements about polonium, the heaviest Group 16 element, is NOT true?
- (A) Polonium is the least metallic of the Group 16 elements.
  - (B) Polonium has the lowest ionization energy of the Group 16 elements.
  - (C) Polonium atoms are the largest of the Group 16 elements.
  - (D) Polonium is expected to be a solid at room temperature and pressure.
  - (E) When <sup>209</sup>Po undergoes alpha decay, it forms <sup>205</sup>Pb .
66. In their metallic form, elements from which of the following groups are usually effective hydrogenation catalysts?
- (A) Alkaline earth metals
  - (B) Platinum metals
  - (C) Halogens
  - (D) Actinides
  - (E) Group 12 metals
67. In CrF<sub>2</sub>(s), the coordination of the six F's around the Cr is a distorted octahedron with four short and two long Cr F bonds. Which of the following best explains this observation?
- (A) F has a -1 anionic charge.
  - (B) Cr<sup>2+</sup> has a low cationic charge.
  - (C) The Jahn-Teller effect
  - (D) Spin-orbit coupling in Cr<sup>2+</sup>
  - (E) The formation of Cr Cr bonds in CrF<sub>2</sub>(s)

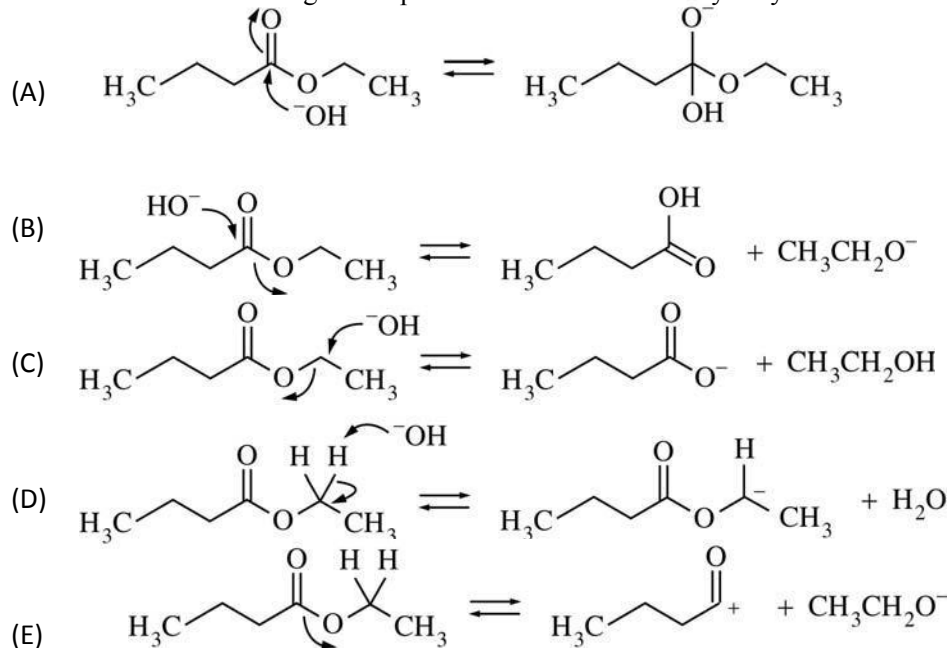


68. Which of the following is the product of the series of reactions shown above?

- (A) 
- (B) 
- (C) 
- (D) 
- (E) 



69. Which of the following is a step in the mechanism of the hydrolysis of the ester shown above?



70. Each of the following molecules can act as a chelating ligand EXCEPT

- (A)  $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$
- (B)  $\text{CH}_3\text{NHCH}_2\text{CH}_2\text{NH}_2$
- (C)  $\text{HC}(\text{CH}_2\text{CH}_2\text{NH}_2)_3$
- (D)  $\text{CH}_3\text{NHCH}_2\text{CH}_2\text{CH}_3$
- (E)  $\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)_3$

71. Which of the following is NOT a desirable property of an indicator to be used in a complexometric titration that involves EDTA?

- (A) The indicator should be a Lewis base.
- (B) The indicator should bind more tightly to the analyte metal than does EDTA.
- (C) The complexation reaction between the indicator and the analyte metal should be reversible.
- (D) The uncomplexed form of the indicator should be a different color than the indicator metal complex.
- (E) The indicator should be highly soluble in the sample.

