

# EXAMPLAR

## Index

- |  |   |
|--|---|
| <p>1. <b><u>MOLE CONCEPT</u></b> (1-10)</p> <ul style="list-style-type: none"><li>• Fill in the Blanks</li><li>• Assertion-Reason</li><li>• Single Choice Correct</li><li>• Multiple Choice Correct</li><li>• Comprehension</li><li>• Subjective Questions</li></ul> <p>2. <b><u>PERIODIC TABLE</u></b> (11-18)</p> <ul style="list-style-type: none"><li>• True and False</li><li>• Fill in the Blanks</li><li>• Assertion-Reason</li><li>• Single Choice Correct</li><li>• Multi Choice Correct</li><li>• Comprehension</li><li>• Subjective Questions</li></ul> <p>3. <b><u>CHEMICAL BONDING</u></b> (19-26)</p> <ul style="list-style-type: none"><li>• True and False</li><li>• Fill in the Blanks</li><li>• Assertion-Reason</li><li>• Single Choice Correct</li><li>• Multiple Choice Correct</li><li>• Match the Column</li><li>• Comprehension</li><li>• Subjective Questions</li></ul> <p>4. <b><u>MOLE CONCEPT</u></b> (27-33)</p> <ul style="list-style-type: none"><li>• Fill in the Blanks</li><li>• Assertion-Reason</li><li>• Single Choice Correct</li><li>• Multiple Choice Correct</li><li>• Comprehension</li><li>• Subjective Questions</li></ul> | <p>5. <b><u>REDOX</u></b> (34-43)</p> <ul style="list-style-type: none"><li>• Fill in the Blanks</li><li>• Assertion-Reason</li><li>• Single Choice Correct</li><li>• Comprehension</li><li>• Subjective Questions</li></ul> <p>6. <b><u>ATOMIC STRUCTURE</u></b> (44-57)</p> <ul style="list-style-type: none"><li>• True and False</li><li>• Fill in the Blanks</li><li>• Assertion-Reason</li><li>• Single Choice Correct</li><li>• Multiple Choice Correct</li><li>• Match the Column</li><li>• Comprehension</li><li>• Subjective Questions</li></ul> <p>7. <b><u>GASEOUS STATE</u></b> (58-68)</p> <ul style="list-style-type: none"><li>• True and False</li><li>• Fill in the Blanks</li><li>• Assertion-Reason</li><li>• Single Choice Correct</li><li>• Multiple Choice Correct</li><li>• Match the Column</li><li>• Comprehension</li><li>• Subjective Questions</li></ul> <p>8. <b><u>CHEMICAL EQUILIBRIUM</u></b> (69-86)</p> <ul style="list-style-type: none"><li>• True and False</li><li>• Fill in the Blanks</li><li>• Assertion-Reason</li><li>• Single Choice Correct</li><li>• Multiple Choice Correct</li><li>• Match the Column</li><li>• Comprehension</li><li>• Subjective Questions</li></ul> |
|--|---|

<p><b>9.     <u>IONIC EQUILIBRIUM</u>     (86-101)</b></p> <ul style="list-style-type: none"> <li>• <i>Assertion–Reason</i></li> <li>• <i>Single Choice Correct</i></li> <li>• <i>Multiple Choice Correct</i></li> <li>• <i>Match the Column</i></li> <li>• <i>Comprehension</i></li> <li>• <i>Subjective Questions</i></li> </ul>	<p><b>11.   <u>THERMOCHEMISTRY</u>     (113-127)</b></p> <ul style="list-style-type: none"> <li>• <i>True and False</i></li> <li>• <i>Fill in the Blanks</i></li> <li>• <i>Assertion–Reason</i></li> <li>• <i>Single Choice Correct</i></li> <li>• <i>Multiple Choice Correct</i></li> <li>• <i>Match the Column</i></li> <li>• <i>Comprehension</i></li> <li>• <i>Subjective Questions</i></li> </ul>
<p><b>10.   <u>THERMODYNAMICS</u>     (102-112)</b></p> <ul style="list-style-type: none"> <li>• <i>True and False</i></li> <li>• <i>Fill in the Blanks</i></li> <li>• <i>Assertion–Reason</i></li> <li>• <i>Single Choice Correct</i></li> <li>• <i>Multiple Choice Correct</i></li> <li>• <i>Match the Column</i></li> <li>• <i>Comprehension</i></li> <li>• <i>Subjective Questions</i></li> </ul>	<p><b>12.   <u>CHEMICAL BONDING</u>     (128-137)</b></p> <ul style="list-style-type: none"> <li>• <i>Assertion–Reason</i></li> <li>• <i>Single Choice Correct</i></li> <li>• <i>Multiple Choice Correct</i></li> <li>• <i>Match the Column</i></li> <li>• <i>Comprehension</i></li> <li>• <i>Subjective Questions</i></li> </ul>

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**MOLE CONCEPT**


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**Fill in the blanks**

- Ratio of number of protons to neutrons in  $3.011 \times 10^{22}$  molecules of  $D_3O^+$  is "\_\_\_\_\_"
- Nitrogen has an atomic number of 7 and oxygen has an atomic number of 8. The total number of electrons in the nitrate ion ( $NO_3^-$ ) is .....
- The maximum number of electrons that can be accommodated in all the orbitals for which  $\ell = 3$  is .....

**True/False**

- The electron density in xy plane of  $3d_{x^2-y^2}$  orbital is zero.
- $3d^6$  configuration is more stable than  $3d^5$ .

**Assertion-Reason**

These questions contains, Statement I (assertion) and Statement II (reason).

(A) Statement-I is true, Statement-II is true ; Statement-II is correct explanation for Statement-I.

(B) Statement-I is true, Statement-II is true ; Statement-II is NOT a correct explanation for statement-I

(C) Statement-I is true, Statement-II is false

(D) Statement-I is false, Statement-II is true

- Statement-I** : 16 g each  $O_2$  and  $O_3$  contains  $\frac{N_A}{2}$  and  $\frac{N_A}{3}$  atoms respectively.

**Because**

**Statement-II** : 16 g  $O_2$  and  $O_3$  contains same no. of atoms.

- Statement-I** : The average mass of one Mg atom is 24.305 amu, which is not the actual mass of one Mg atom.

**Because**

**Statement-II** : Three isotopes,  $^{24}\text{Mg}$ ,  $^{25}\text{Mg}$  and  $^{26}\text{Mg}$ , of Mg are found in nature.

- Statement-I** : A molecule of butane,  $C_4H_{10}$  has a mass of 58.12 amu.

**Because**

**Statement-II** : One mole of butane contains  $6.022 \times 10^{23}$  molecules and has a mass of 58.12 g.

- Statement-I** : Both 12 g. of carbon and 27 g. of aluminium will have  $6.02 \times 10^{23}$  atoms.

**Because**

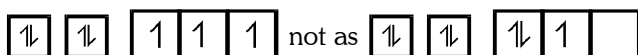
**Statement-II** : Gram atomic mass of an element contains Avogadro's number of atoms.

- Statement-I** : The ground state configuration of Cr is  $3d^5 4s^1$ .

**Because**

**Statement-II** : A set of exactly half filled orbitals containing parallel spin arrangement provide extra stability.

- Statement-I** : The electronic configuration of nitrogen atom is represented as :



**Because**

**Statement-II** : The configuration of ground state of an atom is the one which has the greatest multiplicity.

**12. Statement-I :** The configuration of B atom cannot be  $1s^2 2s^3$ .

**Because**

**Statement-II :** Hund's rule demands that the configuration should display maximum multiplicity.

**13. Statement-1 :** The groundstate configuration of Cr is  $[\text{Ar}] 3d^5 4s^1$

**Statement-2 :** The energy of atom is lesser in  $3d^5 4s^1$  configuration compared to  $3d^4 4s^2$  configuration.

**14. Statement-1 :** Minimum principal quantum number of an orbital belonging to 'g' sub-shell is 5.

**Statement-2 :** For a given value of principal quantum number (n), l may have values 0 to (n-1) only.

### Single Choice Correct

**15.** 112.0 ml of  $\text{NO}_2$  at 1 atm & 273 K was liquefied, the density of the liquid being 1.15 gm/ml. Calculate the volume of and the number of molecules in the liquid  $\text{NO}_2$ .

(A) 0.10 ml and  $3.01 \times 10^{22}$

(B) 0.20 ml and  $3.01 \times 10^{21}$

(C) 0.20 ml and  $6.02 \times 10^{23}$

(D) 0.40 ml and  $6.02 \times 10^{21}$

**16.** The shape of Tobacco Mosaic Virus (TMC) is cylindrical, having length and diameter 3000 Å and 170 Å, respectively. The density of the virus is 0.08 gm/ml. The molecular weight of TMC is

(A) 3.28

(B)  $5.44 \times 10^{-24}$

(C)  $5.44 \times 10^{-18}$

(D)  $3.28 \times 10^6$

**17.** What time, it would take to spend Avogadro's number of rupees at the rate of 10 lac rupees per second?

(A)  $6.023 \times 10^{17}$  sec

(B)  $1.909 \times 10^{10}$  year

(C)  $1.673 \times 10^{14}$  hour

(D) all of these

**18.** The sodium salt of methyl orange has 7% sodium. What is the minimum molecular weight of the compound?

(A) 420

(B) 375

(C) 329

(D) 295

**19.** In the preceding problem, if the compound contains 12.8% nitrogen 9.8% sulphur how many nitrogen and sulphur atoms are present per atom of sodium :

(A) 2 and 1

(B) 1 and 3

(C) 1 and 2

(D) 3 and 1

**20.**  $\text{Na}_2\text{SO}_4 \cdot x\text{H}_2\text{O}$  has 50%  $\text{H}_2\text{O}$ . Hence, x is :

(A) 4

(B) 5

(C) 6

(D) 8

**21.** In the following final result is ....  $0.1 \text{ mol CH}_4 + 3.01 \times 10^{23} \text{ molecules CH}_4 - 9.6 \text{ g CH}_4 = x \text{ mol H atoms}$  :

(A) 0 mol H atom

(B) 0.2 mol H atom

(C) 0.3 mol H atom

(D) 0.4 mol H atom

**22.** In a gaseous mixture an alkane ( $\text{C}_x\text{H}_{2x+2}$ ) and an alkene ( $\text{C}_y\text{H}_{2y}$ ) are taken in 2 : 1 mole ratios, the average molecular weight of mixture is observed to be 20. If the same alkane and alkene are taken in 1 : 2 mole ratios, the average molecular weight of mixture is observed to be 24. Then the value of 'x' and 'y' respectively are :

(A) 2, 1

(B) 1, 2

(C) 2, 3

(D) 3, 2

**23.** 3.06 L of  $\text{H}_2\text{O}_{(\text{vap})}$  is taken at a pressure of 1 atm and 373 K. It is now condensed to  $\text{H}_2\text{O} (l)$  at 373K. Calculate the volume occupied by  $\text{H}_2\text{O} (l)$  (Density of liquid water = 1 g/ml)

(A) 3.06 L


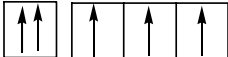

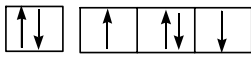
(B) 1.8 ml

(C) 1.8 L

(D) 3.06 ml

- 24.** Nylon is prepared using a compound having formula  $\text{HOOC}(\text{CH}_2)_4\text{COOH}$ . What is the total number of atoms present in 0.73 mg of the above compound :  
 (A)  $6.023 \times 10^{19}$  (B)  $6.023 \times 10^{22}$  (C)  $60.23 \times 10^{23}$  (D) 20
- 25.** A substance has 16% by mass of Sulphur and 4% by mass of Oxygen. Calculate minimum molar mass of the substance.  
 (A) 200 (B) 400 (C) 600 (D) 100
- 26.** In an experiment, it is found that **2.0769 gm** of pure X produces **3.6769 gm** of pure  $\text{X}_2\text{O}_5$ . Then number of moles of X is :  
 (A) 0.04 (B) 0.06 (C) 0.4 (D) 0.02
- 27.** Two isotopes of an element ( atomic mass =  $x + 2.35$ ) have mass ( $x + 2$ ) and ( $x + 7$ ) respectively. Calculate natural abundance of heavier isotope in percentage.  
 (A) 3 (B) 5 (C) 7 (D) 9
- 28.** Two elements A and B form two different sets of compounds  $\text{A}_2\text{B}_3$  and  $\text{A}_3\text{B}_4$ . 2.02 kg of  $\text{A}_2\text{B}_3$  has  $1.806 \times 10^{25}$  atoms of B and 1.44 kg of  $\text{A}_3\text{B}_4$  has  $9.03 \times 10^{24}$  atoms of A. What will be gram molecular mass (GMM) of another compound AB formed from combination of A and B.  
 (A) 75 (B) 86 (C) 94 (D) 97
- 29.** An element exist in three isotopic form  $^{40}\text{X}$ ,  $^{41}\text{X}$  and  $^{42}\text{X}$ .  
 Percentage abundance of  $^{40}\text{X} = 30\%$  by mole.  
 If average atomic mass of 'X' is 41.25. Find out percentage abundance of  $^{41}\text{X}$ .  
**[Divide your answer by 3 and fill OMR sheet]**  
 (A) 2 (B) 3 (C) 5 (D) 7
- 30.** A solution of palmitic acid ( $M = 256$ ) in benzene contains 5 gm acid per litre. When this solution is dropped on surface,  $\text{C}_6\text{H}_6$  gets evaporated and acid forms a unimolecular layer on the surface. If we wish to cover an area  $6000 \text{ cm}^2$  with unimolecular film. What volume of solution in ml should be used? Area covered by one molecule of acid is  $0.32 \text{ nm}^2$ . (**Given :  $N_A = 6 \times 10^{23}$** )  
**Write your answer multiplying with 1000.**  
 (A) 120 ml (B) 140 ml (C) 160 ml (D) 180 ml
- 31.** An element exist in two isotopic forms  $\text{X}^{120}$  and  $\text{X}^{122}$ , in equal abundance. The average atomic mass of element is 121.44. If each atom of  $\text{X}^{120}$  are 10.04 times heavier than one  $\text{C}^{12}$  atom, then how many times each atom of  $\text{X}^{122}$  is heavier than one  $\text{C}^{12}$  atom ?  
 (A) 10.04 (B) 10.4 (C) 10.2 (D) 10.167
- 32.** How many moles of e- weight one Kg : **[JEE 2002]**  
 (A)  $6.023 \times 10^{23}$  (B)  $\frac{1}{9.108} \times 10^{31}$  (C)  $\frac{6.023}{9.108} \times 10^{54}$  (D)  $\frac{1}{9.108 \times 6.023} \times 10^8$
- 33.** Which has maximum number of atoms : **[JEE 2003]**  
 (A) 24 g C(12) (B) 56 g Fe(56) (C) 27 g Al (27) (D) 108 g Ag(108)
- 34.** An alloy of gold and silver contains 38.5% silver by mass and has a density of  $14.6 \text{ g.mL}^{-1}$ . What is the molar concentration of silver in this alloy :  
 (A)  $52.1 \text{ mol.L}^{-1}$  (B)  $45.6 \text{ mol.L}^{-1}$  (C)  $3.57 \text{ mol.L}^{-1}$  (D)  $2.64 \text{ mol.L}^{-1}$

- 35.** "Suvarnabhasm", an ayurvedic drug, is found to contain 400 ppm of colloidal gold. Mass % of gold (atomic mass of Au = 197) will be :  
 (A) 0.040 % (B) 7.88 % (C) 0.0788 % (D)  $4 \times 10^{-4}$  %
- 36.** Which orbit would be the first to have 'g' subshell :-  
 (A)  $3^{\text{rd}}$  (B)  $4^{\text{th}}$  (C)  $5^{\text{th}}$  (D)  $6^{\text{th}}$
- 37.** The decreasing order of energy of the 3d, 4s, 3p, 3s orbitals is :-  
 (A)  $3d > 3s > 4s > 3p$  (B)  $3s > 4s > 3p > 3d$  (C)  $3d > 4s > 3p > 3s$  (D)  $4s > 3d > 3s > 3p$
- 38.** If  $n$  and  $\ell$  are respectively the principle and azimuthal quantum numbers, then the expression for calculating the total number of electrons in any orbit is :-  
 (A)  $\sum_{\ell=1}^{\ell=n} 2(2\ell + 1)$  (B)  $\sum_{\ell=1}^{\ell=n-1} 2(2\ell + 1)$  (C)  $\sum_{\ell=0}^{\ell=n+1} 2(2\ell + 1)$  (D)  $\sum_{\ell=0}^{\ell=n-1} 2(2\ell + 1)$
- 39.** The quantum numbers  $+1/2$  and  $-1/2$  for the electron spin represent :-  
 (A) Rotation of the electron in clockwise and anticlockwise direction respectively.  
 (B) Rotation of the electron in anticlockwise and clockwise direction respectively.  
 (C) Magnetic moment of the electron pointing up and down respectively.  
 (D) Two quantum mechanical spin states which have no classical analogue.
- 40.** What are the values of the orbital angular momentum of an electron in the orbitals 1s, 3s, 3d and 2p :-  
 (A) 0, 0,  $\sqrt{6}\hbar, \sqrt{2}\hbar$  (B) 1, 1,  $\sqrt{4}\hbar, \sqrt{2}\hbar$  (C) 0, 1,  $\sqrt{6}\hbar, \sqrt{3}\hbar$  (D) 0, 0,  $\sqrt{20}\hbar, \sqrt{6}\hbar$
- 41.** If  $m$  = magnetic quantum number and  $\ell$  = azimuthal quantum number then :-  
 (A)  $m = \ell + 2$  (B)  $m = 2\ell^2 + 1$  (C)  $\ell = \frac{m-1}{2}$  (D)  $\ell = 2m + 1$
- 42.** The number of unpaired electrons in  $\text{Mn}^{4+}$  ( $Z = 25$ ) is :-  
 (A) Four (B) Two (C) Five (D) Three
- 43.** Which of the following has maximum number of unpaired electron (atomic number of Fe 26)  
 (A) Fe (B) Fe (II) (C) Fe (III) (D) Fe (IV)
- 44.** Suppose a particle has four quantum numbers such that the permitted values are:  
 $n = 1, 2, 3, \dots$   
 $l = (n - 1), (n - 3), (n - 5), \dots$  but no negative value  
 $j = \left(\ell + \frac{1}{2}\right)$  or  $\left(\ell - \frac{1}{2}\right)$ , the later is not negative  
 $m = -j$  in integer step to  $+j$  what are the other permitted values for  $n = 2$ ?  
 (A)  $l = 1, j = \frac{3}{2}, m = -\frac{3}{2}$  (B)  $l = 0, j = \frac{1}{2}, m = -\frac{1}{2}$   
 (C)  $l = 1, j = \frac{1}{2}, m = -\frac{3}{2}$  (D) All of these

45. Which of the following is / are false.
- (A) Multiplicity in  $\text{Fe}^{3+}$  is greater than  $\text{Co}^{3+}$ .  
 (B)  $\text{Ti}^{3+}$ ,  $\text{Cr}^{+}$ ,  $\text{Sc}^{2+}$  ions are diamagnetic.  
 (C) Value of  $(n + l + m)$  for last electron in Na is 3.  
 (D) Number of neutron in  $1.07 \text{ gm Fe(OH)}_3$  is  $3.25 \times 10^{23}$
46. The orbital diagram in which Hund's rule is violated is
- (I)  (II) 
- (III)  (IV) 
- (A) I & II (B) II & III (C) III & IV (D) II & IV
47. Match the column:
- ('l' and 'm' are respectively the azimuthal and magnetic quantum numbers)
- | Column I   | Column II                               |
|--|---|
| (I) Total number of values of (l) for a shell      | (P) 0, 1, 2, .....(n-1)                 |
| (II) Values of (l) for a shell                     | (Q) +l, .....+2, +1, 0, -1, -2, .....-l |
| (III) Total number of values of (m) for a subshell | (R) (2l + 1)                            |
| (IV) Values of (m) for a subshell                  | (S) n                                   |
| (A) (I) S (II) P (III) R (IV) Q                    | (B) (I) S (II) R (III) P (IV) Q         |
| (C) (I) P (II) S (III) R (IV) Q                    | (D) (I) P (II) R (III) Q (IV) S         |
48. Which of the following statements regarding subshell filling order for a neutral atom is/are correct ?
- (I) Electrons are assigned to the 4s subshell before they are assigned to the 3d subshell  
 (II) Electrons are assigned to the 4f subshell before they are assigned to the 6s subshell  
 (III) Electrons are assigned to the 4d subshell before they are assigned to the 5p subshell
- (A) I only (B) II only (C) I and III (D) I, II and III
49. If the nitrogen atom had electronic configuration  $1s^7$ , it would have energy lower than that of normal ground state configuration  $1s^2 2s^2 2p^3$ , because the electrons would be closer to the nucleus. Yet  $1s^7$  is not observed because it violates :-
- (A) Heisenberg uncertainty principle (B) Hund's rule  
 (C) Pauli's exclusion principle (D) Bohr postulate of stationary orbits
50. The explanation for the presence of three unpaired electrons in the nitrogen atom can be given by
- (A) Pauli's exclusion principle (B) Hund's rule  
 (C) Aufbau's principle (D) Uncertainty principle
51. Which of the following has the maximum number of unpaired electrons ? [JEE 1996]
- (A)  $\text{Mg}^{2+}$  (B)  $\text{Ti}^{3+}$  (C)  $\text{V}^{3+}$  (D)  $\text{Fe}^{2+}$
52. After np orbitals are filled, the next orbital filled will be :-
- (A)  $(n + 1) s$  (B)  $(n + 2) p$  (C)  $(n + 1) d$  (D)  $(n + 2) s$
53. The value of the magnetic moment of a particular ion is 2.83 Bohr magneton. The ion is :-
- (A)  $\text{Fe}^{2+}$  (B)  $\text{Ni}^{2+}$  (C)  $\text{Mn}^{2+}$  (D)  $\text{Co}^{3+}$

54. The electrons, identified by  $n$  &  $l$  ;

[JEE 1999]

- (i)  $n = 4, l = 1$                       (ii)  $n = 4, l = 0$                       (iii)  $n = 3, l = 2$   
 (iv)  $n = 3, l = 1$  can be placed in order of increasing energy, from the lowest to highest as :  
 (A) (iv) < (ii) < (iii) < (i)                      (B) (iii) < (ii) < (iv) < (i)  
 (C) (i) < (iii) < (ii) < (iv)                      (D) (iii) < (i) < (iv) < (ii)

55. The magnetic moment of cobalt of the compound  $\text{Hg}[\text{Co}(\text{SCN})_4]$  is [Given :  $\text{Co}^{+2}$ ]

[JEE 2004]

- (A)  $\sqrt{3}$                       (B)  $\sqrt{8}$                       (C)  $\sqrt{15}$                       (D)  $\sqrt{24}$

56. The magnetic moment of cobalt of the compound  $\text{Hg}[\text{Co}(\text{SCN})_4]$  is [Given :  $\text{Co}^{+2}$ ]

[JEE 2004]

- (A)  $\sqrt{3}$                       (B)  $\sqrt{8}$                       (C)  $\sqrt{15}$                       (D)  $\sqrt{24}$

### Multiple Choice Correct

57\*. X gm A atoms on combining with Y atoms of B form 5 molecules of a compound containing A & B. Find the molecular weight of compound formed. (Atomic weight of B = M)

- (A)  $\frac{(\text{XN}_A + \text{MY})}{5}$                       (B)  $\frac{\text{X} + \text{M}}{5}$                       (C)  $\frac{\text{X} + \text{MY}}{5}$                       (D)  $\left( \frac{\text{X} + \text{MYN}_A}{5} \right)$

58. Calculate mass % & mole % of  $\text{H}_2$  in a mixture of  $\text{H}_2$  and  $\text{O}_2$  if average molecular mass of the mixture is 14.

- (A) 50 % by mole                      (B) 60 % by mole                      (C) 8.57% by mass                      (D) 10% by mass

59\*. Which of the following options is/are incorrect.

- (A) 10 gm of Boron is having 5 mole of nucleons.  
 (B) One atom of an element weight  $1.8 \times 10^{-22}$  gm, then its atomic mass is 108.36  
 (C) 10 gm of  $\text{CaCO}_3$  contains 1 gm atom of C.  
 (D) Number of atoms in 2 moles of  $\text{S}_8$  is greater than 5.5 moles of  $\text{SO}_2$

60. A polymeric organic compound contains 0.07% iron and 0.035% nitrogen by mass. Which of the following statement(s) is/are correct for the compound ? (Fe = 56, N = 14)

- (A) The molecular mass of compound may be 40000.  
 (B) The molecular mass of compound may be 160000.  
 (C) In each molecule of this compound, there are 2 nitrogen atoms per iron atom.  
 (D) In each molecule of this compound, there are 2 iron atoms per nitrogen atom.

61. Which of the following have equal no. of atoms ?

- (A) 12 g  $\text{MgSO}_4$                       (B) 0.2 mole  $\text{CO}_2$                       (C) 5.6 L  $\text{SO}_2$  at STP                      (D) 24 g Ca

62. A mixture of two gases  $\text{H}_2$  and  $\text{O}_2$  has an average molecular mass 12 and is kept at a temperature of  $\frac{200}{3}$  K and pressure 0.821 atm. Select the correct options :

- (A) Mixture contains  $\frac{100}{9}$  % by mass of  $\text{H}_2$  gas.                      (B) Density of mixture is 1.8 gm/ml.  
 (C) Mixture contains  $\frac{100}{3}$  % by mol of  $\text{O}_2$  gas                      (D) Mole ratio of  $\text{O}_2$  and  $\text{H}_2$  gas in the mixture is  $\frac{1}{3}$



63. Which of the statements is / are **true** for a chemical reaction occurring in a closed container?
- (A) Total mass of all reactants and products always remain constant.  
 (B) Average molecular mass of the mixture may change during chemical reaction.  
 (C) Total number of atoms of each element will remain constant in a chemical reaction.  
 (D) Total volume of all reactants and products always remain constant.
64. The magnitude of the spin angular momentum of an electron is given by -
- (A)  $S = \sqrt{s(s+1)} \frac{h}{2\pi}$       (B)  $S = s \frac{h}{2\pi}$       (C)  $S = \frac{\sqrt{3}}{2} \times \frac{h}{2\pi}$       (D)  $S = \pm \frac{1}{2} \times \frac{h}{2\pi}$
65. Gaseous state electronic configuration of nitrogen atom can be represented as : **[JEE 1999]**
- (A)  $\uparrow\downarrow \uparrow\downarrow \uparrow \uparrow \uparrow$       (B)  $\uparrow\downarrow \uparrow\downarrow \uparrow \downarrow \uparrow$       (C)  $\uparrow\downarrow \uparrow\downarrow \uparrow \downarrow \downarrow$       (D)  $\uparrow\downarrow \uparrow\downarrow \downarrow \downarrow \downarrow$
66. The electronic configuration of an element is  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$ . This represents its : **[JEE 2000]**
- (A) excited state      (B) ground state      (C) cationic form      (D) none

### Comprehension

#### Comprehension-1

Azurite is a copper containing mineral that is a mixture of Copper (II) carbonate and copper (II) hydroxide,  $[\text{CuCO}_3]_x \cdot [\text{Cu(OH)}_2]_y$ . If the mineral is 55.31% Cu, 0.58% H and 6.97% C, with the remainder oxygen, what are x and y in the general formula ? **[Cu = 63.5]**

67. What is the value of 'x' in general empirical formula ?
- (A) 7      (B) 2      (C) 3      (D) 4
68. What is the value of 'y' in the general empirical formula b?
- (A) 1      (B) 2      (C) 3      (D) 4
69. If the value of x and y be 1 and 2 respectively. Calculate the % composition of Cu ?
- (A) 50 %      (B) 59.8%      (C) 51.2%      (D) 60%

#### Comprehension-2

Calcium lactate is used in the food and beverage industries. It has also been used medicinally for treatment of various allergies, for treatment of muscular leg cramps, and as an antidote for a variety of poisons, including lead, arsenicals and carbon tetrachloride. A 0.8274 g sample of anhydrous calcium lactate is found by analysis to contain 0.2732 g of C, 0.0382 g H, 0.1520 g Ca and 0.3640 g O. Each mole of calcium lactate is found to contain one mole of calcium ions. Calcium lactate can be crystallised from water as pentahydrate salt.

70. Simplest formula of the calcium lactate is :
- (A)  $\text{CaO}_6\text{C}_6\text{H}_{10}$       (B)  $\text{CaO}_3\text{C}_3\text{H}_5$       (C)  $\text{CaO}_2\text{C}_3\text{H}_3$       (D)  $\text{CaO}_2\text{C}_3\text{H}_5$
71. Formula weight of calcium lactate is :
- (A)  $129 \text{ g mol}^{-1}$       (B)  $111 \text{ g mol}^{-1}$       (C)  $218 \text{ g mol}^{-1}$       (D)  $113 \text{ g mol}^{-1}$
72. How many grams of calcium lactate pentahydrate would be recovered from 1 g of anhydrous salt :
- (A) 1.41 g      (B) 1.00 g      (C) 1.27 g      (D) 1.51 g

**Comprehension-3**

**Read the following rules and answer the questions at the end of it.**

Electrons in various suborbitals of an orbit are filled in increasing order to their energies.

Pairing of electrons in various orbitals of a suborbit takes place only after each orbital is half-filled.

No two electrons in an atom can have the same set of quantum number.

- 73.** Cr ( $Z = 24$ ),  $Mn^+$  ( $Z = 25$ ),  $Fe^{2+}$  ( $Z = 26$ ) and  $Co^{3+}$  ( $Z = 27$ ) are isoelectronic each having 24 electrons.

Thus,

(A) all have configurations as  $[Ar] 4s^1 3d^5$

(B) Cr and  $Mn^+$  have configurations as  $[Ar] 4s^1 3d^5$  while  $Fe^{2+}$  and  $Co^{3+}$  have configurations as  $[Ar] 3d^6$ .

(C) all have configurations as  $[Ar] 3d^6$

(D) all have configurations as  $[Ar] 4s^2 3d^6$

- 74.** A compound of vanadium has a magnetic moment of 1.73 BM. Electronic configuration of the vanadium ion in the compound is :

(A)  $[Ar] 4s^0 3d^1$

(B)  $[Ar] 4s^2 3d^3$

(C)  $[Ar] 4s^1 3d^0$

(D)  $[Ar] 4s^0 3d^5$

- 75.** Which of these ions are expected to be paramagnetic and coloured in aqueous solution ?

(A)  $Fe^{3+}$ ,  $Ti^{3+}$ ,  $Co^{3+}$

(B)  $Cu^+$ ,  $Ti^{4+}$ ,  $Sc^{3+}$

(C)  $Fe^{3+}$ ,  $Ni^{2+}$ ,  $V^{5+}$

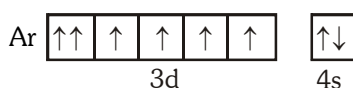
(D)  $Cu^+$ ,  $Cu^{2+}$ ,  $Fe^{2+}$

- 76.** While writing the following electronic configuration of Fe some rules have been violated :

I : Aufbau rule,

II : Hund's rule

III : Pauli's exclusion principle



(A) I, II

(B) II, III

(C) I, III

(D) III

- 77.** How many elements would be in the second period of the periodic table if the spin quantum number ( $m_s$ ) could

have the value of  $-\frac{1}{2}, 0, +\frac{1}{2}$  ?

(A) 8

(B) 10

(C) 12

(D) 18

- 78.** The sub-shell that arises after  $f$  sub-shell is called  $g$  sub-shell.

(A) it contains 18 electrons and 9 orbitals

(B) it corresponds to  $\ell = 4$  and first occurs in 5th energy level

(C) a  $g$ -orbital can have maximum of two electrons

(D) all the above statements are true.

**Subjective Questions**

- 79.** A crystalline hydrated salt on being rendered anhydrous, loses 45.6% of its weight. The percentage composition of anhydrous salt is : Al = 10.5%, K = 15.1%, S = 24.8% and O = 49.6%. Find the empirical formula of the anhydrous and crystalline salt :

- 80.** Two elements C and D combine to form two compounds  $C_xD_y$  &  $C_yD_x$ . 0.5 mole of  $C_yD_x$  weigh 40 gm & 1 molecule of  $C_xD_y$  weigh  $1.66 \times 10^{-25}$  kg. The atomic weight of C and D are 20 & 40 respectively. 'x' & 'y' are respectively.

- 81.** On a reference scale of C, at. weight of Al is 26.98 of Titanium is 47.48. What would be at. weight of Al on a new reference scale where Titanium has a value of 48.

**82.** Three isotopes of an element have mass numbers  $M$ ,  $(M+1)$  and  $(M+2)$ . If the mean mass number is  $(M + 0.5)$ , then the ratio of number may be accepted for  $M$ ,  $(M+1)$  and  $(M+2)$  in the order

**83.** 0.36 gm of a triatomic gas,  $X_3$ , occupies 168 ml at 1 atm & 273 K. The atomic weight of  $X$  is

**84.** A mother cell disintegrate into sixty identical cells and each daughter cell further disintegrate into 24 smaller cells. The smallest cells are uniform cylindrical in shape with diameter of  $120 \text{ \AA}$  and each cell is  $6000 \text{ \AA}$  long. Determine molar mass of the mother cell if density of the smallest cell is  $1.12 \text{ g/cm}^3$  :

**85.** Instead of principal quantum number ( $n$ ), azimuthal quantum number ( $l$ ) & magnetic quantum number  $m$ , a set of new quantum numbers  $s$ ,  $t$  and  $u$  was introduced with similar logic but different values as defined below.

$s = 1, 2, 3, \dots, \infty$  all positive integral values.

$t = (s^2 - 1^2), (s^2 - 2^2), (s^2 - 3^2) \dots$  No negative value

$u = -\frac{(t+1)}{2}$  to  $+\frac{(t+1)}{2}$  (including zero, if any) in integral steps.

Each orbital can have maximum four electrons.

$(s + t)$  rule is defined, similar to  $(n + l)$  rule.

**(i)** Number of electrons that can be accommodated in  $s = 2$  and  $s = 3$  shell.

**(ii)** Number of electrons for which  $s = 2$ ,  $t = 3$  for an element with atomic number 24.

**(iii)** The number of subshells in which the third shell is subdivided equal to

**86.** If for any electron in an orbital another parameter 'B' is defined as

$B = n + l + m$ , where  $n$ ,  $l$ ,  $m$  are the quantum numbers of that orbital then what will be the maximum value of  $B$  for the last electron of  ${}_{35}\text{Br}$ .

**87.** In case of nitrogen, if  $M_1$  represents spin multiplicity if Hund's rule is followed and  $M_2$  represents spin multiplicity

if only Hund's Rule is violated then the value of  $\frac{M_1}{M_2}$  will be:

## ANSWERS

• **Fill in the Blanks**

1. (1)    2. 32    3. 14

• **True and False**

4. False    5. False

• **Assertion-Reason**

6. (D)    7. (A)    8. (A)    9. (A)    10. (A)  
 11. (A)    12. (B)    13. (A)    14. (A)

• **Single Choice Correct**

15. (B)	16. (D)	17. (D)	18. (C)	19. (D)
20. (A)	21. (A)	22. (B)	23. (B)	24. (A)
25. (B)	26. (A)	27. (C)	28. (B)	29. (C)
30. (C)	31. (C)	32. (D)	33. (A)	34. (A)
35. (A)	36. (C)	37. (C)	38. (D)	39. (D)
40. (A)	41. (C)	42. (D)	43. (C)	44. (A)
45. (B)	46. (C)	47. (A)	48. (C)	49. (C)
50. (B)	51. (D)	52. (C)	53. (D)	54. (A)
55. (C)	56. (C)			

• **Multiple Choice Correct**

57. (A)    58. (BC)    59. (ACD)    60. (BC)    61. (ABD)  
 62. (AC)    63. (ABC)    64. (AC)    65. (AD)    66. (BC)

• **Comprehension**

<b>Comprehension 1 :</b>	67. (B)	68. (A)	69. (B)
<b>Comprehension 2 :</b>	70. (A)	71. (C)	72. (A)
<b>Comprehension 3 :</b>	73. (B)	74. (A)	75. (A)
	76. (D)	77. (C)	78. (D)

• **Subjective Questions**

79. $\text{KAlS}_2\text{O}_8, \text{KAlS}_2\text{O}_8 \cdot 12 \text{H}_2\text{O}$	80. $x = 1 \quad y = 2$	81. 27.04
82. 4 : 1 : 1	83. 16	84. $6.6 \times 10^{10} \text{ g}$
85. (i) 28, 76 ; (ii) (0) ; (iii) (3)	86. (6)	87. (2)

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**PERIODIC TABLE**


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**True/False**

1.  $\text{Al}_2\text{O}_3$  is an amphoteric oxide.
2. Third group of periodic table accommodates maximum number of elements.
3. First ionisation potential of Mg is higher than that of Al.
4. The electronic configuration of an element is  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$ . This represents its ground state configuration.
5. Successive ionisation potentials are lower.
6. The alkali metals show increasing electronegativities from Li to Cs.
7. In group I of alkali metals, the ionization potential decreases down the group. Therefore lithium is a poor reducing agent in gaseous state.
8. The decreasing order of electron affinity of F, Cl, Br is  $F > Cl > Br$

**Fill in the blanks**

9. Most electropositive elements belong to ..... group.
10. Most electronegative elements belong to ..... group.
11. Transition elements are characterised by ..... valency.
12. The second ionisation energy of calcium is ..... than the ..... ionisation energy of calcium.
13. The electronegativity of the elements C, N, Si and P increases in the order of .....
14. Total number of inner transition elements are .....
15. Two elements of equal electronegative values they form ..... bond.
16. Among Na, Mg, Al & Si elements ..... element has zero electron affinity.
17. Elements of group ..... have greater tendency to form positive ions than elements of group IIA.
18. In aqueous solution ..... is the best reducing agent among the alkali metals.
19.  $\text{Ca}^{2+}$  has a smaller ionic radius than  $\text{K}^+$  because it has .....
20. Compounds that formally contain  $\text{Pb}^{4+}$  are easily reduced to  $\text{Pb}^{2+}$ . The stability of the lower oxidation state is due to .....

**Assertion-Reason**

These questions contains, Statement I (assertion) and Statement II (reason).

(A) Statement-I is true, Statement-II is true ; Statement-II is correct explanation for Statement-I.

(B) Statement-I is true, Statement-II is true ; Statement-II is NOT a correct explanation for statement-I

(C) Statement-I is true, Statement-II is false

(D) Statement-I is false, Statement-II is false.

21. **Statement -1** : Two successive ionisation energies of Argon are 56.8 eV and 36.8 eV respectively.  
**because**  
**Statement -2** :  $Z_{\text{eff}}$  of Ar ( $3s^2 3p^6$ ) is greater than  $\text{Ar}^+$  ( $3s^2 3p^5$ ).
22. **Statement -1** : Electron affinity of fluorine is greater than chlorine.  
**because**  
**Statement -2** : Ionisation potential of fluorine is less than chlorine.

- 23. Statement -1** : Size of anion is larger than their parent atom.  
**because**  
**Statement -2** :  $Z_{eff}$  of anion is greater than that of their parent atom.
- 24. Statement -1** : Atomic radius of inert gases is largest in the period  
**because**  
**Statement -2** : Effective nuclear charge of inert gases is minimum
- 25. Statement -1** : 2<sup>nd</sup> IP of alkali metals is maximum in the period.  
**because**  
**Statement -2** : Alkali metals has smallest atomic size in the period.
- 26. Statement -1** : First ionization energy of nitrogen is lower than oxygen.  
**because**  
**Statement -2** : Across the period effective nuclear charge decreases.
- 27. Statement -1** : The third period contains only 8 elements and not 18 like 4th period.  
**because**  
**Statement -2** : In III period filling starts from  $3s^1$  and complete at  $3p^6$  whereas in IV period it starts from  $4s^1$  and complete after  $3d^{10}$  and  $4s^2$ .

### Single Choice Correct

- 28.** An element with atomic number 106 has been discovered recently. Which of the following electronic configuration will it posses :-  
 (A)  $[Rn] 5f^{14} 6d^5 7s^1$  (B)  $[Rn] 5f^{14} 6d^5 7s^2$  (C)  $[Rn] 5f^{14} 6d^6 7s^0$  (D)  $[Rn] 5f^{14} 6d^1 7s^2 7p^3$
- 29\*.** Correct order of ionic radii is :-  
 (A)  $Ti^{4+} < Mn^{7+}$  (B)  $^{37}Cl^- < ^{35}Cl^-$  (C)  $K^+ > Cl^-$  (D)  $P^{3+} > P^{5+}$
- 30.** The correct order of stability of  $Al^+$ ,  $Al^{+2}$ ,  $Al^{+3}$  is :-  
 (A)  $Al^{+3} > Al^{+2} > Al^+$  (B)  $Al^{+2} > Al^{+3} > Al^+$   
 (C)  $Al^{+2} < Al^+ > Al^{+3}$  (D)  $Al^{+3} > Al^+ > Al^{+2}$
- 31.** Which of the following general electronic configuration for transition elements is not correct :-  
 (A)  $(n+1)s^{1-2} nd^{1-10}$  (B)  $ns^{1-2} (n-1)d^{1-10}$  (Where  $n = 2, 3, 4, \dots$ )  
 (C)  $ns^{0,1,2} (n-1)s^2 p^6 d^{1-10}$  (D)  $(n-1)d^{1-10} ns^{0-2}$
- 32.** Which of the following decreases in going down the halogen group :-  
 (A) Ionic radius (B) Atomic radius (C) Ionisation potential (D) Boiling point
- 33.** Which of the following has 2<sup>nd</sup> IP < 1<sup>st</sup> IP  
 (A) Mg (B) Ne (C) C (D) None
- 34.** The correct order of decreasing first ionization energy is :-  
 (A)  $Si > Al > Mg > Na$  (B)  $Si > Mg > Al > Na$   
 (C)  $Al > Si > Mg > Na$  (D)  $Mg > Li > Al > Si$
- 35.** The electron affinity  
 (A) Of carbon is greater than oxygen (B) Of fluorine is less than iodine  
 (C) Of  $Cl^-$  is less than Cl (D) Of S is less than oxygen
- 36.** Which will have the maximum value of electron affinity  $O^x$ ,  $O^y$  and  $O^z$  [ $x$ ,  $y$  and  $z$  respectively are 0, -1 and -2] :-  
 (A)  $O^x$  (B)  $O^y$  (C)  $O^z$  (D) All have equal
- 37.** If the atomic number of an element is 58, it will be placed in the periodic table in the -  
 (A) III B gp and 6<sup>th</sup> period (B) IV B gp and 6<sup>th</sup> period  
 (C) VB gp and 7<sup>th</sup> period (D) None of the above

38. Which of the following ion has largest size :-  
 (A)  $F^-$  (B)  $Al^{+3}$  (C)  $Cs^+$  (D)  $O^{2-}$
39. 
$$\begin{array}{cccc} 1 & 2 & 3 & 4 \\ H_3C & -CH & =C & =CH_2 \end{array}$$
  
 In the given compound which carbon atom will show maximum electronegativity -  
 (A) Fourth (B) First  
 (C) Third (D) EN of all the carbon atoms is same
40. (a)  $M^-_{(g)} \rightarrow M_{(g)}$  (b)  $M_{(g)} \rightarrow M^+_{(g)}$  (c)  $M^+_{(g)} \rightarrow M^{+2}_{(g)}$  (d)  $M^{+2}_{(g)} \rightarrow M^{+3}_{(g)}$   
 Minimum and maximum I.P. would be of :-  
 (A) a, d (B) b, c (C) c, d (D) d, a
- 41\*. Which is correct order of size of  $O$ ,  $O^{2-}$ ,  $F^-$  and  $F$  :-  
 (A)  $O^{2-} > O > F^- > F$  (B)  $O > O^{2-} > F > F^-$   
 (C)  $O^{2-} > F^- > F > O$  (D)  $O^{2-} > F^- > O > F$
42. The right order of ionization potential of Li, Be, B & C is :  
 (A)  $C > Be > B > Li$  (B)  $C > B > Be > Li$  (C)  $C > B > Li > Be$  (D)  $B > C > Be > Li$
- 43\*. The correct order of second ionization potential of C, N, O and F is  
 (A)  $C > N > O > F$  (B)  $O > N > F > C$  (C)  $O > F > N > C$  (D)  $F > O > N > C$
44. The correct sequence of the electron affinity of C, N, O and F is :  
 (A)  $C > N < O < F$  (B)  $O > N > C > F$  (C)  $C < N > O < F$  (D)  $C > N > O > F$
45. The decreasing order of the ionization potential of the following elements is :  
 (A)  $Ne > Cl > P > S > Al > Mg$  (B)  $Ne > Cl > P > S > Mg > Al$   
 (C)  $Ne > Cl > S > P > Mg > Al$  (D)  $Ne > Cl > S > P > Al > Mg$
46. One element has atomic weight 39. Its electronic configuration is  $1s^2, 2s^2 2p^6, 3s^2 3p^6 4s^1$ . The true statement for that element is :  
 (A) More (IE) (B) Transition element (C) Isotone with  $^{36}_{18}Ar$  (D) Stable oxide  $M_2O$
- 47\*. Is a data sufficiency problem in which it is to be decided on the basis of given statements whether the given question can be answered or not. (No matter whether the answer is yes or no)  
 If  $\Delta H_{\text{solution}} < 0$  then compound acts as ionic in aqueous solution. Is  $AlCl_3(s)$  ionic in aqueous solution.  
**Statement 1** : L.E. of  $AlCl_3$  is 5137 kJ/mol  
**Statement 2** :  $\Delta H_{\text{HE}}$  of  $Al^{+3}$  ion is - 4665 kJ/mol $^{-1}$  &  $\Delta H_{\text{HE}}$  of  $Cl^-$  is -381 kJ/mol $^{-1}$   
 (A) Statments (A) alone is sufficient but statement (B) is not sufficient  
 (B) Statments (B) alone is sufficient but statement (A) is not sufficient  
 (C) Both statement together are sufficient but neither statement alone is sufficient  
 (D) Statement (A) & (B) together are not sufficient

48. Match List I with List II and select the correct answer using the codes given below :

List I		List II	
A.	$1s^2, 2s^2 2p^6, 3s^2 3p^6, 4s^2$	1.	In
B.	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^1$	2.	Pd
C.	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^6 4d^{10}$	3.	Ca
D.	$1s^2, 2s^2 2p^6, 3d^{10}, 4s^2 4p^6 4d^{10}, 5s^2 5p^1$	4.	Cu
Code : A	B	C	D
(A)	1	3	4
(B)	1	2	4
(C)	3	2	1
(D)	1	3	2

49. Match List I (Atomic Number of Element) with List II (Block to which the Element Belongs) and select the correct answer using the codes given below :

**List I**

(Atomic Number of Element)

- A. 24  
B. 38  
C. 49  
D. 59

**Code : A**

- (A) 2  
(B) 4  
(C) 2  
(D) 4

**B**

- 1  
3  
3  
1

**List II**

(Block to which the element belongs)

1. p  
2. f  
3. s  
4. d

**C**

- 3  
1  
1  
3

**D**

- 4  
2  
4  
2

50. The first ionization potentials (eV) of Be and B respectively are :  
 (A) 8.29 eV, 9.32 eV (B) 9.32 eV, 9.32 eV (C) 8.29 eV, 8.29 eV (D) 9.32 eV, 8.29 eV
- 51\*. If there were 10 periods in the periodic table then how many elements would this period can maximum comprise of.  
 (A) 50 (B) 72 (C) 32 (D) 98
52. If each orbital can hold a maximum of three electrons, the number of elements in 9<sup>th</sup> period of periodic table (long form) are :  
 (A) 48 (B) 162 (C) 50 (D) 75
- 53\*. The electronic configuration of an element is  $1s^2 2s^2 2p^6 3s^2 3p^4$ . The atomic number and the group number of the element 'X' which is just below the above element in the periodic table are respectively.  
 (A) 24 & 6 (B) 24 & 15 (C) 34 & 16 (D) 34 & 8
54. Alkaline earth metals always form dipositive ions due to  
 (A)  $IE_2 - IE_1 > 10 \text{ eV}$  (B)  $IE_2 - IE_1 = 17 \text{ eV}$   
 (C)  $IE_2 - IE_1 < 10 \text{ eV}$  (D) None of these
55. The correct order of second I.P.  
 (A)  $Na < Mg > Al < Si$  (B)  $Na > Mg < Al > Si$   
 (C)  $Na > Mg > Al < Si$  (D)  $Na > Mg > Al > Si$
- 56\*. Two elements A & B are such that B.E. of A-A, B-B & A-B are respectively 81 Kcal/mole, 64 Kcal/mole, 76 kcal/mole & electronegativity of B is 2.4 then the electronic configuration of A is, (if  $X_B > X_A$ )  
 (A)  $1s^2 2s^2 2p^1$  (B)  $[Ne] 3s^2 3p^1$  (C)  $[He] 2s^2 2p^4$  (D)  $[Ne] 3s^2 3p^5$
57. Moving from right to left in a periodic table, the atomic size is: [JEE 1995]  
 (A) increased (B) decreased (C) remains constant (D) none of these
58. The increasing order of electronegativity in the following elements: [JEE 1995]  
 (A) C, N, Si, P (B) N, Si, C, P (C) Si, P, C, N (D) P, Si, N, C
59. One element has atomic weight 39. Its electronic configuration is  $1s^2, 2s^2 2p^6, 3s^2 3p^6 4s^1$ . The true statement for that element is: [JEE 1995]  
 (A) High value of IE (B) Transition element  
 (C) Isotone with  $^{38}_{18}\text{Ar}$  (D) None
60. The number of paired electrons in oxygen atom is: [JEE 1995]  
 (A) 6 (B) 16 (C) 8 (D) 32



- 61.** The decreasing size of  $K^+$ ,  $Ca^{2+}$ ,  $Cl^-$  &  $S^{2-}$  follows the order: [JEE 1995]  
 (A)  $K^+ > Ca^{2+} > S^{2-} > Cl^-$  (B)  $K^+ > Ca^{2+} > Cl^- > S^{2-}$   
 (C)  $Ca^{2+} > K^+ > Cl^- > S^{2-}$  (D)  $S^{2-} > Cl^- > K^+ > Ca^{2+}$
- 62.** Which of the following has the maximum number of unpaired electrons [JEE 1996]  
 (A)  $Mg^{2+}$  (B)  $Ti^{3+}$  (C)  $V^{3+}$  (D)  $Fe^{2+}$
- 63.** The incorrect statement among the following is: [JEE 1997]  
 (A) the first ionisation potential of Al is less than the first ionisation potential of Mg  
 (B) the second ionisation potential of Mg is greater than the second ionisation potential of Na  
 (C) the first ionisation potential of Na is less than the first ionisation potential of Mg  
 (D) the third ionisation potential of Mg is greater than the third ionisation potential of Al
- 64.** The electrons, identified by  $n$  &  $l$  ; [JEE 1999]  
 (i)  $n = 4, l = 1$   
 (ii)  $n = 4, l = 0$   
 (iii)  $n = 3, l = 2$   
 (iv)  $n = 3, l = 1$  can be placed in order of increasing energy, from the lowest to highest as :  
 (A) (iv) < (ii) < (iii) < (i) (B) (iii) < (ii) < (iv) < (i)  
 (C) (i) < (iii) < (ii) < (iv) (D) (iii) < (i) < (iv) < (ii)

### Multiple Choice Correct

- 65.** Ionization energy of an element is :  
 (A) Equal in magnitude but opposite in sign to the electron gain enthalpy of the cation of the element  
 (B) Same as electron affinity of the element  
 (C) Energy required to remove one valence electron from an isolated gaseous atom in its ground state  
 (D) Equal in magnitude but opposite in sign to the electron gain enthalpy of the anion of the element
- 66.** Which one of the following statement (s) is (are) correct? [JEE 1998]  
 (A) The electronic configuration of Cr is  $[Ar] 3d^5 4s^1$ . (Atomic No. of Cr = 24)  
 (B) The magnetic quantum number may have a negative value  
 (C) In silver atom, 23 electrons have a spin of one type and 24 of the opposite type. (Atomic No. of Ag = 47)  
 (D) The oxidation state of nitrogen in  $HN_3$  is -3.
- 67\*.** If Aufbau's principle and Hund's rule were not followed.  
 (A) K would have been d-block element & paramagnetic.  
 (B) Cu would have been s-block element.  
 (C) Cr would have been diamagnetic  
 (D)  $Fe^{+3}$  ion would have 5 unpaired electrons.
- 68\*.** Which of the following pair have nearly the same atomic radii  
 (A) Al and Ga (B) Fe and Ni (C) Zr and Hf (D) Pt & Pd
- 69\*.** Which of the following is false -  
 (A)  $Cr^{2+}$  (g) ion has greater magnetic moment compared to  $Co^{3+}$  (g)  
 (B) The magnitude of ionization potential of iron anion (monoanion) would be equal to electron gain enthalpy of iron.  
 (C) Lanthanide contraction is cause of lower I.P. of Pb than Sn  
 (D) If successive ionization energy are 332, 738, 849, 4080, 4958 (in kJ/mol). Then this element can be of 15th group

### Comprehension Type

Pauling gave method to calculate univalent ion radii by assuming that

- (i) In ionic crystal (let  $M^+X^-$ ) cations and anions are in contact of each other and sum of their radii is equal to interionic distance, i.e.

$$d_{(M^+—X^-)} = r_{M^+} + r_{X^-}$$

- (ii) The radius of an ion having noble gas configuration is inversely proportional to the effective nuclear

$$\text{charge felt at the periphery of the ion, i.e. } r_{(M^+)} = \frac{C}{Z_{\text{eff.}(M^+)}} \text{ and } r_{(X^-)} = \frac{C}{Z_{\text{eff.}(X^-)}}$$

Here C is constant of proportionality whose value depends on electronic configuration of ion.

Thus,

$$d_{(M^+-X^-)} = \frac{C}{Z_{\text{eff.}(M^+)}} + \frac{C}{Z_{\text{eff.}(X^-)}} \text{ pm}$$

$Z_{\text{eff.}}$  is the effective nuclear charge whose value can be calculated by the formula :  $Z_{\text{eff.}} = Z - \sigma$ . Here  $\sigma$  is shielding constant and for neon, the value of  $\sigma$  when calculated by Slater's rule, is found to be 4.5.

- 70\*.** The value of constant C for NaF crystals is [given that interionic distance of NaF = 231 pm] :  
 (A) 231 (B) 115.5 (C) 614.5 (D) 307.25
- 71\*.** The value of univalent radii for  $F^-$  as calculated by Pauling method is (given that interionic distance of NaF = 231 pm) :  
 (A) 94.5 pm (B) 136.5 pm (C) 111.68 pm (D) 115.5 pm
- 72\*.** The value of 'C' for  $Na^+$ ,  $Mg^{2+}$  and  $Al^{3+}$  will be in the order :  
 (A)  $Al^{3+} > Mg^{2+} > Na^+$  (B)  $Al^{3+} < Mg^{2+} < Na^+$   
 (C)  $Al^{3+} = Mg^{2+} = Na^+$  (D) Can't be compared.

### Subjective Questions

- 73\*.**  $Li^+$ ,  $Mg^{2+}$ ,  $K^+$ ,  $Al^{3+}$  (Arrange in increasing order of radii) [JEE 1997]
- 74.** The ionic radii of  $S^{2-}$  and  $Te^{2-}$  are 1.84 and 2.2 Å respectively. What would you predict for the ionic radius of  $Se^{2-}$ .
- 75.** How many chlorine atoms will be ionised ( $Cl \rightarrow Cl^+ + e^-$ ) by the energy released from the process  $Cl + e^- \rightarrow Cl^-$  for  $6.023 \times 10^{23}$  atom (IP for Cl = 1250 kJ mole<sup>-1</sup> and EA = 350 kJ mole<sup>-1</sup>)
- 76.** Na and  $Mg^+$  have same number of electrons. But removal of electron from  $Mg^+$  requires more energy. Explain.
- 77.** Based on location in P.T., which of the following would you expect to be acidic & which basic.  
 (A) CsOH (B) IOH (C)  $Sr(OH)_2$  (D)  $Se(OH)_2$   
 (E) FrOH (F) BrOH
- 78.** From among the elements, choose the following : Cl, Br, F, Al, C, Li, Cs & Xe.  
 (i) The element with highest electron affinity.  
 (ii) The element with lowest ionisation potential.  
 (iii) The element whose oxide is amphoteric.  
 (iv) The element which has smallest radii.  
 (v) The element whose atom has 8 electrons in the outermost shell.
- 79\*.** For the gaseous reaction,  
 $K + F \longrightarrow K^+ F^-$ ,  $\Delta H$  was calculated to be 19 kcal per mole under conditions where the cations and anions were prevented by electrostatic separation from combining with each other. The ionisation potential of K is 4.3 eV atom. What is the electron affinity of F ?
- 80\*.** Total number of enthalpy(s) (out of given nine) of A(g) which is/are **not** associated with conversion of  $A_{(g)}^- \longrightarrow A_{(g)}^{+4}$  :  
 $IE_1, IE_2, IE_3, IE_4, IE_5, IE_6, EGE_1, EGE_2$   
 (IE = ionization energy, EGE = electron gain enthalpy)

- 81\*.** Write the number of pairs in which size of first element or ion is higher as compare to  $\text{I}^{\text{nd}}$  out of following nine pairs.  
(O,S) , (He, Ne) , (Kr, Ne), (Na,  $\text{Na}^+$ ), (Cl,  $\text{Cl}^-$ ), ( $\text{I}^-$ ,  $\text{Cl}^-$ ), ( $\text{Li}_{\text{Aq.}}^+$ ,  $\text{Na}_{\text{Aq.}}^+$ ), (Li, Na), ( $\text{Li}^+$ ,  $\text{Na}^+$ )
- 82\*.** Calculate E.N. of chlorine atom on Pauling scale if I.E. of  $\text{Cl}^-$  is 4eV & of E.A. of  $\text{Cl}^+$  is + 13.0 eV.
- 83\*.** Calculate the E.N. of Cl from the bond energy of ClF (61 KCal/mol). Given that bond energies of  $\text{F}_2$  and  $\text{Cl}_2$  are 38 and 58 KCal/mol respectively. Given : Electronegativity of F = 4.

## ANSWERS

### • True and False

1. True      2. True      3. True      4. True      5. False  
 6. False    7. True      8. False

### • Fill in the Blanks

9. IA group / I      10. VIIA/17      11. Variable  
 12. higher, first    13. Si, P, C, N    14. 28  
 15. (non polar) covalent    16. Mg    17. IA  
 18. Lithium    19. IA    20. IA

### • Assertion-Reason

21. (D)      22. (D)      23. (C)      24. (C)      25. (C)  
 26. (D)      27. (A)

### • Single Choice Correct

28. (A)      29. (D)      30. (A)      31. (D)      32. (C)  
 33. (D)      34. (B)      35. (C)      36. (A)      37. (A)  
 38. (C)      39. (C)      40. (A)      41. (D)      42. (A)  
 43. (C)      44. (A)      45. (B)      46. (D)      47. (C)  
 48. (C)      49. (B)      50. (D)      51. (B)      52. (D)  
 53. (C)      54. (C)      55. (B)      56. (A)      57. (A)  
 58. (C)      59. (C)      60. (A)      61. (D)      62. (D)  
 63. (B)      64. (A)

### • Multiple Choice Correct

65. (AC)      66. (ABC)      67. (ABC)      68. (ABCD)      69. (ACD)

### • Comprehension

70. (C)      71. (B)      72. (D)

### • Subjective Questions

73.  $\text{Al}^{3+} < \text{Mg}^{2+} < \text{Li}^+ < \text{K}^+$
74. Ionic radius of  $\text{Se}^{2-}$  is expected to be in between the ionic radii of  $\text{S}^{2-}$  and  $\text{Te}^{2-}$ . Thus  
 Ionic radius of  $\text{Se}^{2-} = \frac{1.84 + 2.21}{2} = 2.025 \text{ \AA}$
75. Since  $1250 \text{ kJ mole}^{-1}$  energy is required to ionise  $6.023 \times 10^{23}$  atoms. But  $350 \text{ kJ mole}^{-1}$  energy is released  
 hence the no. of ionised atoms =  $\frac{6.023 \times 10^{23} \times 350 \text{ kJ mole}^{-1}}{1250 \text{ kJ mole}^{-1}} = 1.686 \times 10^{23}$
76.  $\text{Mg}^+$  has more  $Z_{\text{eff}}$ .
77. (A) Basic, (B) Acidic, (C), Basic, (D) Acidic, (E) Basic, (F) Acidic.
78. (i) Cl, (ii) Cs, (iii) Al, (iv) F, (v) Xe.      79.  $3.476 \text{ ev.}$
80. (3) ; I.E<sub>5</sub>, I.E<sub>6</sub>, EGE<sub>2</sub> not involved.
81. (4) ; Size of first is greater as compared to second for following :  
 (Kr, Ne) , (Na, Na<sup>+</sup>), (I<sup>-</sup>, Cl<sup>-</sup>), (Li<sup>+</sup>(aq), Na<sup>+</sup>(aq))
82. 3.03 (Pauling)      83. 3.2

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**CHEMICAL BONDING**


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**True/False**

1. The polarising power of a cation is directly proportional to its size.
2. The polarisability of an anion is directly proportional to its charge.
3. Ionic interactions are directional.
4. All molecules having polar bonds are polar.
5. The net dipole in the water molecules is the resultant of its bond dipoles.
6.  $\text{SO}_2$  is polar whereas  $\text{CO}_2$  is non-polar.
7. If all bonds in a molecule are polar, the molecule as a whole must be polar.
8. The bond angle around B in  $\text{BCl}_3$  and  $\text{BF}_3$  is same.
- 9\*. Dipole moment of  $\text{NF}_3$  is less than that of  $\text{NH}_3$ .
10. In ionic bond formation octet is completed.
11. Normally the covalent bond is non-directional.
12.  $\text{O}_2$ ,  $\text{O}_2^-$  and  $\text{O}_2^+$  all are paramagnetic.
13. When bond order increases, bond length decreases.
14.  $\text{SF}_6$  molecule is octahedral.
15. Ethyne is a linear molecule.
16.  $\text{CO}_2$  is a polar molecule but not have polar bond.
17. C–C sigma bond in ethyne is  $\text{sp}^2\text{--sp}^2$ .
18.  $\text{XeF}_4$  molecule is square planar in shape.
19. The bond angle in  $\text{Cl}_2\text{O}$  is equal to that of  $\text{OF}_2$ .
20. HCl is a gas while HF is high boiling point liquid because H–F bond is stronger.
- 21\*. Liquid  $\text{NH}_3$  does not contain H–bond.
22. Odd electron molecule is paramagnetic.
23. During the formation of covalent bond both shared electron having opposite spin.
- 24\*. The solubility of ionic solids decreases when hydration energy of ions increases.
25. Between layers of graphite, bond will be covalent.
- 26\*. The polarising power of  $\text{Zn}^{2+}$  is greater than  $\text{Ca}^{2+}$  ions.
27. The colour of  $\text{PbI}_2$  is yellow. The reason for this is large size of  $\text{Pb}^{+2}$  ion.
28. The H – N – H bond angle in  $\text{NH}_3$  is greater than H – As – H bond angle in  $\text{AsH}_3$ .
29. The dipole moment of  $\text{CH}_3\text{F}$  is greater than that of  $\text{CH}_3\text{Cl}$ .

**Fill in the blanks**

30. Hydrogen bond energy is around .....
31. The valence atomic orbitals on carbon in silver acetylide are ..... hybridised.
32. The hybridisation state of oxygen in water molecule is .....
33. When  $N_2$  goes to  $N_2^+$ , then N–N bond distance ..... and when  $O_2$  goes to  $O_2^+$ , then O–O bond distance .....
34. Among  $N_2O$ ,  $SO_2$ ,  $I_3^+$  and  $I_3^-$ , the linear species are ..... and .....

**Assertion-Reason**

These questions contains, Statement-I (assertion) and Statement-II (reason).

- (A) Statement-I is True, Statement-II is True ; Statement-II is a correct explanation for Statement-I  
 (B) Statement-I is True, Statement-II is True ; Statement-II is NOT a correct explanation for Statement-I  
 (C) Statement-I is True, Statement-II is False.  
 (D) Statement-I is False, Statement-II is True.

- 35\*. **Statement-I** :  $SF_6$  exists but  $SH_6$  does not.

**Because**

**Statement-II** :  $d\pi-p\pi$  bonding cannot take place in  $SH_6$

- 36\*. **Statement-I** : The first ionization energy of Be is greater than that of B.

**Because**

**Statement-II** : The 2p orbital is lower in energy than the 2s.

- 37\*. **Statement-I** :  $CO_2$  is non polar while  $SO_2$  is polar molecule.

**Because**

**Statement-II** : S–O bonds are polar while C–O non polar.

39. **Statement-I** :  $N_2O$ ,  $CO_2$  &  $I_3^-$  are isostructural.

**Because**

**Statement-II** : All three have same hybridised central atom.

- 41\*. **Statement-I** :  $Al(OH)_3$  is amphoteric in nature.

**Because**

**Statement-II** : Al–O and O–H bonds can be broken with equal ease in  $Al(OH)_3$ .

- 42\*. **Statement-I** : Boron does not show univalent nature but unipositive nature of thallium is quite stable.

**Because**

**Statement-II** : Inert pair effect predominates in thallium.

- 43\*. **Statement-I** :  $H_3BO_3$  is monobasic acid in water.

**Because**

**Statement-II** : In water ionise as  $H_3BO_3 \rightleftharpoons H_2BO_3^- + H^+$ .

46. **Statement-I** : Bond order of  $O_2$  and BN is same.

**Because**

**Statement-II** :  $O_2$  and BN are isoelectronic

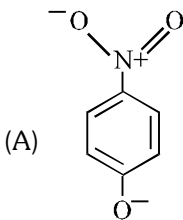
- 47. Statement-I :** In  $\text{NF}_3$  molecule lone pair resides in  $sp^3$  hybrid orbital.  
**Because**  
**Statement-II :**  $\text{NF}_3$  has pyramidal shape.
- 48. Statement-I :** Super oxide ion is paramagnetic whereas peroxide ion is diamagnetic.  
**Because**  
**Statement-II :** Super oxide ion has one unpaired electron whereas peroxide ion has no unpaired electron.
- 49\*. Statement-I :** Although  $\text{PF}_5$ ,  $\text{PCl}_5$  and  $\text{PBr}_5$  are known, the penta halide of nitrogen have not been observed.  
**Because**  
**Statement-II :** Phosphorus has lower electronegativity than nitrogen.
- 50. Statement-I :**  $\text{HNO}_3$  is a stronger acid than  $\text{HNO}_2$ .  
**Because**  
**Statement-II :** In  $\text{HNO}_3$ , there are two N–O linkage whereas in  $\text{HNO}_2$  there is only one.
- 51. Statement-I :**  $\text{H}_2\text{SO}_4$  is more viscous than water.  
**Because**  
**Statement-II :** In  $\text{H}_2\text{SO}_4$ , S has highest oxidation state.
- 52\*. Statement-I :**  $\text{F}_3^-$  ion is known, which has same geometry as  $\text{X}_3^-$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ )  
**Because**  
**Statement-II :** F is most electronegative element.

**Single Choice Correct**

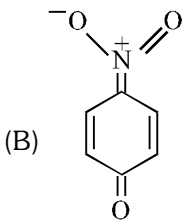
- 53.** Which of the following Lewis dot diagrams is(are) incorrect ?



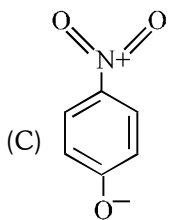
- 54.** The valency of sulphur in sulphuric acid is :  
 (A) 2 (B) 8 (C) 4 (D) 6
- 55\*.** Which of the following has been arranged in increasing order of size of the hybrid orbitals ?  
 (A)  $sp < sp^2 < sp^3$  (B)  $sp^3 < sp^2 < sp$  (C)  $sp^2 < sp^3 < sp$  (D)  $sp^2 < sp < sp^3$
- 58\*.** For  $\text{H}_2\text{O}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{H}_2\text{O}$  and  $\text{HF}$ , the correct order of decreasing strength of hydrogen bonding is :  
 (A)  $\text{H}_2\text{O} > \text{HF} > \text{H}_2\text{O}_2 > \text{H}_2\text{S}$  (B)  $\text{HF} > \text{H}_2\text{O}_2 > \text{H}_2\text{O} > \text{H}_2\text{S}$   
 (C)  $\text{HF} > \text{H}_2\text{O} > \text{H}_2\text{O}_2 > \text{H}_2\text{S}$  (D)  $\text{H}_2\text{O}_2 > \text{H}_2\text{O} > \text{HF} > \text{H}_2\text{S}$
- 59.** Which one of the following does not have intermolecular H-bonding?  
 (A)  $\text{H}_2\text{O}$  (B) o-nitro phenol (C)  $\text{HF}$  (D)  $\text{CH}_3\text{COOH}$

60. The order of strength of hydrogen bonds is:  
 (A)  $ClH \dots Cl > NH \dots N > OH \dots O > FH \dots F$  (B)  $ClH \dots Cl < NH \dots N < OH \dots O < FH \dots F$   
 (C)  $ClH \dots Cl < NH \dots N > OH \dots O > FH \dots F$  (D)  $ClH \dots Cl < NH \dots N < OH \dots O > FH \dots F$
61. The pairs of bases in DNA are held together by :  
 (A) Hydrogen bonds (B) Ionic bonds (C) Phosphate groups (D) Deoxyribose groups
62. The geometry & the type of hybrid orbitals present about the central atom in  $BF_3$  is : [JEE '98]  
 (A) linear,  $sp$  (B) trigonal planar,  $sp^2$  (C) tetrahedral  $sp^3$  (D) pyramidal,  $sp^3$
63. The correct order of increasing C - O bond length of,  $CO$ ,  $CO_3^{2-}$ ,  $CO_2$  is [JEE '99]  
 (A)  $CO_3^{2-} < CO_2 < CO$  (B)  $CO_2 < CO_3^{2-} < CO$  (C)  $CO < CO_3^{2-} < CO_2$  (D)  $CO < CO_2 < CO_3^{2-}$
64. The geometry of  $H_2S$  and its dipole moment are [JEE '99]  
 (A) angular & non zero (B) angular & zero (C) linear & non zero (D) linear & zero
65. In compounds type  $ECl_3$ , where  $E = B, P, As$  or  $Bi$ , the angles  $Cl - E - Cl$  for different  $E$  are in the order [JEE '99]  
 (A)  $B > P = As = Bi$  (B)  $B > P > As > Bi$  (C)  $B < P = As = Bi$  (D)  $B < P < As < Bi$
66. The most likely representation of resonance structure of p-nitrophenoxide is: [JEE '99]
- 

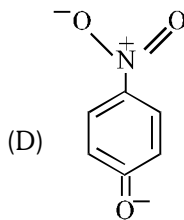
(A)



(B)



(C)



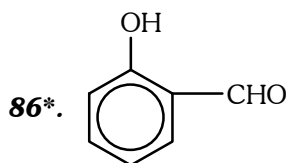
(D)
68. The hybridization of atomic orbitals of nitrogen in  $NO_2^+$ ,  $NO_3^-$  and  $NH_4^+$  are [JEE 2000]  
 (A)  $sp^2$ ,  $sp^3$  and  $sp^2$  respectively (B)  $sp$ ,  $sp^2$  and  $sp^3$  respectively  
 (C)  $sp^2$ ,  $sp$  and  $sp^3$  respectively (D)  $sp^2$ ,  $sp^3$  and  $sp$  respectively
70. Specify hybridization of N and B atoms in a 1 : 1 complex of  $BF_3$  and  $NH_3$  [JEE 2002]  
 (A) N : tetrahedral,  $sp^3$ ; B : tetrahedral,  $sp^3$  (B) N : pyramidal,  $sp^3$ ; B : pyramidal,  $sp^3$   
 (C) N : pyramidal,  $sp^3$ ; B : planar,  $sp^2$  (D) N : pyramidal,  $sp^3$ ; B : tetrahedral,  $sp^3$
71. The nodal plane in the  $\pi$ -bond of ethene is located in [JEE 2002]  
 (A) the molecular plane  
 (B) a plane parallel to the molecular plane  
 (C) a plane perpendicular to the molecular plane which bisects, the carbon-carbon  $\sigma$  bond at right angle.  
 (D) a plane perpendicular to the molecular plane which contains, the carbon-carbon bond.
72. Which of the following are isoelectronic and isostructural ?  $NO_3^-, CO_3^{2-}, ClO_3^-, SO_3$  [JEE 2003]  
 (A)  $NO_3^-, CO_3^{2-}$  (B)  $SO_3, NO_3^-$  (C)  $ClO_3^-, CO_3^{2-}$  (D)  $CO_3^{2-}, SO_3$
73. Which species has the maximum number of lone pair of electrons on the central atom? [JEE 2005]  
 (A)  $ClO_3^-$  (B)  $XeF_4$  (C)  $SF_4$  (D)  $I_3^-$



**Multiple Choice Correct**

- 74.** Atoms combine so that,  
 (A) They can always attain stable configuration to that of nearest noble gas.  
 (B) They can attain stable configuration if possible, to that of nearest noble gas.  
 (C) Their potential energy can increase and hence bond energy may increase.  
 (D) Their potential energy can decrease and hence bond energy may increase.
- 75.** Most ionic compounds have :  
 (A) high melting points and low boiling points  
 (B) high melting points and nondirectional bonds  
 (C) high solubilities in polar solvents and low solubilities in nonpolar solvents  
 (D) three-dimensional arrangements of ions in solid state, and are good conductors of electricity in the molten state
- 77.** Which of the following statements is/are true?  
 (A) Covalent bonds are directional  
 (B) Ionic bonds are nondirectional  
 (C) A polar bond is formed between two atoms which have the same electronegativity value.  
 (D) The presence of polar bonds in a polyatomic molecule suggests that it has zero dipole moment
- 79.** Which of the following species contain coordinate covalent bond :  
 (A)  $AlCl_3$  (B)  $CO$  (C)  $[Fe(CN)_6]^{4-}$  (D)  $N_3^-$
- 80.** Which of the following statement is/are correct  
 (A) Hybridisation is the mixing of pure atomic orbitals having less energy difference  
 (B)  $sp^3d^2$  – hybrid orbitals are at  $90^\circ$  to each other  
 (C)  $sp^3d$  – hybrid orbitals are directed towards the corners of a regular tetrahedron  
 (D)  $sp^3d^2$  – hybrid orbitals are directed towards the corners of a regular octahedron
- 81.**  $sp^3$  hybridisation is in :  
 (A)  $AlH_4^-$  (B)  $CH_3^-$  (C)  $ClO_2^-$  (D)  $NH_2^-$
- 82.** Shape of  $NH_3$  is very similar to :  
 (A)  $SeO_3^{2-}$  (B)  $CH_3^-$  (C)  $BH_3$  (D)  $CH_3^+$
- 83.** Which of the following species are linear ?  
 (A)  $ICl_2^-$  (B)  $I_3^-$  (C)  $N_3^-$  (D)  $ClO_2$
- 84\*.** Which of the following statements are correct?  
 (A) The crystal lattice of ice is formed by covalent as well as hydrogen bonds  
 (B) The density of water increases when heated from  $0^\circ C$  to  $4^\circ C$   
 (C) Above  $4^\circ C$  the thermal agitation of water molecules increases. Therefore, intermolecular distance increases and water starts expanding  
 (D) The density of water decreases from  $0^\circ C$  to a maximum at  $4^\circ C$

85. Molecule(s) having both polar and non polar bonds is / are  
 (A)  $\text{O}_2\text{F}_2$  (B)  $\text{S}_2\text{Cl}_2$  (C)  $\text{N}_2\text{H}_4$  (D)  $\text{S}_2\text{F}_{10}$



- (A) has intermolecular H - bonding (B) has intramolecular H- bonding  
 (C) has low boiling point (D) is steam-volatile
87. Intermolecular hydrogen bonding increases the enthalpy of vapourization of a liquid due to the:  
 (A) decrease in the attraction between molecules  
 (B) increase in the attraction between molecules  
 (C) decrease in the molar mass of unassociated liquid molecules  
 (D) increase in the effective molar mass of hydrogen - bonded molecules

### Match the Column

#### 88. Column-I

- (A)  $\text{XeF}_4$   
 (B)  $\text{BrF}_5$   
 (C)  $\text{ClF}_3$   
 (D)  $\text{SO}_3^{2-}$

#### Column-II

- (P)  $\text{sp}^3\text{d}$  hybridised with 2 lone pair on central atom  
 (Q)  $\text{sp}^3\text{d}^2$  hybridised with 2 lone pair on central atom  
 (R)  $\text{sp}^3$  hybridised with 1 lone pair on central atom  
 (S)  $\text{sp}^3\text{d}^2$  hybridised with 1 lone pair on central atom

### Comprehension

Hybridisation is a theoretical concept, as state of hybridisation cannot be detected even by spectroscopically; unlike intermediates or transition state in various reactions. but it corrects the predictions which are based simple on overlapping of pure atomic orbitals. VSEPR theory predicts precisely shape and bond angle in a given molecule.

89. In which pair of molecules bond angles are not same:  
 (A)  $\text{CCl}_4$  &  $\text{SiCl}_4$  (B)  $\text{NH}_4^+$  &  $\text{NF}_4^+$  (C)  $\text{ClF}_6^+$  &  $\text{SF}_6$  (D) None
90. The molecules / ions which are planar as well as polar.  
 (A)  $\text{BF}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{HF}$ ,  $\text{NH}_2^-$  (B)  $\text{SnCl}_2$ ,  $\text{I}_3^+$ ,  $\text{NH}_2^-$ ,  $\text{IF}_3$   
 (C)  $\text{CO}_3^{2-}$ ,  $\text{I}_3^-$ ,  $\text{SF}_2$ ,  $\text{XeF}_2$  (D)  $\text{NO}_2^-$ ,  $\text{XeF}_4$ ,  $\text{ICl}_4^-$ ,  $\text{NH}_2^+$
91. The correct order of energy levels of hybrid orbitals.  
 (A)  $\text{sp} > \text{sp}^2 > \text{sp}^3$  (B)  $\text{sp} < \text{sp}^2 < \text{sp}^3$  (C)  $\text{sp}^2 > \text{sp}^3 > \text{sp}$  (D)  $\text{sp}^3 > \text{sp} > \text{sp}^2$

### Subjective Questions

92. Explain the structure of Boric acid in solid state.
93. Boiling point of o-Nitrophenol is less than meta and para nitrophenol. Why?
94.  $\text{H}-\text{F}$  is only liquid among halogen acid. Why?
95. Ammonia is more easily liquefied than  $\text{HCl}$ , explain.
96. Why ice floats on water?

- 97.** Water shows maximum density at 4°C. Why?
- 98.** HI is the strongest halogen acid, whereas H-F is the weakest. Why?
- 99.** Wood pieces are used to hold ice-cream. Why?
- 100.**  $\text{KHF}_2$  is possible but not  $\text{KHBr}_2$  or  $\text{KHI}_2$ . Why?
- 101.** o-Nitrophenol is less soluble in  $\text{H}_2\text{O}$  than p-Nitrophenol. Why?
- 102.** o-Hydroxy benzaldehyde is a liquid at room temperature while p-hydroxy benzaldehyde is a high melting solid.
- 103.** Glycerol is more viscous than ethanol. Explain.
- 104.**  $\text{CH}_4$  and  $\text{H}_2\text{O}$  have nearly same molecular weight. Yet  $\text{CH}_4$  has a boiling point 112 K and water 373 K. Explain.
- 105.** The experimental molecular weight of acetic acid is just double than theoretical molecular weight of acetic acid. Why?
- 106.** Although chlorine has same electronegativity as nitrogen but the former does not form effective H-bonding. Explain.

## ANSWERS

• **True and False**

- |           |           |          |           |           |
|-----------|-----------|----------|-----------|-----------|
| 1. False  | 2. True   | 3. False | 4. False  | 5. False  |
| 6. True   | 7. False  | 8. True  | 9. True   | 10. True  |
| 11. False | 12. True  | 13. True | 14. True  | 15. True  |
| 16. False | 17. False | 18. True | 19. False | 20. False |
| 21. False | 22. True  | 23. True | 24. False | 25. False |
| 26. True  | 27. False | 28. True | 29. False |           |

• **Fill in the Blanks**

- |  |                          |
|--|--------------------------|
| 30. $4.2 - 8.4 \text{ kJ mol}^{-1}$    | 31. sp                   |
| 32. $\text{sp}^3$                      | 33. increases, decreases |
| 34. $\text{N}_2\text{O}, \text{I}_3^-$ |                          |

• **Assertion-Reason**

- |         |         |         |         |
|---------|---------|---------|---------|
| 35. (B) | 36. (C) | 37. (C) | 39. (C) |
| 41. (C) | 42. (A) | 43. (C) |         |
| 46. (C) | 47. (A) | 48. (A) | 49. (B) |
| 50. (C) | 51. (B) | 52. (D) |         |

• **Single Choice Correct**

- |         |         |         |         |         |
|---------|---------|---------|---------|---------|
| 53. (A) | 54. (D) | 55. (A) |         |         |
| 58. (C) | 59. (B) | 60. (B) | 61. (A) | 62. (B) |
| 63. (D) | 64. (A) | 65. (B) | 66. (A) |         |
| 68. (B) | 70. (A) | 71. (A) | 72. (A) |         |
| 73. (D) |         |         |         |         |

• **Multiple Choice Correct**

- |           |            |            |          |           |
|-----------|------------|------------|----------|-----------|
| 74. (BD)  | 75. (BCD)  | 77. (AB)   |          |           |
| 79. (BCD) | 80. (ABD)  | 81. (ABCD) | 82. (AB) | 83. (ABC) |
| 84. (ABC) | 85. (ABCD) | 86. (BCD)  | 87. (BD) |           |

• **Match the Column**

88. A-Q, B-S, C-P, D-R

• **Comprehension**

89. (D) 90. (B) 91. (B)

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**MOLE CONCEPT**


---

**Fill in the blanks**

1. Ratio of number of protons to neutrons in  $3.011 \times 10^{22}$  molecules of  $D_3O^+$  is "\_\_\_\_\_"

**Assertion-Reason**

These questions contains, Statement I (assertion) and Statement II (reason).

(A) Statement-I is true, Statement-II is true ; Statement-II is correct explanation for Statement-I.

(B) Statement-I is true, Statement-II is true ; Statement-II is NOT a correct explanation for statement-I

(C) Statement-I is true, Statement-II is false

(D) Statement-I is false, Statement-II is true

2. **Statement-I** : 16 g each  $O_2$  and  $O_3$  contains  $\frac{N_A}{2}$  and  $\frac{N_A}{3}$  atoms respectively.

**Because**

**Statement-II** : 16 g  $O_2$  and  $O_3$  contains same no. of atoms.

3. **Statement-I** : The average mass of one Mg atom is 24.305 amu, which is not the actual mass of one Mg atom.

**Because**

**Statement-II** : Three isotopes,  $^{24}\text{Mg}$ ,  $^{25}\text{Mg}$  and  $^{26}\text{Mg}$ , of Mg are found in nature.

4. **Statement-I** : A molecule of butane,  $C_4H_{10}$  has a mass of 58.12 amu.

**Because**

**Statement-II** : One mole of butane contains  $6.022 \times 10^{23}$  molecules and has a mass of 58.12 g.

5. **Statement-I** : Both 12 g. of carbon and 27 g. of aluminium will have  $6.02 \times 10^{23}$  atoms.

**Because**

**Statement-II** : Gram atomic mass of an element contains Avogadro's number of atoms.

**Single Choice Correct**

6. 112.0 ml of  $NO_2$  at 1atm & 273 K was liquefied, the density of the liquid being 1.15 gm/ml. Calculate the volume of and the number of molecules in the liquid  $NO_2$ .  
 (A) 0.10 ml and  $3.01 \times 10^{22}$  (B) 0.20 ml and  $3.01 \times 10^{21}$   
 (C) 0.20 ml and  $6.02 \times 10^{23}$  (D) 0.40 ml and  $6.02 \times 10^{21}$
7. The shape of Tobacco Mosaic Virus (TMC) is cylindrical, having length and diameter 3000 Å and 170 Å, respectively. The density of the virus is 0.08 gm/ml. The molecular weight of TMC is  
 (A) 3.28 (B)  $5.44 \times 10^{-24}$  (C)  $5.44 \times 10^{-18}$  (D)  $3.28 \times 10^6$
8. What time, it would take to spend Avogadro's number of rupees at the rate of 10 lac rupees per second?  
 (A)  $6.023 \times 10^{17}$  sec (B)  $1.909 \times 10^{10}$  year (C)  $1.673 \times 10^{14}$  hour (D) all of these
9. The sodium salt of methyl orange has 7% sodium. What is the minimum molecular weight of the compound?  
 (A) 420 (B) 375 (C) 329 (D) 295
10. In the preceding problem, if the compound contains 12.8% nitrogen 9.8% sulphur how many nitrogen and sulphur atoms are present per atom of sodium :  
 (A) 2 and 1 (B) 1 and 3 (C) 1 and 2 (D) 3 and 1
11.  $Na_2SO_4 \cdot xH_2O$  has 50%  $H_2O$ . Hence, x is :  
 (A) 4 (B) 5 (C) 6 (D) 8
12. In the following final result is ....  
 $0.1 \text{ mol } CH_4 + 3.01 \times 10^{23} \text{ molecules } CH_4 - 9.6 \text{ g } CH_4 = x \text{ mol H atoms}$  :  
 (A) 0 mol H atom (B) 0.2 mol H atom (C) 0.3 mol H atom (D) 0.4 mol H atom

- 13.** In a gaseous mixture an alkane ( $C_xH_{2x+2}$ ) and an alkene ( $C_yH_{2y}$ ) are taken in 2 : 1 mole ratios, the average molecular weight of mixture is observed to be 20. If the same alkane and alkene are taken in 1 : 2 mole ratios, the average molecular weight of mixture is observed to be 24. Then the value of 'x' and 'y' respectively are :  
 (A) 2, 1 (B) 1, 2 (C) 2, 3 (D) 3, 2
- 14.** 3.06 L of  $H_2O_{(vap)}$  is taken at a pressure of 1 atm and 373 K. It is now condensed to  $H_2O(l)$  at 373K. Calculate the volume occupied by  $H_2O(l)$  (Density of liquid water = 1 g/ml)  
 (A) 3.06 L (B) 1.8 ml (C) 1.8 L (D) 3.06 ml
- 15.** Nylon is prepared using a compound having formula  $HOOC(CH_2)_4COOH$ . What is the total number of atoms present in 0.73 mg of the above compound :  
 (A)  $6.023 \times 10^{19}$  (B)  $6.023 \times 10^{22}$  (C)  $60.23 \times 10^{23}$  (D) 20
- 16.** A substance has 16% by mass of Sulphur and 4% by mass of Oxygen. Calculate minimum molar mass of the substance.  
 (A) 200 (B) 400 (C) 600 (D) 100
- 17.** In an experiment, it is found that **2.0769 gm** of pure X produces **3.6769 gm** of pure  $X_2O_5$ . Then number of moles of X is :  
 (A) 0.04 (B) 0.06 (C) 0.4 (D) 0.02
- 18.** Two isotopes of an element (atomic mass =  $x + 2.35$ ) have mass ( $x + 2$ ) and ( $x + 7$ ) respectively. Calculate natural abundance of heavier isotope in percentage.  
 (A) 3 (B) 5 (C) 7 (D) 9
- 19.** Two elements A and B form two different sets of compounds  $A_2B_3$  and  $A_3B_4$ . 2.02 kg of  $A_2B_3$  has  $1.806 \times 10^{25}$  atoms of B and 1.44 kg of  $A_3B_4$  has  $9.03 \times 10^{24}$  atoms of A. What will be gram molecular mass (GMM) of another compound AB formed from combination of A and B.  
 (A) 75 (B) 86 (C) 94 (D) 97
- 20.** An element exist in three isotopic form  $^{40}X$ ,  $^{41}X$  and  $^{42}X$ .  
 Percentage abundance of  $^{40}X$  = 30% by mole.  
 If average atomic mass of 'X' is 41.25. Find out percentage abundance of  $^{41}X$ .  
**[Divide your answer by 3 and fill OMR sheet]**  
 (A) 2 (B) 3 (C) 5 (D) 7
- 21.** A solution of palmitic acid ( $M = 256$ ) in benzene contains 5 gm acid per litre. When this solution is dropped on surface,  $C_6H_6$  gets evaporated and acid forms a unimolecular layer on the surface. If we wish to cover an area  $6000 \text{ cm}^2$  with unimolecular film. What volume of solution in ml should be used? Area covered by one molecule of acid is  $0.32 \text{ nm}^2$ . **(Given :  $N_A = 6 \times 10^{23}$ )**  
**Write your answer multiplying with 1000.**  
 (A) 120 ml (B) 140 ml (C) 160 ml (D) 180 ml
- 22.** An element exist in two isotopic forms  $X^{120}$  and  $X^{122}$ , in equal abundance. The average atomic mass of element is 121.44. If each atom of  $X^{120}$  are 10.04 times heavier than one  $C^{12}$  atom, then how many times each atom of  $X^{122}$  is heavier than one  $C^{12}$  atom ?  
 (A) 10.04 (B) 10.4 (C) 10.2 (D) 10.167
- 23.** How many moles of e- weight one Kg : **[JEE 2002]**  
 (A)  $6.023 \times 10^{23}$  (B)  $\frac{1}{9.108} \times 10^{31}$  (C)  $\frac{6.023}{9.108} \times 10^{54}$  (D)  $\frac{1}{9.108 \times 6.023} \times 10^8$
- 24.** Which has maximum number of atoms : **[JEE 2003]**  
 (A) 24 g C(12) (B) 56 g Fe(56) (C) 27 g Al (27) (D) 108 g Ag(108)

- 25.** An alloy of gold and silver contains 38.5% silver by mass and has a density of  $14.6 \text{ g.mL}^{-1}$ . What is the molar concentration of silver in this alloy :  
 (A)  $52.1 \text{ mol.L}^{-1}$  (B)  $45.6 \text{ mol.L}^{-1}$  (C)  $3.57 \text{ mol.L}^{-1}$  (D)  $2.64 \text{ mol.L}^{-1}$
- 26.** "Suvarnabhasm", an ayurvedic drug, is found to contain 400 ppm of colloidal gold. Mass % of gold (atomic mass of Au = 197) will be :  
 (A) 0.040 % (B) 7.88 % (C) 0.0788 % (D)  $4 \times 10^{-4}$  %
- 27.** 1 mol of iron (Fe) reacts completely with 0.65 mol  $\text{O}_2$  to give a mixture of only FeO and  $\text{Fe}_2\text{O}_3$ . Mole ratio of ferrous oxide to ferric oxide is :-  
 (A) 3 : 2 (B) 4 : 3 (C) 20 : 13 (D) none of these
- 28.** The molar ratio of  $\text{Fe}^{++}$  to  $\text{Fe}^{+++}$  in a mixture of  $\text{FeSO}_4$  and  $\text{Fe}_2(\text{SO}_4)_3$  having equal number of sulphate ion in both ferrous and ferric sulphate is :-  
 (A) 1 : 2 (B) 3 : 2 (C) 2 : 3 (D) can't be determined
- 29.** If a piece of iron gains 10% of its weight due to partial rusting into  $\text{Fe}_2\text{O}_3$ . The percentage of total iron that has rusted is :-  
 (A) 23 (B) 13 (C) 23.3 (D) 25.67
- 30.** 29.5 mg of an organic compound containing nitrogen was digested according to Kjeldahl's method and the evolved ammonia was absorbed in 20 mL of 0.1 M HCl solution. The excess of the acid required 15 mL of 0.1 M NaOH solution for complete neutralization. The percentage of nitrogen in the compound is : **[AIEEE 2010]**  
 (A) 59.0 (B) 47.4 (C) 23.7 (D) 29.5
- 31\*.** For the estimation of nitrogen, 1.4 g of an organic compound was digested by Kjeldahi method and the evolved ammonia was absorbed in 60 mL of  $\frac{\text{M}}{10}$  sulphuric acid. The unreacted acid required 20 mL of  $\frac{\text{M}}{10}$  sodium hydroxide for complete neutralization. The percentage of nitrogen in the compound is:  
**[JEE Mains\_2014]**  
 (A) 6% (B) 10% (C) 3% (D) 5%
- 32.** The molecular formula of a commercial resin used for exchanging ions in water softening is  $\text{C}_8\text{H}_7\text{SO}_3\text{Na}$  (Mol. wt. 206). What would be the maximum uptake of  $\text{Ca}^{2+}$  ions by the resin when expressed in mole per gram resin ? **[JEE Mains\_2015]**  
 (A)  $\frac{1}{103}$  (B)  $\frac{1}{206}$  (C)  $\frac{2}{309}$  (D)  $\frac{1}{412}$
- 33\*.** 3 g of activated charcoal was added to 50 mL of acetic acid solution (0.06 N) in a flask. After an hour it was filtered and the strength of the filtrate was found to be 0.042 N. The amount of acetic acid adsorbed (per gram of charcoal) is **[JEE Mains\_2015]**  
 (A) 18 mg (B) 36 mg (C) 42 mg (D) 54 mg
- 34.** In Carius method of estimation of halogens, 250 mg of an organic ompound gave 141 mg of AgBr. The percentage of bromine in the compound is: (at mass Ag = 108; Br = 80) **[JEE Mains\_2015]**  
 (A) 24 (B) 36 (C) 48 (D) 60
- 35.** At 300 K and 1 atm, 15 mL of a gaseous hydrocarbon requires 375 mL air containing 20%  $\text{O}_2$  by volume for complete combustion. After combustion the gases occupy 330 mL. Assuming that the water formed is in liquid form and the volumes were measured at the same temperature and pressure, the formula of the hydrocarbon is: **[JEE Mains\_2016]**  
 (A)  $\text{C}_3\text{H}_6$  (B)  $\text{C}_3\text{H}_8$  (C)  $\text{C}_4\text{H}_8$  (D)  $\text{C}_4\text{H}_{10}$

- 36\*.** A 10 gram sample of natural gas containing  $\text{CH}_4$  and  $\text{C}_2\text{H}_4$  was burnt in excess of oxygen to give 29.0 grams of  $\text{CO}_2$  and some water. How many grams of water are formed :  
 (A) 9.42 g (B) 18.81 g (C) 11.42 g (D) 15.31 g
- 37\*.** 50 g of  $\text{ZnS}$  are strongly heated in air to effect partial oxidation and the resultant mass weighed 44 g. What is the ratio of  $\text{ZnO}$  to  $\text{ZnS}$  in the resultant mixture :  
 (A) 13.5 : 30.5 (B) 27 : 12.58 (C) 27 : 15.31 (D) 30.52 : 13.48
- 38.** The % loss in weight after heating a pure sample of potassium chlorate (M. wt. 122.5) will be :  
 (A) 12.25 (B) 24.50 (C) 39.17 (D) 49.0
- 39\*.** Iodobenzene ( $\text{C}_6\text{H}_5\text{I}$ ) is prepared from aniline ( $\text{C}_6\text{H}_5\text{NH}_2$ ) in a two step process as shown below  
 $\text{C}_6\text{H}_5\text{NH}_2 + \text{HNO}_2 + \text{HCl} \rightarrow \text{C}_6\text{H}_5\text{N}_2^+\text{Cl}^- + 2\text{H}_2\text{O}$   
 $\text{C}_6\text{H}_5\text{N}_2^+\text{Cl}^- + \text{KI} \rightarrow \text{C}_6\text{H}_5\text{I} + \text{N}_2 + \text{KCl}$   
 In an actual preparation 9.30 g of aniline was converted to 16.32 g of iodobenzene. The percentage yield of iodobenzene is :  
 (A) 8 % (B) 50 % (C) 75 % (D) 80 %
- 40.** An aqueous solution of concentrated hydrobromic acid contains 48%  $\text{HBr}$  by mass. If the density of the solution is 1.50 g / mL, what is its concentration :  
 (A) 11.4 mol/L (B) 8.9 mol/L (C) 5.9 mol/L (D) 18.5 mol/L

### Multiple Choice Correct

- 41\*.** X gm A atoms on combining with Y atoms of B form 5 molecules of a compound containing A & B. Find the molecular weight of compound formed. (Atomic weight of B = M)  
 (A)  $\frac{(\text{XN}_A + \text{MY})}{5}$  (B)  $\frac{\text{X} + \text{M}}{5}$  (C)  $\frac{\text{X} + \text{MY}}{5}$  (D)  $\left( \frac{\text{X} + \text{MYN}_A}{5} \right)$
- 42.** Calculate mass % & mole % of  $\text{H}_2$  in a mixture of  $\text{H}_2$  and  $\text{O}_2$  if average molecular mass of the mixture is 14.  
 (A) 50 % by mole (B) 60 % by mole (C) 8.57% by mass (D) 10% by mass
- 43\*.** Which of the following options is/are incorrect.  
 (A) 10 gm of Boron is having 5 mole of nucleons.  
 (B) One atom of an element weight  $1.8 \times 10^{-22}$  gm, then its atomic mass is 108.36  
 (C) 10 gm of  $\text{CaCO}_3$  contains 1 gm atom of C.  
 (D) Number of atoms in 2 moles of  $\text{S}_8$  is greater than 5.5 moles of  $\text{SO}_2$
- 44.** A polymeric organic compound contains 0.07% iron and 0.035% nitrogen by mass. Which of the following statement(s) is/are correct for the compound ? (Fe = 56, N = 14)  
 (A) The molecular mass of compound may be 40000.  
 (B) The molecular mass of compound may be 160000.  
 (C) In each molecule of this compound, there are 2 nitrogen atoms per iron atom.  
 (D) In each molecule of this compound, there are 2 iron atoms per nitrogen atom.
- 45.** Which of the following have equal no. of atoms ?  
 (A) 12 g  $\text{MgSO}_4$  (B) 0.2 mole  $\text{CO}_2$  (C) 5.6 L  $\text{SO}_2$  at STP (D) 24 g Ca
- 46.** A mixture of two gases  $\text{H}_2$  and  $\text{O}_2$  has an average molecular mass 12 and is kept at a temperature of  $\frac{200}{3}$  K and pressure 0.821 atm. Select the correct options :  
 (A) Mixture contains  $\frac{100}{9}$  % by mass of  $\text{H}_2$  gas. (B) Density of mixture is 1.8 gm/ml.  
 (C) Mixture contains  $\frac{100}{3}$  % by mol of  $\text{O}_2$  gas (D) Mole ratio of  $\text{O}_2$  and  $\text{H}_2$  gas in the mixture is  $\frac{1}{3}$



47. Which of the statements is / are **true** for a chemical reaction occurring in a closed container?
- (A) Total mass of all reactants and products always remain constant.  
 (B) Average molecular mass of the mixture may change during chemical reaction.  
 (C) Total number of atoms of each element will remain constant in a chemical reaction.  
 (D) Total volume of all reactants and products always remain constant.

### Comprehension

#### Comprehension-1

Azurite is a copper containing mineral that is a mixture of Copper (II) carbonate and copper (II) hydroxide,  $[\text{CuCO}_3]_x \cdot [\text{Cu}(\text{OH})_2]_y$ . If the mineral is 55.31% Cu, 0.58% H and 6.97% C, with the remainder oxygen, what are x and y in the general formula ? **[Cu = 63.5]**

48. What is the value of 'x' in general empirical formula ?  
 (A) 7 (B) 2 (C) 3 (D) 4
49. What is the value of 'y' in the general empirical formula b?  
 (A) 1 (B) 2 (C) 3 (D) 4
50. If the value of x and y be 1 and 2 respectively. Calculate the % composition of Cu ?  
 (A) 50 % (B) 59.8% (C) 51.2% (D) 60%

#### Comprehension-2

Calcium lactate is used in the food and beverage industries. It has also been used medicinally for treatment of various allergies, for treatment of muscular leg cramps, and as an antidote for a variety of poisons, including lead, arsenicals and carbon tetrachloride. A 0.8274 g sample of anhydrous calcium lactate is found by analysis to contain 0.2732 g of C, 0.0382 g H, 0.1520 g Ca and 0.3640 g O. Each mole of calcium lactate is found to contain one mole of calcium ions. Calcium lactate can be crystallised from water as pentahydrate salt.