72. Which of the following compounds exists in stereoisomeric forms?

- (A)  $[\text{Pt}(\text{NH}_3)_4]^{2+}$
- (B)  $[\text{Pt}(\text{NH}_3)_3\text{Cl}]^+$
- (C)  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$
- (D)  $[\text{Pt}(\text{NH}_3)\text{Cl}_3]$
- (E)  $[\text{PtCl}_4]^{2-}$

73. All of the following are recognized as pathways that can reduce the CO<sub>2</sub> level in the atmosphere EXCEPT
- (A) dissolution in the oceans
  - (B) photosynthesis
  - (C) respiration
  - (D) reduced burning of fossil fuels
  - (E) rainfall with dissolved CO<sub>2</sub>
74. Due to electron-electron interactions, it is not possible to obtain exact solutions to the Schrödinger equation for many-electron atoms. One approach that addresses this difficulty uses
- (A) the rigid-rotor approximation
  - (B) the harmonic oscillator approximation
  - (C) the principle of corresponding states
  - (D) effective nuclear charges the Franck-Condon principle
75. Acetic acid is extracted from ether into water. Which of the following actions will NOT increase the fraction of acetic acid removed from ether?
- (A) Raising the pH of the water
  - (B) Increasing the volume of water
  - (C) Decreasing the volume of ether
  - (D) Adding benzoic acid to the water
  - (E) Adding ammonia to the water
76. The ionic strength of an aqueous 0.10 M Pb(NO<sub>3</sub>)<sub>2</sub> solution is
- (A) 0.10 M
  - (B) 0.25 M
  - (C) 0.30 M
  - (D) 0.50 M
  - (E) 0.60 M
77. Which of the following is a strong acid in pure liquid HF?
- (A) H<sub>2</sub>O
  - (B) SbF<sub>5</sub>
  - (C) CH<sub>3</sub>COOH
  - (D) NH<sub>3</sub>
  - (E) NaF
78. Vitamin B<sub>12</sub>, an essential nutrient for humans, contains which of the following elements?
- (A) Cobalt
  - (B) Chromium
  - (C) Copper
  - (D) Zinc
  - (E) Iron
79.  $E_n = n^2 h^2 / 8mL^2$  For a particle of mass  $m$  in a one-dimensional box of length  $L$ , the energy of the particle is given by the equation shown above. How much energy is required to promote the particle from the state with quantum number  $n = 2$  to the state with quantum number  $n = 3$  ?
- (A)  $9h^2/8mL^2$
  - (B)  $5h^2/8mL^2$
  - (C)  $4h^2/8mL^2$
  - (D)  $dh^2/8mL^2$
  - (E) 0

80. A large activation energy implies which of the following about a reaction?

- (A) It is spontaneous.
- (B) It is highly endothermic.
- (C) It is at equilibrium.
- (D) It is very rapid.
- (E) It has a highly temperature-dependent rate constant.

81. In an experiment to test the de Broglie hypothesis, a beam of high-energy electrons with momenta

$$p = m_e u = 6 \times 10^{-24} \text{ kg m/s}$$

would be scattered by a nickel crystal with a pattern similar to that of which of the following?

- (A) X-rays of wavelength  $= h/p$
- (B) Electromagnetic radiation with wavelength  $= p/h$
- (C) A beam of protons with velocity  $u$
- (D) Billiard balls undergoing perfectly elastic collisions
- (E) Visible light with a mixture of frequencies frequently characterized as "white"

82. Which of the following is true about the quantum yield for photodecomposition of a chromophore?

- (A) It depends on the intensity of the light source used for the photolysis.
- (B) It depends on the duration of the light source used for the photolysis.
- (C) It is the reciprocal of the fluorescence lifetime.
- (D) It has a value of either 0 or 1, reflecting the quantum nature of photons.
- (E) It is the ratio of the number of chromophores decomposed to the number of photons absorbed.

83. A characteristic common to polymers that can be made to conduct electricity, such as polyacetylene and polypyrrole, is

- (A) the presence of stereogenic centers of the same configuration
- (B) a monodisperse distribution in molecular weight
- (C) a very low glass transition temperature
- (D) conjugation throughout the polymer chain
- (E) a high degree of cross-linking

84. Which of the following complexes does NOT contain a significant component in the metal-ligand bonding?

- (A)  $[\text{Co}(\text{NH}_3)_6]^{3+}$
- (B)  $[\text{Fe}(\text{CO})_5]$
- (C)  $[\text{CrO}_4]^{2-}$
- (D)  $[\text{Co}(\text{CN})_6]^{3-}$
- (E)  $[\text{Cr}(\text{-C}_6\text{H}_6)_2]$