51. Simplest formula of the calcium lactate is :  
 (A)  $\text{CaO}_6\text{C}_6\text{H}_{10}$  (B)  $\text{CaO}_3\text{C}_3\text{H}_5$  (C)  $\text{CaO}_2\text{C}_3\text{H}_3$  (D)  $\text{CaO}_2\text{C}_3\text{H}_5$
52. Formula weight of calcium lactate is :  
 (A) 129 g mol<sup>-1</sup> (B) 111 g mol<sup>-1</sup> (C) 218 g mol<sup>-1</sup> (D) 113 g mol<sup>-1</sup>
53. How many grams of calcium lactate pentahydrate would be recovered from 1 g of anhydrous salt :  
 (A) 1.41 g (B) 1.00 g (C) 1.27 g (D) 1.51 g

### Subjective Questions

54. A crystalline hydrated salt on being rendered anhydrous, loses 45.6% of its weight. The percentage composition of anhydrous salt is : Al = 10.5%, K = 15.1%, S = 24.8% and O = 49.6%. Find the empirical formula of the anhydrous and crystalline salt :
55. A compound containing Ca, C, N and S was subjected to quantitative analysis and formula mass determination. A 0.25 g of this compound was mixed with  $\text{Na}_2\text{CO}_3$  to convert all Ca into 0.16 g  $\text{CaCO}_3$ . A 0.115 g sample of compound was carried through a series of reactions until all its S was changed into  $\text{SO}_4^{2-}$  and precipitated as 0.344 g  $\text{BaSO}_4$ . A 0.712 g sample was processed to liberate all of its N as  $\text{NH}_3$  and 0.155 g  $\text{NH}_3$  was obtained. The formula mass was found to be 156. Determine the empirical and molecular formula of the compound :
56. One mole of a mixture of  $\text{N}_2$ ,  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  has a mean molar mass of 55.4. On heating to a temperature at which  $\text{N}_2\text{O}_4$  may be dissociated :  $\text{N}_2\text{O}_4 \longrightarrow 2\text{NO}_2$ , the mean molar mass tends to the lower value of 39.6. What is the mole ratio of  $\text{N}_2$  :  $\text{NO}_2$  :  $\text{N}_2\text{O}_4$  in the original mixture?
57. Two elements C and D combine to form two compounds  $\text{C}_x\text{D}_y$  &  $\text{C}_y\text{D}_x$ . 0.5 mole of  $\text{C}_y\text{D}_x$  weigh 40 gm & 1 molecule of  $\text{C}_x\text{D}_y$  weigh  $1.66 \times 10^{-25}$  kg. The atomic weight of C and D are 20 & 40 respectively. 'x' & 'y' are respectively.

- 58.** On a reference scale of C, at. weight of Al is 26.98 of Titanium is 47.48. What would be at. weight of Al on a new reference scale where Titanium has a value of 48.
- 59.** Three isotopes of an element have mass numbers  $M$ ,  $(M+1)$  and  $(M+2)$ . If the mean mass number is  $(M + 0.5)$ , then the ratio of number may be accepted for  $M$ ,  $(M+1)$  and  $(M+2)$  in the order
- 60.** 0.36 gm of a triatomic gas,  $X_3$ , occupies 168 ml at 1 atm & 273 K. The atomic weight of  $X$  is
- 61.** A 1.85 g sample of mixture of  $CuCl_2$  and  $CuBr_2$  was dissolved in water and mixed thoroughly with 1.8 g portion of  $AgCl$ . After reaction, the solid which now contain  $AgCl$  and  $AgBr$  was filtered, dried and weighed to be 2.052 g. What was the % by weight of  $CuBr_2$  in the mixture?
- 62.** A mixture of  $CuSO_4 \cdot 5H_2O$  and  $MgSO_4 \cdot 7H_2O$  was heated until all the water was driven-off. If 5.0 g of mixture gave 3 g of anhydrous salts, what was the percentage by mass of  $CuSO_4 \cdot 5H_2O$  in the original mixture :
- 63\*.** A 0.2 g sample, which is mixture of  $NaCl$ ,  $NaBr$  and  $NaI$  was dissolved in water and excess of  $AgNO_3$  was added. The precipitate containing  $AgCl$ ,  $AgBr$  and  $AgI$  was filtered, dried and weighed to be 0.412 g. The solid was placed in water and treated with excess of  $NaBr$ , which converted all  $AgCl$  into  $AgBr$ . The precipitate was then weighed to be 0.4881 g. It was then placed into water and treated with excess of  $NaI$ , which converted all  $AgBr$  into  $AgI$ . The precipitate was then weighed to be 0.5868 g. What was the percentage of  $NaCl$ ,  $NaBr$  and  $NaI$  in the original mixture :
- 64.** A mother cell disintegrate into sixty identical cells and each daughter cell further disintegrate into 24 smaller cells. The smallest cells are uniform cylindrical in shape with diameter of  $120 \text{ \AA}$  and each cell is  $6000 \text{ \AA}$  long. Determine molar mass of the mother cell if density of the smallest cell is  $1.12 \text{ g/cm}^3$  :
- 65.**  $A_2 + 2B_2 \longrightarrow A_2B_4$   
 $\frac{3}{2}A_2 + 2B_2 \longrightarrow A_3B_4$   
 Two substance  $A_2$  &  $B_2$  react in the above manner when  $A_2$  is limited it gives  $A_2B_4$  in excess gives  $A_3B_4$ .  $A_2B_4$  can be converted to  $A_3B_4$  when reacted with  $A_2$ . Using this information calculate the composition of the final mixture when the mentioned amount of  $A$  &  $B$  are taken :  
 (a) 4 moles  $A_2$  & 4 moles  $B_2$   
 (b)  $\frac{1}{2}$  moles  $A_2$  & 2 moles  $B_2$   
 (c) 1.25 moles  $A_2$  & 2 moles  $B_2$
- 66.** 20% surface sites have adsorbed  $N_2$ . On heating  $N_2$  gas evolved from sites and were collected at 0.001 atm and 298 K in a container of volume is  $2.46 \text{ cm}^3$ . Density of surface sites is  $6.023 \times 10^{14}/\text{cm}^2$  and surface area is  $1000 \text{ cm}^2$ , find out the no. of surface sites occupied per molecule of  $N_2$  : **[JEE 2005]**
- 67.**  $N_2H_4$ , Hydrazine a rocket fuel can be produced according to the following reaction :  
 $ClNH_2 + 2NH_3 \longrightarrow N_2H_4 + NH_4Cl$   
 When 1000 g  $ClNH_2$  is reacted with excess of  $NH_3$ , 473 g  $N_2H_4$  is produced. What is the % yield of the reaction.
- 68\*.** Calculate the percent of  $BaO$  in 29.0 g of a mixture of  $BaO$  and  $CaO$  which just reacts with 100.8 mL of 6.00 M  $HCl$ .  
 $BaO + 2HCl \rightarrow BaCl_2 + H_2O$   
 $CaO + 2HCl \rightarrow CaCl_2 + H_2O$
- 69\*.** 10 ml of ammonia were enclosed in an eudiometer and subjected to electric sparks. The sparks were continued till there was no further increase in volume. The volume after sparking measured 20 ml. Now 30 ml of  $O_2$  were added and sparking was continued again. The new volume then measured 27.5 ml. All volumes were measured under identical conditions of temperature and pressure. V.D. of ammonia is 8.5. If the molecular formula of ammonia is  $N_xH_y$  then calculate  $(x + y)$ . Nitrogen and Hydrogen are diatomic.

# ANSWERS

• **Fill in the Blanks**

1. (1)

• **Assertion-Reason**

2. (D)

3. (A)

4. (A)

5. (A)

• **Single Choice Correct**

6. (B)

7. (D)

8. (D)

9. (C)

10. (D)

11. (A)

12. (A)

13. (B)

14. (B)

15. (A)

16. (B)

17. (A)

18. (C)

19. (B)

20. (C)

21. (C)

22. (C)

23. (D)

24. (A)

25. (A)

26. (A)

27. (B)

28. (B)

29. (C)

30. (C)

31. (B)

32. (D)

33. (A)

34. (A)

35. (BONUS)

36. (B)

37. (D)

38. (C)

39. (D)

40. (B)

• **Multiple Choice Correct**

41. (A)

42. (BC)

43. (ACD)

44. (BC)

45. (ABD)

46. (AC)

47. (ABC)

• **Comprehension**

**Comprehension 1 :**

48. (B)

49. (A)

50. (B)

**Comprehension 2 :**

51. (A)

52. (C)

53. (A)

• **Subjective Questions**

54.  $\text{KAlS}_2\text{O}_8$ ,  $\text{KAlS}_2\text{O}_8 \cdot 12 \text{H}_2\text{O}$

55.  $\text{CaC}_2\text{N}_2\text{S}_2$ ,  $\text{CaC}_2\text{N}_2\text{S}_2$

56. 0.5 : 0.1 : 0.4

57.  $x = 1$   $y = 2$

58. 27.04

59. 4 : 1 : 1

60. 16

61. 34.18

62. 74.4

63\*. 50, 20.23, 29.77

64.  $6.6 \times 10^{10} \text{ g}$

65. (a)  $\text{A}_3\text{B}_4 = 2$  &  $\text{A}_2 = 1$  ; (b)  $\text{A}_2\text{B}_4 = \frac{1}{2}$  &  $\text{B}_2 = 1$  (c)  $\text{A}_2\text{B}_4 = 0.5$  &  $\text{A}_3\text{B}_4 = 0.5$

66. (2)

67. 76.12%

68. 65.65%

69\*. (4)

---

**REDOX**


---

**Fill in the blanks**

- The reactant which reacts completely in a reaction is called .....
- In the reaction  $2 \text{H}_2\text{O}_2 \longrightarrow 2 \text{H}_2\text{O} + \text{O}_2$ , hydrogen peroxide is .....
- In the reaction  $2 \text{KClO}_3 \longrightarrow 2 \text{KCl} + 3 \text{O}_2$ , the element which has been oxidised is ..... and the element which has been reduced is .....
- The compound  $\text{YbBa}_2\text{Cu}_3\text{O}_7$  which shows superconductivity, has copper in oxidation state ..... Assume that the rare earth element ytterbium is in the usual + 3 oxidation state.
- In HCN oxidation number of carbon is .....

**Assertion & Reason**

These questions contains, Statement I (assertion) and Statement II (reason).

(A) Statement-I is true, Statement-II is true ; Statement-II is correct explanation for Statement-I.

(B) Statement-I is true, Statement-II is true ; Statement-II is NOT a correct explanation for statement-I

(C) Statement-I is true, Statement-II is false

(D) Statement-I is false, Statement-II is true

- Statement-I** : The percentage weight of a compound A in a solution is given by

$$\% \text{ of A} = \frac{\text{Mass A}}{\text{Total mass of solution}} \times 100$$

**Because**

**Statement-II** : The mole fraction of a component A is given by,

$$\text{Mole fraction of A} = \frac{\text{No. of moles of A}}{\text{Total no. of moles of all components}}$$

- Statement-I** : A one molal solution prepared at  $20^\circ\text{C}$  will retain the same molality at  $100^\circ\text{C}$ , provided there is no loss of solute or solvent on heating.

**Because**

**Statement-II** : Molality is independent of temperature.

- Statement-I** : The oxidation state of superoxide ion in  $\text{KO}_2$ ,  $\text{CsO}_2$  and  $\text{RbO}_2$  is  $-1/2$ .

**Because**

**Statement-II** : Since the oxidation state of an alkali metal in any compound is always + 1, the oxidation state of oxygen is  $-1/2$  in the  $\text{O}_2^-$  ion.

- Statement-I** : In the redox reaction



the reducing agent is Sn (s),

**Because**

**Statement-II** : In balancing half reaction,  $\text{S}_2\text{O}_3^{2-} \rightarrow \text{S}(\text{s})$ , the number of electrons added on the left is 4.

- Statement-I** : Among  $\text{Br}^-$ ,  $\text{O}_2^{2-}$ ,  $\text{H}^-$  and  $\text{NO}_3^-$ , the ions that could not act as oxidising agents are  $\text{Br}^-$  and  $\text{H}^-$ .

**Because**

**Statement-II** :  $\text{Br}^\ominus$  and  $\text{H}^-$  could not be reduced.

**Single Choice Correct**

- 11.**  $28 \text{NO}_3^- + 3\text{As}_2\text{S}_3 + 4\text{H}_2\text{O} \rightarrow 6\text{AsO}_4^{3-} + 28 \text{NO} + 9\text{SO}_4^{2-} + \text{H}^+$   
 What will be the equivalent mass of  $\text{As}_2\text{S}_3$  in above reaction  
 (A)  $\frac{\text{M.wt.}}{2}$  (B)  $\frac{\text{M.wt.}}{4}$  (C)  $\frac{\text{M.wt.}}{24}$  (D)  $\frac{\text{M.wt.}}{28}$
- 12.** When  $\text{ZnS}$  is boiled with strong nitric acid, the products are zinc nitrate, sulphuric acid and nitrogen dioxide. What are the changes in the oxidation numbers of Zn, S and N.  
 (A) +2, +4, -1 (B) +2, +6, -2 (C) 0, +4, -2 (D) 0, +8, -1
- 13.** When arsenic sulphide is boiled with  $\text{NaOH}$ , sodium arsenite and sodium thioarsenite are formed  
 $x \text{As}_2\text{S}_3 + y \text{NaOH} \longrightarrow \text{Na}_3\text{AsO}_3 + x \text{Na}_3\text{AsS}_3 + \frac{y}{2} \text{H}_2\text{O}$ . What are the values of x and y?  
 (A) 1, 6 (B) 2, 8 (C) 2, 6 (D) 1, 4
- 14.** An element forms two different sulphates in which its weight % is 28 and 37. What is the ratio of oxidation numbers of the element in these sulphates?  
 (A) 1 : 2 (B) 1 : 3 (C) 2 : 1 (D) 3 : 2
- 15.**  $\text{CN}^-$  is oxidised by  $\text{NO}_3^-$  in presence of acid :  
 $a \text{CN}^- + b \text{NO}_3^- + c \text{H}^+ \longrightarrow (a + b) \text{NO} + a \text{CO}_2 + \frac{c}{2} \text{H}_2\text{O}$   
 What are the values of a, b, c in that order :  
 (A) 3,7,7 (B) 3,10,7 (C) 3,10,10 (D) 3,7,10
- 16.** Which of the following solutions will exactly oxidize 25 mL of an acid solution of 0.1 M  $\text{Fe}(\text{II})$  oxalate :-  
 (A) 25 mL of 0.1 M  $\text{KMnO}_4$  (B) 25 mL of 0.2 M  $\text{KMnO}_4$   
 (C) 25 mL of 0.6 M  $\text{KMnO}_4$  (D) 15 mL of 0.1 M  $\text{KMnO}_4$
- 17\*.** 4.9 gm of  $\text{K}_2\text{Cr}_2\text{O}_7$  is taken to prepare 0.1 L of the solution. 10 mL of this solution is further taken to oxidise  $\text{Sn}^{2+}$  ion into  $\text{Sn}^{4+}$  ion  $\text{Sn}^{4+}$  so produced is used in 2<sup>nd</sup> reaction to prepare  $\text{Fe}^{3+}$  ion then the millimoles of  $\text{Fe}^{3+}$  ion formed will be (assume all other components are in sufficient amount) [Molar mass of  $\text{K}_2\text{Cr}_2\text{O}_7 = 294 \text{ g}$ ].  
 (A) 5 (B) 20 (C) 10 (D) none of these
- 18.** 35 mL sample of hydrogen peroxide gives of 500 mL of  $\text{O}_2$  at  $27^\circ\text{C}$  and 1 atm pressure. Volume strength of  $\text{H}_2\text{O}_2$  sample will be :-  
 (A) 10 volume (B) 13 volumes (C) 11 volume (D) 12 volume
- 19.** 20 mL of 0.1 M solution of compound  $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$  is titrated against 0.05 M  $\text{HCl}$ , x mL of  $\text{HCl}$  is used when phenolphthalein is used as an indicator and y mL of  $\text{HCl}$  is used when methyl orange is the indicator in two separate titrations. Hence (y - x) is :-  
 (A) 40 mL (B) 80 mL (C) 120 mL (D) none of these
- 20\*.** 0.10 g of a sample containing  $\text{CuCO}_3$  and some inert impurity was dissolved in dilute sulphuric acid and volume made up to 50 mL. This solution was added into 50 mL of 0.04 M  $\text{KI}$  solution where copper precipitates as  $\text{CuI}$  and  $\text{I}^-$  is oxidized into  $\text{I}_3^-$ . A 10 mL portion of this solution is taken for analysis, filtered and made up free  $\text{I}_3^-$  and then treated with excess of acidic permanganate solution. Liberated iodine required 20 mL of 2.5 mM sodium thiosulphate solution to reach the end point.  
 Determine weight percentage of  $\text{CuCO}_3$  in the original sample.  
 (A) 7.41 (B) 74.1 (C) 61.75 (D) none of these
- 21.** A mixture of  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{C}_2\text{O}_4$  (oxalic acid) and some inert impurity weighing 3.185 g was dissolved in water and the solution made up to 1 litre, 10 mL of this solution required 3 mL of 0.1 N  $\text{NaOH}$  for complete neutralization. In another experiment 100 mL of the same solution in hot condition required 4 mL of 0.02M  $\text{KMnO}_4$  solution for complete reaction. The wt. % of  $\text{H}_2\text{SO}_4$  in the mixture was :-  
 (A) 40 (B) 50 (C) 60 (D) 80

- 22\*.** 0.80 g of sample of impure potassium dichromate was dissolved in water and made upto 500 mL solution. 25 mL of this solution treated with excess of KI in acidic medium and  $I_2$  liberated required 24 mL of a sodium thiosulphate solution. 30 mL of this sodium thiosulphate solution required 15 mL of N/20 solution of pure potassium dichromate. What was the percentage of  $K_2Cr_2O_7$  in given sample?  
 (A) 73.5 % (B) 75.3 % (C) 36.75 % (D) none of these
- 23.** The oxidation number of phosphorus in  $Ba(H_2PO_2)_2$  is : [JEE 1990]  
 (A) +3 (B) +2 (C) +1 (D) -1
- 24.** The number of electrons to balance the following equation :- [JEE 1991]  
 $NO_3^- + 4H^+ + e^- \rightarrow 2H_2O + NO$  is  
 (A) 5 (B) 4 (C) 3 (D) 2
- 25.** What is the volume strength of 1.5 N  $H_2O_2$  : [JEE 1991]  
 (A) 4.8 (B) 8.4 (C) 3.0 (D) 8.0
- 26.** The oxidation states of the most electronegative element in the products of the reaction of  $BaO_2$  with dilute  $H_2SO_4$ . [JEE 1991]  
 (A) 0 and -1 (B) -1 and -2 (C) -2 and 0 (D) -2 and +2
- 27.** For the redox reaction, [JEE 1992]  
 $MnO_4^- + C_2O_4^{2-} + H^+ \rightarrow Mn^{2+} + CO_2 + H_2O$   
 the correct coefficients of the reactants for the balanced reaction are :  

	$MnO_4^-$	$C_2O_4^{2-}$	$H^+$
(A)	2	5	16
(B)	16	5	2
(C)	5	16	2
(D)	2	16	5
- 28.** The number of mole of  $KMnO_4$  that will need to react completely with one mole ferrous oxalate in acidic solution is : [JEE 1997]  
 (A) 2/5 (B) 3/5 (C) 4/5 (D) 1
- 29.** The number of mole of  $KMnO_4$  that will be needed to react with one mole of sulphite ion in acidic solution is : [JEE 1997]  
 (A) 2/5 (B) 3/5 (C) 4/5 (D) 1
- 30.** The equivalent mass of  $MnSO_4$  is half its molecular mass when it is converted to : [JEE 1998]  
 (A)  $Mn_2O_3$  (B)  $MnO_2$  (C)  $MnO_4^-$  (D)  $MnO_4^{2-}$
- 31.** The oxidation number of sulphur in  $S_8$ ,  $S_2F_2$  and  $H_2S$  respectively are : [JEE 1999]  
 (A) 0, +1 and -2 (B) +2, +1 and -2 (C) 0, +1 and +2 (D) -2, +1 and -2
- 32.** The normality of 0.3 M phosphorus acid ( $H_3PO_3$ ) is : [JEE 1999]  
 (A) 0.1 (B) 0.9 (C) 0.3 (D) 0.6
- 33.** Among the following species in which oxidation state of the element is +6 : [JEE 2000]  
 (A)  $MnO_4^-$  (B)  $Cr(CN)_6^{3-}$  (C)  $NiF_6^{2-}$  (D)  $CrO_2Cl_2$
- 34.** Oxidation number of iron in  $Na_2[Fe(CN)_5NO^\oplus]$  is : [JEE 2001]  
 (A) +2 (B) +3 (C) +8/3 (D) none of these
- 35.** An aqueous solution of 6.3 g of oxalic acid dihydrate is made upto 250 mL. The volume of 0.1 N NaOH required to completely neutralise 10 mL of this solution is : [JEE 2001]  
 (A) 40 mL (B) 20 mL (C) 10 mL (D) 4 mL

- 36.** In basic medium  $\text{I}^-$  oxidises by  $\text{MnO}_4^-$ . In this process  $\text{I}^-$  replaces by : **[JEE 2004]**  
 (A)  $\text{IO}_3^-$  (B)  $\text{I}_2$  (C)  $\text{IO}_4^-$  (D)  $\text{IO}^-$
- 37.** Amongst the following, the pair having both the metals in their highest oxidation state is : **[JEE 2004]**  
 (A)  $[\text{Fe}(\text{CN})_6]^{3-}$  and  $[\text{Co}(\text{CN})_6]^{3-}$  (B)  $[\text{CrO}_2\text{Cl}_2]$  and  $[\text{MnO}_4^-]$   
 (C)  $\text{TiO}_2$  and  $\text{MnO}_2$  (D)  $[\text{MnCl}_4]^{2-}$  and  $[\text{NiF}_6]^{-2}$
- 38.**  $\text{O}_3$  does not oxidise : **[JEE 2005]**  
 (A) KI (B)  $\text{FeSO}_4$  (C)  $\text{KMnO}_4$  (D)  $\text{K}_2\text{MnO}_4$
- 39.** An ore of iron, Wustite has the formula  $\text{Fe}_{0.93}\text{O}_{1.00}$ . The mole fraction of total iron present in the form of  $\text{Fe}(\text{II})$  is:-  
 (A) 0.82 (B) 0.85 (C) 0.15 (D) 0.37
- 40.**  $\text{HNO}_3$  oxidises  $\text{NH}_4^+$  ions to nitrogen and itself gets reduced to  $\text{NO}_2$ . The moles of  $\text{HNO}_3$  required by 1 mol of  $(\text{NH}_4)_2\text{SO}_4$  is :-  
 (A) 4 (B) 5 (C) 6 (D) 2
- 41\*.** 25 mL of a 0.1 M solution of a stable cation of transition metal Z reacts exactly with 25 mL of 0.04 M acidified  $\text{KMnO}_4$  solution. Which of the following is most likely to represent the change in oxidation state of Z correctly :-  
 (A)  $\text{Z}^+ \rightarrow \text{Z}^{2+}$  (B)  $\text{Z}^{2+} \rightarrow \text{Z}^{3+}$  (C)  $\text{Z}^{3+} \rightarrow \text{Z}^{4+}$  (D)  $\text{Z}^{2+} \rightarrow \text{Z}^{4+}$
- 42.** How many litres of  $\text{Cl}_2$  at S.T.P. will be liberated by oxidation of  $\text{NaCl}$  with 10 g  $\text{KMnO}_4$  :-  
 (A) 3.54 litres (B) 7.08 litres (C) 1.77 litres (D) none of these
- 43.** During the disproportionation of iodine to iodide and iodate ions, the ratio of iodate and iodide ions formed in alkaline medium is :-  
 (A) 1 : 5 (B) 5 : 1 (C) 3 : 1 (D) 1 : 3

### Match the Column

- | <b>44*.</b> <b>Column-I</b>                                      | <b>Column-II</b>  |
|--|---|
| (A) Eq. wt. of underlined = $\frac{\text{Molecular weight}}{33}$ | (p) When $\text{CrI}_3$ oxidises into $\text{Cr}_2\text{O}_7^{2-}$ and $\text{IO}_4^-$  |
| (B) Eq. wt. of underlined = $\frac{\text{Molecular weight}}{27}$ | (q) When $\text{Fe}(\text{SCN})_2$ oxidises into $\text{Fe}^{3+}$ , $\text{SO}_4^{2-}$ , $\text{CO}_3^{2-}$ and $\text{NO}_3^-$ |
| (C) Eq. wt. of underlined = $\frac{\text{Molecular weight}}{28}$ | (r) When $\text{NH}_4\text{SCN}$ oxidizes into $\text{SO}_4^{2-}$ , $\text{CO}_3^{2-}$ and $\text{NO}_3^-$                      |
| (D) Eq. wt. of underlined = $\frac{\text{Molecular weight}}{24}$ | (s) When $\text{As}_2\text{S}_3$ oxidises into $\text{AsO}_3^-$ and $\text{SO}_4^{2-}$  |

### Comprehension

#### Comprehension-1

Oleum is considered as a solution of  $\text{SO}_3$  in  $\text{H}_2\text{SO}_4$ , which is obtained by passing  $\text{SO}_3$  in solution of  $\text{H}_2\text{SO}_4$ . When 100 g sample of oleum is diluted with desired weight of  $\text{H}_2\text{O}$  then the total mass of  $\text{H}_2\text{SO}_4$  obtained after dilution is known as % labelling in oleum.

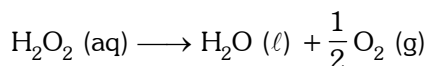
For example, a oleum bottle labelled as '109%  $\text{H}_2\text{SO}_4$ ' means the 109 g total mass of pure  $\text{H}_2\text{SO}_4$  will be formed when 100 g of oleum is diluted by 9 g of  $\text{H}_2\text{O}$  which combines with all the free  $\text{SO}_3$  present in oleum to form  $\text{H}_2\text{SO}_4$  as  $\text{SO}_3 + \text{H}_2\text{O} \longrightarrow \text{H}_2\text{SO}_4$



45. What is the % of free  $\text{SO}_3$  in an oleum that is labelled as '104.5 %  $\text{H}_2\text{SO}_4$ '?  
 (A) 10 (B) 20 (C) 40 (D) none of these
46. 9.0 g water is added into oleum sample labelled as '112%  $\text{H}_2\text{SO}_4$ ' then the amount of free  $\text{SO}_3$  remaining in the solution is :  
 (A) 14.93 L at STP (B) 7.46 L at STP (C) 3.73 L at STP (D) 11.2 L at STP
47. If excess water is added into a bottle sample labelled as '112 %  $\text{H}_2\text{SO}_4$ ' and is reacted with 5.3 g  $\text{Na}_2\text{CO}_3$ , then find the volume of  $\text{CO}_2$  evolved at 1 atm pressure and 300 K temperature after the completion of the reaction:  
 (A) 2.46 L (B) 24.6 L (C) 1.23 L (D) 12.3 L

### Comprehension-3

The strength of  $\text{H}_2\text{O}_2$  is expressed in several ways like molarity, normality, % (w/V), volume strength, etc. The strength of "10 V" means 1 volume of  $\text{H}_2\text{O}_2$  on decomposition gives 10 volumes of oxygen at STP or 1 litre of  $\text{H}_2\text{O}_2$  gives 10 litre of  $\text{O}_2$  at STP. The decomposition of  $\text{H}_2\text{O}_2$  is shown as under :



$\text{H}_2\text{O}_2$  can acts as oxidising as well as reducing agent, as oxidizing agent  $\text{H}_2\text{O}_2$  converted into  $\text{H}_2\text{O}$  and as reducing agent  $\text{H}_2\text{O}_2$  converted into  $\text{O}_2$ , both cases it's n-factor is 2.

$\therefore$  Normality of  $\text{H}_2\text{O}_2$  solution = 2  $\times$  Molarity of  $\text{H}_2\text{O}_2$  solution

48. What is the molarity of "11.2 V" of  $\text{H}_2\text{O}_2$  ?  
 (A) 1 M (B) 2 M (C) 5.6 M (D) 11.2 M
49. What is the percentage strength (% w/V) of "11.2 V"  $\text{H}_2\text{O}_2$  ?  
 (A) 1.7 (B) 3.4 (C) 34 (D) none of these
50. 20 mL of  $\text{H}_2\text{O}_2$  solution is reacted with 80 mL of 0.05 M  $\text{KMnO}_4$  in acidic medium then what is the volume strength of  $\text{H}_2\text{O}_2$  ?  
 (A) 2.8 (B) 5.6 (C) 11.2 (D) none of these
- 51\*. 40 g  $\text{Ba}(\text{MnO}_4)_2$  (mol. wt. = 375) sample containing some inert impurities in acidic medium is completely reacted with 125 mL of "33.6 V" of  $\text{H}_2\text{O}_2$ . What is the percentage purity of the sample ?  
 (A) 28.12 % (B) 70.31 % (C) 85 % (D) none of these

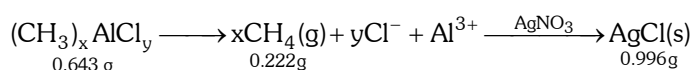
### Subjective Questions

52. A solution containing 4.2 g of KOH and  $\text{Ca}(\text{OH})_2$  is neutralized by an acid. It consumes 0.1 equivalent of acid, calculate the percentage composition of the sample.
53. 10 g  $\text{CaCO}_3$  were dissolved in 250 mL of M HCl and the solution was boiled. What volume of 2 M KOH would be required to equivalence point after boiling? Assume no change in volume during boiling.
54. 1.64 g of mixture of  $\text{CaCO}_3$  and  $\text{MgCO}_3$  was dissolved in 50 mL of 0.8 M HCl. The excess of acid required 16 mL of 0.25 M NaOH for neutralization. Calculate the percentage of  $\text{CaCO}_3$  and  $\text{MgCO}_3$  in the sample.
55. A solution contains  $\text{Na}_2\text{CO}_3$  and  $\text{NaHCO}_3$ . 10 mL of this requires 2 mL of 0.1 M  $\text{H}_2\text{SO}_4$  for neutralisation using Ph indicator. MeOH is then added when a further 2.5 mL of 0.2 M  $\text{H}_2\text{SO}_4$  was needed. Calculate strength of  $\text{Na}_2\text{CO}_3$  and  $\text{NaHCO}_3$ .
- 56\*. A sample containing  $\text{Na}_2\text{CO}_3$  & NaOH is dissolved in 100 mL solution. 10 mL of this solution requires 25 mL of 0.1 N HCl when Ph is used as indicator. If MeOH is used as indicator 10 mL of same solution requires 30 mL of same HCl. Calculate % of  $\text{Na}_2\text{CO}_3$  and NaOH in the sample.



57. It required 40.05 mL of 1 M  $\text{Ce}^{4+}$  to titrate 20 mL of 1 M  $\text{Sn}^{2+}$  to  $\text{Sn}^{4+}$ . What is the oxidation state of the cerium in the product.
58. A volume of 12.53 mL of 0.05093 M  $\text{SeO}_2$  reacted with exactly 25.52 mL of 0.1 M  $\text{CrSO}_4$ . In the reaction,  $\text{Cr}^{2+}$  was oxidized to  $\text{Cr}^{3+}$ . To what oxidation state was selenium converted by the reaction.
59. Potassium acid oxalate  $\text{K}_2\text{C}_2\text{O}_4 \cdot 3\text{H}_2\text{C}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$  can be oxidized by  $\text{MnO}_4^-$  in acid medium. Calculate the volume of 0.1 M  $\text{KMnO}_4$  reacting in acid solution with one gram of the acid oxalate.
60. Metallic tin in the presence of HCl is oxidized by  $\text{K}_2\text{Cr}_2\text{O}_7$  to stannic chloride,  $\text{SnCl}_4$ . What volume of deci-normal dichromate solution would be reduce by 1 g of tin.
61. 5 g sample of brass was dissolved in one litre dil.  $\text{H}_2\text{SO}_4$ . 20 mL of this solution were mixed with KI, liberating  $\text{I}_2$  and  $\text{Cu}^+$  and the  $\text{I}_2$  required 20 mL of 0.0327 N hypo solution for complete titration. Calculate the percentage of Cu in the alloy.
62. 0.84 g iron ore containing x percent of iron was taken in a solution containing all the iron in ferrous condition. The solution required x mL of a dichromatic solution for oxidizing the iron content to ferric state. Calculate the strength of dichromatic solution.
- 63\*. The neutralization of a solution of 1.2 g of a substance containing a mixture of  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ ,  $\text{KHC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  and different impurities of a neutral salt consumed 18.9 mL of 0.5 N NaOH solution. On titration with  $\text{KMnO}_4$  solution, 0.4 g, of the same substance needed 21.55 mL of 0.25 N  $\text{KMnO}_4$ . Calculate the % composition of the substance.
64. 50 g of a sample of  $\text{Ca(OH)}_2$  is dissolved in 50 mL of 0.5 N HCl solution. The excess of HCl was titrated with 0.3 N – NaOH. The volume of NaOH used was 20cc. Calculate % purity of  $\text{Ca(OH)}_2$ .
- 65\*. One g of impure sodium carbonate is dissolved in water and the solution is made up to 250 mL. To 50 mL of this made up solution, 50 mL of 0.1 N – HCl is added and the mix after shaking well required 10 mL of 0.16 N – NaOH solution for complete titration. Calculate the % purity of the sample.
- 66\*. What amount of substance containing 60% NaCl, 37% KCl should be weighed out for analysis so that after the action of 25 mL of 0.1 N  $\text{AgNO}_3$  solution, excess of  $\text{Ag}^+$  is back titrates with 5 mL of  $\text{NH}_4\text{SCN}$  solution. Given that 1 mL of  $\text{NH}_4\text{SCN}$  = 1.1. mL of  $\text{AgNO}_3$ .
67. 50 mL of an aqueous solution of  $\text{H}_2\text{O}_2$  were treated with an excess of KI solution and dilute  $\text{H}_2\text{SO}_4$ , the liberated iodine required 20 mL of 0.1 N  $\text{Na}_2\text{S}_2\text{O}_3$  solution for complete interaction. Calculate the concentration of  $\text{H}_2\text{O}_2$  in g/l.
68. 10 g sample of bleaching powder was dissolved into water to make the solution one litre. To this solution 35 mL of 1.0 M Mohr salt solution was added containing enough  $\text{H}_2\text{SO}_4$ . After the reaction was complete, the excess Mohr salt required 30 mL of 0.1 M  $\text{KMnO}_4$  for oxidation. Find out the % of available  $\text{Cl}_2$  approximately is (mol wt. 71).
- 69\*. Calculate the amount (in milligrams) of  $\text{SeO}_3^{-2}$  in solution on the basis of following data 20 mL of M/60 solution of  $\text{KBrO}_3$  was added to a definite volume of  $\text{SeO}_3^{-2}$  solution. The bromine evolved was removed by boiling and excess of  $\text{KBrO}_3$  was back titrated with 5 mL of M/25 solution of  $\text{NaAsO}_2$ . The reactions are given below. (Atomic mass of K = 39, Br = 80, As = 75, Na = 23, O = 16, Se = 79)
- (a)  $\text{SeO}_3^{-2} + \text{BrO}_3^- + \text{H}^+ \longrightarrow \text{SeO}_4^{-2} + \text{Br}_2 + \text{H}_2\text{O}$
- (b)  $\text{BrO}_3^- + \text{AsO}_2^- + \text{H}_2\text{O} \longrightarrow \text{Br}^- + \text{AsO}_4^{-3} + \text{H}^+$
70. A 1.0 g sample of  $\text{Fe}_2\text{O}_3$  solid of 55.2% purity is dissolved in acid and reduced by heating the solution with zinc dust. The resultant solution is cooled and made upto 100.0 mL. An aliquot of 25.0 mL of this solution requires 17.0 mL of 0.0167 M solution of an oxidant for titration. Calculate the number of moles of electrons taken up by the oxidant in the reaction of the above titration.

- 71.** How much quantity of zinc will have to be reacted with excess of dilute HCl solution to produce sufficient hydrogen gas for completely reacting with the oxygen obtained by decomposing 5.104 g of potassium chlorate?
- 72.** 1.0 g of a sample containing NaCl, KCl and some inert impurity is dissolved in excess of water and treated with excess of AgNO<sub>3</sub> solution. A 2.0 g precipitate of AgCl separates out. Also sample is 23% by mass in sodium. Determine mass percentage of KCl in the sample :
- 73.** 2.5 g of a sample containing Na<sub>2</sub>CO<sub>3</sub> ; NaHCO<sub>3</sub> and some non-volatile impurity on gentle heating loses 12% of its weight. Residue is dissolved in 100 mL water and its 10 mL portion required 15 mL 0.1 M aqueous solution of BaCl<sub>2</sub> for complete precipitation of carbonates. Determine mass percentage of Na<sub>2</sub>CO<sub>3</sub> in the original sample?
- 74.** Based on the following information, determine value x and y :



- 75\*.** A 5.0 g sample of felspar containing Na<sub>2</sub>O, K<sub>2</sub>O and some inert impurity is dissolved in dilute HCl solution and NaCl and KCl formed are separated by fractional crystallization. During crystallization some less soluble impurities also come out. Mass of NaCl, KCl and impurity accompanying these salts was found to be 6.47 g. Solid crystal was then re-dissolved and required 300 mL of 0.3 M AgNO<sub>3</sub> for complete precipitation of chlorides. The precipitate thus, obtained was found to contain 4.23 % insoluble impurity. Determine mass percentage of Na<sub>2</sub>O and K<sub>2</sub>O in the original sample :
- 76.** Pb(NO<sub>3</sub>)<sub>2</sub> and KI reacts in aqueous solution to form a yellow precipitate of PbI<sub>2</sub>. In one series of experiments, the masses of two reactants varied, but the total mass of the two was held constant at 5.0 g. What maximum mass of PbI<sub>2</sub> can be produced in the above experiment :
- 77.** A sample is a mixture of Mohr's salts and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>. A 0.5 g sample on treatment with excess of BaCl<sub>2</sub> solution gave 0.75 g BaSO<sub>4</sub>. Determine percentage composition of the salt mixture . What weight of Fe<sub>2</sub>O<sub>3</sub> would be obtained if 0.2 g of the sample were ignited in air ?
- 78.** A chloride mixture is prepared by grinding together pure BaCl<sub>2</sub>·2H<sub>2</sub>O, KCl and NaCl. What is the smallest and largest volume of 0.15 M AgNO<sub>3</sub> solution that may be used for complete precipitation of chloride from a 0.3 g sample of the mixture which may contain any one or all of the constituents ?
- 79.** One mole of a mixture of N<sub>2</sub>, NO<sub>2</sub> and N<sub>2</sub>O<sub>4</sub> has a mean molar mass of 55.4. On heating to a temperature at which N<sub>2</sub>O<sub>4</sub> may be dissociated : N<sub>2</sub>O<sub>4</sub> → 2NO<sub>2</sub>, the mean molar mass tends to the lower value of 39.6. What is the mole ratio of N<sub>2</sub> : NO<sub>2</sub> : N<sub>2</sub>O<sub>4</sub> in the original mixture?
- 80.** A sea water sample has a density of 1.03 g/cm<sup>3</sup> and 2.8% NaCl by mass. A saturated solution of NaCl in water is 5.45 M NaCl. How much water would have to be evaporated from 1.00 × 10<sup>6</sup> L of the sea water before NaCl would precipitate ?
- 81.** One litre of milk weighs 1.035 kg. The butter fat is 4% (v/v) of milk has density of 875 kg/m<sup>3</sup>. Find the density of fat free skimmed milk.
- 82\*.** A 1g sample of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> containing some inert material was entirely reduced with conc. HCl. The chlorine liberated was passed through hot solution of NaOH at 80°C, and it completely disproportionates to form ClO<sub>3</sub><sup>-</sup> and Cl<sup>-</sup>. This NaClO<sub>3</sub> was isolated and its reduction with KI (aq) liberated iodine, giving Cl<sup>-</sup>. The iodine thus liberated required 100 mL of decinormal hypo solution for complete titration. What is the percentage purity of the dichromate sample?
- 83.** 2.5g of mixture of crystalline oxalic acid (H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O) and sodium oxalate (Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>) was dissolved in 100 mL of water. 50 mL of this solution was titrated against N/10 NaOH solution when 119.05 mL of the base was found necessary to reach the end point with phenolphthalein as the indicator. 1g of the mixture was dissolved in water and the solution titrated against N/10 KMnO<sub>4</sub> in the presence of dil. H<sub>2</sub>SO<sub>4</sub>. What is the volume of KMnO<sub>4</sub> needed for getting the end point with 0.5g of the mixture?

- 84\*.** 0.6213 g of sample contains an unknown amount of  $\text{As}_2\text{O}_3$ . The sample was treated with HCl resulting in formation of  $\text{AsCl}_3$  (g) which was distilled into a beaker of water. The hydrolysis reaction is as follows :  

$$\text{AsCl}_3 + 2\text{H}_2\text{O} \rightarrow \text{HAsO}_2 + 3\text{H}^+ + 3\text{Cl}^-$$
 The amount of  $\text{HAsO}_2$  was determined by titration with 0.04134 M  $\text{I}_2$ , requiring 23.04 mL to reach the equivalence point. The redox products in the titration were  $\text{H}_3\text{AsO}_4$  and  $\text{I}^-$ . Find the amount of  $\text{KMnO}_4$  needed to oxidize As in  $\text{As}_2\text{O}_3$  to its maximum possible oxidation state in acidic medium.
- 85\*.** In the presence of fluoride ion,  $\text{Mn}^{2+}$  can be titrated with  $\text{MnO}_4^-$ , both reactants being converted to a complex of Mn(III). A 0.545 g sample containing  $\text{Mn}_3\text{O}_4$  was dissolved and all manganese was converted to  $\text{Mn}^{2+}$ . Titration in the presence of fluoride ion consumed 31.1 mL of  $\text{KMnO}_4$  that was 0.177 N against oxalate.  
 (a) write a balanced chemical equation for the reaction, assuming that the complex is  $\text{MnF}_4^-$ .  
 (b) what was the % of  $\text{Mn}_3\text{O}_4$  in the sample ?
- 86\*.** A steel sample is to be analysed for Cr and Mn simultaneously. By suitable treatment the Cr is oxidized to  $\text{Cr}_2\text{O}_7^{2-}$  and the Mn to  $\text{MnO}_4^-$ . A 10.00 g sample of steel is used to produce 250.0 mL of a solution containing  $\text{Cr}_2\text{O}_7^{2-}$  and  $\text{MnO}_4^-$ . A 10.00 mL portion of this solution is added to a  $\text{BaCl}_2$  solution and by proper adjustment of the acidity, the chromium is completely precipitated as  $\text{BaCrO}_4$ ; 0.0549 g is obtained. A second 10.00 mL portion of this solution requires exactly 15.95 mL of 0.0750 M standard  $\text{Fe}^{2+}$  solution for its titration (in acid solution). Calculate the % of Mn and % of Cr in the steel sample.
- 87\*.** 1.16 g  $\text{CH}_3(\text{CH}_2)_n\text{COOH}$  was burnt in excess air and the resultant gases ( $\text{CO}_2$  and  $\text{H}_2\text{O}$ ) were passed through excess NaOH solution. The resulting solution was divided in two equal parts. One part required 50 mL of 1 N HCl for neutralization using phenolphthalein as indicator. Another part required 80 mL of 1 N HCl for neutralization using methyl orange as indicator. Find the value of n and the amount of excess NaOH solution taken initially.
- 88\*.** A 1.5 g sample containing oxalic acid and some inert impurity was dissolved in enough water and volume made up to 250 mL. A 20 mL portion of this solution was then mixed with 30 mL of an alkali solution. The resulting solution was then treated with stoichiometric amount of  $\text{CaCl}_2$  just needed for precipitation of oxalate as  $\text{CaC}_2\text{O}_4$ . Solution was filtered off and filtrate was finally titrated against 0.1 M HCl solution. 8.0 mL of acid was required to reach the equivalence point. At last, the above neutral solution was treated with excess of  $\text{AgNO}_3$  solution and  $\text{AgCl}$  obtained was washed, dried and weighed to be 0.4305 g. Determine mass percentage of oxalic acid in the original sample :
- 89\*.** A 1 g sample containing NaOH as the only basic substance and some inert impurity was left exposed to atmosphere for a very long time so that part of NaOH got converted into  $\text{Na}_2\text{CO}_3$  by absorbing  $\text{CO}_2$  from atmosphere. The resulting sample was dissolved in water and volume made upto 100 mL. A 20 mL portion of this solution required 16 mL 0.25 M HCl solution to reach the equivalence point when methyl orange was used as indicator. In a separate analysis, 20 mL portion of the same solution was taken along with phenolphthalein indicator and mixed with 50 mL of 0.1 M HCl solution. An additional 9.00 mL 0.1 M  $\text{Ba}(\text{OH})_2$  solution was required to just restore the pink colour of solution. Determine mass percentage of NaOH in the original sample and mass percentage of  $\text{Na}_2\text{CO}_3$  in the sample after exposure to atmosphere.
- 90.** A 5.0 cm<sup>3</sup> solution of  $\text{H}_2\text{O}_2$  liberates 0.508 g of iodine from an acidified KI solution. Calculate the strength of  $\text{H}_2\text{O}_2$  solution in terms of volume strength at STP. **[JEE 1995]**
- 91\*.** A 3.00 g sample containing  $\text{Fe}_3\text{O}_4$ ,  $\text{Fe}_2\text{O}_3$  and an inert impure substance, is treated with excess of KI solution in presence of dilute  $\text{H}_2\text{SO}_4$ . The entire iron is converted into  $\text{Fe}^{2+}$  along with the liberation of iodine. The resulting solution is diluted to 100 mL. A 20 mL of the diluted solution require 11 mL of 0.5 M  $\text{Na}_2\text{S}_2\text{O}_3$  solution to reduce the iodine present. A 50 mL of diluted solution after complete extraction of the iodine requires 12.80 mL of 0.25  $\text{KMnO}_4$  solution in dilute  $\text{H}_2\text{SO}_4$  medium for the oxidation of  $\text{Fe}^{2+}$ . Calculate the percentages of  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$  in the original sample. **[JEE 2000]**

- 92\*.** One litre of a mixture of  $O_2$  and  $O_3$  at NTP was allowed to react with an excess of acidified solution of KI. The Iodine liberated required 40 mL of M/10 sodium thiosulphate solution for titration. What is the percent of ozone in the mixture? Ultraviolet radiation of wavelength 300 nm can decompose ozone. Assuming that one photon can decompose one ozone molecule, how many photons would have been required for the complete decomposition of ozone in the original mixture? **[JEE 1997]**
- 93\*.** A sample of hard water contains 96 ppm of  $SO_4^{2-}$  and 183 ppm of  $HCO_3^-$ , with  $Ca^{2+}$  as the only cation. How many moles of CaO will be required to remove  $HCO_3^-$  from 1000 kg of this water? If 1000 kg of this water is treated with the amount of CaO calculate above, what will be the concentration (in ppm) of residual  $Ca^{2+}$  ions (Assume  $CaCO_3$  to be completely insoluble in water)? If the  $Ca^{2+}$  ions in one litre of the treated water are completely exchanged with hydrogen ions, what will be its pH (one ppm means one part of the substance in one million part of water, weight / weights)? **[JEE 1997]**
- 94.** An aqueous solution containing 0.10 g  $KIO_3$  (formula wt. 214.0) was treated with an excess of KI solution. The solution was acidified with HCl. The liberated  $I_2$  consumed 45.0 mL of thiosulphate solution to decolourise the blue starch – iodine complex. Calculate the molarity of the sodium thiosulphate solution. **[JEE 1998]**
- 95.** How many millilitre of 0.5 M  $H_2SO_4$  are needed to dissolve 0.5 g of copper II carbonate? **[JEE 1999]**
- 96.** Hydrogen peroxide solution (20 mL) reacts quantitatively with a solution of  $KMnO_4$  (20 mL) acidified with dilute  $H_2SO_4$ . The same volume of  $KMnO_4$  solution is just decolorized by 10 mL of  $MnSO_4$  in neutral medium simultaneously forming a dark brown precipitate of hydrated  $MnO_2$ . The brown precipitate is dissolved in 10 mL of 0.2 M sodium oxalate under boiling condition in the presence of dilute  $H_2SO_4$ . Write the balanced equations involved in the reactions and calculate the molarity of  $H_2O_2$ . **[JEE 2001]**
- 97.** A sample of oleum is such that ratio of "free  $SO_3$ " by "combined  $SO_3$ " is equal to unity. Calculate its labelling in terms of percentage oleum.
- 98.** In a solution the concentration of  $CaCl_2$  is 5 M & that of  $MgCl_2$  is 5 m. The specific gravity of solution is 1.05, calculate the concentration of  $Cl^-$  in the solution in terms of Molarity.
- 99\*.** 1.2475 g of crystalline copper sulphate was dissolved in water and excess of KI was added. The liberated iodine consumed 50 mL N/10  $Na_2S_2O_3$  solution to reach the end point of the titration. Calculate the number of water molecules of hydration in crystalline copper sulphate salt.
- 100.** 25 mL of a solution containing HCl was treated with excess of M/5  $KIO_3$  and KI solution of unknown concentration where  $I_2$  liberated is titrated against a standard solution of 0.021 M  $Na_2S_2O_3$  solution whose 24 mL were used up. Find the strength of HCl and volume of  $KIO_3$  solution consumed :
- 101\*.** A sample of steel weighing 0.6 g and containing S as an impurity was burnt in a stream of  $O_2$ , when S was converted to its oxide  $SO_2$ .  $SO_2$  was then oxidized to  $SO_4^{2-}$  by using  $H_2O_2$  solution containing 30 mL of 0.04 M NaOH. 22.48 mL of 0.024 M HCl was required to neutralize the base remaining after oxidation. Calculate the % of S in the sample :

# ANSWERS

## • Fill in the Blanks

- |   |                                |
|---|--------------------------------|
| 1. Limiting Reagent                                       | 2. Oxidised as well as reduced |
| 3. Oxygen has been oxidised and chlorine has been reduced | 4. +7/3                        |
| 5. +2   |                                |

## • Assertion-Reason

- |        |        |        |        |         |
|--------|--------|--------|--------|---------|
| 6. (B) | 7. (A) | 8. (A) | 9. (B) | 10. (A) |
|--------|--------|--------|--------|---------|

## • Single Choice Correct

- |         |         |         |         |         |
|---------|---------|---------|---------|---------|
| 11. (D) | 12. (D) | 13. (A) | 14. (D) | 15. (D) |
| 16. (D) | 17. (C) | 18. (B) | 19. (B) | 20. (B) |
| 21. (A) | 22. (A) | 23. (C) | 24. (C) | 25. (B) |
| 26. (B) | 27. (A) | 28. (B) | 29. (A) | 30. (B) |
| 31. (A) | 32. (D) | 33. (D) | 34. (A) | 35. (A) |
| 36. (A) | 37. (B) | 38. (C) | 39. (B) | 40. (C) |
| 41. (D) | 42. (A) | 43. (A) |         |         |

## • Match the Column

44. (A) → q ; (B) → p ; (C) → s ; (D) → r

## • Comprehension

- |                          |         |         |         |         |
|--------------------------|---------|---------|---------|---------|
| <b>Comprehension 1 :</b> | 45. (B) | 46. (C) | 47. (C) |         |
| <b>Comprehension 2 :</b> | 48. (A) | 49. (B) | 50. (B) | 51. (B) |

## • Subjective Questions

- |  |   |
|--|---|
| 52. KOH = 35%, Ca(OH) <sub>2</sub> = 65%                             | 53. V = 25 mL   |
| 54. MgCO <sub>3</sub> = 51.22%, CaCO <sub>3</sub> = 48.78 %          | 55. 4.24 g/L ; 5.04 g/L   |
| 56. 39.85% ; 60.15%  | 57. +3  |
| 58. zero   | 59. V = 31.68 mL  |
| 60. 337 mL   | 61. 41.53 %   |
| 62. 0.15 N   | 63. H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> ·2H <sub>2</sub> O = 14.36%, KH <sub>2</sub> O <sub>4</sub> ·H <sub>2</sub> O=81.71% |
| 64. 1.406 %  | 65. 90.1%   |
| 66. 0.1281 g   | 67. 0.68 g/L  |
| 68. 7.1%   | 69. 84mg  |
| 70. (6.23)   | 71. 8.124 g Zn  |
| 72. 29.28  | 73. 53.3 % Na <sub>2</sub> CO <sub>3</sub>  |
| 74. 2, 1   | 75. 31.16, 37.34  |
| 76. 3.464 g  | 77. 18.77 mg  |
| 78. 16.38 ml, 34.18 ml   | 79. 0.5 : 0.1 : 0.4   |
| 80. 9.095 × 10 <sup>5</sup> L  | 81. 1.041 g/mL  |
| 82. 58.8%  | 83. 77.45 mL  |
| 84. 0.06 g   | 85. 61.67%  |
| 86. Cr = 2.821% , Mn = 1.498%  | 87. n = 4, NaOH = 6.4 g   |
| 88. 82.5   | 89. 80, 36.05 %   |
| 90. 4.48   | 91. Fe <sub>2</sub> O <sub>3</sub> = 48.1 % , Fe <sub>3</sub> O <sub>4</sub> = 33.9%  |
| 92. 6.57% O <sub>3</sub> (by weight), 1.2 × 10 <sup>21</sup> photons | 93. 1.5, 40 ppm, pH = 2.6989  |
| 94. 0.0623 M   | 95. 8.097 ml  |
| 96. 0.1 M  | 97. 110.11 %  |
| 98. [Cl <sup>-</sup> ] = 13.36 M                                     | 99*. (5)  |
| 100. V <sub>KIO<sub>3</sub></sub> = 0.42mL , [HCl] = 0.02016 N       | 101*. 1.76 %  |

## ATOMIC STRUCTURE

### True/False

- The electron density in xy plane of  $3d_{x^2-y^2}$  orbital is zero.
- $3d^6$  configuration is more stable than  $3d^5$ .
- The potential energy of an electron in an orbit is twice in magnitude as compared to its kinetic energy.
- The increasing order for the values of  $e/m$  (charge/mass) for electron (e), proton (p), neutron (n) and alpha particle ( $\alpha$ ) is  $n < \alpha < p < e$ .
- The orbital  $3d_{xy}$  has no probability of finding electron along x and y-axis.

### Fill in the blanks

- Nitrogen has an atomic number of 7 and oxygen has an atomic number of 8. The total number of electrons in the nitrate ion ( $\text{NO}_3^-$ ) is .....
- $h/\pi$  is the angular momentum of the electron in the ..... orbit of  $\text{He}^+$ .
- An emission spectrum has electromagnetic radiation of definite .....
- The maximum number of electrons that can be accommodated in all the orbitals for which  $\ell = 3$  is .....
- The values of  $n_1$  and  $n_2$  in the Paschen spectral series of hydrogen atom are ..... and ..... respectively.

### Assertion-Reason

These questions contains, Statement I (assertion) and Statement II (reason).

(A) Statement-I is true, Statement-II is true ; Statement-II is correct explanation for Statement-I.

(B) Statement-I is true, Statement-II is true ; Statement-II is NOT a correct explanation for statement-I

(C) Statement-I is true, Statement-II is false

(D) Statement-I is false, Statement-II is true

- Statement-I** : Nodal plane of  $p_x$  atomic orbital is yz plane.

**Because**

**Statement-II** : In  $p_x$  atomic orbital electron density is zero in the yz plane.

- Statement-I** : No two electrons in an atom can have the same values of four quantum numbers.

**Because**

**Statement-II** : No two electrons in an atom can be simultaneously in the same shell, same subshell, same orbitals and have same spin.

- Statement-I** : p-orbital has dumb-bell shape.

**Because**

**Statement-II** : Electrons present in p-orbital can have one of three values for 'm', i.e. 0, +1, -1.

- Statement-I** : The ground state configuration of Cr is  $3d^5 4s^1$ .

**Because**

**Statement-II** : A set of exactly half filled orbitals containing parallel spin arrangement provide extra stability.

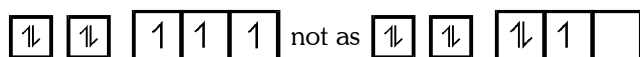


15. **Statement-I** : Limiting line in the balmer series has a wavelength of  $36.4 \mu\text{m}$ .

**Because**

**Statement-II** : Limiting lines is obtained for a jump of electron from  $n = \infty$  to  $n = 2$  for Balmer series.

16. **Statement-I** : The electronic configuration of nitrogen atom is represented as :



**Because**

**Statement-II** : The configuration of ground state of an atom is the one which has the greatest multiplicity.

17. **Statement-I** : The configuration of B atom cannot be  $1s^2 2s^3$ .

**Because**

**Statement-II** : Hund's rule demands that the configuration should display maximum multiplicity.

18. **Statement-1** : The groundstate configuration of Cr is  $[\text{Ar}] 3d^5 4s^1$

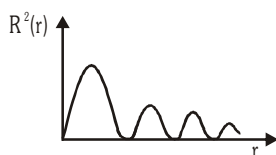
**Statement-2** : The energy of atom is lesser in  $3d^5 4s^1$  configuration compared to  $3d^4 4s^2$  configuration.

19. **Statement-1** : Minimum principal quantum number of an orbital belonging to 'g' sub-shell is 5.

**Statement-2** : For a given value of principal quantum number ( $n$ ),  $l$  may have values 0 to  $(n-1)$  only.

### Single Choice Correct

20. The binding energy of an electron in the ground state of the He atom is equal to 24.6 eV. The energy required to remove both the electrons from the atom will be  
 (A) 59 eV (B) 81 eV (C) 79 eV (D) None of these
21. Given  $\Delta H$  for the process  $\text{Li}(\text{g}) \longrightarrow \text{Li}^{+3}(\text{g}) + 3e^-$  is 19800 kJ/mole &  $IE_1$  for Li is 520 then  $IE_2$  &  $IE_1$  of  $\text{Li}^+$  are respectively (approx value) :-  
 (A) 11775, 7505 (B) 19280, 520 (C) 11775, 19280 (D) Data insufficient
- 22\*. From the following observations predict the type of orbital :  
 Observation 1 : x y plane acts as nodal plane  
 Observation 2 : The angular function of the orbital intersect the three axis at origin only.  
 Observation 3 :  $R^2(r)/r$  curve is obtained for the orbital is



- (A)  $5p_z$  (B)  $6d_{xy}$  (C)  $6d_{x^2-y^2}$  (D)  $6d_{yz}$
23. For which orbital angular probability distribution is maximum at an angle of  $45^\circ$  to the axial direction :-  
 (A)  $d_{x^2-y^2}$  (B)  $d_{z^2}$  (C)  $d_{xy}$  (D)  $P_x$
24. Which orbit would be the first to have 'g' subshell :-  
 (A)  $3^{\text{rd}}$  (B)  $4^{\text{th}}$  (C)  $5^{\text{th}}$  (D)  $6^{\text{th}}$
25. The decreasing order of energy of the 3d, 4s, 3p, 3s orbitals is :-  
 (A)  $3d > 3s > 4s > 3p$  (B)  $3s > 4s > 3p > 3d$  (C)  $3d > 4s > 3p > 3s$  (D)  $4s > 3d > 3s > 3p$

26. If  $n$  and  $\ell$  are respectively the principle and azimuthal quantum numbers, then the expression for calculating the total number of electrons in any orbit is :-

(A)  $\sum_{\ell=1}^{\ell=n} 2(2\ell+1)$       (B)  $\sum_{\ell=1}^{\ell=n-1} 2(2\ell+1)$       (C)  $\sum_{\ell=0}^{\ell=n+1} 2(2\ell+1)$       (D)  $\sum_{\ell=0}^{\ell=n-1} 2(2\ell+1)$

27. If wavelength is equal to the distance travelled by the electron in one second, then :-

(A)  $\lambda = \frac{h}{pv}$       (B)  $\lambda = \frac{h}{m}$       (C)  $\lambda = \sqrt{\frac{h}{p}}$       (D)  $\lambda = \sqrt{\frac{h}{m}}$

28. According to Schrodinger model nature of electron in an atom is :-

- (A) Particles only      (B) Wave only  
(C) Both simultaneously      (D) Sometimes waves and sometimes particle

29. Which describes orbital :-

- (A)  $\psi$       (B)  $\psi^2$       (C)  $|\psi^2|\psi$       (D) All

30. In order to have the same wavelength for the electron (mass  $m_e$ ) and the neutron (mass  $m_n$ ) their velocities should be in the ratio (electron velocity/neutron velocity) :-

- (A)  $m_n/m_e$       (B)  $m_n \times m_e$       (C)  $m_e/m_n$       (D) one

31. The quantum numbers  $+1/2$  and  $-1/2$  for the electron spin represent :-

- (A) Rotation of the electron in clockwise and anticlockwise direction respectively.  
(B) Rotation of the electron in anticlockwise and clockwise direction respectively.  
(C) Magnetic moment of the electron pointing up and down respectively.  
(D) Two quantum mechanical spin states which have no classical analogue.

32. Which is true about  $\psi$  :-

- (A)  $\psi$  represents the probability of finding an electron around the nucleus  
(B)  $\psi$  represent the amplitude of the electron wave  
(C) Both A and B  
(D) None of these

33. Consider an electron in the  $n^{\text{th}}$  orbit of a hydrogen atom in the Bohr model. The circumference of the orbit can be expressed in terms of the de Broglie wavelength  $\lambda$  of the electron as :-

- (A)  $(0.529) n\lambda$       (B)  $\sqrt{n}\lambda$       (C)  $(13.6) \lambda$       (D)  $n\lambda$

34. A particle X moving with a certain velocity has a de Broglie wave length of  $1\text{Å}$ . If particle Y has a mass of 25% that of X and velocity 75% that of X, de Broglie's wave length of Y will be :-

- (A)  $3\text{Å}$       (B)  $5.33\text{Å}$       (C)  $6.88\text{Å}$       (D)  $48\text{Å}$

35. What are the values of the orbital angular momentum of an electron in the orbitals 1s, 3s, 3d and 2p :-

- (A)  $0, 0, \sqrt{6}\hbar, \sqrt{2}\hbar$       (B)  $1, 1, \sqrt{4}\hbar, \sqrt{2}\hbar$       (C)  $0, 1, \sqrt{6}\hbar, \sqrt{3}\hbar$       (D)  $0, 0, \sqrt{20}\hbar, \sqrt{6}\hbar$

36. If  $m$  = magnetic quantum number and  $\ell$  = azimuthal quantum number then :-

- (A)  $m = \ell + 2$       (B)  $m = 2\ell^2 + 1$       (C)  $\ell = \frac{m-1}{2}$       (D)  $\ell = 2m + 1$

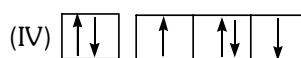
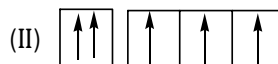
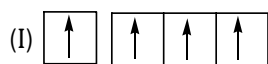
37. The number of unpaired electrons in  $\text{Mn}^{4+}$  ( $Z = 25$ ) is :-

- (A) Four      (B) Two      (C) Five      (D) Three



- 38.** After np orbitals are filled, the next orbital filled will be :-  
 (A)  $(n + 1) s$  (B)  $(n + 2) p$  (C)  $(n + 1) d$  (D)  $(n + 2) s$
- 39.** The value of the magnetic moment of a particular ion is 2.83 Bohr magneton. The ion is :-  
 (A)  $\text{Fe}^{2+}$  (B)  $\text{Ni}^{2+}$  (C)  $\text{Mn}^{2+}$  (D)  $\text{Co}^{3+}$
- 40.** In Bohr's model of the hydrogen atom the ratio between the period of revolution of an electron in the orbit of  $n = 1$  to the period of the revolution of the electron in the orbit  $n = 2$  is :-  
 (A) 1 : 2 (B) 2 : 1 (C) 1 : 4 (D) 1 : 8
- 41.** Let  $\nu_1$  be the frequency of the series limit of the Lyman series,  $\nu_2$  be the frequency of the first line of the Lyman series, and  $\nu_3$  be the frequency of the series limit of the Balmer series :-  
 (A)  $\nu_1 - \nu_2 = \nu_3$  (B)  $\nu_2 - \nu_1 = \nu_3$  (C)  $\nu_3 = 1/2 (\nu_1 - \nu_2)$  (D)  $\nu_1 + \nu_2 = \nu_3$
- 42.** The energies of energy levels A, B and C for a given atom are in the sequence  $E_A < E_B < E_C$ . If the radiations of wavelengths  $\lambda_1$ ,  $\lambda_2$  and  $\lambda_3$  are emitted due to the atomic transitions C to B, B to A and C to A respectively then which of the following relations is correct :-  
 (A)  $\lambda_1 + \lambda_2 + \lambda_3 = 0$  (B)  $\lambda_3 = \lambda_1 + \lambda_2^2$  (C)  $\lambda_3 = \lambda_1 + \lambda_2$  (D)  $\lambda_3 = \frac{\lambda_1 \lambda_2}{\lambda_1 + \lambda_2}$
- 43.** The wavelengths of photons emitted by electron transition between two similar levels in H and  $\text{He}^+$  are  $\lambda_1$  and  $\lambda_2$  respectively. Then :-  
 (A)  $\lambda_2 = \lambda_1$  (B)  $\lambda_2 = 2\lambda_1$  (C)  $\lambda_2 = \lambda_1/2$  (D)  $\lambda_2 = \lambda_1/4$
- 44.** If first ionization potential of an atom is 16 V, then the first excitation potential will be :-  
 (A) 10.2 V (B) 12 V (C) 14 V (D) 16 V
- 45.** In which transition minimum energy is emitted :-  
 (A)  $\infty \rightarrow 1$  (B)  $2 \rightarrow 1$  (C)  $3 \rightarrow 2$  (D)  $n \rightarrow (n - 1)$  ( $n \geq 4$ )
- 46.** No. of visible lines when an electron returns from 5<sup>th</sup> orbit to ground state in H spectrum :-  
 (A) 5 (B) 4 (C) 3 (D) 10
- 47.** Which of the following has maximum number of unpaired electron (atomic number of Fe 26)  
 (A) Fe (B) Fe (II) (C) Fe (III) (D) Fe (IV)
- 48.** Suppose a particle has four quantum numbers such that the permitted values are:  
 $n = 1, 2, 3, \dots$   
 $l = (n - 1), (n - 3), (n - 5), \dots$  but no negative value  
 $j = \left(\ell + \frac{1}{2}\right)$  or  $\left(\ell - \frac{1}{2}\right)$ , the later is not negative  
 $m = -j$  in integer step to  $+j$  what are the other permitted values for  $n = 2$ ?  
 (A)  $l = 1, j = \frac{3}{2}, m = -\frac{3}{2}$  (B)  $l = 0, j = \frac{1}{2}, m = -\frac{1}{2}$   
 (C)  $l = 1, j = \frac{1}{2}, m = -\frac{3}{2}$  (D) All of these
- 49.** Which of the following is / are false.  
 (A) Multiplicity in  $\text{Fe}^{3+}$  is greater than  $\text{Co}^{3+}$ . (B)  $\text{Ti}^{3+}$ ,  $\text{Cr}^+$ ,  $\text{Sc}^{2+}$  ions are diamagnetic.  
 (C) Value of  $(n + l + m)$  for last electron in Na is 3. (D) Number of neutron in  $1.07 \text{ gm Fe}(\text{OH})_3$  is  $3.25 \times 10^{23}$

50. The orbital diagram in which Hund's rule is violated is



(A) I & II

(B) II & III

(C) III & IV

(D) II & IV

51. Match the column:

('l' and 'm' are respectively the azimuthal and magnetic quantum numbers)

**Column I**

**Column II**

(I) Total number of values of (l) for a shell

(P) 0, 1, 2, .....(n-1)

(II) Values of (l) for a shell

(Q) +l, .....+2, +1, 0, -1, -2, .....-l

(III) Total number of values of (m) for a subshell

(R) (2l + 1)

(IV) Values of (m) for a subshell

(S) n

(A) (I) S (II) P (III) R (IV) Q

(B) (I) S (II) R (III) P (IV) Q

(C) (I) P (II) S (III) R (IV) Q

(D) (I) P (II) R (III) Q (IV) S

52. Which of the following statements regarding subshell filling order for a neutral atom is/are correct ?

(I) Electrons are assigned to the 4s subshell before they are assigned to the 3d subshell

(II) Electrons are assigned to the 4f subshell before they are assigned to the 6s subshell

(III) Electrons are assigned to the 4d subshell before they are assigned to the 5p subshell

(A) I only

(B) II only

(C) I and III

(D) I, II and III

53. If the nitrogen atom had electronic configuration  $1s^7$ , it would have energy lower than that of normal ground state configuration  $1s^2 2s^2 2p^3$ , because the electrons would be closer to the nucleus. Yet  $1s^7$  is not observed because it violates :-

(A) Heisenberg uncertainty principle

(B) Hund's rule

(C) Pauli's exclusion principle

(D) Bohr postulate of stationary orbits

54. The explanation for the presence of three unpaired electrons in the nitrogen atom can be given by

(A) Pauli's exclusion principle

(B) Hund's rule

(C) Aufbau's principle

(D) Uncertainty principle

55. Which of the following has the maximum number of unpaired electrons ?

[JEE 1996]

(A)  $Mg^{2+}$

(B)  $Ti^{3+}$

(C)  $V^{3+}$

(D)  $Fe^{2+}$

56. The electrons, identified by n & l ;

[JEE 1999]

(i)  $n = 4, l = 1$

(ii)  $n = 4, l = 0$

(iii)  $n = 3, l = 2$

(iv)  $n = 3, l = 1$  can be placed in order of increasing energy, from the lowest to highest as :

(A) (iv) < (ii) < (iii) < (i) (B) (iii) < (ii) < (iv) < (i) (C) (i) < (iii) < (ii) < (iv) (D) (iii) < (i) < (iv) < (ii)

57. Rutherford's experiment, which established the nuclear model of atom, used a beam of :-

[JEE 2002]

(A)  $\beta$  - particles, which impinged on a metal foil and get absorbed.

(B)  $\gamma$  - rays, which impinged on a metal foil and ejected electron.

(C) Helium atoms, which impinged on a metal foil and got scattered.

(D) Helium nuclei, which impinged on a metal foil and got scattered.

58. The magnetic moment of cobalt of the compound  $Hg[Co(SCN)_4]$  is [Given :  $Co^{+2}$ ]

[JEE 2004]

(A)  $\sqrt{3}$

(B)  $\sqrt{8}$

(C)  $\sqrt{15}$

(D)  $\sqrt{24}$

**59.** The radius of which of the following orbit is same as that of the first Bohr's orbit of hydrogen atom?

[JEE 2004]

- (A)  $\text{He}^+$  ( $n = 2$ )      (B)  $\text{Li}^{2+}$  ( $n = 2$ )      (C)  $\text{Li}^{2+}$  ( $n = 3$ )      (D)  $\text{Be}^{3+}$  ( $n = 2$ )

**60.** The magnetic moment of cobalt of the compound  $\text{Hg}[\text{Co}(\text{SCN})_4]$  is [Given :  $\text{Co}^{+2}$ ]

[JEE 2004]

- (A)  $\sqrt{3}$       (B)  $\sqrt{8}$       (C)  $\sqrt{15}$       (D)  $\sqrt{24}$

### Multi Choice Correct

**61.** Which of the following statements is/are incorrect ?

- (A) Lanthanum is the first element of lanthanides      (B) Actinium violates the Aufbau's principle.  
 (C) Chromium violates the Pauli's exclusion principle.      (D) Total 10 exchanges are possible for d electrons in Zn.

**62.** Bohr's theory is not applicable to -

- (A) He      (B)  $\text{Li}^{2+}$       (C)  $\text{He}^{2+}$       (D) the H-atom

**63.** In which transition, one quantum of energy is emitted -

- (A)  $n = 4 \rightarrow n = 2$       (B)  $n = 3 \rightarrow n = 1$       (C)  $n = 4 \rightarrow n = 1$       (D)  $n = 2 \rightarrow n = 1$

**64.** Choose the correct relation on the basis of Bohr's theory -

- (A) velocity of electron  $\propto \frac{1}{n}$       (B) frequency of revolution  $\propto \frac{Z^2}{n^3}$   
 (C) radius of orbit  $\propto n^2 Z$       (D) force on electron  $\propto \frac{Z^3}{n^4}$

**65.** The magnitude of the spin angular momentum of an electron is given by -

- (A)  $S = \sqrt{s(s+1)} \frac{h}{2\pi}$       (B)  $S = s \frac{h}{2\pi}$       (C)  $S = \frac{\sqrt{3}}{2} \times \frac{h}{2\pi}$       (D)  $S = \pm \frac{1}{2} \times \frac{h}{2\pi}$

**66.** A hydrogen - like atom has ground state binding energy 122.4 eV. Then :

- (A) its atomic number is 3  
 (B) an photon of 90 eV can excite it to a higher state  
 (C) an 80 eV photon cannot excite it to a higher state  
 (D) an electron of 8.2 eV and a photon of 91.8 eV are emitted when a 100 eV electron interacts with it

**67\*.** In a hydrogen like sample two different types of photons A and B are produced by electronic transition. Photon B has its wavelength in infrared region if photon A has more energy than B, then the photon A may belong to the region.

- (A) ultraviolet      (B) visible      (C) infrared      (D) None

**68\*.** Hydrogen atoms in a particular excited state 'n', when all returned to ground state, 6 different photons are emitted. Which of the following is/are incorrect.

- (A) Out of 6 different photons only 2 photons have wavelength equal to that of visible light.  
 (B) If highest energy photon emitted from the above sample is incident on the metal plate having work function 8 eV, AKE of liberated photo-electron may be equal to or less than 4.75 eV.  
 (C) Total number of radial nodes in all the orbitals of nth shell is 24.  
 (D) Total number of angular nodes in all the orbitals in (n-1)th shell is 23.

- 69\*.** In a H-like sample electrons make transition from 4th excited state to 2<sup>nd</sup> state then  
 (A) 10 different spectral lines are observed  
 (B) 6 different spectral lines are observed  
 (C) number of lines belonging to the balmier series is 3  
 (D) Number of lines belonging to paschen series is 2.
- 70.** Gaseous state electronic configuration of nitrogen atom can be represented as : [JEE 1999]  
 (A)  $\uparrow\downarrow \uparrow\downarrow \uparrow \uparrow \uparrow$  (B)  $\uparrow\downarrow \uparrow\downarrow \uparrow \downarrow \uparrow$  (C)  $\uparrow\downarrow \uparrow\downarrow \uparrow \downarrow \downarrow$  (D)  $\uparrow\downarrow \uparrow\downarrow \downarrow \downarrow \downarrow$
- 71.** The electronic configuration of an element is  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$ . This represents its : [JEE 2000]  
 (A) excited state (B) ground state (C) cationic form (D) none
- 72.** Which is true about an electron -  
 (A) rest mass of electron is  $9.1 \times 10^{-28}$  g  
 (B) mass of electron increases with the increase in velocity  
 (C) molar mass of electron is  $5.48 \times 10^{-4}$  g/mole  
 (D)  $e/m$  of electron is  $1.7 \times 10^8$  coulomb/g
- 73.** In a hydrogen like sample electron is in 2<sup>nd</sup> excited state, the Binding energy of 4th state of this sample is 13.6 eV, then  
 (A) A 25 eV photon can set free the electron from the second excited state of this sample.  
 (B) 3 different types of photon will be observed if electrons make transition up to ground state from the second excited state  
 (C) If 23 eV photon is used then K. E. of the-ejected electron is 1 eV.  
 (D) 2<sup>nd</sup> line of Balmer series of this sample has same energy value as 1st excitation energy of H-atoms.
- 74\*.** A hydrogen like atom in ground state absorbs 'n' photons having the same energy and it emits exactly 'n' photons when electronic transition takes place. Then the energy of the absorbed photon may be  
 (A) 91.8 eV (B) 40.8 eV (C) 48.4 eV (D) 54.4 eV

### Match the Column

- 75\*.** Frequency = f, Time period = T, Energy of n<sup>th</sup> orbit =  $E_n$ , radius of n<sup>th</sup> orbit =  $r_n$ , Atomic number = Z, Orbit number = n :

#### Column-I

- (A) f  
 (B) T  
 (C)  $E_n$   
 (D)  $\frac{1}{r_n}$

#### Column-II

- (p)  $n^3$   
 (q)  $Z^2$   
 (r)  $\frac{1}{n^2}$   
 (s) Z

- 76.** Match the following:

#### Column I

- (A) Orbital with equal number of radial and angular nodes  
 (B) Orbital with number of radial nodes less than the number of angular nodes  
 (C) Orbital with zero radial nodes but two angular node.

#### Column II

- (p)  $3d_{x^2-y^2}$   
 (q)  $2p_z$   
 (r)  $3p_x$   
 (s)  $5d_{xy}$

**77. Column-I**

- (A) Aufbau principle
- (B) de broglie
- (C) Angular momentum
- (D) Hund's rule
- (E) Balmer series
- (F) Planck's law

**Column-II**

- (p) Line spectrum in visible region
- (q) Orientation of an electron in an orbital
- (r) Photon
- (s)  $\lambda = h/mv$
- (t) Electronic configuration
- (u)  $mvr$

**Comprehension**

**Read the following rules and answer the questions at the end of it.**

Electrons in various suborbits of an orbit are filled in increasing order to their energies.

Pairing of electrons in various orbitals of a suborbit takes place only after each orbital is half-filled.

No two electrons in an atom can have the same set of quantum number.

- 78.** Cr ( $Z = 24$ ),  $Mn^+$  ( $Z = 25$ ),  $Fe^{2+}$  ( $Z = 26$ ) and  $Co^{3+}$  ( $Z = 27$ ) are isoelectronic each having 24 electrons.

Thus,

- (A) all have configurations as  $[Ar] 4s^1 3d^5$
- (B) Cr and  $Mn^+$  have configurations as  $[Ar] 4s^1 3d^5$  while  $Fe^{2+}$  and  $Co^{3+}$  have configurations as  $[Ar] 3d^6$ .
- (C) all have configurations as  $[Ar] 3d^6$
- (D) all have configurations as  $[Ar] 4s^2 3d^6$

- 79.** A compound of vanadium has a magnetic moment of 1.73 BM. Electronic configuration of the vanadium ion in the compound is :

- (A)  $[Ar] 4s^0 3d^1$
- (B)  $[Ar] 4s^2 3d^3$
- (C)  $[Ar] 4s^1 3d^0$
- (D)  $[Ar] 4s^0 3d^5$

- 80.** Which of these ions are expected to be paramagnetic and coloured in aqueous solution ?

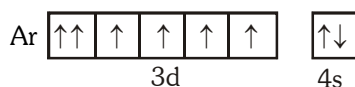
- (A)  $Fe^{3+}$ ,  $Ti^{3+}$ ,  $Co^{3+}$
- (B)  $Cu^+$ ,  $Ti^{4+}$ ,  $Sc^{3+}$
- (C)  $Fe^{3+}$ ,  $Ni^{2+}$ ,  $V^{5+}$
- (D)  $Cu^+$ ,  $Cu^{2+}$ ,  $Fe^{2+}$

- 81.** While writing the following electronic configuration of Fe some rules have been violated :

I : Aufbau rule,

II : Hund's rule

III : Pauli's exclusion principle



- (A) I, II
- (B) II, III
- (C) I, III
- (D) III

- 82.** How many elements would be in the second period of the periodic table if the spin quantum number ( $m_s$ ) could

have the value of  $-\frac{1}{2}, 0, +\frac{1}{2}$  ?

- (A) 8
- (B) 10
- (C) 12
- (D) 18

- 83.** The sub-shell that arises after  $f$  sub-shell is called  $g$  sub-shell.

- (A) it contains 18 electrons and 9 orbitals
- (B) it corresponds to  $\ell = 4$  and first occurs in 5th energy level
- (C) a  $g$ -orbital can have maximum of two electrons
- (D) all the above statements are true.

**Subjective Questions**

- 84\*.** An alpha particle after passing through a potential difference of  $2 \times 10^6$  volt falls on a silver foil. The atomic number of silver is 47. Calculate :
- the K.E. of the alpha-particle at the time of falling on the foil.
  - K.E. of the  $\alpha$ -particle at a distance of  $5 \times 10^{-14}$  m from the nucleus,
  - the shortest distance from the nucleus of silver to which the  $\alpha$ -particle reaches.
- 85\*.** A beam of some kind of particle of velocity  $2 \times 10^7$  m/s is scattered by a gold ( $z = 79$ ) foil. Find specific charge of this particle (charge / mass) if the distance of closest approach is  $7.9 \times 10^{-14}$  m.
- 86\*.** A certain dye absorbs light of  $\lambda = 4530 \text{ \AA}$  and then fluorescence light of  $5080 \text{ \AA}$ . Assuming that under given conditions 47% of the absorbed energy is re-emitted out as fluorescence, calculate the ratio of number of quanta emitted out to the number of quanta absorbed. radiations. Find the wavelength of these induced radiations.
- 87.** The  $IP_1$  of H is 13.6 V. It is exposed to electromagnetic waves of  $1028 \text{ \AA}$  and gives out induced.
- 88.** An electron in a hydrogen like species is in the excited state  $n_2$ . The wavelength for the transition from  $n_2$  to  $n_1 = 2$  is 48.24 nm. The corresponding wavelength for the transition  $n_2$  to  $n_1 = 3$  is 142.46 nm. Find the value of  $n_2$  and  $Z$  and report the H like atom.
- 89\*.** When electromagnetic radiation of wavelength 300 nm falls on the surface of sodium, electrons are emitted with a kinetic energy of  $1.68 \times 10^5 \text{ J mol}^{-1}$ . What is the minimum energy needed to remove an electron from sodium ? What is the maximum wavelength that will cause a photoelectron to be emitted?
- 90.** How long would it take a radio wave of frequency  $6 \times 10^3 \text{ sec}^{-1}$  to travel from mars to the earth, a distance of  $8 \times 10^7 \text{ km}$  ?
- 91.** The energy levels of hypothetical one electron atom are shown below.
- |          |   |              |
|----------|---|--------------|
| 0 eV     | — | $n = \infty$ |
| -0.50 eV | — | $n = 5$      |
| -1.45 eV | — | $n = 4$      |
| -3.08 eV | — | $n = 3$      |
| -5.3 eV  | — | $n = 2$      |
| -15.6 eV | — | $n = 1$      |
- Find the ionisation potential of atom?
  - Find the short wavelength limit of the series terminating at  $n = 2$  ?
  - Find the wave no. of photon emitted for the transition made by the electron from third orbit to first orbit ?
  - Find the minimum energy that an electron will have after interacting with this atom in the ground state, if the initial kinetic energy of the electron is (i) 6eV (ii) 11 eV ?
- 92.** Suppose  $10^{-17} \text{ J}$  of light energy is needed by the interior of the human eye to see an object. How many photons of green light ( $\lambda = 550 \text{ nm}$ ) are needed to generate this minimum amount of energy?
- 93.** Find the number of photons of radiation of frequency  $5 \times 10^{13} \text{ s}^{-1}$  that must be absorbed in order to melt one g ice when the latent heat of fusion of ice is  $330 \text{ J/g}$ .
- 94.** The eyes of certain member of the reptile family pass a single visual signal to the brain when the visual receptors are struck by photons of wavelength 850 nm. If a total energy of  $3.15 \times 10^{-14} \text{ J}$  is required to trip the signal, what is the minimum number of photons that must strike the receptor?
- 95.** To what series does the spectral lines of atomic hydrogen belong if its wave number is equal to the difference between the wave number of the following two lines of the Balmer series 486.1 and 410.2 nm. What is the wavelength of this ?

- 96.** Calculate the threshold frequency of metal if the binding energy is  $180.69 \text{ kJ mol}^{-1}$  of electron.
- 97.** Calculate the binding energy per mole when threshold wavelength of photon is  $240 \text{ nm}$ .
- 98.** A metal was irradiated by light of frequency  $3.2 \times 10^{15} \text{ s}^{-1}$ . The photoelectron produced had its KE, 2 times the KE of the photoelectron which was produced when the same metal was irradiated with a light of frequency  $2.0 \times 10^{15} \text{ s}^{-1}$ . What is work function ?
- 99.** U.V. light of wavelength  $800 \text{ \AA}$  &  $700 \text{ \AA}$  falls on hydrogen atoms in their ground state & liberates electrons with kinetic energy  $1.8 \text{ eV}$  and  $4 \text{ eV}$  respectively. Calculate planck's constant.
- 100.** A potential difference of  $20 \text{ kV}$  is applied across an X-ray tube. Find the minimum wavelength of X-ray generated.
- 101.** The K.E. of an electron emitted from tungsten surface is  $3.06 \text{ eV}$ . What voltage would be required to bring the electron to rest.
- 102.** What is de-Broglie wavelength of a He-atom in a container at room temperature.  $\left( \text{Use } U_{\text{avg.}} = \sqrt{\frac{8kT}{\pi m}} \right)$
- 103.** Through what potential difference must an electron pass to have a wavelength of  $500 \text{ \AA}$ .
- 104.** A proton is accelerated to one tenth of the velocity of light. If its velocity can be measured with a precision  $\pm 1\%$ . What must be its uncertainty in position ?
- 105.** To what effective potential a proton beam be subjected to give its protons a wavelength of  $1 \times 10^{-10} \text{ m}$ .
- 106.** Calculate the number of exchange pairs of electrons present in configuration of Cu according to Aufbau principle considering 3d orbitals.
- 107.** He atom can be excited to  $1s^1 2p^1$  by  $\lambda = 58.44 \text{ nm}$ . If lowest excited state for He lies  $4857 \text{ cm}^{-1}$  below the above. Calculate the energy for the lower excitation state.
- 108.** A certain dye absorbs  $4530 \text{ \AA}$  and fluorescence at  $5080 \text{ \AA}$  these being wavelengths of maximum absorption that under given conditions 47% of the absorbed energy is emitted. Calculate the ratio of the no. of quanta emitted to the number absorbed.
- 109.** The dissociation energy of  $\text{H}_2$  is  $430.53 \text{ kJ/mol}$ . If  $\text{H}_2$  is exposed to radiant energy of wavelength  $253.7 \text{ nm}$ , what % of radiant energy will be converted into K.E ?
- 110.** Iodine molecule dissociates into atoms after absorbing light of  $4500 \text{ \AA}$  If one quantum of radiation is absorbed by each molecule, calculate the K.E. of iodine atoms.  
(Bond energy of  $\text{I}_2 = 240 \text{ kJ/mol}$ )
- 111.** What is de-Broglie wavelength associated with an  $e^-$  accelerated through potential difference of  $100 \text{ kV}$  ?
- 112.** Calculate the de-broglie wavelength associated with motion of earth (mass  $6 \times 10^{24} \text{ kg}$ ) orbiting around the sun at a speed of  $3 \times 10^6 \text{ m/s}$ .
- 113.** A base ball of mass  $200 \text{ g}$  is moving with velocity  $30 \times 10^2 \text{ cm/s}$ . If we can locate the base ball with error equal in magnitude to the  $\lambda$  of the light used ( $5000 \text{ \AA}$ ), how will the uncertainty in momentum compared with the total momentum of base ball ?
- 114.** An electron has a speed of  $40 \text{ m/s}$ , accurate up  $99.99\%$ . What is the uncertainty in locating position?

**115.** Instead of principal quantum number ( $n$ ), azimuthal quantum number ( $l$ ) & magnetic quantum number  $m$ , a set of new quantum numbers  $s$ ,  $t$  and  $u$  was introduced with similar logic but different values as defined below.

$s = 1, 2, 3, \dots, \infty$  all positive integral values.

$t = (s^2 - 1^2), (s^2 - 2^2), (s^2 - 3^2) \dots$  No negative value

$u = -\frac{(t+1)}{2} \text{ to } +\frac{(t+1)}{2}$  (including zero, if any) in integral steps.

Each orbital can have maximum four electrons.

$(s + t)$  rule is defined, similar to  $(n + l)$  rule.

(i) Number of electrons that can be accommodated in  $s = 2$  and  $s = 3$  shell.

(ii) Number of electrons for which  $s = 2$ ,  $t = 3$  for an element with atomic number 24.

(iii) The number of subshells in which the third shell is subdivided equal to

**116.** Calculate the Rydberg constant  $R$  if  $\text{He}^+$  ions are known to have the wavelength difference between the first (of the longest wavelength) lines of Balmer and Lyman series equal to 133.7 nm.

**117.** Calculate the wavelength in angstrom of photon that is emitted when an  $e^-$  in Bohr orbit  $n = 2$  returns to the orbit  $n = 1$ . The ionization potential of the ground state of hydrogen atom is  $2.17 \times 10^{-11}$  erg/atom.

**118.** One mole  $\text{He}^+$  ions are excited. Spectral analysis showed existence of 50% ions in 3<sup>rd</sup> orbit, 25% in 2<sup>nd</sup> and rest in ground state. Calculate total energy evolved when all the ions return to the ground state.

**119.** Calculate the frequency of  $e^-$  in the first Bohr orbit in a H-atom.

**120.** How many electrons are present in P-shell.

**121.** According to Aufbau's Principle, the maximum of electron that can be accommodated in the outermost orbit (ab) and the penultimate orbit (cd) is :

**122.** To what series does the spectral lines of atomic hydrogen belong if its wave number is equal number is equal to the difference between the wave numbers of the following two lines of the Balmer series 486.1 and 410.2 nm? What is the wavelength of this line ?

**123.** Hydrogen atom in its ground state is excited by means of monochromatic radiation of wavelength 975 Å. How many different lines are possible in the resulting spectrum? Calculate the longest wavelength amongst them.

**124.** Identify number of correct statements.

(A) Weight of 0.002 gm-atom of fluorine is 38 mg.

(B) Average atomic weight of an element is the weight of most of the atoms.

(C) The value of ' $l$ ' for 5th electron of any element ( $Z > 5$ ) will be same.

(D) In case of CO weight of carbon atoms is equal to weight of oxygen atoms.

(E) The value of ' $m$ ' must be zero for last electron of Ne.

(F) To obtain 0.1 mole of  $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$  weight of oxygen required is 64 g.

(G)  $\text{N}^{3-}$  and  $\text{P}^{3-}$  are isoelectronic.

(H) Hydrogen(H) and Deuterium (D) are isobars.

**125.** Find the number of electrons having the value of azimuthal quantum number ' $l$ ' = 1 for  $\text{Cd}^{2+}$ .

**126.** (a) The Schrodinger wave equation for hydrogen atom is

[IIT-2004]

$$\psi_{2s} = \frac{1}{4(2\pi)^{1/2}} \left( \frac{1}{a_0} \right)^{3/2} \left( 2 - \frac{r_0}{a_0} \right) e^{-r/a}$$

Where  $a_0$  is Bohr's radius. Let the radial node in 2s be at  $r_0$ . Then find  $r_0$  in terms of  $a_0$ .

(b) A base ball having mass 100 g moves with velocity 100 m/s. Find out the value of wavelength of base ball.



- 127.** (a) Calculate velocity of electron in first Bohr orbit of hydrogen atom (Given  $r = a_0$ ) [IIT-2005]  
 (b) Find de-Broglie wavelength of the electron in first Bohr orbit.  
 (c) Find the orbital angular momentum of 2p-orbital in terms of  $h/2\pi$  units.
- 128.** Find the quantum number 'n' corresponding to the excited state of  $\text{He}^+$  ion if on transition to the ground state that ion emits two photons in succession with wavelengths 108.5 and 30.4 nm.
- 129\*.** A gas of identical H-like atom has some atoms in the lowest (ground) energy level A and some atoms in a particular upper (excited) energy level B and there are no atoms in any other energy level. The atoms of the gas make transition to a higher energy level by absorbing monochromatic light of photon energy 2.7 eV. Subsequently, the atoms emit radiation of only six different photons energies. Some of the emitted photons have energy 2.7 eV. Some have more and some have less than 2.7 eV.  
 (a) Find the principal quantum number of initially excited level B.  
 (b) Find the ionisation energy for the gas atoms.  
 (c) Find the maximum and the minimum energies of the emitted photons.
- 130\*.** A hydrogen like atom (atomic number Z) is in a higher excited state of quantum number n. This excited atom can make a transition to the first excited state by successively emitting two photons of energies 10.20 eV and 17.00 eV respectively. Alternatively, the atom from the same excited state can make a transition to the second excited state by successively emitting two photons of energy 4.25 eV and 5.95 eV respectively. Determine the values of n and z (ionisation energy of hydrogen atom = 13.6 eV).
- 131.** An energy of 68 eV is required to excite a hydrogen like atom from its second Bohr orbit to the third. The nuclear charge is Ze. Find the value of Z, the kinetic energy of the electron in the first Bohr orbit and the wavelength of the radiation required to eject the electrons from the first Bohr orbit to infinity.
- 132.** The ionisation energy of a H-like Bohr atom is 4 Rydbergs.  
 (i) What is the wavelength of radiation emitted when the  $e^-$  jumps from the first excited state to the ground state?  
 (ii) What is the radius of first Bohr orbit for this atom? [1 Rydberg =  $2.18 \times 10^{-18}$  J]
- 133\*.** Photon having wavelength 12.4 nm was allowed to strike a metal plate having work function 25 eV. Calculate the -  
 (a) Maximum kinetic energy of photoelectrons emitted in eV.  
 (b) Wavelength of electron with maximum kinetic energy in  $\text{\AA}$ .  
 (c) Calculate the uncertainty in wavelength of emitted electron, if the uncertainty in the momentum is  $6.62 \times 10^{-28}$  kg m/sec.
- 134\*.** Electron present in single electron species jumps from energy level 3 to 1. Emitted photons when passed through a sample containing excited  $\text{He}^+$  ion causes further excitation to some higher energy level (Given  $E_n = 13.6 \frac{Z^2}{n^2}$ ) : Determine .  
 (i) Atomic number of single electron species.  
 (ii) Principal quantum number of initial excited level & higher energy of  $\text{He}^+$
- 135\*.** The angular momentum of an electron in a Bohr's orbit of H-atom is  $3.1652 \times 10^{-34}$  kg-m<sup>2</sup>/sec. Calculate the wave number in terms of Rydberg constant (R) of the spectral line emitted when an electron falls from this level to the ground state. (Use  $h = 6.626 \times 10^{-34}$  Js).
- 136.** If for any electron in an orbital another parameter 'B' is defined as  $B = n + l + m$ , where n, l, m are the quantum numbers of that orbital then what will be the maximum value of B for the last electron of  ${}_{35}\text{Br}$ .
- 137.** In case of nitrogen, if  $M_1$  represents spin multiplicity if Hund's rule is followed and  $M_2$  represents spin multiplicity if only Hund's Rule is violated then the value of  $\frac{M_1}{M_2}$  will be:

## ANSWERS

• **True and False**

1. False      2. False      3. True      4. True      5. True

• **Fill in the Blanks**

6. 32      7. 2<sup>nd</sup>      8. frequency or wavelength      9. 14  
 10. 3, (4, 5, 6,....)

• **Assertion-Reason**

11. (A)      12. (A)      13. (B)      14. (A)      15. (A)  
 16. (A)      17. (B)      18. (A)      19. (A)

• **Single Choice Correct**

- |         |         |         |         |         |
|---------|---------|---------|---------|---------|
| 20. (C) | 21. (A) | 22. (D) | 23. (C) | 24. (C) |
| 25. (C) | 26. (D) | 27. (D) | 28. (B) | 29. (B) |
| 30. (A) | 31. (D) | 32. (B) | 33. (D) | 34. (B) |
| 35. (A) | 36. (C) | 37. (D) | 38. (A) | 39. (B) |
| 40. (D) | 41. (A) | 42. (D) | 43. (D) | 44. (B) |
| 45. (D) | 46. (C) | 47. (C) | 48. (A) | 49. (B) |
| 50. (C) | 51. (A) | 52. (C) | 53. (C) | 54. (B) |
| 55. (D) | 56. (A) | 57. (D) | 58. (C) | 59. (D) |
| 60. (C) |         |         |         |         |

• **Multi Choice Correct**

- |           |            |            |            |          |
|-----------|------------|------------|------------|----------|
| 61. (ACD) | 62. (AC)   | 63. (ABCD) | 64. (ABD)  | 65. (AC) |
| 66. (ACD) | 67*. (ABC) | 68*. (CD)  | 69*. (BCD) | 70. (AD) |
| 71. (BC)  | 72. (ABCD) | 73. (AB)   | 74. (AB)   |          |

• **Match the Column**

- 75\*. (A) → q ; (B) → p ; (C) → q,r ; (D) → r,s  
 76. (A) - (rs), (B) - (qp), (C) - (p)  
 77. (A) → t; (B) → s ; (C) → u ; (D) → q ; (E) → p; (F) → r

• **Comprehension**

78. (B)      79. (A)      80. (A)      81. (D)      82. (C)  
 83. (D)

• **Subjective Questions**

84. (i)  $6.4 \times 10^{-13}$  J    (ii)  $2.1 \times 10^{-13}$  J,    (iii)  $3.4 \times 10^{-14}$  m  
 85.  $1.39 \times 10^8$  C/kg  
 86. 0.526  
 87. I induced = 1028 Å, II induced = 1216 Å, III induced = 6568 Å  
 88.  $n_2 = 5$ ,  $Z = 3$ ,  $\text{Li}^{2+}$ .  
 89. 517 nm.  
 90.  $2.66 \times 10^2$  sec  
 91. (a) 15.6 eV      (b) 233.9 nm,  
       (c)  $1.008 \times 10^7 \text{ m}^{-1}$       (d) (i) electron will not interact (ii) 0.7 eV  
 92. 28 photons      93.  $10^{22}$       94.  $1.35 \times 10^5$   
 95. Brackett ;  $2.63 \times 10^{-4}$  m      96.  $4.5 \times 10^{14} \text{ s}^{-1}$       97. 497 kJ/mol  
 98. 319.2 kJ/mol      99.  $6.57 \times 10^{-34}$  Js      100. 0.62 A°  
 101. 3.06 V      102. 0.79 A°      103.  $6.03 \times 10^{-4}$  volt  
 104.  $1.05 \times 10^{-13}$  m      105. 0.0826 volts      106. (16)

- 107.**  $3.3 \times 10^{-18} \text{ J}$       **108.** 0.527      **109.** 8.68 %  
**110.**  $2.186 \times 10^{-20} \text{ Joules}$       **111.** 3.88 pm      **112.**  $3.68 \times 10^{-65} \text{ m}$   
**113.**  $1.75 \times 10^{-29}$       **114.** 0.0144 m      **115.** (i) 28, 76 ; (ii) (0) ; (iii) (3)  
**116.**  $1.096 \times 10^7 \text{ m}^{-1}$       **117.**  $1220 \text{ A}^\circ$       **118.**  $331.13 \times 10^4 \text{ J}$   
**119.**  $6530 \times 10^{12} \text{ Hz}$       **120.** (72)      **121.** (818)  
**122.**  $n_1 = 4, n_2 = 6, 2.63 \times 10^{-4} \text{ cm}$       **123.** six,  $18800 \text{ A}^\circ$   
**124.** (3)      **125.** (18)      **126.** (a)  $r_0 = 2a_0$  ; (b)  $6.626 \times 10^{-35} \text{ m}$   
**127.** (a)  $2.197 \times 10^6 \text{ m/s}$   
           (b)  $3.31 \text{ \AA}$   
           (c)  $\sqrt{2} \cdot \frac{h}{2\pi}$   
**128.**  $n = 5$       **129\*.** (a)  $n = 2$ , (b) 14.4 eV, (c) 13.5eV, 0.7eV  
**130\*.**  $n = 6, Z = 3$       **131.** 6 ; 489.6 eV,  $25.28 \text{ A}^\circ$   
**132.**  $300.89 \text{ A}^\circ, 2.645 \times 10^{-9} \text{ cm}$       **133\*.** (a) 75 eV ; (b)  $1.414 \text{ A}^\circ$  ; (c)  $2 \times 10^{-14} \text{ m}$   
**134\*.** (i)  $Z = 1$  (ii) For  $\text{He}^+$  ion this energy corresponds to excitation from 2 to 6.  
**135\*.**  $R \left( \frac{8}{9} \right)$       **136.** (6)      **137.** (2)

## GASEOUS STATE

### True / False

1. The volume occupied by 32 g of oxygen is greater than that occupied by 16 g of methane, both being at the same T and P.
2. A real gas can be liquefied if its temperature is greater than its critical temperature.
3. Kinetic energy of gaseous molecules is zero at 0°C.
4. The term  $V_m - b$  in vander waals equation represents the available volume where molecules of the gas can move.
5. The average speed of a gas varies linearly with increases of temperature.
6. A mixture of ideal gaseous is cooled upto liquid helium temperature (4.22 K) to form an ideal solution.
7. For a vander waals gas  $V_c = 3b$ ,  $P_c = a/27b^2$ ,  $T_c = 8a/27bR$ . Numerically the compressibility factor of a vander waals gas at the critical points is  $Z = 0.375$ .