85. In an experiment to determine riboflavin by fluorescence spectrometry, a series of riboflavin standards was analyzed and gave a calibration line with a slope of 1000 ppm and a y-intercept of 25. If a sample gave a fluorescence reading of 750, the riboflavin concentration (in ppm) of the sample

- (A) 0.0750
- (B) 0.0775
- (C) 0.725

- (D) 0.775
- (E) 7.50

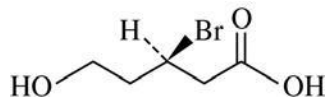
86. The rate constant for a first-order reaction R  $\rightarrow$  P is 0.010 s<sup>-1</sup>. The concentration of R decreases to one-half of its initial value after

- (A)  $\frac{2}{0.010}$  s
- (B)  $\frac{\ln 2}{0.010}$  s
- (C)  $\frac{1}{2(0.010)}$  s
- (D)  $\frac{1}{4(0.010)}$  s
- (E) 5(0.010) s

87. The activated-complex theory (or transition state theory) assumes that an equilibrium exists between the

- (A) activated complex and reactants only
- (B) activated complex and products only
- (C) products and reactants only
- (D) reactants, activated complex, and products
- (E) system (reaction) and surroundings

88.



Oxidation of (*R*)-3-bromo-5-hydroxypentanoic acid, shown above, yields the corresponding 3-bromopentanedicarboxylic acid product that is

- (A) a mixture of two diastereomers in unequal amounts
- (B) a racemic mixture
- (C) a single pure enantiomer
- (D) a meso compound
- (E) an achiral compound

89. The radiation in the wavelength range 400-800 nm corresponds to

- (A) ultra-violet
- (B) Infra-red

(C) visible

(D) Far IR

(E) CV

90. For an organic compound, the mass spectrum has the following  $m/e$  values: 124, 122 (low abundance), 43 (base peak), 107, 109, The organic compound is:

(A) *n*-Propyl chloride

(B) *n*-propylalcohol

(C) *n*-Propyl bromide

(D) Butyl bromide

(E) None

91. The entropy of the system increases in the order

(A) gas < liquid < solid

(B) solid < liquid < gas

(C) gas < solid < liquid

(D) Liquid < gas < gas

(E) None of these

92. Which of the following gases will have the lowest rate of diffusion?

(A) H<sub>2</sub>

(B) N<sub>2</sub>

(c) F<sub>2</sub>

(D) O<sub>2</sub>

(E) Cl<sub>2</sub>

93. In *p*-type semiconductors, the conductivity is due to

(A) negative holes

(B) positive holes

(C) mobile electrons

(D) valence electrons

(E) Free radicals

94 . The voltage of a solar cell is

(A) very high

(B) high

(C) not very high

(D) none of these

(E) Low

95. When a non-volatile solute is added to a solvent, the freezing point of the solvent-----.

(A) increases

(B) remains the same



- (C) decreases
- (D) Slowly increases
- (E) none of these

96. Why doesn't catalyst shift the equilibrium position?

- (A) it speeds up both the forward and reverse reaction
- (B) it is recoverable unchanged at the end of a reaction
- (C) it increases the concentration of both the reactants and products equally
- (D) it provides a surface site at which the reaction can occur.
- (E) it is recoverable forward and reverse reaction.

97. For first-order reactions the rate constant,  $k$ , has the unit(s)

- (A)  $l \text{ mol}^{-1}$
- (B)  $\text{time}^{-1}$
- (C)  $(\text{mol}/l)^{-1} \text{ time}^{-1}$
- (D)  $\text{time mol } l^{-1}$
- (E)  $l / \text{mol } l^{-1}$

98. The signal (s) for a compound like  $A\text{-CH}_2\text{-CH}_2\text{-B}$  will be:

- (A) two triplets
- (B) two singlets
- (C) one singlet
- (D) one triplet
- (E) three triplet

99. Which of the solvents cannot be used in NMR spectroscopy?

- A)  $\text{CCl}_4$
- (B)  $\text{CS}_2$
- (C)  $\text{CHCl}_3$
- (D)  $(\text{CCl}_3)_2\text{C=O}$
- (E)  $\text{CDCl}_3$

100. Which of the following are microwave active?

- (A)  $\text{HCl}$
- (B)  $\text{CO}_2$
- (C)  $\text{H}_2$
- (D)  $\text{O}_2$
- (E)  $\text{N}_2$