### Fill in the blanks

8. The value of PV for 5.6 L of an ideal gas is ..... RT at STP.
9. The density of an ideal gas ..... with increase in temperature of the gas, provided the pressure remains constant.
10. The unit of vander waals constant 'a' in SI units is .....
11. 0.5 L of a certain gas at STP weighs 0.58 g. Its molar mass is ..... g mol<sup>-1</sup>.
12. The root means square speed of methane gas will be ..... that of helium gas both having the same temperature and pressure.
13. (i) The rate of diffusion of a gas is ..... proportional to ..... or square root of molecular mass.  
(ii) The total energy of one mole of gas (ideal monoatomic) at 27°C is ..... calorie.  
(iii) Equal masses of SO<sub>2</sub> and O<sub>2</sub> are kept in a vessel at 27°C. The total pressure is 2 atm. The partial pressure of SO<sub>2</sub> is .....
14. (i) There is no effect of ..... on the motion of gas molecules.  
(ii) If the density of a gas at 27°C and 1 atmospheric pressure is 1.8 g lit<sup>-1</sup>, its molecular mass is .....  
(iii) If the speed of a molecule at 27°C is 0.25 metre sec<sup>-1</sup>, its speed at 927°C will be .....  
(iv) A steel vessel of capacity 22.4 litre contains 2 g of hydrogen, 8g of oxygen and 22 g of carbon dioxide at a temperature of 0°C. The total pressure of the gas is .....
15. A gas has a volume of 580 cm<sup>3</sup> at a certain pressure. If its pressure is increased by 0.96 atm, its volume becomes 100 cm<sup>3</sup>. The new pressure of the gas is .....

### Assertion & Reason

These questions contains, Statement I (assertion) and Statement II (reason).

(A) Statement-I is true, Statement-II is true ; Statement-II is correct explanation for Statement-I.

(B) Statement-I is true, Statement-II is true ; Statement-II is NOT a correct explanation for statement-I

(C) Statement-I is true, Statement-II is false

(D) Statement-I is false, Statement-II is true

16. **Statement-I** : Plot of P Vs. 1/V (volume) is a straight line.

**Because**

**Statement-II** : Pressure is directly proportional to volume.

17. **Statement-I** : Absolute zero is a theoretically possible temperature at which the volume of the gas becomes zero.

**Because**

**Statement-II** : The total kinetic energy of the molecule is zero at this temperature.

- 18. Statement-I :** Critical temperature of the gas is the temperature at which it occupies 22.4 L of volume.  
**Because**  
**Statement-II :** Molar volume of every gas at NTP is 22.4 L.
- 19. Statement-I :** Excluded volume or co-volume equals to  $(v-nb)$  for  $n$  moles.  
**Because**  
**Statement-II :** Co-volume depends on the effective size of gas molecules.
- 20. Statement-I :** Most probable velocity is the velocity possessed by maximum fraction of molecules at the same temperature.  
**Because**  
**Statement-II :** On collision, more and more molecules acquire higher speed at the same temperature.
- 21. Statement-I :** The diffusion rate of oxygen is smaller than that of nitrogen.  
**Because**  
**Statement-II :** Molecular size of nitrogen is smaller than that of oxygen.

### Single Choice Correct

- 22\*.** A certain volume of argon gas (Mol Wt. 40) requires 45 s to effuse through a hole at a certain pressure and temperature. The same volume of another gas of unknown molecular weight requires 60 s to pass through the same hole under the same conditions of temperature and pressure. The molecular weight of the gas is  
 (A) 53 (B) 35 (C) 71 (D) 120
- 23\*.** Two closed vessel A and B of equal volume containing air at pressure  $P_1$  and temperature  $T_1$  are connected to each other through a narrow open tube. If the temperature of one is now maintained at  $T_1$  and other at  $T_2$  (where  $T_1 > T_2$ ) then that what will be the final pressure ?  
 (A)  $\frac{T_1}{2P_1T_2}$  (B)  $\frac{2P_1T_2}{T_1 + T_2}$  (C)  $\frac{2P_1T_2}{T_1 - T_2}$  (D)  $\frac{2P_1}{T_1 + T_2}$
- 24\*.** A balloon containing 1 mole air at 1 atm initially is filled further with air till pressure increases to 4 atm. The initial diameter of the balloon is 1 m and the pressure at each stage is proportion to diameter of the balloon. How many no. of moles of air added to change the pressure from 1 atm to 4 atm :  
 (A) 80 (B) 257 (C) 255 (D) 256
- 25\*.** What is the density of wet air with 75% relative humidity at 1 atm and 300 K? Given : vapour pressure of  $H_2O$  is 30 torr and average molar mass of air is  $29 \text{ g mol}^{-1}$  :  
 (A) 1.614 g/L (B) 0.96 g/L (C) 1.06 g/L (D) 1.164 g/L
- 26\*.** Consider the following statements :  
 The coefficient B in the virial equation on state
- $$PV_m = RT \left( 1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \dots \right)$$
- a : is independent of temperature  
 b : is equal to zero at Boyle temperature  
 c : has the dimension of molar volume

Which of the above statements are correct.

- (A) a and b (B) a and c (C) b and c (D) a, b and c

**27\*.** Consider the following statements : If the vander Waal's parameters of two gases are given as

a (atm lit<sup>2</sup> mol<sup>-2</sup>)      b (lit mol<sup>-1</sup>)

Gas X : 6.5      0.056

Gas Y : 8.0      0.011

then a :  $V_c(X) < V_c(Y)$

b :  $P_c(X) < P_c(Y)$

c :  $T_c(X) < T_c(Y)$

Select correct alternate :

- (A) a alone (B) a and b (C) a, b and c (D) b and c

**28\*.** At low pressures, the vander Waal's equation is written as :

$$\left[ p + \frac{a}{V^2} \right] V = RT$$

The compressibility factor is then equal to :

- (A)  $\left( 1 - \frac{a}{RTV} \right)$  (B)  $\left( 1 - \frac{RTV}{a} \right)$  (C)  $\left( 1 + \frac{a}{RTV} \right)$  (D)  $\left( 1 + \frac{RTV}{a} \right)$

**29\*.** NH<sub>3</sub> gas is liquefied more easily than N<sub>2</sub>. Hence :

(A) vander Waal's constants 'a' and 'b' of NH<sub>3</sub> > that of N<sub>2</sub>

(B) vander Waal's constants 'a' and 'b' of NH<sub>3</sub> < that of N<sub>2</sub>

(C) a (NH<sub>3</sub>) > a (N<sub>2</sub>) but b (NH<sub>3</sub>) < b (N<sub>2</sub>)

(D) a (NH<sub>3</sub>) < a (N<sub>2</sub>) but b (NH<sub>3</sub>) > b (N<sub>2</sub>)

**30\*.** For the non-zero values of force of attraction between gas molecules, gas equation will be :

- (A)  $PV = nRT - \frac{n^2a}{V}$  (B)  $PV = nRT + nbP$  (C)  $PV = nRT$  (D)  $P = \frac{nRT}{V-b}$

**31.** Compressibility factor for H<sub>2</sub> behaving as real gas is :

- (A) 1 (B)  $\left( 1 - \frac{a}{RTV} \right)$  (C)  $\left( 1 + \frac{Pb}{RT} \right)$  (D)  $\frac{RTV}{(1-a)}$

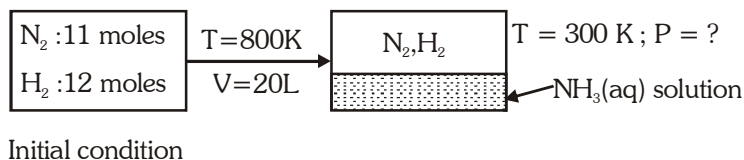
**32.** Equal masses of methane and oxygen are mixed in an empty container at 25°C. The fraction of the total pressure exerted by oxygen is :

- (A) 1/3 (B) 1/2 (C) 2/3 (D) (1/3) (273/298)

**33.** On the surface of the earth at 1 atm pressure, a balloon filled with H<sub>2</sub> gas occupies 500 mL. This volume 5/6 of its maximum capacity. The balloon is left in air. It starts rising. The height above which the balloon will burst if temperature of the atmosphere remains constant and the pressure decreases 1 mm for every 100 cm rise of height is :

- (A) 120 m (B) 136.67 m (C) 126.67 m (D) 100 m

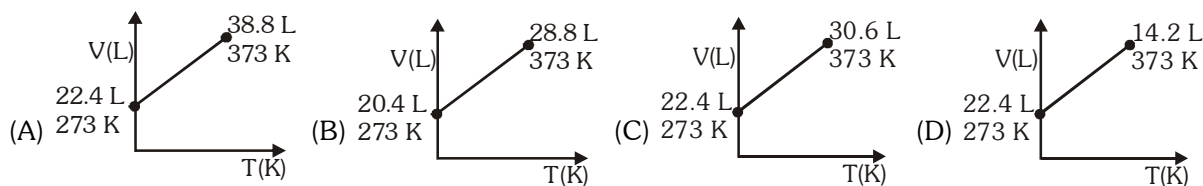
- 34\*. 11 moles  $N_2$  and 12 moles of  $H_2$  mixture reacted in 20 litre vessel at 800 K. After equilibrium was reached, 6 mole of  $H_2$  was present. 3.58 litre of liquid water is injected in equilibrium mixture and resultant gaseous mixture suddenly cooled to 300 K. What is the final pressure of gaseous mixture ? Neglect vapour pressure of liquid solution. Assume (i) all  $NH_3$  dissolved in water (ii) no change in volume of liquid (iii) no reaction of  $N_2$  and  $H_2$  at 300 K :



- (A) 18.47 atm      (B) 60 atm      (C) 22.5 atm      (D) 45 atm
35. The ratio between the r.m.s. velocity of  $H_2$  at 50 K and that of  $O_2$  at 800 K is. [JEE 1996]  
 (A) 4      (B) 2      (C) 1      (D) 1/4
36. X ml  $H_2$  gas effuses through a hole in a container in 5 sec. The time taken for the effusion of the same volume of the gas specified below under identical conditions is [JEE 1996]  
 (A) 10 sec, He      (B) 20 sec,  $O_2$       (C) 25 sec, CO      (D) 55 sec,  $CO_2$
37. One mole of  $N_2O_4$  (g) at 300 K is kept in a closed container under one atm. It is heated to 600 K when 20% by mass of  $N_2O_4$  (g) decomposes to  $NO_2$  (g). The resultant pressure is. [JEE 1996]  
 (A) 1.2 atm      (B) 2.4 atm      (C) 2.0 atm      (D) 1.0 atm
38. According to Graham's law, at a given temperature the ratio of the rates of diffusion  $\frac{r_A}{r_B}$  of gases A and B is given by. [JEE 1997]  
 (A)  $\frac{P_A}{P_B} \left( \frac{M_A}{M_B} \right)^{1/2}$       (B)  $\left( \frac{M_A}{M_B} \right) \left( \frac{P_A}{P_B} \right)^{1/2}$       (C)  $\frac{P_A}{P_B} \left( \frac{M_B}{M_A} \right)^{1/2}$       (D)  $\frac{M_A}{M_B} \left( \frac{P_B}{P_A} \right)^{1/2}$
39. A gas will approach ideal behaviour at : [JEE 1999]  
 (A) low temperature and low pressure      (B) low temperature and high pressure  
 (C) low pressure and high temperature      (D) high temperature and high pressure
40. The compressibility of a gas is less than unity at STP. Therefore : [JEE 2000]  
 (A)  $V_m > 22.4$  L      (B)  $V_m < 22.4$  L      (C)  $V_m = 22.4$  L      (D)  $V_m = 44.8$  L
41. The r.m.s. velocity of hydrogen is  $\sqrt{7}$  times the r.m.s. velocity of nitrogen. If T is the temperature of the gas [JEE 2000]  
 (A)  $T(H_2) = T(N_2)$       (B)  $T(H_2) > T(N_2)$       (C)  $T(H_2) < T(N_2)$       (D)  $T(H_2) = \sqrt{7} T(N_2)$
42. The root mean square velocity of an ideal gas at constant pressure varies with density as : [JEE 2001]  
 (A)  $d^2$       (B)  $d$       (C)  $d^{1/2}$       (D)  $1/d^{1/2}$

43. Which one of the following V, T plots represents the behaviour of one mole of an ideal gas at one atm?

[JEE 2002]



44. Positive deviation from ideal behaviour takes place because of.

[JEE 2003]

- (A) molecular interaction between atoms and  $\frac{PV}{nRT} > 1$
- (B) molecular interaction between atoms and  $\frac{PV}{nRT} < 1$
- (C) finite size of atoms and  $\frac{PV}{nRT} > 1$
- (D) finite size of atoms and  $\frac{PV}{nRT} < 1$

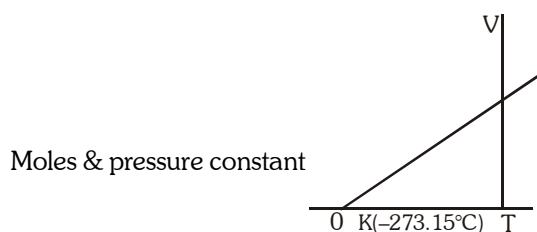
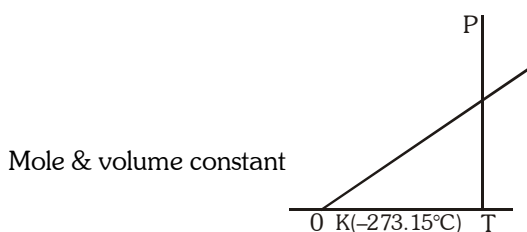
45. The ratio of the rate of diffusion of helium and methane under identical condition of pressure and temperature will be :

[JEE 2005]

- (A) 4 (B) 2 (C) 1 (D) 0.5

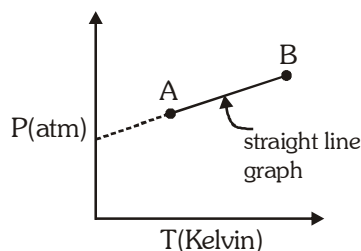
### Multi Choice Correct

46\*. What conclusions would you draw from the following graphs for ideal gas :



- (A) As the temperature is reduced, the volume as well as pressure increase under given condition.
- (B) As the temperature is reduced, the volume becomes zero and the pressure reaches infinity under given condition.
- (C) As the temperature is reduced, the volume as well as the pressure decrease under given condition.
- (D) A point is reached where theoretically, the volume as well as the pressure become zero under given condition.

47. For a fixed amount of an ideal gas P vs T plot is given as shown. Identify the **incorrect** option :



- (A) The change from A to B should be isochoric
- (B) Volume first increases reaches maxima and then decreases
- (C)  $PV = nRT$  is not applicable
- (D) None of the statements are correct



### Match the Column

48\*. Match the entries in **column I** with entries in **Column II** and then pick out correct options.

#### Column I

(A)  $\frac{1}{V^2}$  vs P for ideal gas at

constant T and n.

(B) V vs  $\frac{1}{T}$  for ideal gas at

constant P and n

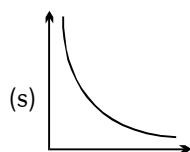
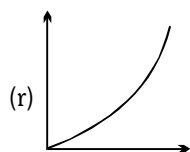
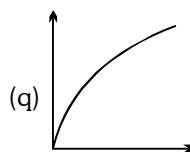
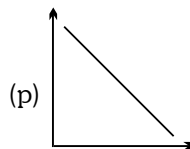
(C) log P vs log V for ideal gas

at constant T and n.

(D) V vs  $\frac{1}{P^2}$  for ideal gas

at constant T and n.

#### Column II



### Comprehension

The rate of change of pressure (p) of a gas at constant temperature and constant external pressure due to effusion of gas from a vessel of constant volume is related to rate of change of number of molecules present by

$$\frac{dp}{dt} = \frac{kT}{V} \frac{dN}{dt}$$

where k = Boltzmann constant, T = temperature, V = volume of vessel & N = No. of molecules and

$$\frac{dN}{dt} = \frac{-pA_0}{(2\pi mkT)^{1/2}}, \text{ where } A_0 = \text{area of orifice and } m = \text{mass of molecule.}$$

49\*. Time required for pressure inside vessel to reduce to 1/e of its initial value in ( $\ln e = 1$ )

(A)  $\left(\frac{2\pi m}{kT}\right)^{1/2} \frac{V}{A_0}$      
 (B)  $\left(\frac{kT}{2\pi m}\right)^{1/2} \frac{V}{A_0}$      
 (C)  $\left(\frac{2\pi mkT}{A_0}\right)^{1/2}$      
 (D)  $\frac{2\pi m}{kT} \frac{V}{A_0}$

50\*. If the gas inside the vessel had molecular weight 9 times the gas in previous example and area of orifice was doubled and temperature maintained at 4T, time required for pressure to fall to 1/e times of its initial value would be (t = answer of previous option)

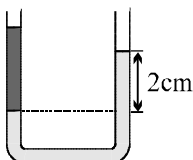
(A) 1.33 t     
 (B) 4.24 t     
 (C) 0.75 t     
 (D) 1.125 t

51\*. The incorrect statement (s) is/are.

- [I] Pressure will not fall to zero in infinite time.  
 [II] Time required for pressure to decrease to half its initial value is independent of initial pressure.  
 [III] The relations given above are true for real gases also.
- (A) I (B) II (C) III (D) I and III

### Subjective Questions

52\*. The liquids shown in the fig. in the two arms are mercury (specific gravity = 13.6) and water. If the difference of heights of the mercury columns in 2 cm. Find the height  $h$  of the water column.



53\*. A glass bulb of volume  $400 \text{ cm}^3$  is connected to another bulb of volume  $200 \text{ cm}^3$  by means of a tube of negligible volume. The bulbs contain dry air and are both at a common temperature and pressure of  $20^\circ\text{C}$  and  $1.00 \text{ atm}$ . The larger bulb is immersed in steam at  $100^\circ\text{C}$ ; the smaller, in melting ice at  $0^\circ\text{C}$ . Find the final common pressure.

54\*. 1500 mL flask contains 400 mg  $\text{O}_2$  and 60 mg  $\text{H}_2$  at  $100^\circ\text{C}$ .

(a) What is the total pressure in the flask?

(b) If the mixture is permitted to react to form water vapour at  $100^\circ\text{C}$ , what will be their partial pressures?

55. Calculate the temperature values at which the molecules of the first two members of the homologous series  $\text{C}_n\text{H}_{2n+2}$  will have the same rms speed as  $\text{CO}_2$  gas at 770 K. The normal b.p. of n-butane is 273 K. Assuming ideal gas behaviour of n-butane upto this temperature, calculate the mean velocity and the most probable velocity of its molecules at this temperature.

56. Calculate the temperature at which the root mean square velocity, average velocity and most probable velocity of oxygen gas are all equal to  $1500 \text{ ms}^{-1}$ .

57. The density of mercury is  $13.6 \text{ g/cm}^3$ . Estimate the  $b$  value.

58\*. The vander waals constants for gases A, B and C are as follows :

Gas	$a/\text{dm}^6 \text{ kPa mol}^{-2}$	$b/\text{dm}^3 \text{ mol}^{-1}$
A	405.3	0.027
B	1215.9	0.030
C	607.95	0.032

Which gas has (i) the highest critical temperature, (ii) the largest molecular volume, and (iii) most ideal behaviour around STP?

59. The vander waals constant for  $\text{O}_2$  are  $a = 1.36 \text{ atm L}^2 \text{ mol}^{-2}$  and  $b = 0.0318 \text{ L mol}^{-1}$ . Calculate the temperature

at which  $\text{O}_2$  gas behaves, ideally for longer range of pressure.

60. Calculate from the vander waal's equation, the temperature at which 192 g of  $\text{SO}_2$  would occupy a vol. of  $10 \text{ dm}^3$  at 15 atm pressure. [ $a = 6.7 \text{ atm L}^2 \text{ mol}^{-2}$ ,  $b = 0.0564 \text{ L mol}^{-1}$ ]

- 61\*.** Calculate the pressure of 15 mol neon at 30°C in a 12 litre container using  
 (i) the ideal gas equation  
 (ii) the vander waals equation  
 [ $a = 0.2107 \text{ atm L}^2 \text{ mol}^{-2}$ ,  $b = 0.0171 \text{ L mol}^{-1}$ ]
- 62.** A mixture of ideal gases is cooled upto liquid He temperature (4.22 K) to form an ideal solution. Is this statement **true** or **false**. Justify your answer in not more than two lines. **[JEE 1996]**
- 63.** The absolute temperature of an ideal gas is ..... to/than the average kinetic energy of the gas molecules. **[JEE 1997]**
- 64.** One way of writing the equation for state for real gases is,  $P\bar{V} = RT \left[ 1 + \frac{B}{\bar{V}} + \dots \right]$  where B is constant. Derive an approximate expression for 'B' in terms of Vander Waals constant 'a' & 'b'. **[JEE 1997]**
- 65.** Calculate the total pressure in a 10 litre cylinder which contains 0.4 g He, 1.6 g oxygen and 1.4 g nitrogen at 27°C. Also calculate the partial pressure of He gas in the cylinder. Assume ideal behaviour for gases. **[JEE 1997]**
- 66.** An evacuated glass vessel weighs 50.0 g when empty, 148.0 g when filled with a liquid of density 0.98 g/mL and 50.5 g when filled with an ideal gas at 760 mm Hg at 300 K. Determine the molecular weight of the gas. **[JEE 1998]**
- 67.** Using Vander Waals equation, calculate the constant "a" when 2 moles of a gas confined in a 4 litre flask exerts a pressure of 11.0 atm at a temperature of 300 K. The value of "b" is 0.05 litre mol<sup>-1</sup>. **[JEE 1998]**
- 68.** The pressure exerted by 12 g of an ideal gas at temperature t°C in a vessel of volume V is one atm. When the temperature is increased by 10 degrees at the same volume, the pressure increases by 10%. Calculate the temperature 't' and volume 'V'. [molecular weight of gas = 120] **[JEE 1999]**
- 69.** One mole of N<sub>2</sub> gas at 0.8 atm takes 38 sec to diffuse through a pin hole, whereas one mole of an unknown compound of Xenon with F at 1.6 atm takes 57 sec to diffuse through the same hole. Calculate the molecular formula of the compound. **[JEE 1999]**
- 70.** If the pressure of a fixed amount of an ideal gas is proportional to its temperature, then under these conditions frequency of collision and their impact both increase in proportion to the square root of temperature. True/False. **[JEE 2000]**
- 71.** Calculate the pressure exerted by one mole of CO<sub>2</sub> gas at 273 K, if the Vander Waals constant  $a = 3.592 \text{ dm}^6 \text{ atm mol}^{-2}$ . Assume that the volume occupied by CO<sub>2</sub> molecules is negligible. **[JEE 2000]**
- 72.** The compression factor (compressibility factor) for one mole of a vander Waals gas at 0°C and 100 atmos phere pressure is found to be 0.5. Assuming that the volume of a gas molecule is negligible, calculate the vander waals constant 'a'. **[JEE 2001]**
- 73.** The density of the vapour of a substance at 1 atm pressure and 500 K is 0.36 Kg m<sup>-3</sup>. The vapour effuse through a small hole at a rate of 1.33 times faster than oxygen under the same condition. **[JEE 2002]**  
 (a) Determine  
 (i) mol. wt. ; (ii) molar volume ; (iii) compressibility factor (z) of the vapour  
 (iv) which forces among the gas molecules are dominating the attractive or the repulsive.  
 (b) If the vapour behaves ideally at 1000 K, determine the average translational K.E. of a molecule.

- 74.** The average velocity of gas molecules is 400 m/sec. Calculate its (rms) velocity at the same temperature. **[JEE 2003]**
- 75.**  $C_v$  value of He is always  $3R/2$  but  $C_v$  value of  $H_2$  is  $3R/2$  at low temperature and  $5R/2$  at moderate temperature and more than  $5R/2$  at higher temperature explain in two to three lines. **[JEE 2003]**
- 76.** For a real gas obeying vander Waal's equation a graph is plotted between  $PV_m$  (y-axis) and  $P$  (x-axis) where  $V_m$  is molar volume. Find y-intercept of the graph. **[JEE 2005]**
- 77.** The temperature and the relative humidity of air are  $20^\circ\text{C}$  and 80% on a certain day. Find the fraction of the mass of water vapour that will condense if the temperature falls to  $5^\circ\text{C}$ . Saturation vapour pressures at  $20^\circ\text{C}$  and  $5^\circ\text{C}$  are 17.5 mm and 6.5 mm of Hg respectively.
- 78\*.** 6.0 g of He having average velocity  $4 \times 10^2 \text{ ms}^{-1}$  is mixed with 12.0 g of  $\text{Ne}^{20}$  having the same average velocity. What is the average kinetic energy per mole in the mixture?
- 79.** Molar volume of He at 10.1325 MPa and 273 K is 0.011075 times its molar volume at 101.325 kPa. Calculate radius of He atom assuming negligible 'a'.
- 80\*.** Pressure of He gas confined in a steel chamber drops from 4.0 to 1.0 atmosphere in 4.0 hours due to diffusion through a pin-hole in the steel chamber. If an equimolar mixture of He and methane gas at 20 atmosphere and the same temperature are confined in the same chamber, what will be the partial pressure of He and methane after 1.0 hour. Assume rate of diffusion to be linear function of gas pressure and inverse function of square root of molar masses.
- 81\*.** A mixture of  $\text{CH}_4$  &  $\text{O}_2$  is used as an optimal fuel if  $\text{O}_2$  is present in thrice the amount required theoretically for combustion of  $\text{CH}_4$ . Calculate number of effusions steps required to convert a mixture containing 1 part of  $\text{CH}_4$  in 193 parts mixture (parts by volume). If calorific value (heat evolved when 1 mole is burnt) of  $\text{CH}_4$  is 100 cal/mole & if after each effusion 90% of  $\text{CH}_4$  is collected. find out what initial mole of each gas in initial mixture required for producing 1000 cal of energy after processing. [Given  $(0.9)^5 = 0.6$ ]
- 82\*.** A water gas mixture has the composition by volume of 50%  $\text{H}_2$ , 45% CO and 5%  $\text{CO}_2$ .  
 (i) Calculate the volume in litres at STP of the mixture which on treatment with excess steam will contain 5 litres of  $\text{H}_2$ . The stoichiometry for the water gas shift reaction is  

$$\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$$
  
 (ii) Find the density of the water gas mixture in  $\text{kg/m}^3$ .  
 (iii) Calculate the moles of the absorbants KOH,  $\text{Ca}(\text{OH})_2$  and ethanolamine.  
 $\text{HO}-\text{CH}_2-\text{CH}_2-\text{NH}_2$  required respectively to collect the  $\text{CO}_2$  gas obtained.
- 83\*.** Calculate the pressure exerted by 22 g of carbon dioxide in  $0.5 \text{ dm}^3$  at 298.15 K using :  
 (a) the ideal gas law and (b) vander waals equation. Given :  
 $[a = 363.76 \text{ kPa dm}^6 \text{ mol}^{-2} \quad \text{and} \quad b = 42.67 \text{ cm}^3 \text{ mol}^{-1}]$
- 84\*.** The compressibility factor for  $\text{N}_2$  at  $-50^\circ\text{C}$  and 800 atm pressure is 1.95 and at  $100^\circ\text{C}$  and 200 atm, it is 1.10. A certain mass of nitrogen occupied one litre at  $-50^\circ\text{C}$  and 800 atm. Calculate the volume occupied by the same quantity of  $\text{N}_2$  at  $100^\circ\text{C}$  and 200 atm.
- 85.** At 273.15 K and under a pressure of 10.1325 MPa, the compressibility factor of  $\text{O}_2$  is 0.927. Calculate the mass of  $\text{O}_2$  necessary to fill a gas cylinder of  $100 \text{ dm}^3$  capacity under the given conditions.

## ANSWERS

• **True and False**

1. False      2. False      3. False      4. True      5. False  
 6. False      7. True

• **Fill in the Blanks**

8. 0.25      9. decreases  
 10.  $\text{Pa m}^6 \text{mol}^{-2}$       11. 26  
 12.  $\frac{1}{2}$       13. (i) inversely, square root of density, (ii) 900, (iii)  $\frac{2}{3}$   
 14. (i) gravity (ii) 44.33 (iii) 0.5 m/s (iv) 1.75 atm  
 15. 1.16 atm

• **Assertion-Reason**

16. (C)      17. (B)      18. (D)      19. (D)      20. (C)  
 21. (C)

• **Single Choice Correct**

22. (C)      23. (B)      24. (C)      25. (D)      26\*. (C)  
 27\*. (D)      28\*. (A)      29\*. (C)      30\*. (A)      31. (C)  
 32. (A)      33. (C)      34\*. (C)      35. (C)      36. (B)  
 37. (B)      38. (C)      39. (C)      40. (B)      41. (C)  
 42. (D)      43. (C)      44. (C)      45. (B)

• **Multi Choice Correct**

46. (CD)      47. (ABC)

• **Match the Column**

- 48\*. (A) - (r), (B) - (s), (C) - (p), (D) - (q)

• **Comprehension**

- 49\*. (A)      50\*. (A)      51\*. (C)

• **Subjective Questions**

52. 27.2 cm      53. 1.13 atm  
 54. (a) 0.867 atm      (b) 0.102 atm  
 55. 280 K, 525 K,  $3.157 \times 10^2 \text{ m/s}$ ,  $2.798 \times 10^2 \text{ m/s}$   
 56.  $R_{\text{RMS}}$  2886 K,  $T_{\text{av}} = 3399 \text{ K}$ ,  $T_{\text{mp}} = 4330 \text{ K}$   
 57.  $58.997 \text{ cm}^3$       58\*. (i) B (ii) C (iii) A  
 59. 521 K      60.  $350.5^\circ\text{C}$

- 61\*.** (i) 31.1 atm (ii) 31.4 atm  
**62.** Yes it is false statement  
**63.** directly proportional  
**64.**  $B = \left( b - \frac{a}{RT} \right)$   
**65.** 0.492 atm, 0.246 atm  
**66.** 123  
**67.**  $6.46 \text{ atm L}^2 \text{ mol}^{-2}$   
**68.**  $-173^\circ\text{C}$ , 0.82 L  
**69.**  $\text{XeF}_6$   
**70.** True  
**71.** 0.99 atm  
**72.**  $1.2544 \text{ atm L}^2 \text{ mol}^{-2}$   
**73.** (a) (i) 18.1 g/mol (ii)  $50.25 \text{ L mol}^{-1}$  (iii) 1.224 (iv) repulsive (b)  $2.07 \times 10^{-20} \text{ J}$   
**74.** 434.17 m/sec  
**75.** Since  $\text{H}_2$  is diatomic and He is monoatomic degree of freedom for mono is 3 and only translational but for diatomic, vibrational and rotational are also to be considered.  
**76.** RT  
**77.** 0.51  
**78\*.** 807.84 J  
**79.** 134 pm  
**80\*.**  $P_{\text{He}} = 7.07 \text{ atm}$ ,  $P_{\text{CH}_4} = 8.4 \text{ atm}$   
**81\*.** 10 Steps, 27.78 mol  $\text{CH}_4$ , 5333.3 mol  $\text{O}_2$   
**82\*.** (i) 5.263 L,  
 (ii)  $0.7 \text{ kg/m}^3$ ,  
 (iii)  $\text{KOH} = 0.2348 \text{ moles}$ ,  $\text{Ca(OH)}_2 = 0.1174 \text{ moles}$ , ethanolamine = 0.2348 moles  
**83\*.** (a)  $2.479 \times 10^3 \text{ kPa}$  (b) 2225.55 kPa  
**84\*.** 3.77 L  
**85.** 15.40 kg

**CHEMICAL EQUILIBRIUM**
**True / False**

1. Van't Hoff's equation gives the quantitative relation between change in value of  $K$  with change in temperature.
2. The value of equilibrium constant changes with change in the initial concentration of the reactants.
3.  $K_p$  is related to  $K_c$  as  $K_p = K_c (RT)^{\Delta n}$ .
4. Introduction of inert gas in a gaseous reaction ( $\Delta n_g \neq 0$ ) at equilibrium keeping pressure constant has no effect on equilibrium state.
5. For the reaction,  $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ ,  $K_p = K_c (RT)$ .
6. For the reaction,  $N_2 + 3H_2 \rightleftharpoons 2NH_3$ , the equilibrium expression may be written as  $K = \frac{[NH_3]^2}{[N_2][H_2]^3}$ .
7. A catalyst increases the value of the equilibrium constant for a reaction.
8. In case of endothermic reaction, the equilibrium shifts in backward direction on increasing the temperature.
9. For the reaction,  $H_2 + I_2 \rightleftharpoons 2HI$ , the equilibrium constant,  $K$  is dimensionless.
10. The reaction  $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ ,  $\Delta H = -X \text{ kJ}$ , is favoured by high pressure and high temperature.
11. The larger value of  $K$  indicates that the product is more stable relative to reactants.
12. Extent of a reaction can always be increased by increasing the temperature.
13. Solubilities of all solids in water increase with increase in temperature.
14. Dissolution of all gases in water is accompanied by evolution of heat.
15. For the reaction,  $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ ,  $K_p = p_{CO_2}$ .
16. If concentration quotient of reaction is less than  $K$ , the net reaction is proceeding in the backward direction.
17. The value of  $K$  increases with increase in pressure.
18. A very high value of  $K$  indicates that at equilibrium most of the reactants are converted into products.
19. The value of  $K$  for the reaction,  $N_2 + 3H_2 \rightleftharpoons 2NH_3$ , can be increased by applying high pressure or by using a catalyst.
20. For a reaction the value of  $Q$  greater than  $K$  indicates that the net reaction is proceeding in backward direction.

**Fill in the blanks**

21.  $K$  for the reaction  $2A + B \rightleftharpoons 2C$  is  $1.5 \times 10^{12}$ . This indicates that at equilibrium the concentration of ..... would be maximum.
22.  $K$  for the reaction  $X_2 + Y_2 \rightleftharpoons 2XY$  is 100.  $K$  for this reaction  $XY \rightleftharpoons \frac{1}{2}X_2 + \frac{1}{2}Y_2$  would be .....
23. Compared to  $K$  for the dissociation,  $2H_2S \rightleftharpoons 2H^+ + 2HS^-$ , then  $K'$  for the  $H^+ + HS^- \rightleftharpoons H_2S$  would have .....
24. For the reaction,  $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ , at equilibrium, increase in pressure shifts the equilibrium in ..... direction.
25. When the reaction is at equilibrium, the value of  $\Delta G$  is .....

26. The value of  $K$  for a reaction can be changed by changing .....
27. The law of mass action was proposed by .....
28. The degree of dissociation of  $\text{PCl}_5$  [ $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$ ], ..... with increase in pressure at equilibrium.
29. If concentration quotient,  $Q$  is greater than  $K_c$ , the net reaction is taking place in ..... direction.
30. The reaction,  $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$  would be favoured by ..... pressure.
31. The reaction  $\text{N}_2 + \text{O}_2 \rightleftharpoons 2\text{NO} - \text{Heat}$ , would be favoured by ..... temperature.
32. The equilibrium constant for a reaction decreases with increase in temperature, the reaction must be .....
33. For the reaction,  $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$ ,  $K_p$  and  $K_c$  are related as .....
34.  $\Delta G^\circ$  is related to  $K$  by the relation .....
35. Vant Hoff's equation is .....
36. Dimensions of equilibrium constant,  $K_c$  for the reaction  $2\text{NH}_3 \rightleftharpoons \text{N}_2 + 3\text{H}_2$ , are .....
37.  $K_p$  is related to  $K_c$  as .....
38. Solubility of a gas in water ..... with increase in temperature.
39. Introduction of inert gas at constant volume to a gaseous reaction at equilibrium results in formation of ..... product.
40. The product is more stable than reactants in reaction having .....  $K$ .

### Assertion-Reason

These questions contains, Statement I (assertion) and Statement II (reason).

(A) Statement-I is true, Statement-II is true ; Statement-II is correct explanation for Statement-I.

(B) Statement-I is true, Statement-II is true ; Statement-II is NOT a correct explanation for statement-I

(C) Statement-I is true, Statement-II is false

(D) Statement-I is false, Statement-II is true

41. **Statement-I** : The melting point of ice decreases with increase of pressure.  
**Because**  
**Statement-II** : Ice contracts on melting.
- 42\*. **Statement-I** : The equilibrium of  $\text{A}(\text{g}) \rightleftharpoons \text{B}(\text{g}) + \text{C}(\text{g})$  is not affected by changing the volume.  
**Because**  
**Statement-II** :  $K_c$  for the reaction does not depend on volume of the container.
43. **Statement-I** : For the reaction  $\text{A}(\text{g}) \rightleftharpoons \text{B}(\text{g}) + \text{C}(\text{g})$ ,  $K_p = 1$  atm. If we start with equal moles of all gases at 9 atm of initial pressure, then at equilibrium partial pressure of A increases.  
**Because**  
**Statement-II** : Reaction quotient  $Q_p > K_p$  hence equilibrium shifts in backward direction.
- 44\*. **Statement-I** : For a reaction at equilibrium, the Gibb's free energy of reaction is minimum at constant temp. and pressure.  
**Because**  
**Statement-II** : The Gibb's free energy of both reactants and products increases and become equal at equilibrium.



- 45. Statement-I :** Equilibrium constant for the reverse reaction is the inverse of the equilibrium constant for the reaction in the forward direction.  
**Because**  
**Statement-II :** Equilibrium constant depends upon the way in which the reaction is written.
- 46. Statement-I :** For the reaction  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$  if the volume of vessel is reduced to half of its original volume, equilibrium concentration of all gases will be doubled.  
**Because**  
**Statement-II :** According to Le Chatelier's principle, reaction shifts in a direction that tends to minimize the effect of the stress.
- 47. Statement-I :** For the reaction at certain temperature  
 $\text{A}(\text{g}) + \text{B}(\text{g}) \rightleftharpoons \text{C}(\text{g})$   
 there will be no effect by addition of inert gas at constant volume.  
**Because**  
**Statement-II :** Molar concentration of all gases remains constant.
- 48. Statement-I :** The catalyst does not alter the equilibrium constant.  
**Because**  
**Statement-II :** For the catalysed reaction and uncatalysed reaction  $\Delta H$  remains same and equilibrium constant depends on  $\Delta H$ .

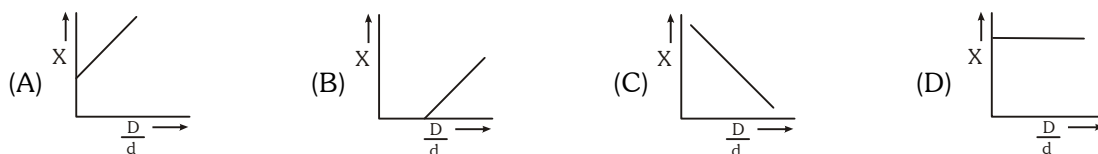
**Single Choice Correct**

- 49\*.** For reaction :  $\text{A}(\text{s}) \rightleftharpoons \text{B}(\text{g}) + \text{C}(\text{g})$ . What will be the value of natural logarithm of ratio of total pressure at 400

K to that at 300 K  $\left[ = \ln \frac{P_{400}}{P_{300}} \right]$  if  $\Delta H = 16.628 \text{ kJ}$ . [Given :  $R = 8.314 \text{ J/K-mole}$ ]

- (A)  $\frac{5}{3}$  (B)  $\frac{5}{6}$  (C)  $\frac{3}{5}$  (D)  $\frac{6}{5}$

- 50.** In the above question, x varies with  $\frac{D}{d}$  according to :



- 51\*.** In a 7.0 L evacuated chamber, 0.50 mol  $\text{H}_2$  and 0.50 mol  $\text{I}_2$  react at  $427^\circ\text{C}$ .  
 $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$ . At the given temperature,  $K_C = 49$  for the reaction.

- (i) What is the total pressure (atm) in the chamber?  
 (A) 83.14 (B) 831.4 (C) 8.21 (D) None
- (ii) What is the value of  $K_p$ ?  
 (A) 7 (B) 49 (C) 24.5 (D) None
- (iii) How many moles of the iodine remain unreacted at equilibrium?  
 (A) 0.388 (B) 0.112 (C) 0.25 (D) 0.125
- (iv) What is the partial pressure (atm) of HI in the equilibrium mixture?  
 (A) 6.385 (B) 12.77 (C) 40.768 (D) 646.58

- 52.** The reaction  $A + B \rightleftharpoons C + D$  is studied in a one litre vessel at  $250^\circ\text{C}$ . The initial concentration of A was  $3n$  and that of B was  $n$ . When equilibrium was attained, equilibrium concentration of C was found to be equal to the equilibrium concentration of B. What is the concentration of D at equilibrium :  
 (A)  $n/2$  (B)  $(3n - 1/2)$  (C)  $(n - n/3)$  (D)  $n$
- 53\*.** The value of  $K_p$  for the reaction  

$$2\text{H}_2\text{O}(\text{g}) + 2\text{Cl}_2\text{O}(\text{g}) \rightleftharpoons 4\text{HCl}(\text{g}) + \text{O}_2(\text{g})$$
 is  $0.03 \text{ atm}$  at  $427^\circ\text{C}$ , when the partial pressure are expressed in atmosphere then the value of  $K_C$  for the same reaction is :  
 (A)  $5.23 \times 10^{-4}$  (B)  $7.34 \times 10^{-4}$  (C)  $3.2 \times 10^{-3}$  (D)  $5.43 \times 10^{-5}$
- 54.** 2 moles each of  $\text{SO}_3$ ,  $\text{CO}$ ,  $\text{SO}_2$  and  $\text{CO}_2$  is taken in a one lit. vessel. If  $K_C$  for  $\text{SO}_3 + \text{CO} \rightleftharpoons \text{SO}_2 + \text{CO}_2$  is  $1/9$  then :  
 (A) total no. of moles at equilibrium are less than 8 (B)  $n(\text{SO}_3) + n(\text{CO}_2) = 4$   
 (C)  $[n(\text{SO}_2)/n(\text{CO})] < 1$  (D) both (B) and (C)
- 55\*.** Sulphide ion in alkaline solution reacts with solid sulphur to form polysulphide ions having formulae  $\text{S}_2^{2-}$ ,  $\text{S}_3^{2-}$ ,  $\text{S}_4^{2-}$  and so on. The equilibrium constant for the formation of  $\text{S}_2^{2-}$  is 12 ( $K_1$ ) & for the formation of  $\text{S}_3^{2-}$  is 132 ( $K_2$ ), both from S and  $\text{S}^{2-}$ . What is the equilibrium constant for the formation of  $\text{S}_3^{2-}$  from  $\text{S}_2^{2-}$  and S ?  
 (A) 11 (B) 12 (C) 132 (D) None of these
- 56\*.** For the reaction  $\text{CO}(\text{g}) + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2(\text{g}) + \text{H}_2(\text{g})$  at a given temperature the equilibrium amount of  $\text{CO}_2(\text{g})$  can be increased by :  
 (A) adding a suitable catalyst (B) adding an inert gas  
 (C) decreasing the volume of the container (D) increasing the amount of  $\text{CO}(\text{g})$

[JEE 1998]

**Multi Choice Correct**

- 57\*.** The equilibrium between, gaseous isomers A, B and C can be represented as

Reaction	Equilibrium constant
$\text{A}(\text{g}) \rightleftharpoons \text{B}(\text{g})$ :	$K_1 = ?$
$\text{B}(\text{g}) \rightleftharpoons \text{C}(\text{g})$ :	$K_2 = 0.4$
$\text{C}(\text{g}) \rightleftharpoons \text{A}(\text{g})$ :	$K_3 = 0.6$

If one mole of A is taken in a closed vessel of volume 1 litre, then

- (A)  $[\text{A}] + [\text{B}] + [\text{C}] = 1 \text{ M}$  at any time of the reactions  
 (B) Concentration of C is  $4.1 \text{ M}$  at the attainment of equilibrium in all the reactions  
 (C) The value of  $K_1$  is  $\frac{1}{0.24}$   
 (D) Isomer [A] is least stable as per thermodynamics.

**Comprehension**

**Read the following passage carefully and answer the questions.**

Effect of temperature on the equilibrium process is analysed by using the thermodynamics

From the thermodynamics relation

$$\Delta G^0 = -2.30 \text{ RT log } k \quad \dots\dots\dots (1)$$

$\Delta G^0$  : Standard free energy change

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad \dots\dots\dots (2)$$

$\Delta H^0$  : Standard heat of the reaction.

From (1) & (2)

$$-2.3 \text{ RT log } k = \Delta H^0 - T\Delta S^0 \quad \Delta S^0 : \text{Standard entropy change}$$

$$\Rightarrow \log k = -\frac{\Delta H^0}{2.3\text{RT}} + \frac{\Delta S^0}{2.3\text{R}} \quad \dots\dots\dots (3)$$

Clearly if a plot of  $\log k$  vs  $1/T$  is made then it is a straight line having slope  $= \frac{-\Delta H^\circ}{2.3R}$

and Y intercept  $= \frac{\Delta S^\circ}{2.3R}$

If at temp.  $T_1$  equilibrium constant be  $k_1$  and at temperature  $T_2$  equilibrium constant be  $k_2$  then :

The above equation reduces to:

$$\Rightarrow \log k_1 = -\frac{\Delta H^\circ}{2.3RT_1} + \frac{\Delta S^\circ}{2.3R} \quad \dots\dots\dots (4)$$

$$\Rightarrow \log k_2 = -\frac{\Delta H^\circ}{2.3RT_2} + \frac{\Delta S^\circ}{2.3R} \quad \dots\dots\dots (5)$$

Subtracting (4) from (5) we get

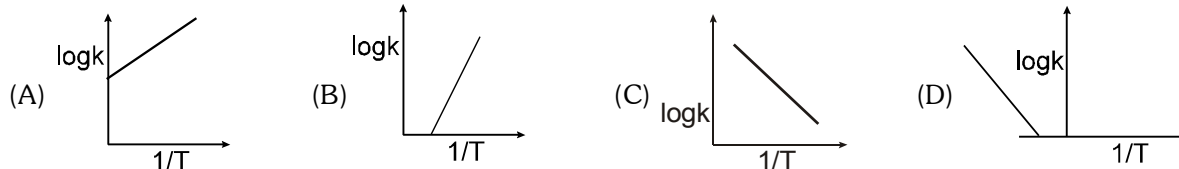
$$\Rightarrow \log \frac{k_2}{k_1} = \frac{\Delta H^\circ}{2.30R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

From the above relation we can conclude that the value of equilibrium constant increases with increase in temperature for endothermic reaction but value of equilibrium constant decreases with the increase in temperature for exothermic reaction.

**58\***. If standard heat of dissociation of  $\text{PCl}_5$  is 230 cal then slope of the graph of  $\log k$  vs  $\frac{1}{T}$  is :

- (A) +50                                      (B) - 50                                      (C) 10                                      (D) None

**59\***. For exothermic reaction if  $\Delta S_0 < 0$  then the sketch of  $\log k$  vs  $\frac{1}{T}$  may be :



**60\***. If for a particular reversible reaction at :  
 $k_C = 57$  at  $355^\circ\text{C}$  and  $k_C = 69$  at  $450^\circ$  then :

- (A)  $\Delta H < 0$                                       (B)  $\Delta H > 0$   
 (C)  $\Delta H = 0$                                       (D)  $\Delta H$  whose sign can't be determined

### Subjective Questions

**61.** Rate of disappearance of the reactant A at two different temperature is given by  $A \rightleftharpoons B$

$$\frac{-d[A]}{dt} = (2 \times 10^{-2} \text{ S}^{-1}) [A] - 4 \times 10^{-3} \text{ S}^{-1} [B] ; 300 \text{ K}$$

$$\frac{-d[A]}{dt} = (4 \times 10^{-2} \text{ S}^{-1}) [A] - 16 \times 10^{-4} \text{ S}^{-1} [B] ; 400 \text{ K}$$

Calculate heat of reaction in the given temperature range. When equilibrium is set up.

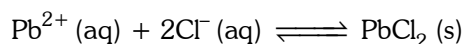
**62.** Among the solubility rules, the statement that all chlorides are soluble except  $\text{Hg}_2\text{Cl}_2$ ,  $\text{AgCl}$ ,  $\text{PbCl}_2$ , and  $\text{CuCl}$ .

(a) Write the expression for the equilibrium constant for the reaction represented by the equation

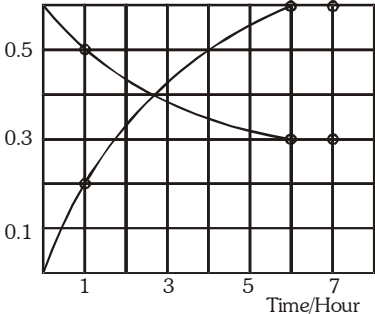


Is K greater than 1, less than 1, or about equal to 1? Explain your answer.

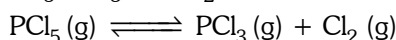
(b) Write the expression for the equilibrium constant for the reaction represented by the equation



Is K greater than 1, less than 1, or about equal to 1? Explain your answer.

- 63\*.** At 1400 K,  $K_c = 2.5 \times 10^{-3}$  for the reaction  $\text{CH}_4(\text{g}) + 2\text{H}_2\text{S} \rightleftharpoons \text{CS}_2(\text{g}) + 4\text{H}_2(\text{g})$ . A 10.0 L reaction vessel at 1400 K contains 2.0 mol of  $\text{CH}_4$ , 3.0 mol of  $\text{CS}_2$ , 3.0 mol of  $\text{H}_2$  and 4.0 mol of  $\text{H}_2\text{S}$ . Is this reaction mixture at equilibrium? If not, in which direction does the reaction proceed to reach equilibrium?
- 64.** At a certain temperature, the reaction  $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$  has an equilibrium constant  $K_c = 5.8 \times 10^{-2}$ . Calculate the equilibrium concentrations of  $\text{PCl}_5$ ,  $\text{PCl}_3$  and  $\text{Cl}_2$  if only  $\text{PCl}_5$  is present initially, at a concentration of 0.160 M.
- 65\*.** The system  $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$  maintained in a closed vessel at  $60^\circ\text{C}$  & pressure of 5 atm has an average (i.e. observed) molecular weight of 69, calculate  $K_p$ . At what pressure at the same temperature would the observed molecular weight be (230/3)?
- 66.** The vapour density of  $\text{N}_2\text{O}_4$  at a certain temperature is 30. Calculate the percentage dissociation of  $\text{N}_2\text{O}_4$  at this temperature.  $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$ .
- 67\*.** In the esterification  $\text{C}_2\text{H}_5\text{OH}(\ell) + \text{CH}_3\text{COOH}(\ell) \rightleftharpoons \text{CH}_3\text{COOC}_2\text{H}_5(\ell) + \text{H}_2\text{O}(\ell)$  an equimolar mixture of alcohol and acid taken initially yields under equilibrium, the water with mole fraction = 0.333. Calculate the equilibrium constant.
- 68.** Solid Ammonium carbamate dissociates as:  $\text{NH}_2\text{COONH}_4(\text{s}) \rightleftharpoons 2\text{NH}_3(\text{g}) + \text{CO}_2(\text{g})$ . In a closed vessel solid ammonium carbamate is in equilibrium with its dissociation products. At equilibrium, ammonia is added such that the partial pressure of  $\text{NH}_3$  at new equilibrium now equals the original total pressure. Calculate the ratio of total pressure at new equilibrium to that of original total pressure.
- 69\*.** A sample of  $\text{CaCO}_3(\text{s})$  is introduced into a sealed container of volume 0.821 litre & heated to 1000 K until equilibrium is reached. The equilibrium constant for the reaction  $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$  is  $4 \times 10^{-2}$  atm at this temperature. Calculate the mass of  $\text{CaO}$  present at equilibrium.
- 70\*.** (a) Water gas, a mixture of  $\text{H}_2$  and  $\text{CO}$ , is an important industrial fuel produced by the reaction of steam with red-hot coke, essentially pure carbon. Write the expression for the equilibrium constant for the reversible reaction.
- $$\text{C}(\text{s}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + \text{H}_2(\text{g}) \quad \Delta H = 131.30 \text{ kJ}$$
- (b) Assume that equilibrium has been established and predict how the concentration of each reactant and product will differ at a new equilibrium if (1) more C is added. (2)  $\text{H}_2\text{O}$  is removed. (3)  $\text{CO}$  is added (4) the pressure on the system is increased. (5) the temperature of the system is increased.
- 71.** The progress of the reaction  $\text{A} \rightleftharpoons \text{nB}$  with time, is presented in figure, Determine
- the value of n.
  - the equilibrium constant K.
  - the initial rate of conversion of A.
- 
- 72.** The  $K_p$  for reaction  $\text{A} + \text{B} \rightleftharpoons \text{C} + \text{D}$  is 1.34 at  $60^\circ\text{C}$  and 6.64 at  $100^\circ\text{C}$ . Determine the free energy change of this reaction at each temperature and  $\Delta H^\circ$  for the reaction over this range of temperature?
- 73.** At 100 K, then value of  $K_c$  for the reaction  $\text{C}(\text{s}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + \text{H}_2(\text{g})$  is  $3.0 \times 10^{-2}$ . Calculate equilibrium concentrations of  $\text{H}_2\text{O}$ ,  $\text{CO}_2$  and  $\text{H}_2$  in the reaction mixture obtained by heating 6.0 mole of steam and an excess of solid carbon in a 5.0 L container. What is the molar composition of the equilibrium mixture?

- 74\*.** When 1.0 mol of  $\text{PCl}_5$  is introduced into a 5.0 L container at 500 K, 78.5 % of the  $\text{PCl}_5$  dissociates to give an equilibrium mixture of  $\text{PCl}_5$ ,  $\text{PCl}_3$  and  $\text{Cl}_2$ .

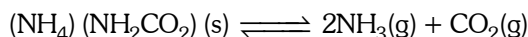


- (a) Calculate the values of  $K_c$  and  $K_p$ .  
 (b) If the initial concentrations in a particular mixture of reactants and products are  $[\text{PCl}_5] = 0.5 \text{ M}$ ,  $[\text{PCl}_3] = 0.15 \text{ M}$ , and  $[\text{Cl}_2] = 0.6 \text{ M}$ , in which direction does the reaction proceed to reach equilibrium? What are the concentrations when the mixture reaches equilibrium?
- 75.** The vapour pressure of water at  $25^\circ\text{C}$  is 0.0313 atm. Calculate the values of  $K_p$  and  $K_c$  at  $25^\circ\text{C}$  for the equilibrium  $\text{H}_2\text{O}(\ell) \rightleftharpoons \text{H}_2\text{O}(\text{g})$ .
- 76.** When 0.5 mol of  $\text{N}_2\text{O}_4$  is placed in a 4.00 L reaction vessel and heated at 400 K, 79.3 % of the  $\text{N}_2\text{O}_4$  decomposes to  $\text{NO}_2$ . Calculate  $K_c$  and  $K_p$  at 400 K for the reaction  $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2 \text{NO}_2(\text{g})$ .
- 77.** The equilibrium constant of the reaction  $2 \text{C}_3\text{H}_6(\text{g}) \rightleftharpoons \text{C}_2\text{H}_4(\text{g}) + \text{C}_4\text{H}_8(\text{g})$  is found to fit the expression

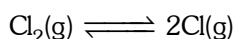
$$\ln K = -1.04 - \frac{1088}{T}$$

Calculate the standard reaction enthalpy and entropy at 400 K.

- 78\*.** The decomposition of solid ammonium carbamate,  $(\text{NH}_4)(\text{NH}_2\text{CO}_2)$ , to gaseous ammonia and carbon dioxide is an endothermic reaction.

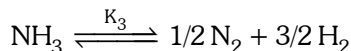
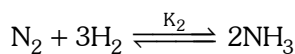


- (a) When solid  $(\text{NH}_4)(\text{NH}_2\text{CO}_2)$  is introduced into an evacuated flask at  $25^\circ\text{C}$ , the total pressure of gas at equilibrium is 0.116 atm. What is the value of  $K_p$  at  $25^\circ\text{C}$  ?  
 (b) Given that the decomposition reaction is at equilibrium, how would the following changes affect the total quantity of  $\text{NH}_3$  in the flask once equilibrium is re-established?  
 (i) Adding  $\text{CO}_2$   
 (ii) Adding  $(\text{NH}_4)(\text{NH}_2\text{CO}_2)$   
 (iii) Removing  $\text{CO}_2$   
 (iv) Increasing the total volume  
 (v) Adding neon  
 (vi) Increasing the temperature
- 79.** A container contains three gases. A, B and C in equilibrium  $\text{A} \rightleftharpoons 2\text{B} + \text{C}$   
 At equilibrium the concentration of A was 3 M, and of B was 4 M. On doubling the volume of container, the new equilibrium concentration of B was 3M. Calculate  $K_c$  and initial equilibrium concentration of C.
- 80.** A mixture of hydrogen & iodine in the mole ratio 1.5 : 1 is maintained at  $450^\circ\text{C}$ . After the attainment of equilibrium  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$ , it is found on analysis that the mole ratio of  $\text{I}_2$  to HI is 1 : 18. Calculate the equilibrium constant & the number of moles of each species present under equilibrium, if initially, 127 g of iodine were taken.
- 81.** The equilibrium constant for the reaction  $\text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}_2(\text{g}) + \text{H}_2(\text{g})$  is 7.3 at  $450^\circ\text{C}$  & 1 atm pressure. The initially concentration of water gas [ $\text{CO}$  &  $\text{H}_2$  in equimolar ratio] & steam are 2 moles & 5 moles respectively. Find the number of moles of  $\text{CO}$ ,  $\text{H}_2$ ,  $\text{CO}_2$  &  $\text{H}_2\text{O}$  (vapour) at equilibrium.
- 82.** At  $1200^\circ\text{C}$ , the following equilibrium is established between chlorine atoms & molecule.



The composition of equilibrium mixture may be determined by measuring the rate of effusion of the mixture through a pin hold. It is found that at  $1200^\circ\text{C}$  and 1 atm pressure the mixture effuses 1.16 times as fast as krypton effuses under the same condition. Calculate the equilibrium constant  $K_c$ .

- 83.**  $\Delta G^\circ$  (298 K) for the reaction  $1/2\text{N}_2 + 3\text{H}_2 \xrightleftharpoons{K_1} \text{NH}_3$  is  $-16.5 \text{ kJ mol}^{-1}$ . Find the equilibrium constant ( $K_1$ ) at  $25^\circ\text{C}$ . What will be the equilibrium constants  $K_2$  and  $K_3$  for the following reactions :



- 84.** For the reaction,  $\text{N}_2\text{O}_5(\text{g}) = 2\text{NO}_2(\text{g}) + 0.5\text{O}_2(\text{g})$ , calculate the mole fraction of  $\text{N}_2\text{O}_5(\text{g})$  decomposed at a constant volume & temperature, if the initial pressure is 600 mm Hg & the pressure at anytime is 960 mm Hg. Assume ideal gas behaviour. **[JEE 1998]**

- 85.** The degree of dissociation is 0.4 at 400 K & 1.0 atm for the gaseous reaction  $\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2(\text{g})$ . Assuming ideal behaviour of all gases. Calculate the density of equilibrium mixture at 400 K & 1.0 atm pressure. **[JEE 1999]**

- 86.** When 3.06 g of solid  $\text{NH}_4\text{HS}$  is introduced into a two litre evacuated flask at  $27^\circ\text{C}$ , 30% of the solid decomposes into gaseous ammonia and hydrogen sulphide. **[JEE 1999]**

(i) Calculate  $K_c$  &  $K_p$  for the reaction at  $27^\circ\text{C}$ .

(ii) What would happen to the equilibrium when more solid  $\text{NH}_4\text{HS}$  is introduced into the flask?

- 87.** When 1-pentyne (A) is treated with 4N alcoholic KOH at  $175^\circ\text{C}$ , it is converted slowly into an equilibrium mixture of 1.3% 1-pentyne (A), 95.2% 2-pentyne (B) & 3.5 % of 1,2-pentadiene (C). The equilibrium was maintained at  $175^\circ\text{C}$ . Calculate  $\Delta G^\circ$  for the following equilibria.

$$\text{B} = \text{A} \quad \Delta G_1^\circ = ?$$

$$\text{B} = \text{C} \quad \Delta G_2^\circ = ?$$

From the calculated value of  $\Delta G_1^\circ$  &  $\Delta G_2^\circ$  indicate the order of stability of A, B & C. Write a reasonable reaction mechanism sharing all intermediate leading to A, B & C. **[JEE 2001]**

- 88.**  $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$  **[JEE 2004]**

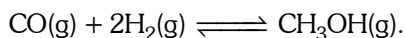
This reaction is carried out at 298 K and 20 bar. 5 mol each of  $\text{N}_2\text{O}_4$  and  $\text{NO}_2$  are taken initially :

Given :  $\Delta G^\circ_{\text{N}_2\text{O}_4} = 100 \text{ kJ mol}^{-1}$ ;  $\Delta G^\circ_{\text{NO}_2} = 50 \text{ kJ mol}^{-1}$

(i) Find  $\Delta G$  for reaction at 298 K under given condition.

(ii) Find the direction in which the reaction proceeds to achieve equilibrium.

- 89\*.** 0.15 mole of CO taken in a 2.5 litre flask is maintained at 750 K along with a catalyst so that the following reaction can take place ;

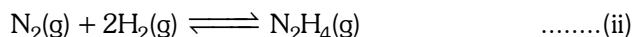
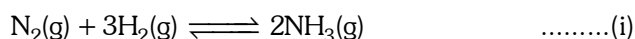


Hydrogen is introduced untill the total pressure of the system is 8.5 atm at equilibrium and 0.08 mole of methanol is formed. Calculate :

(i)  $K_p$  &  $K_c$  ;

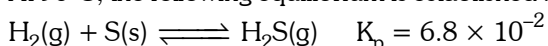
(ii) the final pressure if the same amount of CO and  $\text{H}_2$  as before are used, but with no catalyst so that the reaction does not take place.

- 90.** In a vessel, two equilibrium are simultaneously established at the same temperature as follows :



Initially the vessel contains  $\text{N}_2$  and  $\text{H}_2$  in the molar ratio of 9 : 13. The equilibrium pressure is  $7P_0$ , in which pressure due to ammonia is  $P_0$  and due to hydrogen is  $2P_0$ . Find the values of equilibrium constant ( $K_p$ 's) for both the reactions.

- 91.** At  $90^\circ\text{C}$ , the following equilibrium is established :



If 0.2 mol of hydrogen and 1.0 mol of sulphur are heated to  $90^\circ\text{C}$  in a 1.0 litre vessel, what will be the partial pressure of  $\text{H}_2\text{S}$  at equilibrium ?

- 92\*.** At  $817^{\circ}\text{C}$ ,  $K_p$  for the reaction between pure  $\text{CO}_2$  and excess hot graphite to form  $2\text{CO}(\text{g})$  is 10 atm.
- What is the analysis of the gases at equilibrium at  $817^{\circ}\text{C}$  & a total pressure of 4.0 atm? What is the partial pressure of  $\text{CO}_2$  at equilibrium?
  - At what total pressure will the gas mixture analyze 6%,  $\text{CO}_2$  by volume?
- 93.** For the reaction  $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ , equilibrium mixture contains  $\text{NO}_2$  at  $P = 1.1$  atm &  $\text{N}_2\text{O}_4$  at  $P = 0.28$  atm at 350 K. The volume of the container is doubled. Calculate the equilibrium pressures of the two gases when the system reaches new equilibrium.
- 94.** The degree of dissociation of HI at a particular temperature is 0.8. Find the volume of 1.5 M sodium thiosulphate solution required to react completely with the iodine present at equilibrium in acidic conditions, when 0.135 mol each of  $\text{H}_2$  and  $\text{I}_2$  are heated at 440 K in a closed vessel of capacity 2.0 L.
- 95\*.**  $\text{SO}_3$  decomposes at a temperature of 1000 K and at a total pressure of 1.642 atm. At equilibrium, the density of mixture is found to be 1.28 g/L in a vessel of 90 litres. Find the degree of dissociation of  $\text{SO}_3$  for  $\text{SO}_3 \rightleftharpoons \text{SO}_2 + 1/2\text{O}_2$ .
- 96.** The density of an equilibrium mixture of  $\text{N}_2\text{O}_4$  and  $\text{NO}_2$  at 101.32  $\text{KPa}$  is  $3.62 \text{ g dm}^{-3}$  at 288 K and  $1.84 \text{ g dm}^{-3}$  at 348 K. What is the heat of the reaction for  $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2(\text{g})$ .
- 97\*.** The equilibrium constant for the following reaction at 1395 K.
- $$2\text{H}_2\text{O} \rightleftharpoons 2\text{H}_2 + \text{O}_2 \quad K_1 = 2.1 \times 10^{-13}$$
- $$2\text{CO}_2 \rightleftharpoons 2\text{CO} + \text{O}_2 \quad K_2 = 1.4 \times 10^{-12}$$
- Calculate the value of  $K$  for the reaction :  $\text{H}_2 + \text{CO}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}$
- 98.** A mixture of  $\text{N}_2$  &  $\text{H}_2$  are in equilibrium at 600 K at a total pressure of 80 atm. If the initial ratio of  $\text{N}_2$  and  $\text{H}_2$  are 3 : 1 and at equilibrium  $\text{NH}_3$  is 10% by volume, calculate  $K_p$  of reaction at given temperature.

## ANSWERS

• **True and False**

- |           |           |           |           |           |
|-----------|-----------|-----------|-----------|-----------|
| 1. True   | 2. False  | 3. True   | 4. False  | 5. True   |
| 6. True   | 7. False  | 8. False  | 9. True   | 10. False |
| 11. True  | 12. False | 13. False | 14. True  | 15. True  |
| 16. False | 17. False | 18. True  | 19. False | 20. True  |

• **Fill in the Blanks**

- |   |                                  |                                |
|---|----------------------------------|--------------------------------|
| 21. product C   | 22. $\frac{1}{10}$               | 23. $\frac{1}{\sqrt{K}}$       |
| 24. backward  | 25. zero                         | 26. Temperature                |
| 27. Guldberg and Waage  | 28. decreases                    | 29. backward                   |
| 30. high  | 31. high                         | 32. exothermic                 |
| 33. $K_p = K_c(RT)$   | 34. $\Delta G^\circ = -RT \ln K$ |                                |
| 35. $\log \frac{K_2}{K_1} = \frac{\Delta H^\circ}{2.303R} \left[ \frac{T_2 - T_1}{T_2 T_1} \right]$ | 36. $\text{mol}^2 \text{L}^{-2}$ | 37. $K_p = K_c(RT)^{\Delta n}$ |
| 38. decreases   | 39. same amount of               | 40. large value of             |

• **Assertion - Reason**

- |         |          |         |          |         |
|---------|----------|---------|----------|---------|
| 41. (A) | 42*. (D) | 43. (A) | 44*. (C) | 45. (A) |
| 46. (B) | 47. (A)  | 48. (A) |          |         |

• **Single Choice Correct**

- |         |          |                      |                    |
|---------|----------|----------------------|--------------------|
| 49. (B) | 50. (B)  | 51. (i) (C) (ii) (B) | (iii) (B) (iv) (A) |
| 52. (A) | 53*. (A) | 54. (D)              | 55*. (A) 56*. (D)  |

• **Multi Choice Correct**

57. (ACD)

• **Comprehension**

- 58\*. (B)      59\*. (B)      60\*. (B)

• **Subjective Questions**

61. Vant holf equation

$$\log \frac{K_2}{K_1} = \frac{\Delta H}{2.303R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]$$

$$\log 2 \times 10^{-2} \quad \text{At } 300\text{K} \quad K_1 = \frac{2 \times 10^{-2}}{4 \times 10^{-3}} = 5$$

$$\text{At } 400\text{K} \quad K_2 = \frac{4 \times 10^{-2}}{16 \times 10^{-4}} = 25$$

$$\log \frac{25}{5} = \frac{\Delta H}{2.303 \times 8.314} \left[ \frac{1}{300} - \frac{1}{400} \right] \quad \Delta H = 16.06 \times 10^3 \text{ J}$$



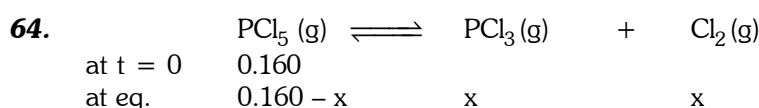
62. (a)  $k_{eq} = \frac{[Ag^+][Cl^-]}{[AgCl]} = [Ag^+][Cl^-]$  (as conc. of solid is 1)

$k_{eq} < 1$ , AgCl is insoluble, so conc. of ions are much less than 1 M.

(b)  $k_{eq} = \frac{1}{[Pb^{2+}][Cl^-]^2}$

$k_{eq} > 1$ , as PbCl<sub>2</sub> is insoluble of conc. of ions are much less than 1 M.

63\*.  $Q = \frac{[CS_2][H_2]^4}{[H_2S]^2[CH_4]} = \frac{\left(\frac{3}{10}\right)\left(\frac{3}{10}\right)^4}{\left(\frac{4}{10}\right)^2\left(\frac{2}{10}\right)} = 7.6 \times 10^{-2}$

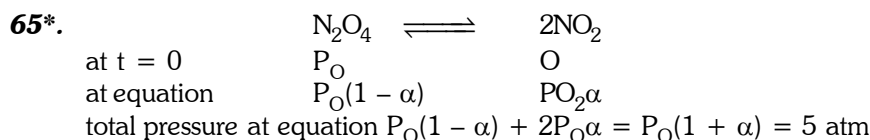


$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{x^2}{(0.16 - x)} = 5.8 \times 10^{-2}$$

$$\Rightarrow x = 0.071$$

so, conc. of PCl<sub>3</sub> = Cl<sub>2</sub> = 0.071

conc. of PCl<sub>5</sub> = 0.16 - 0.071 = 0.089



$$\text{average molecular mass} = \frac{P_O(1 - \alpha) \times 92 + 2P_O\alpha \times 46}{P_O(1 + \alpha)} = 69$$

$$\Rightarrow \frac{P_O \times 92(1 - \alpha + \alpha)}{P_O(1 + \alpha)} = 69$$

$$\Rightarrow (1 + \alpha) = \frac{92}{69}$$

$$\Rightarrow \alpha = \frac{92}{69} - 1 = \frac{23}{69}$$

and P<sub>O</sub>(1 + α) = 5

$$P_O = \frac{5}{1 + \alpha} = \frac{5}{92} \times 69$$

$$K_P = \frac{(2P_O\alpha)^2}{P_O(1 - \alpha)} = \frac{4P_O\alpha^2}{(1 - \alpha)}$$

$$= \frac{4 \times \frac{5}{92} \times 69 \times \left(\frac{23}{69}\right)^2}{\left(1 - \frac{23}{69}\right)} = 2.5 \text{ atm}$$

(ii) Average molecular mass =  $\frac{P_O(1 - \alpha) \times 92 + 2P_O\alpha \times 46}{P_O(1 + \alpha)} = \frac{230}{3}$

$$\Rightarrow \frac{92P_O(1 - \alpha + \alpha)}{P_O(1 + \alpha)} = \frac{230}{3}$$

$$\Rightarrow 1 + \alpha = \frac{92 \times 3}{230} = \frac{276}{230} = \frac{12}{10}$$

$$\alpha = \frac{12}{10} - 1 = \frac{2}{10} = 0.2$$

$$\text{Now } K_p = \frac{(2\alpha P_0)^2}{P(1-\alpha)} = \frac{4\alpha^2 P_0}{(1-\alpha)} = 2.5$$

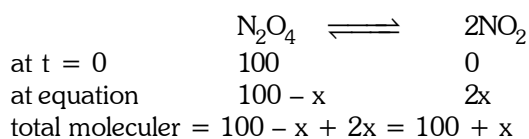
$$\Rightarrow \frac{4 \times 0.2 \times 0.2 \times P_0}{1 - 0.2} = 2.5$$

$$\Rightarrow P_0 = 12.5$$

$$\text{Total pressure at equation} = P_0(1 + \alpha) = 12.5(1 + 0.2) = 15 \text{ atm.}$$

**66.** Vapour density = 30

$$\text{So molecular mass} = 30 \times 2 = 60$$

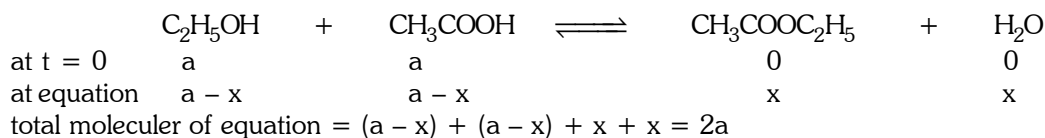


$$\text{Average molecular mass} = \frac{(100 - x)92 + (2x + 46)}{100 + x} = 60$$

$$\Rightarrow \frac{9200}{100 + x} = 60$$

$$\Rightarrow x = 53.33\%$$

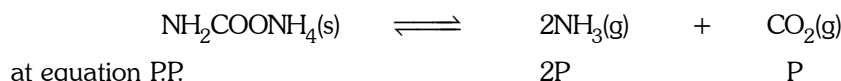
**67\*.**



$$\text{as given in equation mole fraction of } \text{H}_2\text{O} = \frac{x}{2a} = 0.333 \quad x = 0.666a$$

$$x = K_{eq} = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]}{[\text{C}_2\text{H}_5\text{OH}][\text{CH}_3\text{COOH}]} = \frac{0.666a \times 0.666a}{(a - 0.666a) \times (a - 0.666a)} = 4$$

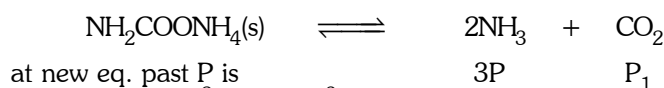
**68.**



$$\text{so } K_p = [\text{NH}_3]^2 [\text{CO}_2] = (2P)^2 (P) = 3P^2$$

$$\text{total pressure} = 2P + P = 3P$$

$$\text{If }^{\text{nd}} \text{ case : Now P.P. of } \text{NH}_3 = \text{Total pressure of case I} = 3P$$



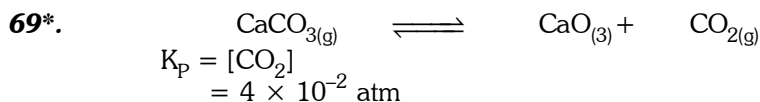
$$\text{so } K_p = [3P]^2 [P_1] = 4P^3$$

$$\Rightarrow P_1 = \frac{4P}{9}$$

$$\text{so total pressure at new equation} = 3 \text{ P.P. of } \text{NH}_3 + \frac{4P}{9} \text{ P.P. of } \text{CO}_2$$

$$= \frac{31P}{9}$$

$$\text{Ratio of total pressure} = \frac{31P/9}{3P} = \frac{31}{27}$$



so moles of  $\text{CO}_2 = \frac{PV}{RT} = \frac{4 \times 10^{-2} \times 0.821}{0.0821 \times 1000} = 4 \times 10^{-4}$

Moles of  $\text{CaO} = \text{moles of } \text{CO}_2 = 4 \times 10^{-4}$   
 out of  $\text{CaO} = 4 \times 10^{-4} \times 56 = 224 \times 10^{-4} \text{ g} = 22.4 \text{ mg}$

- 70\*.** (a)  $K = [\text{CO}][\text{H}_2] / [\text{H}_2\text{O}]$  ;  
 (b) in each of the following cases the mass of carbon will change, but its concentration (activity) will not change.  
 1.  $[\text{H}_2\text{O}]$  no change,  $[\text{CO}]$  no change,  $[\text{H}_2]$  no change ;    2.  $[\text{H}_2\text{O}]$  decrease,  $[\text{CO}]$  decrease,  $[\text{H}_2]$  decrease ;  
 3.  $[\text{H}_2\text{O}]$  increase,  $[\text{CO}]$  increase,  $[\text{H}_2]$  decrease ;    4.  $[\text{H}_2\text{O}]$  increase,  $[\text{CO}]$  decrease,  $[\text{H}_2]$  decrease ;  
 5.  $[\text{H}_2\text{O}]$  decrease,  $[\text{CO}]$  increase,  $[\text{H}_2]$  increase ;

- 71.** Each small cube represents 0.1 mol and 1 hour.  
 (i) In one hour 0.1 mole decreases, but 0.2 mole increases of B so it is  $A \rightarrow 2B$ , (value of  $n = 2$ )  
 (ii) At equilibrium moles of  $A = 0.3$ ,  $B = 0.6$

so  $K_{eq} = \frac{[\text{B}]^2}{[\text{A}]} = \frac{(0.6)^2}{(0.3)} = 1.2 \text{ mol/L}$

(iii) In 1 hour conversion of A decreases from 0.6 to 0.5 so rate  $= \frac{0.1}{1} \text{ moles hour}^{-1}$

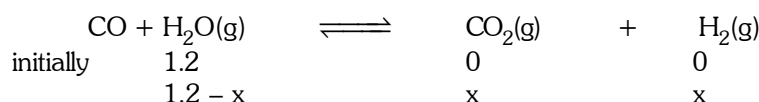
**72.** (i)  $\log \frac{K_2}{K_1} = \frac{\Delta H}{2.303R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$

$\log \frac{6.64}{1.34} = \frac{\Delta H}{2.303 \times 8.314} \times \left( \frac{1}{333} - \frac{1}{373} \right)$

(ii)  $\Delta G^\circ = -RT \ln K$   
 $= -8.314 \times 333 \times \ln 1.34$   
 $= -810 \text{ J/mol}$

(iii)  $\Delta G^\circ = -RT \ln K$   
 $= -8.314 \times 373 \times \ln 6.64$   
 $= -5872 \text{ J/mol}$

**73.** initial conc. of  $\text{H}_2\text{O} = \frac{6}{5} = 1.2 \text{ M}$

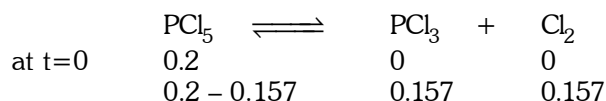


$K_C = \frac{[\text{CO}_2][\text{H}_2]}{[\text{H}_2\text{O}]} = \frac{x^2}{1.2 - x} = 3 \times 10^{-2} \quad x = 0.18$

so  $[\text{CO}_2] = [\text{H}_2] = 0.18$  and  $[\text{H}_2\text{O}] = 0.02 \text{ M}$

**74\*.** initial conc. of  $\text{PCl}_5 = \frac{1}{5} = 0.2 \text{ M}$

78.5% of 0.2  $= 0.2 \times \frac{78.5}{100} = 0.157$



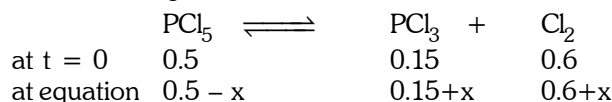
$$K_C = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} = \frac{0.157 \times 0.157}{0.2 - 0.157} = 0.573$$

$$K_P = K_C (RT)^1 \quad (\text{As } \Delta n_g = 2 - 1 = 1)$$

$$= 0.573 \times 500 \times 0.0821 = 23.5$$

$$(b) \quad Q = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} = \frac{0.15 \times 0.6}{0.5} = 0.18$$

$Q < K_C$  so reaction will proceed in forward direction.



$$\text{so} \quad \frac{(0.15 + x)(0.6 + x)}{(0.5 - x)} = 0.573$$

$$x = 0.135$$

$$\text{so conc. of } \text{PCl}_5 = 0.5 - 0.135 = 0.365$$

$$\text{Cl}_2 = 0.6 + 0.135 = 0.735$$

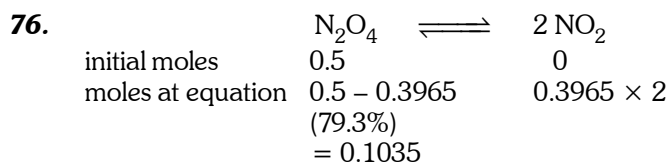
$$\text{PCl}_3 = 0.15 + 0.135 = 0.285$$

**75.**  $K_P = P_{(\text{H}_2\text{Og})} = 0.0313 \text{ atm}$

$$\Delta n_g = 1 - 0 = 1$$

$$\text{so } K_P = K_C (RT)^1$$

$$\text{so } K_C = \frac{K_P}{RT} = \frac{0.0313}{0.0821 \times 298} = 1.28 \times 10^{-3}$$



$$\text{so at equation conc. of } \text{N}_2\text{O}_4 = \frac{0.1035 \text{ mole}}{4 \text{ litre}}$$

$$\text{NO}_2 = \frac{0.3965 \times 2}{4} = \frac{0.3965}{2} \quad \text{now } K_C = \frac{[\text{NO}]^2}{[\text{N}_2\text{O}_4]} = \frac{(0.3965/2)^2}{(0.1035/2)} = 1.51$$

$$K_P = K_C (RT)^1 \quad (\text{as } \Delta n_g = 2 - 1 = 1)$$

$$= 1.51 \times 0.0821 \times 400 = 49.6$$

**77.**  $\ln K = -1.04 - \frac{1088}{T}$

$$RT \ln K = -R \times T \times 1.04 - R \times 1088$$

$$= -8.64T - 9045 \quad \dots\dots\dots(1)$$

we know that

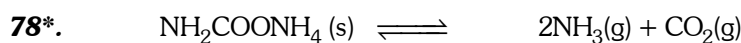
$$\Delta G^\circ = -RT \ln K = \Delta H - T\Delta S^\circ$$

$$\text{so } RT \ln k = -\Delta H + T\Delta S \quad \dots\dots\dots(2)$$

from equation (1) and (2)

$$\Delta H = 9045 \text{ J/mol} = 9.04 \text{ KJ/mole}$$

$$\Delta S = -8.64 \text{ J mol}^{-1} \text{ K}^{-1}$$



$$\text{at eq.} \quad \quad \quad 2P \quad \quad P$$

$$\text{total pressure at eq.} = 3P = 0.116$$

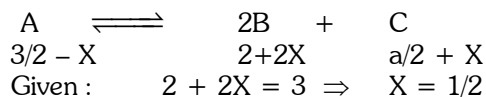
$$P = 0.03866$$

$$K_P = (P_{\text{NH}_3})^2 (P_{\text{CO}_2}) = (2P)^2 (P) = 4P^3 = 4(0.03866)^3 = 2.31 \times 10^{-4}$$

79. Let equilibrium concentration of C be a M.

$$K_c = \frac{(4^2)(a)}{3} = \frac{16a}{3} \quad \dots(1)$$

on doubling volume all concentration are halved and equilibrium shifts forward



$$K_c = \frac{(3)^2 \left( \frac{a}{2} + \frac{1}{2} \right)}{\left( \frac{3}{2} - \frac{1}{2} \right)} \quad \dots (2)$$

$$\text{From (1) \& (2),} \quad \frac{16a}{3} = \frac{9(a+1)}{2}$$

$$\Rightarrow 32a = 27a + 27$$

$$\Rightarrow 5a = 27$$

$$a = 5.4$$

$$K_c = \frac{9(3.2)}{(1)} = 28.8$$

80.  $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$   
 $1.5a - x \quad a - x \quad 2x$

$$\begin{aligned}
 \frac{a-x}{2x} &= \frac{1}{18} \Rightarrow 9a - 9x = x \\
 x &= 9a/10
 \end{aligned}$$

$$K_c = \frac{[2(9a/10)]^2}{\left(1.5a - \frac{9a}{10}\right)(a - 9a/10)} = \frac{81 \times 4}{6 \times 1} = 54$$

81.  $CO + H_2O \rightleftharpoons CO_2 + H_2$   
 $1-x \quad 5-x \quad x \quad 1+x$

$$\frac{x(1+x)}{(1-x)(5-x)} = 7.3 \quad \text{Solving } x = 0.938$$

82.  $\frac{r_{mix}}{r_{Kr}} = \sqrt{\frac{M_{Kr}}{M_{avg}}} = 1.16$

$$\text{Solving, } M_{\text{average}} = \frac{83.8}{1.16^2}$$

$$\frac{71}{M_{avg.}} = 1 + \alpha. \quad K_p = \frac{4\alpha^2}{1 - \alpha^2}$$

$$\Rightarrow K_c = \frac{K_p}{(0.0821)(1473)} = 6.3 \times 10^{-4}$$

83.  $-16.5 \times 10^3 = -8.314 \times 298 \times 2.303 \log K_1$   
 $K_2 = K_1^2$

$$K_3 = \frac{1}{K_1}$$

let initial pressure of NO be p and of NO<sub>2</sub> be 2p

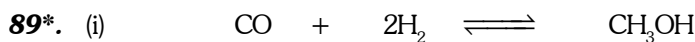
84. Fraction decomposed = 0.4

85. 4.54 g dm<sup>-3</sup>

86. (i)  $K_c = 8.1 \times 10^{-5} \text{ mol}^2 \text{ L}^2$ ;  $K_p = 4.84 \times 10^{-2} \text{ atm}^2$ ,  
 (ii) No effect;

87.  $15991 \text{ J mol}^{-1}$ ,  $12304 \text{ J mol}^{-1}$ ;  $B > C > A$

88. (i)  $5.705 \times 10^3 \text{ J mol}^{-1}$   
 (ii) Since initial Gibbs free energy change of the reaction is positive, so the reverse reaction will take place.



$$\begin{array}{ccccccc} t = 0 & 0.15 & a & & 0 & & \\ t = \infty & 0.15-x & a-2x & & x = 0.08 & & \end{array}$$

Total moles finally

$$= 0.15 + a - 2(0.08)$$

$$= a - 0.01$$

$$\Rightarrow 8.5 (2.5) = (a - 0.01) (0.0821) (750)$$

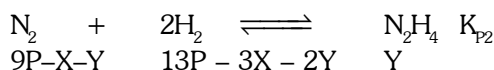
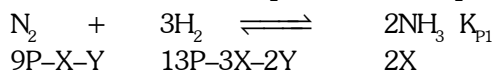
$$a = 0.355$$

Hence at equilibrium  $[\text{CO}] = 0.07\text{M}$ ,  $[\text{H}_2] = 0.195 \text{ M}$   $[\text{CH}_3\text{OH}] = 0.08$

$$\therefore K_c = \frac{0.08/2.5}{\left(\frac{0.195}{2.5}\right)^2 \left(\frac{0.07}{2.5}\right)}$$

- (ii) Total moles =  $0.15 + 0.355 = 0.505$   
 $P(2.5) = (0.505) (0.0821) 750$   
 $P = 12.43 \text{ atm}$

90. Let initial pressure of  $\text{N}_2$  be  $9P$  and of  $\text{H}_2$  be  $13P$



$$9P-X-Y+13P-3X-2Y+2X+Y=7P_0 \quad \dots (1)$$

$$2X = P_0 \quad \dots (2)$$

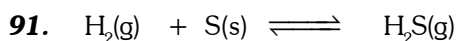
$$13P-3X-2Y = 2P_0 \quad \dots (3)$$

$$\text{Solving } x = P_0/2 \quad Y = 3P_0/2 \quad P = P_0/2$$

$$K_{p1} = \frac{(P_0)^2}{(4.5P_0 - 0.5P_0 - 1.5P_0)(6.5P_0 - 1.5P_0 - 3P_0)^3}$$

$$= \frac{P_0^2}{(2.5P_0)(8P_0^3)} = \frac{1}{20P_0^2}$$

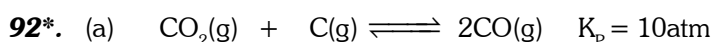
$$\text{and } K_{p2} = \frac{3}{20P_0^2}$$



$$\begin{array}{ccc} 0.2-x & & x \\ K_p = K_c = 6.8 \times 10^{-2} & & \end{array}$$

$$\frac{x}{0.2-x} = 6.8 \times 10^{-2} \Rightarrow x = 0.012$$

$$P_{\text{H}_2\text{S}} = (x) RT = 0.012 (0.0821) (363)$$



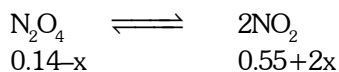
$$\begin{array}{ccc} P_0-x & & 2x \end{array}$$

$$\frac{4x^2}{P_0-x} = 10 \text{ \& } P_0 + x = 4$$

- (b) Let total pressure be  $P$  atm  
 $P_{\text{CO}_2} = 0.06 P$        $P_{\text{CO}_2} = 0.94 P$

$$K_p = 10 = \frac{(0.94P)^2}{0.06P} \Rightarrow P = 0.08 \text{ atm}$$

- 93.**  $K_p = 1.1^2/0.28 \text{ atm}$   
 On doubling volume



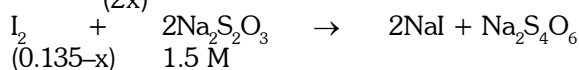
$$\frac{(0.55+2x)^2}{0.14-x} = \frac{1.1^2}{0.28}$$

- 94.**  $2\text{HI} \rightleftharpoons \text{H}_2 + \text{I}_2$   
 $1-0.8 \quad \quad \quad 0.4 \quad \quad \quad 0.4$

$$K_c = \frac{0.4 \times 0.4}{0.2^2} = 4$$

Let  $x$  mol of  $\text{H}_2$  &  $\text{I}_2$  react

$$4 = \frac{(0.135-x)^2}{(2x)^2}$$

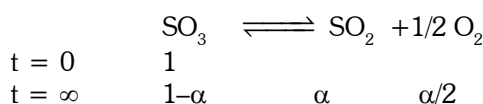


If  $V$  L of hypo are used

$$(0.135-x) \times 2 = 1.5 V$$

Let initially a mole  $\text{I}_2$  &  $(1.5 a)$  mol  $\text{H}_2$  be present

- 95\*.**  $M_{\text{average}} = \frac{12.8 \times 0.0821 \times 1000}{1.642} = 64$



$$\frac{80}{64} = 1 + \alpha/2 \Rightarrow \alpha = 0.5$$

- 96.** At 288 K,  $M_{\text{avg.}} = \frac{3.62 \times 0.0821 \times 288}{1}$

$$\frac{92}{M_{\text{avg.}}} = 1 + \alpha \Rightarrow K_{p1} = \frac{4\alpha^2}{1-\alpha^2}$$

$$\text{Similarly at 348K, } M'_{\text{avg.}} = \frac{1.84 \times 0.0821 \times 348}{1}$$

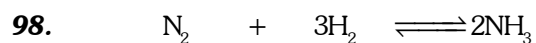
$$\frac{92}{M'_{\text{avg.}}} = 1 + \alpha' \Rightarrow K_{p2} = \frac{4\alpha'^2}{1-\alpha'^2}$$

$$\log \frac{K_{p2}}{K_{p1}} = \frac{\Delta H^\circ}{2.303R} \left[ \frac{1}{288} - \frac{1}{348} \right]$$

- 97\*.**  $K_1 = \frac{[\text{H}_2]^2[\text{O}_2]}{[\text{H}_2\text{O}]^2} \quad K_2 = \frac{[\text{CO}]^2[\text{O}_2]}{[\text{CO}_2]^2}$

$$K = \frac{[\text{CO}][\text{H}_2\text{O}]}{[\text{H}_2][\text{CO}_2]} = \frac{[\text{CO}][\text{O}_2]^{1/2}}{[\text{CO}_2]} \times \frac{[\text{H}_2\text{O}]}{[\text{H}_2][\text{O}_2]^{1/2}}$$

$$= \sqrt{\frac{K_2}{K_1}} = \sqrt{\frac{1.4 \times 10^{-12}}{2.1 \times 10^{-13}}} = 2.58$$



$$t=0 \quad 60\text{atm} \quad 20\text{atm}$$

$$t=\infty \quad 60-x \quad 20\text{atm} \quad 2x$$

$$\frac{2x}{80-2x} = \frac{1}{10} \Rightarrow 20x = 80 - 2x \Rightarrow x = \frac{80}{22}$$

$$\Rightarrow K_p = \frac{\left[2\left(\frac{80}{22}\right)\right]^2}{\left[60 - \frac{80}{22}\right]\left[20 - \frac{240}{22}\right]^3}$$



## IONIC EQUILIBRIUM

### Assertion-Reason

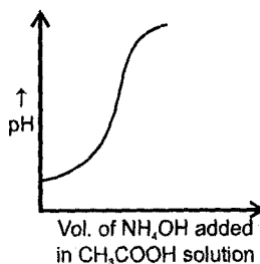
- Statement-1** : solubility of  $\text{BaSO}_4$  in  $0.1 \text{ M Na}_2\text{SO}_4$  is  $10^{-9} \text{ M}$  hence its  $K_{\text{sp}}$  is  $10^{-18}$ .

**Statement-2** : because for  $\text{BaSO}_4$   $K_{\text{sp}} = (s)^2$  [symbols have their usual meanings].

(A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement -1.  
 (B) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.  
 (C) Statement-1 is True, Statement-2 is False.  
 (D) Statement - 1 is False, Statement -2, is True.
- Statement-1** : It is difficult to distinguish the strengths of the strong acids such as  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ ,  $\text{HBr}$ ,  $\text{HI}$  or  $\text{HClO}_4$  in dilute aqueous solutions.

**Statement-2** : In dilute aqueous solution all strong acids donate a proton to water and are essentially. 100% ionised to produce a solution containing  $\text{H}_3\text{O}^+$  ions plus the anions of strong acid .

(A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.  
 (B) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.  
 (C) Statement-1 is True, Statement-2 is False.  
 (D) Statement-1 is False, Statement-2 is True.
- Statement-1** : The titration curve for weak acid and weak base is as follows :



For this titration no suitable indicator is present.

- Statement-2** : Indicator should change its colour sharply for indication of reaction to be complete so its pH-range should lie perfectly within sharp change to avoid experimental error.
- (A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.  
 (B) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.  
 (C) Statement-1 is True, Statement-2 is False.  
 (D) Statement-1 is False, Statement-2 is True.
- Statement-1** :  $0.20 \text{ M}$  solution of  $\text{NaCN}$  is more basic than  $0.20 \text{ M}$  solution of  $\text{NaF}$ .

**Statement-2** :  $0.20 \text{ M}$  solution of  $\text{NaCN}$  is more basic than  $0.20 \text{ M}$  solution of  $\text{CH}_3\text{COONa}$ .

(A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.  
 (B) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.  
 (C) Statement-1 is True, Statement-2 is False.  
 (D) Statement-1 is False, Statement-2 is True.
  - Statement-1** : A substance that can either act as an acid or a base is called ampholyte.

**Statement-2** : Bisulphide ion ( $\text{HS}^-$ ) and bicarbonate ion ( $\text{HCO}_3^-$ ) are ampholytes.

(A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.  
 (B) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.  
 (C) Statement-1 is True, Statement-2 is False.  
 (D) Statement-1 is False, Statement-2 is True.
  - Statement-1** : pH of amphiprotic anion is always independent upon concentration.

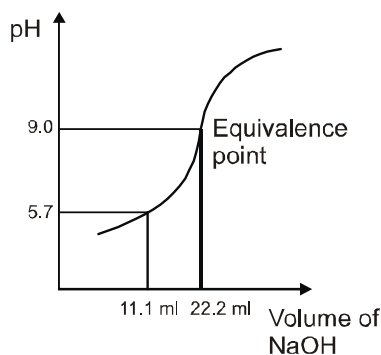
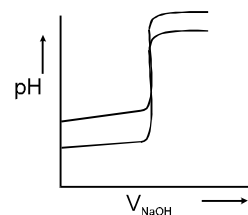
**Statement-2** : pH of amphiprotic anion is given by  $\frac{1}{2}[\text{p}K_1 + \text{p}K_2]$  where  $\text{p}K_1$  and  $\text{p}K_2$  are the dissociation const. of the acid in which amphiprotic anion is formed –

(A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.  
 (B) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.  
 (C) Statement-1 is True, Statement-2 is False.  
 (D) Statement-1 is False, Statement-2 is True.

**Single Choice Correct**

7. How many gm of solid NaOH must be added to 100 ml of a buffer solution which is 0.1 M each w.r.t. Acid HA and salt  $\text{Na}^+ \text{A}^-$  to make the pH of solution 5.5. Given  $\text{p}K_a(\text{HA}) = 5$ . (Use  $\text{antilog}(0.5) = 3.16$ )  
 (A)  $2.08 \times 10^{-1}$  (B)  $3.05 \times 10^{-3}$  (C)  $2.01 \times 10^{-2}$  (D) None of these
8. What % of the carbon in the  $\text{H}_2\text{CO}_3 - \text{HCO}_3^-$  buffer should be in the form of  $\text{HCO}_3^-$  so as to have a neutral solution? ( $K_a = 4 \times 10^{-7}$ )  
 (A) 20 % (B) 40 % (C) 60 % (D) 80%
- 9\*. If  $K_1$  &  $K_2$  be first and second ionisation constant of  $\text{H}_3\text{PO}_4$  and  $K_1 \gg K_2$  which is incorrect.  
 (A)  $[\text{H}^+] = [\text{H}_2\text{PO}_4^-]$  (B)  $[\text{H}^+] = \sqrt{K_1[\text{H}_3\text{PO}_4]}$   
 (C)  $K_2 = [\text{HPO}_4^{2-}]$  (D)  $[\text{H}^+] = 3[\text{PO}_4^{3-}]$
10. An aqueous solution contains 0.01 M  $\text{RNH}_2$  ( $K_b = 2 \times 10^{-6}$ ) &  $10^{-4}$  M NaOH. The concentration of  $\text{OH}^-$  is nearly :  
 (A)  $2.414 \times 10^{-4}$  (B)  $10^{-4}$  M (C)  $1.414 \times 10^{-4}$  (D)  $2 \times 10^{-4}$
11.  $\text{p}K_a$  of acetic acid is 4.74, which implies that:  
 (A) pH of 1 N acetic acid is 4.74  
 (B) at pH 4.74, the dissociation of acetic acid is maximum  
 (C) at pH 4.74 half of acetic acid molecules are dissociated in the solution  
 (D) at pH 4.74, the dissociation of acetic acid is minimum.
12. Pure water is added into the following solutions causing a 10% increase in volume of each :  
 (A) 0.1 M  $\text{NaHCO}_3$  (B) 0.2 M NaOH  
 (C) 0.3 M  $\text{NH}_3 - 0.2$  M  $\text{NH}_4^+$  system (D) 0.4 M  $\text{CH}_3\text{COONH}_4$   
 The greatest % change in pH would be observed in which case (A), (B), (C) or (D) ?
13. pH of an aqueous solution of NaCl at  $85^\circ\text{C}$  should be  
 (A) 7 (B)  $> 7$  (C)  $< 7$  (D) 0
14. Which of the following solution will have pH close to 1.0?  
 (A) 100 ml of M/100 HCl + 100 ml of M/10 NaOH (B) 55 ml of M/10 HCl + 45 ml of M/10 NaOH  
 (C) 10 ml of M/10 HCl + 90 ml of M/10 NaOH (D) 75 ml of M/5 HCl + 25 ml of M/5 NaOH
15. A certain acidic buffer solution contains equal concentration of  $\text{X}^-$  and HX. The  $K_b$  for  $\text{X}^-$  is  $10^{-10}$ . The pH of the buffer is :  
 (A) 4 (B) 7 (C) 10 (D) 14
16. At what pH will a  $1 \times 10^{-4}$  M solution of an indicator will  $K_b(\text{indicator}) = 1 \times 10^{-11}$  change colour?  
 (A) 7.0 (B) 3.0 (C) 5.5 (D) 11.0
17. One litre of saturated solution of  $\text{CaCO}_3$  is evaporated to dryness, 7.0 g of residue is left. The solubility product for  $\text{CaCO}_3$  is:  
 (A)  $4.9 \times 10^{-3}$  (B)  $4.9 \times 10^{-5}$  (C)  $4.9 \times 10^{-9}$  (D)  $4.9 \times 10^{-7}$
- 18\*. What will happen if the pH of the solution of 0.001 M  $\text{Mg}(\text{NO}_3)_2$  solution is adjusted to pH = 9 ( $K_{sp}$  of  $\text{Mg}(\text{OH})_2 = 8.9 \times 10^{-12}$ )  
 (A) ppt will take place (B) ppt will not take place  
 (C) Solution will be saturated (D) None of these
19. Equal volume of two solution having pH = 2 and pH = 10 are mixed together at  $90^\circ\text{C}$ . Then pH of resulting solution is : (Take  $K_w$  at  $90^\circ\text{C} = 10^{-12}$ )  
 (A)  $2 + \log 2$  (B)  $10 - \log 2$  (C) 7 (D) 6

- 20\*.** Which of the following is true  
 (A)  $pK_b$  for  $OH^-$  is  $-1.74$  at  $25^\circ C$   
 (B) The equilibrium constant for the reaction between  $HA$  ( $pK_a = 4$ ) and  $NaOH$  at  $25^\circ C$  will be equal to  $10^{10}$ .  
 (C) The pH of a solution containing  $0.1 M HCOOH$  ( $K_a = 1.8 \times 10^{-4}$ ) and  $0.1 M HOCN$ . ( $K_a = 3.2 \times 10^{-4}$ ) will be nearly  $(3 - \log 7)$ .  
 (D) All the above are correct.
- 21.** When  $0.1 M NaOH$  is added in  $0.1 M aq NH_3$  then which statement is going to wrong. ( $K_b = 2 \times 10^{-5}$ )  
 (A) degree of dissociation approaches to zero (B) change in pH would be  $1.85$   
 (C) conc of  $[Na^+] = 0.1$ ,  $[NH_3] = 0.1$ ,  $[OH^-] = 0.2$  (D) on addition of  $OH^-$   $K_b$  of  $NH_4OH$  does not changes.
- 22\*.** Which is/are correct statements :  
 (a) In any strong acid's solution, the concentration of  $[OH^-]$  will be zero.  
 (b) If  $\Delta G^\circ$  of a reaction is positive, then the reaction will not proceed at all, in the forward direction for any concentrations of reactants and products.  
 (c) When titration curves are drawn for  
 (i)  $1 M HCl$  ( $50 mL$ ) with  $1 M NaOH$  and  
 (ii)  $0.01 M HCl$  ( $50 mL$ ) with  $0.01 M NaOH$  on the same graph paper they look like:  
 (A) a & b (B) c only (C) b only (D) a & c
- 23.** A solution prepared by dissolving  $2.8 gm$  of lime,  $CaO$  in enough water to make  $1.00 L$  of lime water ( $Ca(OH)_2(aq)$ ). If solubility of  $Ca(OH)_2$  in water is  $1.48 gm$ . The pH of the solution obtained will be:  
 [ $\log 2 = 0.3$ , Atomic masses are  $Ca = 40$ ,  $O = 16$ ,  $H = 1$ ]  
 (A)  $12.3$  (B)  $12.6$  (C)  $1.3$  (D)  $13$
- 24.** Pure  $AgCl(s)$  is added to (i)  $0.01 M AgNO_3$  solution (ii)  $0.025 M KCl$  solution and both suspensions are shaken well. What is the ratio of the  $[Cl^-]$  in the first solution to the  $[Ag^+]$  in the second solution?  $S_{AgCl} = 1.7 \times 10^{-10}$ .  
 (A) nearly  $2.5$  (B) nearly  $2.0$  (C) nearly  $3.0$  (D) nearly  $1.5$
- 25\*.** The curve represents a titration of weak monoprotic acid with  $NaOH$ . Calculate the initial concentration of the acid using the data given in the curve. Assume that the final volume to be  $100 mL$  :

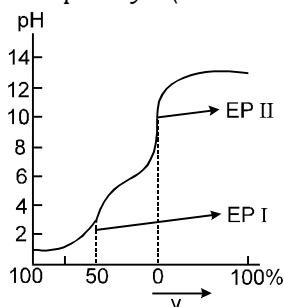


- (A)  $1.8 \times 10^{-5}$  (B)  $2.6 \times 10^{-2}$  (C)  $3 \times 10^{-4}$  (D)  $2.6 \times 10^{-6}$
- 26.** A solution is  $0.1 M$  each in  $HCl$  and  $CH_3COOH$ .  $20 mL$  of this solution is titrated against  $0.1 M NaOH$ . By how many units does the pH change from the beginning to the stage when the  $HCl$  is almost completely neutralized?  $K_a$  for acetic acid is  $1.8 \times 10^{-5}$ .  
 (A)  $2.03$  (B)  $0.775$  (C)  $1.87$  (D)  $3.172$
- 27.** The pH of  $0.1 M$  solution of the following salts increases in the order- **[JEE 1999]**  
 (A)  $NaCl < NH_4Cl < NaCN < HCl$  (B)  $HCl < NH_4Cl < NaCl < NaCN$   
 (C)  $NaCN < NH_4Cl < NaCl < HCl$  (D)  $HCl < NaCl < NaCN < NH_4Cl$
- 28.** An aqueous solution of  $6.3 g$  oxalic acid dihydrate is made up to  $250 mL$ . The volume of  $0.1 N NaOH$  required to completely neutralise  $10 mL$  of this solution is- **[JEE 2001]**  
 (A)  $40 mL$  (B)  $20 mL$  (C)  $10 mL$  (D)  $4 mL$

- 29.** For sparingly soluble salt  $ApBq$ , the relationship of its solubility product ( $L_s$ ) with its solubility ( $S$ ) is-  
**[JEE 2001]**  
 (A)  $L_s = S^{p+q}, p^p \cdot q^q$  (B)  $L_s = S^{p+q}, p^p \cdot q^p$  (C)  $L_s = S^{pq} p^p \cdot q^q$  (D)  $L_s = S^{pq}, (pq)^{p+q}$
- 30.** A solution which is  $10^{-3}$  M each in  $Mn^{2+}$ ,  $Fe^{2+}$ ,  $Zn^{2+}$  and  $Hg^{2+}$  is treated with  $10^{-16}$  M sulphide ion. If  $K_{sp}$ ,  $MnS$ ,  $FeS$ ,  $ZnS$  and  $HgS$  are  $10^{-15}$ ,  $10^{-23}$ ,  $10^{-20}$  and  $10^{-54}$  respectively, which one will precipitate first? **[JEE 2003]**  
 (A)  $FeS$  (B)  $MnS$  (C)  $HgS$  (D)  $ZnS$
- 31.**  $HX$  is a weak acid ( $K_a = 10^{-5}$ ). It forms a salt  $NaX$  (0.1 M) on reacting with caustic soda. The degree of hydrolysis of  $NaX$  is-  
**[JEE 2004]**  
 (A) 0.01 % (B) 0.0001 % (C) 0.1 % (D) 0.5 %
- 32\*.**  $CH_3NH_2$  (0.1 mole,  $K_b = 5 \times 10^{-4}$ ) is added to 0.08 moles of  $HCl$  and the solution is diluted to one litre, resulting hydrogen ion concentration is-  
**[JEE 2005]**  
 (A)  $1.6 \times 10^{-11}$  (B)  $8 \times 10^{-11}$  (C)  $5 \times 10^{-5}$  (D)  $2 \times 10^{-2}$
- 33.**  $CH_3NH_2$  (0.1 mole,  $K_b = 5 \times 10^{-4}$ ) is added to 0.08 moles of  $HCl$  and the solution is diluted to one litre, resulting hydrogen ion concentration is  
 (A)  $1.6 \times 10^{-11}$  (B)  $8 \times 10^{-11}$  (C)  $5 \times 10^{-5}$  (D)  $2 \times 10^{-2}$  **[JEE 2005]**

### Multiple Choice Correct

- 34\*.** A weak acid (or base) is titrated against a strong base (or acid), volume  $v$  of strong base (or acid) is plotted against pH of the solution in Fig. The weak protolyte (i.e. acid or base) could be



- (A)  $Na_2CO_3$  (B)  $Na_2C_2O_4$  (C)  $H_2C_2O_4$  (D)  $CH_2(COOH)_2$
- 35.** Which of the following are true for an acid-base titration?  
 (A) Indicators catalyse the acid base reactions by releasing or accepting  $H^+$  ions.  
 (B) Indicators do not significantly affect the pH of the solution to which they are added.  
 (C) Acid-base reactions do not occur in absence of indicators.  
 (D) Indicators have different colours in dissociated and undissociated forms.
- 36.** The charge balance condition for a solution is written as  $[Na^+] + [H^+] = [Cl^-] + [Br^-] + [I^-] + [OH^-]$ . The solution could be :  
 (A)  $NaCl / NaBr / NaI$  simultaneously (B)  $NaCl / NaBr / HBr / HI$  simultaneously  
 (C)  $NaOH / HCl / HBr / HI$  simultaneously (D)  $NaI / HI / HBr / HCl$  simultaneously
- 37\*.** Successive acid dissociation constants for a tri basic acid,  $H_3XO_3$ , are  $K_1 = 7.5 \times 10^{-10}$ ,  $K_2 = 2 \times 10^{-13}$ ,  $K_3 = 1.6 \times 10^{-14}$ . Decimolar aqueous solutions of which of the following are expected to be basic?  
 (A)  $H_3XO_3$  (B)  $NaH_2XO_3$  (C)  $Na_2HXO_3$  (D)  $Na_3XO_3$
- 38\*.** When 0.1 mol arsenic acid,  $H_3AsO_4$  is dissolved in 1L buffer solution of  $pH = 4$ , which of the following hold good?  $K_1 = 2.5 \times 10^{-4}$ ,  $K_2 = 5 \times 10^{-8}$ ,  $K_3 = 2 \times 10^{-13}$  for arsenic acid [ $<$  sign denotes that the higher concentration is at least 100 times more than the lower one]  
 (A)  $[H_3AsO_4] < [H_2AsO_4^-]$  (B)  $[H_2AsO_4^-] < [HAsO_4^{2-}]$   
 (C)  $[HAsO_4^{2-}] < [AsO_4^{3-}]$  (D)  $[AsO_4^{3-}] < [HAsO_4^{2-}]$

39. Which of the following statement(s) is/are correct ? [JEE 1998]
- (A) the pH of  $1.0 \times 10^{-8}$  M solution of HCl is 8  
 (B) the conjugate base of  $\text{H}_2\text{PO}_4^-$  is  $\text{HPO}_4^{2-}$   
 (C) autoprotolysis constant of water increases with temperature  
 (D) when a solution of a weak monoprotic acid is titrated against a strong base, at half - neutralization point  $\text{pH} = (1/2) \text{pK}_a$ .
40. A buffer solution can be prepared from a mixture of- [JEE 1999]
- (A) sodium acetate and acetic acid in water  
 (B) sodium acetate and hydrochloric acid in water  
 (C) ammonia and ammonium chloride in water  
 (D) ammonia and sodium hydroxide in water.

**Match the Column**

41\*. Match the column.

**Column I**

**Column II**

- (A)  $\left( \begin{array}{l} 10 \text{ litre of } 0.03 \text{ N } (\text{OH})_2 \text{ (strong diacidic base)} \\ + \\ 5 \text{ litre of } 0.08 \text{ M } \text{HNO}_3 \\ + \\ 485 \text{ litre of } 0.01 \text{ M } \text{NaNO}_3 \end{array} \right)$  (p)  $\text{pH} \approx 3.7$
- (B)  $\left( \begin{array}{l} 10 \text{ ml of } 0.5 \text{ M } \text{RNH}_3\text{Cl} (\text{K}_h = 10^{-9}) \\ + \\ 40 \text{ ml of } 0.125 \text{ M } \text{KOH} \end{array} \right)$  (q)  $\text{pH} \approx 11$
- (C)  $\left( \begin{array}{l} 100 \text{ ml of } 0.8 \text{ M } \text{HCO}_3^- \\ + \\ 100 \text{ ml of } 0.4 \text{ M } \text{CO}_3^{2-} \\ \text{(for } \text{H}_2\text{CO}_3, \text{ use } \text{K}_{a1} = 4 \times 10^{-7} \text{ \& } \text{K}_{a2} = 4 \times 10^{-11}) \end{array} \right)$  (r)  $\text{pH} \approx 7$
- (D) Saturated aqueous of  $\text{Co}(\text{OH})_3$  ( $\text{K}_{\text{sp}} = 2.7 \times 10^{-43}$ ) (s)  $\text{pH} \approx 10$

42\*. Match the following :

If  $\text{K}_a$  of HCN =  $5 \times 10^{-10}$ ,  $\text{K}_a$  of HOCN =  $3.2 \times 10^{-4}$ ,  $\text{K}_b$  of  $\text{NH}_3$  =  $1.8 \times 10^{-5}$ ,  $\text{K}_a$  of  $\text{CH}_3\text{COOH}$  =  $1.8 \times 10^{-5}$

**Column-I**

**Column-II**

- (A)  $0.1 \text{ M } \text{NH}_4\text{CN}$  (p)  $\text{pH} > 7$   
 (B)  $100 \text{ ml of } 10^{-1} \text{ M } \text{NaCl} + 100 \text{ ml of } 10^{-1} \text{ M } \text{HCl} + 300 \text{ ml of } 10^{-1} \text{ M } \text{NaOH}$  (q)  $\text{pH} \neq 7$   
 (C)  $10^{-1} \text{ M } \text{HCl} + 10^{-1} \text{ M } \text{HCN}$  (r)  $\text{pH} < 7$   
 (D)  $10^{-1} \text{ M } \text{NH}_4\text{OCN}$  (s)  $\text{pH} = 7$

43. (Use  $\log 1.8 = 0.26$ ,  $\text{K}_a$  of formic acid =  $1.8 \times 10^{-4}$ ,  $\text{K}_a$  of acetic acid =  $1.8 \times 10^{-5}$ ,  $\text{K}_b$  of ammonia =  $1.8 \times 10^{-5}$ ,  $\text{K}_{a1}$  of  $\text{H}_2\text{S}$  =  $10^{-7}$  and  $\text{K}_{a2}$  of  $\text{H}_2\text{S}$  =  $10^{-14}$ , for the following matchings)

Match the entries of column II for which the equality or inequality given in the column I are satisfied.

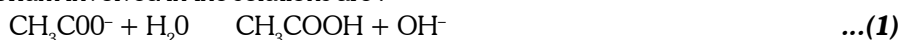
**Column I**

**Column II**

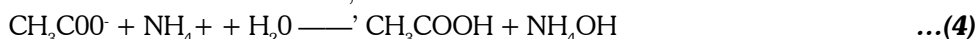
- (A)  $10^{-5} \text{ M } \text{HCl}$  solution  $> 0.1 \text{ M } \text{H}_2\text{S}$  solution (p)  $\alpha_{\text{water}}$  (degree of dissociation of water)  
 (B)  $\text{CH}_3\text{COOH}$  solution at pH equal to 4.74 (q)  $[\text{OH}^-]$   
      $= \text{NH}_4\text{OH}$  solution at pH equal to 9.26  
 (C)  $0.1 \text{ M } \text{CH}_3\text{COOH}$  solution =  $1.0 \text{ M } \text{HCOOH}$  solution (r)  $\alpha$  (degree of dissociation of weak electrolytes)  
 (D)  $0.1 \text{ M}$  of a weak acid  $\text{HA}$  ( $\text{K}_b = 10^{-5}$ ) solution (s) pH  
      $< 0.01 \text{ M}$  of a weak acid  $\text{HA}_2$  ( $\text{K}_a = 10^{-8}$ ) solution

**Comprehension****Comprehension-1**

Consider a solution of  $\text{CH}_3\text{COONH}_4$  which is a salt of weak acid & weak base. The equilibrium involved in the solutions are :



If we add these three reactions, then the net reaction is



Both  $\text{CH}_3\text{COO}^-$  and  $\text{NH}_4^+$  get hydrolysed independently and their hydrolysis depends on

- (i) their initial concentration
- (ii) the value of  $K_h$  which is  $\frac{K_w}{K_a}$  for  $\text{CH}_3\text{COO}^-$  and  $\frac{K_w}{K_b}$  for  $\text{NH}_4^+$ .

Since both of the ions were produced from the same salt, their initial concentrations are same. Therefore

unless & until the value of  $\frac{K_w}{K_a}$  and  $K_b$  is same, the degree of hydrolysis of ion can't be same.

To explain why we assume that degree of hydrolysis of cation and anion is same, we need to now look at the third reaction i.e., combination of  $\text{H}^+$  and  $\text{OH}^-$  ions. It is obvious that this reaction happens only because one reaction produced  $\text{H}^+$  ion and the other produced  $\text{OH}^-$  ions. We can also note that this reaction causes both the hydrolysis reaction to occur more since their product ions are being consumed. Keep this thing in mind that the equilibrium which has smaller value of equilibrium constant is affected more by the common ion effect. For the same reason if for any reason a reaction is made to occur to a greater extent by the consumption of any one of the product ion, the reaction with the smaller value of equilibrium constant tends to get affected more. Therefore we conclude that firstly the hydrolysis of both the ions occurs more in the presence of each other (due to consumption of the product ions) than in each other's absence. Secondly the hydrolysis of the ion which occurs to a lesser extent (due to smaller value of  $K_h$ ) is affected more than the one whose  $K_h$  is greater. Hence we can see that the degree of hydrolysis of both the ions would be close to each other when they are getting hydrolysed in the presence of each other.

**44\*.** In the hydrolysis of salt of weak acid & weak base :

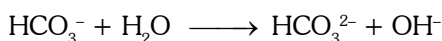
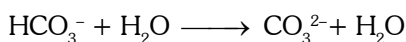
- (A) degree of hydrolysis of cation and anion is different  
 (B) degree of hydrolysis of cation and anion is same  
 (C) degree of hydrolysis of cation and anion is different and they can never be assumed same.  
 (D) degree of hydrolysis of cation and anion is different but they are very close to each other when they are getting hydrolysed in the presence of each other.

**45\*.** For 0.1 M  $\text{CH}_3\text{COONH}_4$  salt solution given,  $K_{a_{\text{CH}_3\text{COOH}}} = K_{b_{\text{NH}_4\text{OH}}} = 2 \times 10^{-5}$ .

In this case : degree of hydrolysis of cation and anion is

- (A) exactly same  
 (B) slightly different  
 (C) can't say  
 (D) different but can be taken approximately same

**46\*.** In a solution of  $\text{NaHCO}_3$ , the amphiprotic anion can undergo ionization to form  $\text{H}^+$  ion and hydrolysis to form  $\text{OH}^-$  ion. ionization



To calculate pH, suitable approximation is :

- (A)  $[\text{CO}_3^{2-}] = [\text{HCO}_3^-]$   
 (B) degree of ionization = degree of Hydrolysis  
 (C) both (A) and (B)  
 (D) neither 'A' nor 'B'

**Comprehension-2**

The product of the concentrations of the ions of an electrolyte raised to power of their coefficients in the balanced chemical equation in the solution at any concentration is called ionic product. Its value is not constant and varies with change in concentration. Ionic product of the saturated solution is called solubility product  $K_{sp}$ .

- (i) When  $K_{ip} = K_{sp}$ , the solution is just saturated and no precipitation takes place.
- (ii) When  $K_{ip} < K_{sp}$ , the solution is unsaturated and precipitation will not take place.
- (iii) When  $K_{ip} > K_{sp}$ , the solution is supersaturated and precipitation takes place.

47. The solubility product  $K_{sp}$  of sparingly soluble salt MX at  $25^\circ\text{C}$  is  $2.5 \times 10^{-9}$ . The solubility of the salt in  $\text{mol L}^{-1}$  at this temperature is  
 (A)  $1 \times 10^{-14}$  (B)  $5 \times 10^{-8}$  (C)  $1.25 \times 10^{-9}$  (D)  $5 \times 10^{-5}$
48. Which of the following is most soluble?  
 (A)  $\text{Bi}_2\text{S}_3$  ( $K_{sp} = 1 \times 10^{-70}$ ) (B)  $\text{MnS}$  ( $K_{sp} = 7 \times 10^{-16}$ )  
 (C)  $\text{CuS}$  ( $K_{sp} = 8 \times 10^{-37}$ ) (D)  $\text{Ag}_2\text{S}$  ( $K_{sp} = 6 \times 10^{-51}$ )
49. The concentration of  $\text{Ag}^+$  ions in a given saturated solution of  $\text{AgCl}$  at  $25^\circ\text{C}$  is  $1.06 \times 10^{-5}$  g ion per litre. The solubility product of  $\text{AgCl}$  is :  
 (A)  $0.353 \times 10^{-10}$  (B)  $0.530 \times 10^{-10}$  (C)  $1.12 \times 10^{-10}$  (D)  $2.12 \times 10^{-10}$

**Comprehension-3**

Potash alum is  $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ . As a strong electrolyte, it is considered to be 100 % dissociated into  $\text{K}^+$ ,  $\text{Al}^{3+}$  and  $\text{SO}_4^{2-}$ . The solution is acidic because of the hydrolysis of  $\text{Al}^{3+}$ , but not so acidic as might be expected, because the  $\text{SO}_4^{2-}$  can sponge up some of the  $\text{H}_3\text{O}^+$  by forming  $\text{HSO}_4^-$ . Given a solution made by dissolving 11.85 gm of  $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  in enough water to make  $100 \text{ cm}^3$  of solution. What is  $[\text{H}_3\text{O}^+]$  of the solution if

50. None of the ion is hydrolysing.  
 (A)  $10^{-7} \text{ M}$  (B) less than  $10^{-7} \text{ M}$  (C) More than  $10^{-7} \text{ M}$  (D) 0.0
51. Only  $\text{Al}^{3+}$  is hydrolysing and its first hydrolysis constant is  $1.4 \times 10^{-5} \text{ M}$   
 (A)  $1.87 \times 10^{-3} \text{ M}$  (B)  $6.24 \times 10^{-4} \text{ M}$  (C)  $0.09 \text{ M}$  (D) None of these
52. Only  $\text{SO}_4^{2-}$  is hydrolysing and acid dissociation constant of  $\text{HSO}_4^-$  in water is  $1.25 \times 10^{-2}$ .  
 (A)  $1.26 \times 10^{-3} \text{ M}$  (B)  $6.32 \times 10^{-7} \text{ M}$  (C)  $1.58 \times 10^{-8} \text{ M}$  (D) None of these
53. Both  $\text{Al}^{3+}$  and  $\text{SO}_4^{2-}$  are hydrolysing.  
 (A)  $2.93 \times 10^{-4} \text{ M}$  (B)  $0.0114 \text{ M}$  (C)  $5.43 \times 10^{-6} \text{ M}$  (D) None of these

**Subjective Questions**

54. The value of  $K_w$  at the physiological temperature ( $37^\circ\text{C}$ ) is  $2.56 \times 10^{-14}$ . What is the pH at the neutral point of water at this temperature?
55. All environmental chemist needs a carbonate buffer of pH 10.00 to study the effects of the acidification of limestone-rich soils. How many grams of  $\text{Na}_2\text{CO}_3$  must be added to 1.5 L of freshly prepared  $0.20 \text{ M NaHCO}_3$  to make the buffer?  $K_a$  of  $\text{HCO}_3^- = 4.7 \times 10^{-11}$ . ( $\log 4.7 = 0.672$ )
- 56\*. The dissociation constant for hydrogen sulphide (dissociated into  $2\text{H}^+$  and  $\text{S}^{2-}$ ) is  $1.1 \times 10^{-22}$  at  $18^\circ\text{C}$ . What is the concentration of sulphide ion in a  $0.1 \text{ N}$  hydrochloric acid solution which is saturated with hydrogen sulphide at  $18^\circ\text{C}$ , assuming that the concentration of  $\text{H}_2\text{S}$  is  $0.1 \text{ M}$ ?
57. Calculate the extent of hydrolysis of  $0.005 \text{ M K}_2\text{CrO}_4$ . [ $K_2 = 3.1 \times 10^{-7}$  for  $\text{H}_2\text{CrO}_4$ ]  
 (It is essentially strong for first ionization).
58. A solution of ammonia bought for cleaning the windows was found to be 10% ammonia by mass, having a density of  $0.935 \text{ g mL}^{-1}$ . What is the pH of the solution. Take  $K_b$  for protonation of ammonia =  $5.5 \times 10^{-6}$ .



- 59.** A handbook states that the solubility of methylamine  $\text{CH}_3\text{NH}_2$  (g) in water at 1 atm pressure at  $25^\circ\text{C}$  is 959 volumes of  $\text{CH}_3\text{NH}_2$  (g) per volume of water ( $pK_b = 3.39$ ) :-  
 (a) Estimate the max. pH that can be attained by dissolving methylamine in water.  
 (b) What molarity NaOH (aq.) would be required to yield the same pH?
- 60\*.** Mixture of solutions. Calculate the pH of the following solution.  
 Use data of above question & For  $\text{H}_2\text{CO}_3$ ;  $K_1 = 4.2 \times 10^{-7}$ ,  $K_2 = 4.8 \times 10^{-11}$   
 (a) 40 mL of 0.050 M  $\text{Na}_2\text{CO}_3$  + 50 mL of 0.040 M HCl;  
 (b) 40 mL of 0.020 M  $\text{Na}_3\text{PO}_4$  + 40 mL of 0.040 M HCl;  
 (c) 50 mL of 0.10 M  $\text{Na}_3\text{PO}_4$  + 50 mL of 0.10 M  $\text{NaH}_2\text{PO}_4$ ;  
 (d) 40 mL of 0.10 M  $\text{H}_3\text{PO}_4$  + 40 mL of 0.10 M  $\text{Na}_3\text{PO}_4$ .
- 61.** A buffer solution was prepared by dissolving 0.05 mol formic acid & 0.06 mol sodium formate in enough water to make 1.0 L of solution.  $K_a$  for formic acid is  $1.80 \times 10^{-4}$ .  
 (a) Calculate the pH of the solution.  
 (b) If this solution were diluted to 10 times its volume, what would be the pH?  
 (c) If the solution in (b) were diluted to 10 times its volume, what would be the pH?
- 62.** Calculate the  $\text{OH}^-$  concentration and the  $\text{H}_3\text{PO}_4$  concentration of a solution prepared by dissolving 0.1 mol of  $\text{Na}_3\text{PO}_4$  in sufficient water to make 1 L of solution  $K_1 = 7.1 \times 10^{-3}$ ,  $K_2 = 6.3 \times 10^{-8}$ ,  $K_3 = 4.5 \times 10^{-13}$ .
- 63\*.** A buffer solution was prepared by dissolving 0.02 mol propionic acid & 0.015 mol sodium propionate in enough water to make 1.00 L of solution. ( $K_a$  for propionic acid is  $1.34 \times 10^{-5}$ )  
 (a) What is the pH of the buffer.  
 (b) What would be the pH change if  $1.0 \times 10^{-5}$  mol HCl were added to 10 ml of the buffer.  
 (c) What would be the pH change if  $1.0 \times 10^{-5}$  mol NaOH were added to 10 ml of the buffer.  
 (d) Also report the percent change in pH of original buffer in cases (b) and (c).
- 64.** Describe how would you prepare a phosphate buffer at a pH of about 7.40. Given for  $\text{H}_3\text{PO}_4$   
 $K_{a1} = 7.5 \times 10^{-3}$ ,  $K_{a2} = 6.2 \times 10^{-8}$ ,  $K_{a3} = 4.8 \times 10^{-13}$ .
- 65.**  $pK_1$  and  $pK_2$  for pyrophosphoric acid ( $\text{H}_4\text{P}_2\text{O}_7$ , a tetraprotic acid) are 0.80 and 2.2 respectively. Neglecting the third and fourth dissociations, find the concentration of the divalent anion in a 0.05 M acid solution.
- 66.** A weak acid (50.0 mL) was titrated with 0.1 M NaOH. The pH values when 10.0 mL and 25.0 mL of base have been added are found to be 4.16 and 4.76, respectively. Calculate  $K_a$  of the acid and pH at the equivalence point.
- 67.** Bromophenol blue is an acid indicator with a  $K_a$  value of  $6 \times 10^{-5}$ . What % of this indicator is in its basic form at a pH of 5?
- 68\*.** An acid indicator has a  $K_a$  of  $3 \times 10^{-5}$ . The acid form of the indicator is red & the basic form is blue. By how much must the pH change in order to change the indicator from 75% red to 75% blue?
- 69.** Calculate the pH during the titration of 40.00 ml of 0.1 M propanoic acid (HPr;  $K_a = 1 \times 10^{-5}$ ) after adding the following volumes of 0.1 M NaOH : ( $\log 2 = 0.3$ ,  $\log 3 = 0.48$ )  
 (a) 0.00 ml (b) 30.00 ml (c) 40.00 ml (d) 50.00 ml.
- 70\*.** A small quantity of phenolphthalein is added to a decinormal solution of sodium butyrate at  $25^\circ\text{C}$ . Calculate the ratio of the coloured to the colourless form of the indicator.  $K_a$  for butyric acid =  $1.5 \times 10^{-5}$  at  $25^\circ\text{C}$ .  $K$  for the indicator =  $3.16 \times 10^{-10}$  and  $K_w = 10^{-14}$  at  $25^\circ\text{C}$ .
- 71.** How many mol CuI ( $K_{sp} = 5 \times 10^{-12}$ ) will dissolve in 1.0 L of 0.10 M NaI solution?
- 72.** What mass of  $\text{Pb}^{2+}$  ion is left in solution when 50.0 mL of 0.20 M  $\text{Pb}(\text{NO}_3)_2$  is added to 50.0 mL of 1.5 M NaCl? [Given  $K_{sp}$  for  $\text{PbCl}_2 = 1.7 \times 10^{-4}$ ]



- 73\*.** How much AgBr could dissolve in 1.0 L of 0.40 M  $\text{NH}_3$ ? Assume that  $\text{Ag}(\text{NH}_3)_2^+$  is the only complex formed.  
 $[K_f(\text{Ag}(\text{NH}_3)_2^+) = 1 \times 10^8; K_{sp}(\text{AgBr}) = 5 \times 10^{-13}]$
- 74.**  $K_{sp}$  of  $\text{PbBr}_2$  is  $2.56 \times 10^{-7}$ . If the salt is 80% dissociated in solution, calculate the solubility of salt in g per litre.
- 75.**  $K_{sp}$  for  $\text{PbCl}_2$  is  $10^{-13}$ . What will be  $[\text{Pb}^{2+}]$  in a solution prepared by mixing 100 mL of 0.1 M  $\text{Pb}(\text{NO}_3)_2$  and 1 mL of 1 M HCl?
- 76\*.** Given :  $\text{Ag}(\text{NH}_3)_2^+ \rightleftharpoons \text{Ag}^+ + 2 \text{NH}_3$ ,  $K_c = 6.2 \times 10^{-8}$  &  $K_{sp}$  of  $\text{AgCl} = 1.8 \times 10^{-10}$  at 298 K. Calculate the concentration of the complex in 1.0 M aqueous ammonia. **[JEE 1998]**
- 77.** What will be the resultant pH when 200 mL of an aqueous solution of HCl (pH = 2.0) is mixed with 300 mL of an aqueous solution of NaOH (pH = 12.0)? **[JEE 1998]**
- 78.** The solubility of  $\text{Pb}(\text{OH})_2$  in water is  $6.7 \times 10^{-6}$  M. Calculate the solubility of  $\text{Pb}(\text{OH})_2$  in a buffer solution of pH = 8. **[JEE 1999]**
- 79\*.** The average concentration of  $\text{SO}_2$  in the atmosphere over a city on a certain day is 10 ppm, when the average temperature is 298 K. Given that the solubility of  $\text{SO}_2$  in water at 298 K is 1.3653 moles litre<sup>-1</sup> and the  $\text{pK}_a$  of  $\text{H}_2\text{SO}_3$  is 1.92, estimate the pH of rain on that day. **[JEE 2000]**
- 80.** 500 mL of 0.2 M aqueous solution of acetic acid is mixed with 500 mL of 0.2 M HCl at 25 °C.  
 (a) Calculate the degree of dissociation of acetic acid in the resulting solution and pH of the solution.  
 (b) If 6g of NaOH is added to the above solution, determine final pH. Assume there is no change in volume on mixing.  $K_a$  of acetic acid is  $1.75 \times 10^{-5}$  M. **[JEE 2002]**
- 81.** Will the pH of water be same at 4 °C and 25 °C? Explain. **[JEE 2003]**
- 82.** 0.1 M of HA is titrated with 0.1 M NaOH, calculate the pH at end point.  
 Given  $K_a(\text{HA}) = 5 \times 10^{-6}$  and  $\alpha \ll 1$ . **[JEE 2004]**
- 83.** Salt mixture containing  $\text{Cu}_3(\text{AsO}_4)_2$  ( $K_{sp} = 8 \times 10^{-36}$ ) and  $\text{Pb}_3(\text{AsO}_4)_2$  ( $K_{sp} = 4.096 \times 10^{-36}$ ) is shaken with water. Find the concentration of metal cations in the solution at equilibrium. Neglect any hydrolysis of the dissolved ions.
- 84\*.** (a) At what minimum pH will  $1.0 \times 10^{-3}$  mol of  $\text{Al}(\text{OH})_3$  go into 1 L solution as  $[\text{Al}(\text{OH})_4^-]$ .  
 (b) At what minimum pH will  $1.0 \times 10^{-3}$  mol of  $\text{Al}(\text{OH})_3$  go into 1 L solution as  $\text{Al}^{3+}$ ?  
 Given :  $K_{sp}[\text{Al}(\text{OH})_3] = 5.0 \times 10^{-33}$  and for  $[\text{Al}(\text{OH})_4^-] \rightleftharpoons \text{Al}^{3+} + 4\text{OH}^-$ ,  $K = 1.3 \times 10^{-34}$ .
- 85.** What is the pH of a 1.0 M solution of acetic acid? To what volume must 1 litre of the solution be diluted so that the pH of the resulting solution will be twice the original value. Given  $K_a = 1.8 \times 10^{-5}$  :-
- 86\*.** Mixture of solutions. Calculate the pH of the following solutions.  
 For  $\text{H}_3\text{PO}_4$ ;  $K_{a1} = 7.5 \times 10^{-3}$ ,  $K_{a2} = 6.2 \times 10^{-8}$ ,  $K_{a3} = 10^{-12}$   
 (a) 50 mL of 0.12 M  $\text{H}_3\text{PO}_4$  + 20 mL of 0.15 M NaOH;  
 (b) 50 mL of 0.12 M  $\text{H}_3\text{PO}_4$  + 40 mL of 0.15 M NaOH;  
 (c) 40 mL of 0.12 M  $\text{H}_3\text{PO}_4$  + 40 mL of 0.18 M NaOH;  
 (d) 40 mL of 0.10 M  $\text{H}_3\text{PO}_4$  + 40 mL of 0.25 M NaOH.
- 87.** When a 40 mL of a 0.1 M weak base is titrated with 0.16 M HCl, the pH of the solution at the end point is 5.23. What will be the pH if 15 mL of 0.12 M NaOH is added to the resulting solution :-
- 88.** How many moles of sodium hydroxide can be added to 1.00 L of a solution 0.1 M in  $\text{NH}_3$  & 0.1 M in  $\text{NH}_4\text{Cl}$  without changing the pOH by more than 1.00 unit? Assume no change in volume.  $K_b(\text{NH}_3) = 1.8 \times 10^{-5}$ .

- 89\***. If 0.00050 mol  $\text{NaHCO}_3$  is added to 1 litre of a buffered solution at pH 8.00, how much material will exist in each of the three forms  $\text{H}_2\text{CO}_3$ ,  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$ ? For  $\text{H}_2\text{CO}_3$ ,  $K_1 = 5 \times 10^{-7}$ ,  $K_2 = 5 \times 10^{-13}$ .
- 90.** How much  $\text{Na}_2\text{HPO}_4$  must be added to one litre of 0.005 M solution of  $\text{NaH}_2\text{PO}_4$  in order to make a 1 L of the solution of pH = 6.7?  $K_1 = 7.1 \times 10^{-3}$ ,  $K_2 = 6.3 \times 10^{-8}$ ,  $K_3 = 4.5 \times 10^{-13}$  for  $\text{H}_3\text{PO}_4$ .
- 91\***. Liquid ammonia ionises to a slight extent. At  $-50^\circ\text{C}$ , its self ionisation constant  $K_{\text{NH}_3} = [\text{NH}_4^+][\text{NH}_2^-] = 10^{-30}$ . How many amide ions are present per  $\text{cm}^3$  of pure liquid ammonia.
- 92.** Calculate the pH of a solution obtained by mixing 0.1 litre of a strong acid solution of pH = 4 and 0.2 lit, solution of strong base of pH = 10.
- 93\***. If both the functional groups of salicylic acid,  $\text{HOC}_6\text{H}_4\text{COOH}$ , ionise in water, with  $K_a = 1 \times 10^{-3}$  for the  $-\text{COOH}$  group and  $4.2 \times 10^{-13}$  for the  $-\text{OH}$  group, calculate pH of the saturated solution of the acid. (Solubility of salicylic acid in water = 1.725 g/L,  $\log 2 = 0.3$ ).

## ANSWERS

### Assertion-Reason

1. (D)      2. (A)      3. (A)      4. (B)      5. (B)  
 6. (B)

### Single Choice Correct

7. (A)      8. (D)      9. (D)      10. (D)      11. (C)  
 12. (B)      13. (C)      14. (D)      15. (A)      16. (B)  
 17. (A)      18. (B)      19. (D)      20. (D)      21. (C)  
 22. (B)      23. (B)      24. (A)      25. (B)      26. (A)  
 27. (B)      28. (A)      29. (A)      30. (C)      31. (A)  
 32. (B)      33. (B)

### Multiple Choice Correct

34. (CD)      35. (BD)      36. (ABCD)      37. (BCD)      38. (CD)  
 39. (BC)      40. (AC)

### Match the Column

- 41\*. (A - p), (B - q), (C - s), (D - r)      42. (A - p, q); (B - p, q); (C - q, r); (D - q, r)  
 43. (A - p, q, r, s); (B - p, r); (C - r); (D - p, q, s)

### Comprehension

- Comprehension 1 :**      44\*. (D)      45\*. (C)      46\*. (C)  
**Comprehension 2 :**      47. (D)      48. (B)      49. (C)  
**Comprehension 3 :**      50. (A)      51. (A)      52. (C)      53. (A)

### Subjective Questions

54.  $pK_w = 14 - \log 2.56 = 13.59 \approx 13.6$

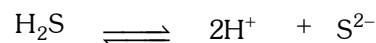
$$pH = \frac{pK_w}{2} = 6.795$$

55. Ans. 15 g  $Na_2CO_3$   
For  $Na_2CO_3 + NaHCO_3$  buffer

$$pH = pK_a \text{ of } HCO_3^- + \log \frac{[CO_3^{2-}]}{[HCO_3^-]}$$

56. Ans.  $1.1 \times 10^{-21} M$

HCl saturated  $H_2S$  solution, in presence of 0.1 N HCl



$$0.1 M \quad \quad 0.10 \quad \quad 0$$

$$0.1 - x \quad \quad 0.1 + x \quad \quad x$$

$$\therefore K_a = \frac{x \times (0.1 + x)^2}{0.1 - x}$$

Where  $x \ll 0.1$

57. Ans. 0.26%

For anionic hydrolysis of  $A^{2-}$

$$h = \sqrt{\frac{K_h}{C}} \text{ where } K_h = \frac{K_w}{K_{a2}}$$

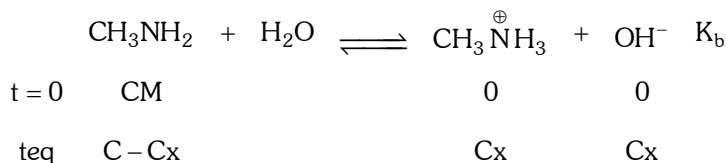
58. **Ans. pH = 11.74**

For ammonia solution i.e.  $\text{NH}_4\text{OH}$

$$\text{pOH} = \frac{1}{2} \text{p}K_b - \frac{1}{2} \log C$$

$$\text{where } C = \frac{10}{100} \times \frac{935}{17} \text{ M}$$

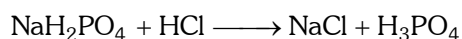
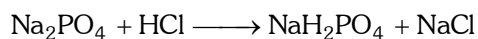
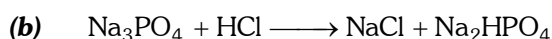
59. (a) **13.097** (b) **0.1252**



$$[\text{OH}^-] = \text{Cx} \quad \text{and} \quad K_b = \frac{\text{Cx}^2}{1 - x}$$

60. (a) **8.347** (b) **4.66** (c) **9.6** (d) **7.2**

(a) 2mg mol of  $\text{H}_2\text{CO}_3$  will form after completion of reaction for weak acid of type  $\text{H}_2\text{A}$ , most of  $[\text{H}^+]$  occurs from 1<sup>st</sup> ionization only.



Taken amount of reagents will results in formation of 0.8mg mol of  $\text{NaH}_2\text{PO}_4$   $\therefore \text{pH} = \frac{\text{p}K_{a1} + \text{p}K_{a2}}{2}$

(c) In this case mainly  $\text{PO}_4^{3-}$  hydrolysis occurs.

(d) 
$$[\text{H}^+]^3 = \frac{[\text{H}_3\text{PO}_4] \times K_1 \times K_2 \times K_3}{[\text{PO}_4^{3-}]}$$

61. (a) **pH = 3.823**

(b) **pH = 3.846**

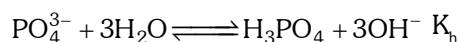
(c) **pH = 3.9899**

For buffer of  $\text{HCOOH}$  &  $\text{HCOONa}$ .

$$\text{pH} = \text{p}K_a + \log \frac{[\text{HCOO}^-]}{[\text{HCOOH}]}$$

With dilution degree of hydrolysis of  $\text{HCOO}^-$  & degree of dissociation of  $\text{HCOOH}$  changes.

62.  **$[\text{OH}^-] = 3.73 \times 10^{-2} \text{ M}$ ,  $[\text{H}_3\text{PO}_4] = 5.93 \times 10^{-18} \text{ M}$**



$$[\text{H}_3\text{PO}_4] = \text{Ch}$$

$$[\text{OH}^-] = 3\text{Ch}$$

$$K_h = \frac{\text{Ch} \times (3\text{Ch})^3}{\text{C} - \text{Ch}} = 27\text{h}^4\text{C}^3 \quad (\text{Assuming } h \ll 1)$$

$$\text{and } K_h = \frac{K_w}{K_1 K_2 K_3}$$

63. (a)  $pH = 4.75$  (b)  $pH = 4.697$  (c)  $pH = 4.798$

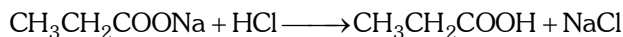
(d) 1.116% on acid addition, 1.03% on base addition.

For acidic buffer of  $CH_3CH_2COOH + CH_3CH_2COONa$

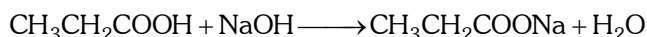
$$K_a = \frac{[H^+][CH_3CH_2COO^-]}{[CH_3CH_2COOH]}$$

$$\therefore pH = pK_a + \log \frac{[CH_3CH_2COO^-]}{[CH_3CH_2COOH]}$$

On adding of a HCl



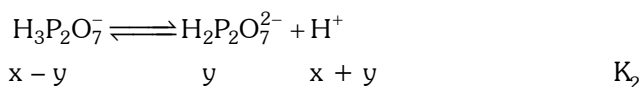
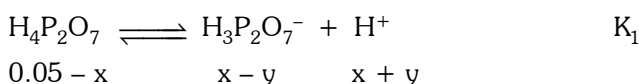
On adding of NaOH



64.  $\frac{[Na_2HPO_4]}{[NaH_2PO_4]} = 1.55 M$

Mixture of weak acid & its salt with strong base is acidic buffer.

65.  $[H_2P_2O_7^{2-}] = 4.9 \times 10^{-3} M$



$$[H^+] = 2[H_2P_2O_7^{2-}] + [H_3P_2O_7^-]$$

$$K_2 = \frac{[H^+][H_2P_2O_7^{2-}]}{[H_3P_2O_7^-]}$$

$$K_1 = \frac{[H^+][H_3P_2O_7^-]}{[H_4P_2O_7]}$$

$$0.05 = [H_4P_2O_7] + [H_3P_2O_7^-] + [H_2P_2O_7^{2-}]$$

Alternatively, if we assume that in weak diprotic acid most of  $[H^+]$  comes from 1<sup>st</sup> ionization only.

Then

$$K_1 = \frac{x^2}{0.05 - x} \quad \text{where } [H^+] = xM$$

$$\& \quad K_2 = \frac{[H^+][H_2P_2O_7^{2-}]}{[H_3P_2O_7^-]}$$

66.  $K_a = 1.73 \times 10^{-5}$   $pH = 8.73$

68.  $\Delta pH = 0.954$

70. 0.257

72. 12 mg

74. 1.84 g/lit

76.  $[Ag(NH_3)_2^+] = 0.0539$

78.  $s = 1.203 \times 10^{-3} M$

67. 85.71%

69. (a)  $pH = 3$  (b)  $pH = 5.48$ , (c)  $pH = 8.85$ , (d)  $pH = 12.05$

71.  $[Cu^+] = 5 \times 10^{-11} M$

73.  $2.8 \times 10^{-3} M$

75.  $9.4 \times 10^{-2} \text{ mol litre}^{-1}$

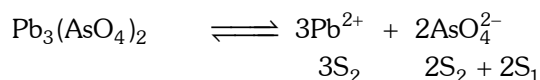
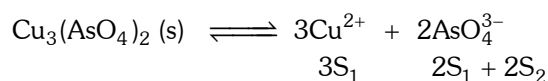
77.  $pH = 11.3010$

79. 3.925

80. (a) 0.0175 %, pH = 1, (b) 4.75      81. NO

82. pH = 9

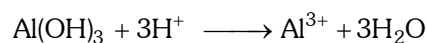
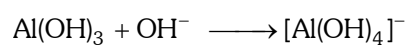
83.  $[Cu^{+2}] = 8.825 \times 10^{-8}$ ,  $[Pb^{+2}] = 7.119 \times 10^{-8}$



$$8 \times 10^{-36} = (3S_1)^3 \times (2S_1 + 2S_2)^2$$

$$4.096 \times 10^{-36} = (3S_2)^3 \times (2S_1 + 2S_2)^2$$

84\*. (a) pH = 9.415      (b) pH = 4.23



$$[OH^-]_{\text{required}} = [Al(OH)_3] \text{ present}$$

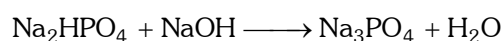
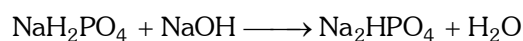
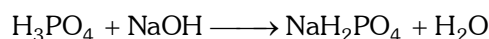
$$[H^+]_{\text{required}} = 3[Al(OH)_3] \text{ present}$$

85.  $V = 2.77 \times 10^4 L$

For weak acid of type HA, having  $\alpha < 1$

$$pH = \frac{1}{2}pK_a - \frac{1}{2}pK_a - \frac{1}{2}\log C$$

86\*. (a) 2.12      (b) 4.66      (c) 7.2      (d) 12



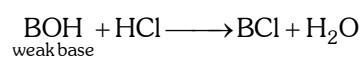
$$(a) \text{ pH} = pK_{a1} + \log \frac{[H_2PO_4^-]}{[H_3PO_4]}$$

$$(b) \text{ pH} = \frac{pK_{a1} + pK_{a2}}{2}$$

$$(c) \text{ pH} = pK_{a2} + \log \frac{[HPO_4^{2-}]}{[H_2PO_4^-]}$$

$$(d) \text{ pH} = pK_{a3} + \log \frac{[PO_4^{3-}]}{[HPO_4^{2-}]}$$

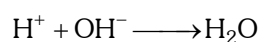
87. **Ans. 9.1628**



$\therefore$  Cationic hydrolysis occurs

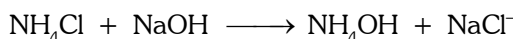
$$pH = 7 - \frac{1}{2}pK_b - \frac{1}{2}\log C$$

Addition of NaOH is resulting solution will cause neutralization.



**88. 0.0818 moles**

On addition of NaOH in this buffer solution.



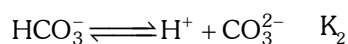
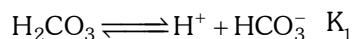
t = 0	0.1 M	xM	0.1M	0
t	0.1-x	0	0.1 + x	x

$$[\text{pOH}]_i = \text{p}K_b + \log \frac{[0.1]}{[0.1]}$$

$$[\text{pOH}]_f = \text{p}K_b + \log \frac{[0.1 - x]}{[0.1 + x]}$$

$$\Delta \text{pOH} = 1$$

$$\therefore -\log \frac{[0.1 - x]}{[0.1 + x]} = 1 \quad \text{or} \quad \frac{[0.1 + x]}{[0.1 - x]} = 10$$

**89\*.  $[\text{H}_2\text{CO}_3] = 9.85 \times 10^{-6} \text{ M}$ ,  $[\text{HCO}_3^-] = 4.9 \times 10^{-4} \text{ M}$ ,  $[\text{CO}_3^{2-}] = 2.45 \times 10^{-8} \text{ M}$** 


$$5 \times 10^{-7} = \frac{10^{-8} \times [\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]}$$

$$5 \times 10^{-13} = 10^{-8} \times \frac{[\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}$$

$$[\text{H}^+] = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}]$$

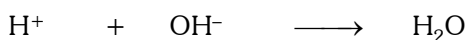
**90. Ans. 1.6 m mole**

 For solution containing  $\text{Na}_2\text{HPO}_4$  &  $\text{NaH}_2\text{PO}_4$ 

$$K_{a2} = \frac{[\text{H}^+][\text{HPO}_4^-]}{[\text{H}_2\text{PO}_4^-]}$$

**91\*.  $6 \times 10^5$  ions**

$$[\text{NH}_2^-] = \sqrt{K_{\text{NH}_3}}$$

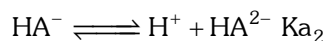
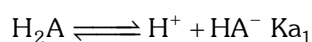
**92. Ans. 9.5228**


$$10^{-2} \text{ mg mol} \quad 2 \times 10^{-2} \text{ mg mol} \quad 0$$

$$[\text{OH}^-]_{\text{left}} = \frac{10^{-2}}{0.3} \text{ M}$$

**93\*. Ans. 2.45**

$$\text{In saturated solution } [\text{Salicylic acid}] = \frac{1.725 / (\text{M.wt}) \text{ salicylacacid}}{1}$$

 salicylic acid will behave like weak diprotic acid in the solution  
 for weak diprotic acid of type  $\text{H}_2\text{A}$ 

 $\therefore K_{a1} > K_{a2} \quad \therefore$  Most of  $[\text{H}^+]$  will be from first ionization only.

$$\therefore 1 \times 10^{-3} = \frac{[\text{H}^+][\text{HA}^-]}{[\text{H}_2\text{A}]} = \frac{x^2}{\frac{1.725}{(\text{M.wt}) \text{ Salicylic acid}} - x}$$

## THERMODYNAMICS

### True/False

1. Pressure is an intensive property.
2. Like  $U$  and  $H$ ,  $S$  is also a state function.
3. When a system undergoes a change at constant pressure, it is referred to an isothermal process.
4. The work done by a gas during free expansion is equal to zero.
5. First law of T.D. is applicable to all processes irrespective to whether they are reversible or irreversible.
6. All spontaneous process proceed in one direction only.
7. Positive value of  $\Delta S_{\text{system}}$  during the process can be taken as sole criterion of spontaneity.
8. The  $\Delta H$  of a reaction is independent of temperature.

### Fill in the blanks

9. According to IUPAC conventions work done on the surroundings is .....
10. A system is said to be ..... if it can neither exchange matter nor energy with surrounding.
11. The efficiency of a carnot engine can be increased by ..... sink temperature when the source temperature is held constant.
12. Entropy change of a system is determine by the ..... and ..... states only, irrespective of how the system has changed its states.
13. Solidification of liquid shows ..... in entropy.
14. When  $\text{Fe(s)}$  is dissolved in a aqueous  $\text{HCl}$  in a closed rigid vessel, the work done is .....
15. For Non-spontaneous process at constant  $T$  &  $P$   $\Delta G$  is .....

### Assertion-Reason

These questions contains, Statement I (assertion) and Statement II (reason).

(A) Statement-I is true, Statement-II is true ; Statement-II is correct explanation for Statement-I.

(B) Statement-I is true, Statement-II is true ; Statement-II is NOT a correct explanation for Statement-I

(C) Statement-I is true, Statement-II is false.

(D) Statement-I is false, Statement-II is true.

16. **Statement-I :** The heat absorbed during the isothermal expansion of an ideal gas against vacuum is zero.

**Because**

**Statement-II :** The volume occupied by the molecules of an ideal gas is zero.

17. **Statement-I :** The magnitude of the work involved in an isothermal expansion is greater than that involved in an adiabatic expansion.

**Because**

**Statement-II :**  $P$ - $V$  curve ( $P$  on  $y$ -axis and  $V$  on  $x$ -axis) decrease more rapidly for reversible adiabatic expansion compared to reversible isothermal expansion starting from same initial state.

18. **Statement-I :** Entropy change in reversible adiabatic expansion of an ideal gas is zero.

**Because**

**Statement-II :** The increase in entropy due to volume increase just compensate the decrease in entropy due to fall in temperature.



**19. Statement-I :** The standard free energy changes of all spontaneously occurring reactions are negative.

**Because**

**Statement-II :** The standard free energies of the elements in their standard states at 1 bar and 298 K are taken as zero.

**20. Statement-I :** Enthalpy and entropy of any elementary substance in the standard states are taken as zero.

**Because**

**Statement-II :** At absolute zero, particles of the perfectly crystalline substance become completely ordered.

**21. Statement-I :** A reaction which is spontaneous and accompanied by decrease of randomness must be exothermic.

**Because**

**Statement-II :** All exothermic reactions are accompanied by decrease of randomness.

**22. Statement-I :** Decrease of free energy during the process under constant temperature and pressure provides a measure of its spontaneity.

**Because**

**Statement-II :** A spontaneous change must have +ve sign of  $\Delta S_{\text{system}}$ .

### Single Choice Correct

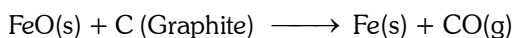
**23\*.** For a perfectly crystalline solid  $C_{p.m.} = aT^3$ , where  $a$  is constant. If  $C_{p.m.}$  is 0.42 J/K-mol at 10 K, molar entropy at 10 K is

- (A) 0.42 J/K-mol                      (B) 0.14 J/K-mol                      (C) 4.2 J/K-mol                      (D) zero

**24\*.** Given the following data :

Substance	$\Delta H^\circ$ (kJ/mol)	$S^\circ$ (J/mol K)	$\Delta G^\circ$ (kJ/mol)
FeO(s)	-266.3	57.49	-245.12
C (Graphite)	0	5.74	0
Fe(s)	0	27.28	0
CO(g)	-110.5	197.6	-137.15

Determine at what temperature the following reaction is spontaneous ?



- (A) 298 K  
 (B) 668 K  
 (C) 966 K  
 (D)  $\Delta G^\circ$  is +ve, hence the reaction will never be spontaneous

**25\*.** The piece of zinc at a temperature of 20.0°C weighing 65.38 g is dropped into 180 g of boiling water ( $T = 100^\circ\text{C}$ ). The specific heat of zinc is  $0.400 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1}$  and that of water is  $4.20 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1}$ . What is the final common temperature reached by both the zinc and water :-

- (A) 97.3°C                      (B) 33.4°C                      (C) 80.1°C                      (D) 60.0°C

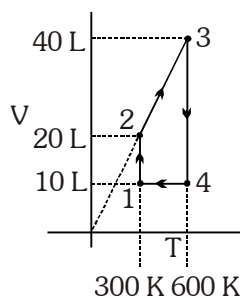
**26\*.** A vessel contains 100 litres of a liquid  $x$ . Heat is supplied to the liquid in such a fashion that, heat given = change in enthalpy. The volume of the liquid increases by 2 litres. If the external pressure is one atm, and 202.6 Joules of heat were supplied then, [ $U \rightarrow$  total internal energy] :-

- (A)  $\Delta U = 0$ ,  $\Delta H = 0$                       (B)  $\Delta U = +202.6 \text{ J}$ ,  $\Delta H = +202.6 \text{ J}$   
 (C)  $\Delta U = -202.6 \text{ J}$ ,  $\Delta H = -202.6 \text{ J}$                       (D)  $\Delta U = 0$ ,  $\Delta H = +202.6 \text{ J}$

- 27\*.** What is the net work done (**in calories**) by 1 mole of monoatomic ideal gas in a process described by 1, 2, 3, 4 in given V-T graph.

**Use :  $R = 2 \text{ cal / mole K}$**

**$\ln 2 = 0.7$**



- (A) - 600 cal  
(B) - 660 cal  
(C) + 660 cal  
(D) + 600 cal

- 28.** How much energy must be supplied to change 36 g of ice at  $0^\circ\text{C}$  to water at room temperature  $25^\circ\text{C}$

Data for water,  $\Delta H_{\text{fusion}}^\circ = 6.01 \text{ kJ mol}^{-1}$   $C_{p,\text{liquid}} = 4.18 \text{ J.K}^{-1} \text{ g}^{-1}$

- (A) 12 kJ (B) 16 kJ (C) 19 kJ (D) 22 kJ

- 29\*.** One mole of an ideal diatomic gas ( $C_V = 5 \text{ cal}$ ) was transformed from initial  $25^\circ\text{C}$  and 1 L to the state when temperature is  $100^\circ\text{C}$  and volume 10L. The entropy change of the process can be expressed as ( $R = 2 \text{ calories/mol.K}$ ) :-

- (A)  $3 \ln \frac{298}{373} + 2 \ln 10$  (B)  $5 \ln \frac{373}{298} + 2 \ln 10$  (C)  $7 \ln \frac{373}{298} + 2 \ln \frac{1}{10}$  (D)  $5 \ln \frac{373}{298} + 2 \ln \frac{1}{10}$

- 30.** Calculate the total entropy change for the transition at 368 K of 1 mol of sulphur from the monoclinic to the rhombic solid state, if  $\Delta H = -401.7 \text{ J mol}^{-1}$  for the transition. Assume the surrounding to be an ice-water both at  $0^\circ\text{C}$  :-

- (A)  $-1.09 \text{ JK}^{-1}$  (B)  $1.47 \text{ JK}^{-1}$  (C)  $0.38 \text{ JK}^{-1}$  (D) None of these

- 31\*.** One mole of an ideal monoatomic gas expands isothermally against constant external pressure of 1 atm from initial volume of 1L to a state where its final pressure becomes equal to external pressure. If initial temperature of gas is 300 K, then entropy change of system in the above process is :-

( $R = 0.082 \text{ L atm mol}^{-1} \text{ K}^{-1} = 8.3 \text{ J mol}^{-1} \text{ K}^{-1}$ )

- (A) 0 (B)  $R \ln(24.6)$  (C)  $R \ln(2490)$  (D)  $\frac{3}{2} R \ln(24.6)$

- 32\*.** The enthalpy change for a given reaction at 298 K is  $-x \text{ J mol}^{-1}$  ( $x$  being positive). If the reaction occurs spontaneously at 298 K, the entropy change at that temperature :

- (A) Can be negative but numerically larger than  $\frac{x}{298}$   
(B) Can be negative but numerically smaller than  $\frac{x}{298}$   
(C) Cannot be negative  
(D) Cannot be positive

- 33\*.** One mole of a real gas is subjected to heating at constant volume from  $(P_1, V_1, T_1)$  state to  $(P_2, V_1, T_2)$  state. Then it is subjected to irreversible adiabatic compression against constant external pressure  $P_3 \text{ atm}$  till system reaches final state  $(P_3, V_2, T_3)$ . If the constant volume molar heat capacity of real gas is  $C_V$ . Find out correct expression for  $\Delta H$  from state 1 to state 3.

- (A)  $C_V(T_3 - T_1) + (P_3 V_1 - P_1 V_1)$  (B)  $C_V(T_2 - T_1) + (P_3 V_2 - P_1 V_1)$   
(C)  $C_V(T_2 - T_1) + (P_3 V_1 - P_1 V_1)$  (D)  $C_p(T_2 - T_1) + (P_3 V_1 - P_1 V_1)$

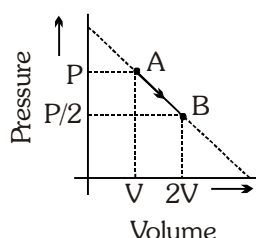
- 34\*.** When two equal sized pieces of the same metal at different temperatures  $T_h$  (hot piece) and  $T_c$  (cold piece) are brought into contact into thermal contact and isolated from its surrounding. The total change in entropy of system is given by ? [ $C_V (\text{J/K})$  = heat capacity of metal]

- (A)  $C_V \ln \frac{T_c + T_h}{2T_c}$  (B)  $C_V \ln \frac{T_2}{T_1}$  (C)  $C_V \ln \frac{(T_c + T_h)^2}{2T_h \cdot T_c}$  (D)  $C_V \ln \frac{(T_c + T_h)^2}{4T_h \cdot T_c}$

- 35\*.** The enthalpy of tetramerization of X in gas phase ( $4X(g) \rightarrow X_4(g)$ ) is  $-100 \text{ kJ/mol}$  at  $300 \text{ K}$ . The enthalpy of vaporisation for liquid X and  $X_4$  are respectively  $30 \text{ kJ/mol}$  and  $72 \text{ kJ/mol}$  respectively.  
 $\Delta S$  for tetramerization of X in liquid phase is  $-125 \text{ J / K mol}$  at  $300 \text{ K}$ .  
 What is the  $\Delta G$  at  $300 \text{ K}$  for tetramerization of X in liquid phase ?  
 (A)  $-52 \text{ kJ/mol}$  (B)  $-89.5 \text{ kJ/mol}$  (C)  $-14.5 \text{ kJ/mol}$  (D) None of these
- 36.** The change in entropy of 2 moles of an ideal gas upon isothermal expansion at  $243.6 \text{ K}$  from 20 litre until the pressure becomes 1 atm, is :  
 (A)  $1.385 \text{ cal / K}$  (B)  $-1.2 \text{ cal / K}$  (C)  $1.2 \text{ cal / K}$  (D)  $2.77 \text{ cal / K}$
- 37.** Molar heat capacity of water in equilibrium with ice at constant pressure is :- [IIT-JEE-1997]  
 (A) zero (B)  $\infty$   
 (C)  $40.45 \text{ kJ K}^{-1} \text{ mol}^{-1}$  (D)  $75.48 \text{ JK}^{-1} \text{ mol}^{-1}$
- 38.** Which of the following statement is false ? [IIT-JEE-2001]  
 (A) Work is a state function  
 (B) temperature is a state function  
 (C) Change of state is completely defined when initial and final states are specified  
 (D) Work appears at the boundary of the system
- 39\*.** One mole of non-ideal gas undergoes a change of state ( $2.0 \text{ atm}, 3.0 \text{ L}, 95 \text{ K}$ ) to ( $4.0 \text{ atm}, 5.0 \text{ L}, 245 \text{ K}$ ) with a change in internal energy ( $\Delta U$ ) =  $30.0 \text{ L-atm}$ . The change in enthalpy ( $\Delta H$ ) of the process in  $\text{L-atm}$  :- [IIT-JEE-2002]  
 (A) 40.0 (B) 42.3  
 (C) 44.0 (D) not defined, because pressure is not constant
- 40.** Two mole of an ideal gas is expanded isothermally and reversibly from 1 litre to 10 litre at  $300 \text{ K}$ . The enthalpy change (in  $\text{kJ}$ ) for the process is :- [IIT-JEE-2004]  
 (A)  $11.4 \text{ kJ}$  (B)  $-11.4 \text{ kJ}$  (C)  $0 \text{ kJ}$  (D)  $4.8 \text{ kJ}$
- 41.** The enthalpy of vapourization of a liquid is  $30 \text{ kJ mol}^{-1}$  and entropy of vapourization is  $75 \text{ J mol}^{-1} \text{ K}$ . The boiling point of the liquid at 1 atm is :- [IIT-JEE-2004]  
 (A)  $250 \text{ K}$  (B)  $400 \text{ K}$  (C)  $450 \text{ K}$  (D)  $600 \text{ K}$
- 42\*.** One mole of monoatomic ideal gas expands adiabatically at initial temp. T against a constant external pressure of 1 atm from one litre to two litre. Find out the final temp. ( $R = 0.0821 \text{ litre. atm K}^{-1} \text{ mol}^{-1}$ ) [IIT-JEE-2005]  
 (A) T (B)  $\frac{T}{(2)^{\frac{5}{3}-1}}$  (C)  $T - \frac{2}{3 \times 0.0821}$  (D)  $T + \frac{2}{3 \times 0.0821}$

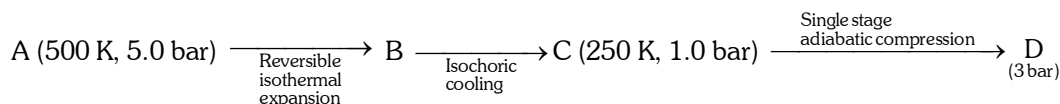
### Multi Choice Correct

- 43\*.** An ideal gas is taken from state A (Pressure P, Volume V) to the state B (Pressure  $P/2$ , Volume  $2V$ ) along a straight line path in PV diagram as shown in the adjacent figure.  
 Select the correct statement(s) among the following.



- (A) The work done by gas in the process A to B exceeds the work that would be done by it if the system were taken from A to B along the isotherm.
- (B) In the T-V diagram, the path AB become part of parabola
- (C) In the P-T diagram, the path AB becomes a part of hyperbola.
- (D) In going from A to B, the temperature T of the gas first increases to a maximum value then decreases.

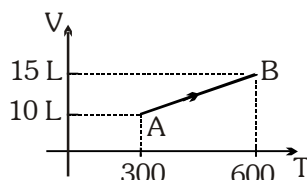
**44\*.** Two moles of an ideal gas ( $C_{v,m} = 3/2R$ ) is subjected to following change of state.



The correct statement is / are :

- (A) The pressure at B is 2.0 bar (B) The temperature at D is 450 K
- (C)  $\Delta H_{CD} = 1000 R$  (D)  $\Delta U_{BC} = 375 R$

**45\*.** If one mole monoatomic ideal gas was taken through process AB as shown in figure, then select correct option(s).



- (A)  $w_{AB} = -1496.52 J$  (B)  $q_{AB} = 5237.82 J$  (C)  $\Delta H_{AB} = 3741.3 J$  (D)  $\Delta S_{AB}$  is +ve

**46\*.** Which of the following statement(s) is/are correct :

- (A) Reversible isothermal compression of an ideal gas represents the limiting minimum value of the workdone ( $|w|$ ) by the surrounding on the system.
- (B) In an irreversible process, the cyclic integral of work is not zero.
- (C) For thermodynamic changes in adiabatic process  $T^{\left(\frac{C_{p,m}}{R}\right)} \cdot P = \text{constant}$
- (D) Work done by 1 mole of a real (vander waals) gas  $W = -RT \ln \frac{V_2 - b}{V_1 - b} - a \left[ \frac{V_1 \times V_2}{V_2 - V_1} \right]$

## Comprehension

### Comprehension-1

An ideal gas, having ratio of specific heat  $\gamma$  undergoes a process in which its internal energy relates to the volume as  $U = \alpha\sqrt{V}$ , where  $\alpha$  is a constant. If the gas is expanded from volume  $V_1$  to  $V_2$ .

**47\*.** The work performed by gas is :

- (A)  $2\alpha(\gamma - 1) [\sqrt{V_2} - \sqrt{V_1}]$  (B)  $\alpha(\gamma - 1) [\sqrt{V_2} - \sqrt{V_1}]$  (C)  $2\alpha(\gamma - 1) [V_2 - V_1]$  (D)  $\alpha(\gamma - 1) [V_2 - V_1]$

**48\*.** If the ideal gas is diatomic and its increase in internal energy is 100 J then the work performed by gas is: (Ignore vibrational degree of freedom)

- (A) 80 J (B) 180 J (C) 100 J (D) 20 J

**49\*.** In the above question, the heat supplied to gas is :

- (A) 80 J (B) 180 J (C) 100 J (D) 20 J

**Comprehension-2**

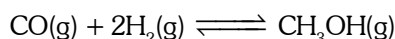
Standard Gibb's energy of reaction ( $\Delta_r G^\circ$ ) at a certain temperature can be computed as  $\Delta_r G^\circ = \Delta_r H^\circ - T \Delta_r S^\circ$  and the change in the value of  $\Delta_r H^\circ$  and  $\Delta_r S^\circ$  for a reaction with temperature can be computed as follows :

$$\Delta_r H_{T_2}^\circ - \Delta_r H_{T_1}^\circ = \Delta_r C_p (T_2 - T_1)$$

$$\Delta_r S_{T_2}^\circ - \Delta_r S_{T_1}^\circ = \Delta_r C_p \ln \left( \frac{T_2}{T_1} \right)$$

$$\Delta_r G^\circ = \Delta_r H^\circ - T \Delta_r S^\circ \quad \text{and} \quad \Delta_r G^\circ = -RT \ln K_{eq}$$

Consider the following reaction :



Given :

$$\Delta_r H^\circ (\text{CH}_3\text{OH, g}) = -201 \text{ kJ/mol ;}$$

$$S^\circ (\text{CH}_3\text{OH, g}) = 240 \text{ J/K-mol ;}$$

$$S^\circ (\text{CO, g}) = 198 \text{ J/mol-K ;}$$

$$C_{p,m}^\circ (\text{CO}) = 29.4 \text{ J/mol-K ;}$$

$$\Delta_r H^\circ (\text{CO, g}) = -114 \text{ kJ/mol}$$

$$S^\circ (\text{H}_2, \text{g}) = 29 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$C_{p,m}^\circ (\text{H}_2) = 28.8 \text{ J/mol-K}$$

$$C_{p,m}^\circ (\text{CH}_3\text{OH}) = 44 \text{ J/mol-K}$$

and  $\ln \left( \frac{320}{300} \right) = 0.06$ , all data at 300 K

**50.**  $\Delta_r S^\circ$  at 300 K for the reaction is :

- (A) 152.6 J/K-mol      (B) 181.6 J/K-mol      (C) -16 J/K-mol      (D) none of these

**51.**  $\Delta_r H^\circ$  at 300 K for the reaction is :

- (A) -87 kJ/mol      (B) 87 kJ/mol      (C) -315 kJ/mol      (D) -288 kJ/mol

**52\*.**  $\Delta_r S^\circ$  at 320 K is :

- (A) 155.18 J/mol-K      (B) 150.02 J/mol-K      (C) 172 J/mol-K      (D) 18.58 J/mol-K

**53\*.**  $\Delta_r H^\circ$  at 320 K is :

- (A) -288.86 kJ/mol      (B) -289.1 kJ/mol      (C) -87.86 kJ/mol      (D) none of these

**54\*.**  $\Delta_r G^\circ$  at 320 K is :

- (A) -48295.2 kJ/mol      (B) -240.85 kJ/mol      (C) 93.80 kJ/mol      (D) -81.91 kJ/mol

**Comprehension-3**

9.0 g ice at 0°C is mixed with 36 g of water at 50°C in a thermally insulated container. Using the following data, answer the question that follow ?

$$C_p (\text{H}_2\text{O}) = 4.18 \text{ Jg}^{-1}\text{K}^{-1} ; \Delta H_{\text{fusion}} (\text{ice}) = 335 \text{ J g}^{-1}$$

**55.** Final temperature of water is

- (A) 304.43 K      (B) 296.97 K      (C) 303.93 K      (D) 287 K

**56\*.**  $\Delta S_{\text{ice}}$  is

- (A) 11.04 JK<sup>-1</sup>      (B) 3.16 JK<sup>-1</sup>      (C) 14.2 JK<sup>-1</sup>      (D) 7.84 JK<sup>-1</sup>

**57\*.**  $\Delta S_{\text{water}}$  is

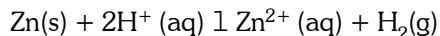
- (A) -12.64 JK<sup>-1</sup>      (B) -0.34 JK<sup>-1</sup>      (C) -5.42 JK<sup>-1</sup>      (D) 12.64 JK<sup>-1</sup>

**58.** What is the total entropy change in the process ?

- (A) -1.56 JK<sup>-1</sup>      (B) -1.60 JK<sup>-1</sup>      (C) 1.56 JK<sup>-1</sup>      (D) 1.60 JK<sup>-1</sup>

**Subjective Questions**

- 59\*.** One mole of solid Zn is placed in excess of dilute  $\text{H}_2\text{SO}_4$  at  $27^\circ\text{C}$ , in a cylinder fitted with a piston. Find the value of  $\Delta E$ ,  $q$  and  $w$  for the process if the area of piston is  $500\text{ cm}^2$  and it moves out by  $50\text{ cm}$  against a pressure of  $1\text{ atm}$  during the reaction. The heat given to surrounding is  $36.5\text{ kJ}$ .



- 60\*.** Methane (Considered to be an ideal gas) initially at  $25^\circ\text{C}$  and  $1\text{ bar}$  pressure is heated at constant pressure until the volume has doubled. The variation of the molar heat capacity with absolute temperature is given by :

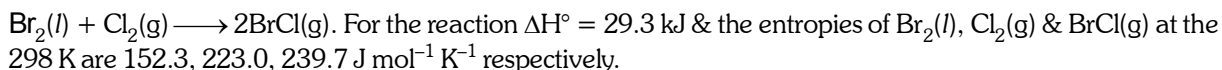
$$C_p = 22.34 + 48.1 \times 10^{-3} T \text{ where } C_p \text{ is in } \text{JK}^{-1} \text{ mol}^{-1}. \text{ Calculate molar (a) } \Delta H \text{ (b) } \Delta U.$$

- 61.** One mole of  $\text{NaCl(s)}$  on melting absorbed  $30.5\text{ kJ}$  of heat and its entropy is increased by  $28.8\text{ JK}^{-1}$ . What is the melting point of sodium chloride ?

- 62\*.** Oxygen is heated from  $300\text{ K}$  to  $600\text{ K}$  at a constant pressure of  $1\text{ bar}$ . What is the increases in molar entropy? The molar heat capacity in  $\text{JK}^{-1} \text{ mol}^{-1}$  for the  $\text{O}_2$  is.

$$C_p = 25.5 + 13.6 \times 10^{-3} T - 42.5 \times 10^{-7} T^2$$

- 63.** Calculate the free energy change at  $298\text{ K}$  for the reaction :



- 64.** Using the data given below, establish that the vaporization of  $\text{CCl}_4(\text{l})$  at  $298\text{ K}$  to produce  $\text{CCl}_4(\text{g})$  at  $1\text{ atm}$  pressure does not occur spontaneously.

$$\text{Given : } \text{CCl}_4(\text{l}, 1\text{ atm}) \longrightarrow \text{CCl}_4(\text{g}, 1\text{ atm}) ; \Delta S^\circ = 94.98\text{ JK}^{-1} \text{ mol}^{-1}$$

$$\Delta H_f^\circ(\text{CCl}_4, \text{g}) = -106.7\text{ kJ mol}^{-1} \text{ \& } \Delta H_f^\circ(\text{CCl}_4, \text{l}) = -139.3\text{ kJ mol}^{-1}$$

- 65\*.** From the given table answer the following questions :



- (i) Calculate  $\Delta_r H^\circ_{298}$  (ii) Calculate  $\Delta_r G^\circ_{298}$   
 (iii) Calculate  $\Delta_r S^\circ_{298}$  (iv) Calculate  $\Delta_r E^\circ_{298}$   
 (v) Calculate  $S^\circ_{298}[\text{H}_2\text{O}(\text{g})]$

	$\text{CO}(\text{g})$	$\text{CO}_2(\text{g})$	$\text{H}_2\text{O}(\text{g})$	$\text{H}_2(\text{g})$
$\Delta H_{298}^\circ$ (-kJ/mole)	-26.42	-94.05	-57.8	0
$\Delta G_{298}^\circ$ (-kJ/mole)	-32.79	-94.24	-54.64	0
$S_{298}^\circ$ (-Cal/kmole)	47.3	51.1	?	31.2

- 66\*.** Compute  $\Delta_r G$  for the reaction  $\text{H}_2\text{O}(\text{l}, 1\text{ atm}, 323\text{ K}) \rightarrow \text{H}_2\text{O}(\text{g}, 1\text{ atm}, 323\text{ K})$

$$\text{Given that : } \Delta_{\text{vap}} H \text{ at } 373\text{ K} = 40.639\text{ kJ mol}^{-1}, C_p(\text{H}_2\text{O}, \text{l}) = 75.312\text{ J K}^{-1} \text{ mol}^{-1},$$

$$C_p(\text{H}_2\text{O}, \text{g}) = 33.305\text{ J K}^{-1} \text{ mol}^{-1}.$$

- 67\*.** (a) An ideal gas undergoes a single state expansion against a constant opposing pressure from  $(P_1, V_1, T)$  to  $(P_2, V_2, T)$ . What is the largest mass  $m$  which can be lifted through a height  $h$  in this expansion ?  
 (b) The system (a) restored to its initial state by a single state compression. What is the smallest mass  $m'$  which must fall through the height  $h$  to restore system?  
 (c) What is the net mass lowered through height  $h$  in the cyclic transformation in (a) and (b) ?

- 68\*.** A sample of argon gas at  $1\text{ atm}$  pressure and  $27^\circ\text{C}$  expands reversibly and adiabatically from  $1.25\text{ dm}^3$  to  $2.50\text{ dm}^3$ . Calculate the enthalpy change in this process.  $C_{v,m}$  for argon is  $12.48\text{ JK}^{-1} \text{ mol}^{-1}$ . [IIT-JEE-2000]

- 69.** Show that the reaction  $\text{CO(g)} + \frac{1}{2} \text{O}_2 \text{(g)} \longrightarrow \text{CO}_2 \text{(g)}$  at 300 K is spontaneous and exothermic, when the standard entropy is  $-0.094 \text{ kJ mol}^{-1} \text{ K}^{-1}$ . The standard Gibbs free energies of formation for  $\text{CO}_2$  and CO are  $-394.4$  and  $-137.2 \text{ kJ mol}^{-1}$ , respectively. **[IIT-JEE-2001]**
- 70\*.** Two moles of a perfect gas undergoes the following processes : **[IIT-JEE-2002]**
- a reversible isobaric expansion from (1.0 atm, 20.0 L) to (1.0 atm, 40.0 L) ;
  - a reversible isochoric change of state from (1.0 atm, 40.0 L) to (0.5 atm, 40.0 L) ;
  - a reversible isothermal compression from (0.5 atm, 40.0 L) to (1.0 atm, 20.0 L) ;
- Sketch with labels each of the processes on the same P–V diagram.
  - Calculate the total work (w) and the total heat change (q) involved in the above processes.
  - What will be the values of  $\Delta U$ ,  $\Delta H$  and  $\Delta S$  for the overall process ?
- 71\*.** One mole of a liquid (1 bar, 100 mL) is taken in an adiabatic container and the pressure increases steeply to 100 bar. Then at a constant pressure of 100 bar, volume decreases by 1 mL. Find  $\Delta U$  and  $\Delta H$ . **[IIT-JEE-2004]**
- 72.** The increase in entropy of 1 kg of ice at 200 K which is heated to 400 K (super heated steam) at constant atmospheric pressure, will be :
- Given that  $C_p(\text{ice}) = 2.09 \times 10^3 \text{ J/kg degree}$  ;  $C_p(\text{water}) = 4.18 \times 10^3 \text{ J/kg degree}$   
 $C_p(\text{steam}) = 2.09 \times 10^3 \text{ J/kg degree}$  ;  $L_f(\text{C}, 273 \text{ K}) = 3.34 \times 10^5 \text{ J/kg}$  ;  
 $L_v(\text{water}, 273 \text{ K}) = 22.6 \times 10^5 \text{ J/kg}$
- 73\*.** Calculate workdone in adiabatic compression of one mole of an ideal gas (monoatomic) from an initial pressure of 1 atm to final pressure of 2 atm. Initial temperature = 300 K
- If process is carried out reversibly.
  - If process is carried out irreversible against 2 atm external pressure.
- Compute the final volume reached by gas in two cases.
- 74\*.**  $20.0 \text{ dm}^3$  of an ideal gas (diatomic  $C_{v,m} = 5 R/2$ ) at 673 K and 0.7 MPa expands until pressure of the gas is 0.2 MPa. Calculate q, w,  $\Delta U$  and  $\Delta H$  for the process if the expansion is :
- Isothermal and reversible
  - Adiabatic and reversible
  - Isothermal and adiabatic
  - Against 0.2 MPa and adiabatic
  - Against 0.2 MPa and isothermal.
- 75\*.** One mole of an ideal gas is expanded isothermally at 298 K until its volume is tripled. Find the values of  $\Delta S_{\text{gas}}$  and  $\Delta S_{\text{total}}$  under the following conditions.
- Expansion is carried out reversibly.
  - Expansion is carried out irreversibly where 836.6 J of heat is less absorbed than in (i)
  - Expansion is free.
- 76\*.** 10 g of neon initially at a pressure of 506.625 kPa and temperature of 473 K expand adiabatically to a pressure of 202.65 kPa. Calculate entropy change of the system and total entropy change for the following ways of carrying out this expansion.
- Expansion is carried out reversibly.
  - Expansion occurs against a constant external pressure of 202.65 kPa.
  - Expansion is free expansion.
- 77.** Pressure over 1000 mL of a liquid is gradually increases from 1 bar to 1001 bar under adiabatic conditions. If the final volume of the liquid is 990 mL, calculate  $\Delta U$  and  $\Delta H$  of the process, assuming linear variation of volume with pressure.

- 78\*.** One mole of ideal monoatomic gas was taken through reversible isochoric heating from 100 K to 1000 K. Calculate  $\Delta S_{\text{system}}$ ,  $\Delta S_{\text{surr}}$ , and  $\Delta S_{\text{total}}$  in
- when the process carried out reversibly
  - when the process carried out irreversibly (one step)
- 79\*.** Fixed amount of an ideal gas contained in a sealed rigid vessel ( $V = 24.6$  litre) at 1.0 bar is heated reversibly from  $27^\circ\text{C}$  to  $127^\circ\text{C}$ . Determine change in Gibb's energy (in Joule) if entropy of gas  $S = 10 + 10^{-2} T$  (J/K).
- 80\*.** A 32 g sample of  $\text{CH}_4$  gas initially at 101.325 kPa and 300 K is heated to 550 K.  $C_{p,m}/\text{JK}^{-1} \text{mol}^{-1} = 12.552 + 8.368 \times 10^{-2} T/\text{K}$ . Assuming  $\text{CH}_4$  behaves ideally, compute  $w$ ,  $q$ ,  $\Delta U$  and  $\Delta H$  for (a) an isobaric reversible process and (b) an isochoric reversible process.
- 81\*.** At 298 K,  $\Delta H^\circ_{\text{combustion}}(\text{sucrose}) = -5737 \text{ kJ/mol}$  &  $\Delta G^\circ_{\text{combustion}}(\text{sucrose}) = -6333 \text{ kJ/mol}$ . Estimate additional non-PV work that is obtained by raising temperature to 310 K. Assume  $\Delta_r C_p = 0$  for this temperature change.



# ANSWERS

## • True and False

1. True      2. True      3. False      4. True      5. True  
 6. True      7. False      8. False

## • Fill in the blanks

9. Negative      10. Isolated      11. Decreasing      12. (i) initial (ii) final  
 13. decrease      14. zero      15. positive

## • Assertion-Reason

16. (B)      17. (A)      18. (A)      19. (B)      20. (D)  
 21. (C)      22. (C)

## • Single Choice Correct

23. (B)      24. (C)      25. (A)      26. (D)      27. (C)  
 28. (B)      29\*. (B)      30. (C)      31\*. (B)      32\*. (D)  
 33\*. (C)      34\*. (D)      35\*. (C)      36. (D)      37. (B)  
 38. (A)      39\*. (C)      40. (C)      41. (B)      42\*. (C)

## • Multi Choice Correct

43. (ABD)      44. (ABC)      45. (BD)      46. (AB)

## • Comprehension

- Comprehension 1 :**      47\*. (A)      48\*. (A)      49\*. (B)  
**Comprehension 2 :**      50. (C)      51. (A)      52\*. (A)  
                                  53\*. (C)      54\*. (D)  
**Comprehension 3 :**      55. (B)      56\*. (C)      57\*. (A)  
                                  58. (C)

## • Subjective Questions

59.  $\Delta E = -39.03 \text{ kJ/mole}$ ;  $q = -36.5 \text{ kJ}$ ;  $w = -2.53 \text{ kJ}$

60\*. (a)  $13.064 \text{ kJ mol}^{-1}$       (b)  $10.587 \text{ kJ mol}^{-1}$       61.  $T = 1059 \text{ K}$

62\*.  $21.18 \text{ J K}^{-1} \text{ mol}^{-1}$       63.  $-1721.8 \text{ J}$

64.  $\Delta G^\circ = 4.3 \text{ kJ mol}^{-1} > 0$

65\*. (i)  $-9.83 \text{ kcal mol}^{-1}$       (ii)  $-6.81 \text{ kcal mol}^{-1}$       (iii)  $-10.13 \text{ cal/K mol}$       (iv)  $-9.83 \text{ kcal/mol}$   
 (v)  $+45.13 \text{ cal/K mole}$

66\*.  $\Delta_r G = 5.59 \text{ kJ mol}^{-1}$

67\*. (a)  $m = \frac{nRT}{gh} \left( 1 - \frac{P_2}{P_1} \right)$ , (b)  $m' = \frac{nRT}{gh} \left( \frac{P_1}{P_2} - 1 \right)$ , (c)  $m' - m = \frac{nRT}{gh} \left( \frac{(P_1 - P_2)^2}{P_1 P_2} \right)$

68\*.  $\Delta H = -114.52 \text{ J}$

69.  $\Delta H^\circ = -285.4 \text{ kJ/mol}$ ,  $\Delta G^\circ = -257.2 \text{ kJ/mol}$

70\*. (ii)  $-w = q = 620.77 \text{ J}$ , (iii)  $\Delta H = 0$ ,  $\Delta U = 0$ ,  $\Delta S = 0$

**71\*.**  $\Delta U = 0.1 \text{ litre atm}$ ,  $\Delta H = 9.9 \text{ litre atm}$

**72.**  $9390 \text{ J kg}^{-1}$

**73\*.** (a)  $T_2 = 395.8$ ;  $V_2 = 16.24 \text{ L}$ ;  $w_{\text{rev}} = 1194.72 \text{ J}$ , (b)  $V_2^1 = 17.24 \text{ L}$ ;  $T_2^1 = 420 \text{ K}$ ;  $w_{\text{irrev}} = 1496.52 \text{ J}$

**74\*.** (i)  $q = -w = 17.54 \text{ kJ}$ ,  $\Delta U = 0$  and  $\Delta H = 0$ ; (ii)  $q = 0$ ,  $w = \Delta U = -10.536 \text{ kJ}$  and  $\Delta H = -14.75 \text{ kJ}$   
 (iii)  $q = 0$ ,  $w = 0$ ,  $\Delta U = 0$  and  $\Delta H = 0$ ; (iv)  $q = 0$ ;  $\Delta U = w = -7.14 \text{ kJ}$ ;  $\Delta H = -9.996 \text{ kJ}$   
 (v)  $q = -w = 9.94 \text{ kJ}$ ,  $\Delta U = \Delta H = 0$

**75\*.** (i)  $\Delta S_{\text{gas}} = -\Delta S_{\text{surr}}$  and  $\Delta S_{\text{total}} = 0$ , (ii)  $\Delta S_{\text{total}} = 2.808 \text{ J K}^{-1}$ ,  
 (iii)  $\Delta S_{\text{total}} = \Delta S_{\text{sys}} = 9.134 \text{ J K}^{-1}$

**76\*.** (i)  $\Delta S_{\text{sys}} = 0$ ;  $\Delta S_{\text{surr}} = 0$  and  $\Delta S_{\text{total}} = 0$ , (ii)  $\Delta S_{\text{surr}} = 0$ ;  $\Delta S_{\text{total}} = \Delta S_{\text{sys}} = 0.957 \text{ JK}^{-1}$   
 (iii)  $\Delta S_{\text{sys}} = \Delta S_{\text{total}} = 3.81 \text{ JK}^{-1}$

**77.**  $\Delta U = 501 \text{ J}$ ;  $\Delta H = 99.5 \text{ kJ}$

**78\*.** (i) Rev. process  $\Delta S_{\text{sys}} = \frac{3}{2} R \ln 10$ ;  $\Delta S_{\text{surr}} = -\frac{3}{2} R \ln 10$ ,  
 (ii) Irr. process  $\Delta S_{\text{sys}} = \frac{3}{2} R \ln 10$ ;  $\Delta S_{\text{surr}} = -\frac{3}{2} (0.9)$ ;  $\Delta S_{\text{total}} = \frac{3}{2} R (1.403)$

**79\*.**  $-530 \text{ J}$

**80\*.** (a)  $q_p = \Delta H = 24.058 \text{ kJ}$ ,  $w = -4.157 \text{ kJ}$ ,  $\Delta U = 19.90 \text{ kJ}$ ;  
 (b)  $\Delta U = 19.90 \text{ kJ}$ ,  $\Delta H = 24.058$ ;  $w = 0$

**81\*.**  $24 \text{ kJ/mol}$

**THERMOCHEMISTRY**
**True/False**

1.  $\Delta H_f^\circ$  (C, diamond)  $\neq 0$
2. For a particular reaction  $\Delta E = \Delta H + P\Delta V$
3. If BE (bond energy) of  $N \equiv N$  bond is  $x_1$  that of  $H - H$  bond is  $x_2$  and  $N - H$  bond is  $x_3$  then enthalpy change of the reaction is  

$$N_2 + 3H_2 \longrightarrow 2NH_3 \qquad \Delta H_r = x_1 + 3x_2 - 2x_3$$
4. Enthalpy change is dependent on temperature and on the path adopted.
5. Heat of hydrogenation of ethene is  $x_1$  and that of benzene is  $x_2$ , hence resonance energy of benzene is  $(x_1 - x_2)$ .
6. The enthalpies of elements are always taken to be zero.
7. Heat of neutralisation of weak acid-strong base is not constant.
8. Resonance energy is always negative.
9. For reaction  $2A(g) + B(g) \longrightarrow 3C(g)$   $\Delta H = -x$  kJ then for reaction  $\frac{3}{2}C(g) \longrightarrow A(g) + \frac{B}{2}(g)$   $\Delta H = \frac{x}{2}$  kJ.

**Fill in the blanks**

10. The combustion of a substance is always .....
11. If heat content of X is smaller than that of Y then the process  $X \rightarrow Y$  is .....
12.  $C(\text{Diamond}) \longrightarrow C(\text{Graphite}) + x$  kJ. The heat change in this process is called .....
13. As per reaction,  $N_2(g) + 2O_2(g) \longrightarrow 2NO_2(g)$   $-66$  kJ the value of  $\Delta H_f^\circ$  of  $NO_2$  is .....
14. Heats of combustion of methane, carbon and hydrogen are  $-212$ ,  $-94$ ,  $-68$  kcal  $\text{mol}^{-1}$ . The heat of formation of  $CH_4$  is .....
15. The heat of neutralisation of 1 mole of  $HClO_4$  with 1 gm-equivalent of  $NaOH$  in aqueous solutions is .....  $\text{kJ mol}^{-1}$ .
16. The heat of combustion of graphite and carbon monoxide respectively are  $-393.5$   $\text{kJ mol}^{-1}$  and  $-283$   $\text{kJ mol}^{-1}$ . Thus heat of formation of carbon monoxide in  $\text{kJ mol}^{-1}$  is .....
17. For the reaction,  
 $C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(l)$  at constant temperature,  $\Delta H - \Delta U$  is .....

**Assertion-Reason**

These questions contains, Statement I (assertion) and Statement II (reason).

(A) Statement-I is true, Statement-II is true ; Statement-II is correct explanation for Statement-I.

(B) Statement-I is true, Statement-II is true ; Statement-II is NOT a correct explanation for statement-I

(C) Statement-I is true, Statement-II is false

(D) Statement-I is false, Statement-II is true

18. **Statement-I** : Enthalpy of neutralization of  $CH_3COOH$  by  $NaOH$  is less than that of  $HCl$  by  $NaOH$ .

**Because**

**Statement-II** : Enthalpy of neutralization of  $CH_3COOH$  is less because of the absorption of heat in the ionization process.

19. **Statement-I** : Enthalpy changes are positive when  $Na_2SO_4 \cdot 10H_2O$ ,  $CuSO_4 \cdot 5H_2O$  and salts like  $NaCl$ ,  $KCl$ , etc., which do not form hydrates are dissolved in water. But enthalpy changes are negative when anhydrous salts capable of forming hydrates are dissolved in water.

**Because**

**Statement-II** : The difference in the behaviour is due to large differences in the molecular weight of hydrated and anhydrous salts. The substances with larger molecular weights usually show positive enthalpy changes on dissolution.

- 20. Statement-I :** Heat of neutralisation of HF (aq.), a weak acid, with NaOH (aq.) is more than 13.7 kcal, in an exothermic reaction.  
**Because**  
**Statement-II :** Some heat is lost in the ionisation of a weak acid.
- 21. Statement-I :** Enthalpy of formation of HCl is equal to bond energy of HCl.  
**Because**  
**Statement-II :** Enthalpy of formation and bond energy both involve the formation of one mole of HCl from the elements.
- 22. Statement-I :** Enthalpy of atomization is the heat of reaction  $\text{H}_2\text{O(l)} \longrightarrow \text{H}_2\text{O(g)}$ .  
**Because**  
**Statement-II :** Gaseous molecules are far apart of each other due to less attraction.
- 23. Statement-I :** The enthalpy of formation of  $\text{H}_2\text{O(l)}$  is greater than that of  $\text{H}_2\text{O(g)}$ .  
**Because**  
**Statement-II :** Enthalpy change is negative for the condensation reaction,  $\text{H}_2\text{O(g)} \longrightarrow \text{H}_2\text{O(l)}$ .
- 24. Statement-I :** As temperature increases, heat of reaction also increases for exothermic as well as for endothermic reactions.  
**Because**  
**Statement-II :**  $\Delta H$  varies with temperature as given by  $\Delta H_2 \text{ (at } T_2) = \Delta H_1 \text{ (at } T_1) + \Delta C_p(T_2 - T_1)$
- 25. Statement-I :** Heat of combustion is always negative.  
**Because**  
**Statement-II :** Heat of combustion is used to calculate of fuels.

### Single Choice Correct

- 26\*.** A gas mixture 3.67 L in volume contain  $\text{C}_2\text{H}_4$  and  $\text{CH}_4$  is proportion of 2 : 1 by moles and is at  $25^\circ\text{C}$  and 1 atm. If the  $\Delta H_c$  ( $\text{C}_2\text{H}_4$ ) and  $\Delta H_c$  ( $\text{CH}_4$ ) are  $-1400$  and  $-900$  kJ/mol find heat evolved on burning this mixture:-  
 (A) 20.91 kJ (B) 50.88 kJ (C) 185 kJ (D) 160 kJ
- 27.** The fat, glyceryl trioleate, is metabolized via the following reaction. Given the enthalpies of formation, calculate the energy (kJ) liberated when 1.00 g of this fat reacts.  
 (Atomic weights: C = 12.01, H = 1.008, O = 16.00).  

$$\text{C}_{57}\text{H}_{104}\text{O}_6(\text{s}) + 80 \text{O}_2(\text{g}) \rightarrow 57 \text{CO}_2(\text{g}) + 52 \text{H}_2\text{O}(\text{l})$$
  
 $\Delta H^\circ \text{C}_{57}\text{H}_{104}\text{O}_6 = -70870$  kJ/mole  
 $\Delta H^\circ \text{H}_2\text{O}(\text{l}) = -285.8$  kJ/mole  
 $\Delta H^\circ \text{CO}_2(\text{g}) = -393.5$  kJ/mole  
 (A) 40.4 (B) 33.4 (C) 37.8 (D) 42.6
- 28.** A sheet of 15.0 g of gold at  $25.0^\circ\text{C}$  is placed on a 30.0 g sheet of copper at  $45.0^\circ\text{C}$ . What is the final temperature of the two metals assuming that no heat is lost to the surroundings. The specific heats of gold and copper are  $0.129 \text{ J/g}^\circ\text{C}$  and  $0.385 \text{ J/g}^\circ\text{C}$  respectively.  
 (A) 42.1 (B) 40.1 (C) 41.1 (D) 43.4
- 29.** Calculate the heat of combustion (kJ) of propane,  $\text{C}_3\text{H}_8$  using the listed standard enthalpy of reaction data:  

$$\text{C}_3\text{H}_8(\text{g}) + 5 \text{O}_2(\text{g}) \rightarrow 3 \text{CO}_2(\text{g}) + 4 \text{H}_2\text{O}(\text{g})$$
  

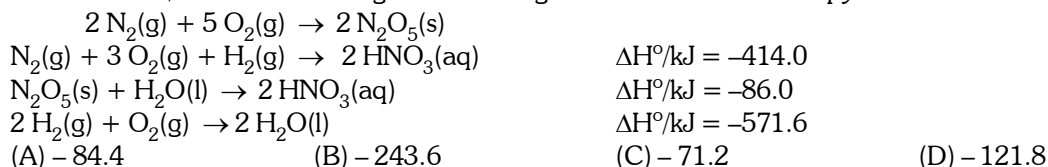
$$3 \text{C}(\text{s}) + 4 \text{H}_2(\text{g}) \rightarrow \text{C}_3\text{H}_8(\text{g}) \quad \Delta H^\circ/\text{kJ} = -103.8$$
  

$$\text{C}(\text{s}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) \quad \Delta H^\circ/\text{kJ} = -393.5$$
  

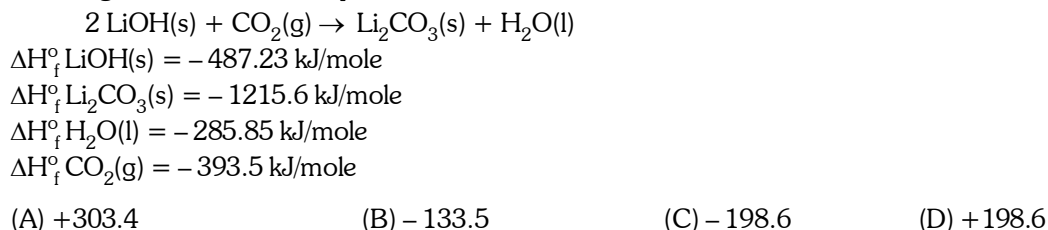
$$\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g}) \quad \Delta H^\circ/\text{kJ} = -241.8$$
  
 (A)  $-2043.9$  (B)  $-1532.9$  (C)  $-1021.9$  (D)  $-739.1$
- 30.** Use the given standard enthalpies of formation to determine the heat of reaction of the following reaction:  

$$\text{C}_2\text{H}_5\text{OH}(\text{l}) + 3 \text{O}_2(\text{g}) \rightarrow 2 \text{CO}_2(\text{g}) + 3 \text{H}_2\text{O}(\text{g}) \quad \Delta H^\circ_f \text{C}_2\text{H}_5\text{OH}(\text{l}) = -277.7 \text{ kJ/mole}$$
  
 $\Delta H^\circ_f \text{CO}_2(\text{g}) = -393.5$  kJ/mole  
 $\Delta H^\circ_f \text{H}_2\text{O}(\text{g}) = -241.8$  kJ/mole  
 (A)  $-1456.3$  (B)  $-1234.7$  (C)  $-1034.0$  (D)  $-1119.4$

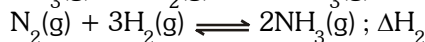
- 31.** Calculate  $\Delta H^\circ/\text{kJ}$  for the following reaction using the listed standard enthalpy of reaction data:



- 32\*.** Use the given standard enthalpies of formation to determine the heat of reaction of the following reaction :



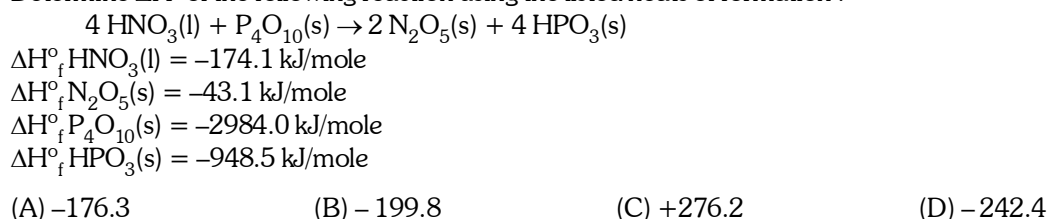
- 33\*.**  $\text{NH}_3(\text{g}) + 3\text{Cl}_2(\text{g}) \rightleftharpoons \text{NCl}_3(\text{g}) + 3\text{HCl}(\text{g}) ; -\Delta H_1$



The heat of formation of  $\text{NCl}_3(\text{g})$  in the terms of  $\Delta H_1$ ,  $\Delta H_2$  and  $\Delta H_3$  is ?

- (A)  $\Delta H_f = -\Delta H_1 + \frac{\Delta H_2}{2} - \frac{3}{2} \Delta H_3$       (B)  $\Delta H_f = \Delta H_1 + \frac{\Delta H_2}{2} - \frac{3}{2} \Delta H_3$   
 (C)  $\Delta H_f = \Delta H_1 - \frac{\Delta H_2}{2} - \frac{3}{2} \Delta H_3$       (D) None of these

- 34.** Determine  $\Delta H^\circ$  of the following reaction using the listed heats of formation :

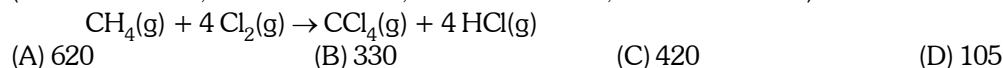


- 35\*.** If  $x_1$ ,  $x_2$  and  $x_3$  are enthalpies of H-H, O=O and O-H bonds respectively, and  $x_4$  is the enthalpy of vaporisation of water, estimate the standard enthalpy of combustion of hydrogen.

- (A)  $x_1 + \frac{x_2}{2} - 2x_3 + x_4$     (B)  $x_1 + \frac{x_2}{2} - 2x_3 - x_4$     (C)  $x_1 + \frac{x_2}{2} - x_3 + x_4$     (D)  $2x_1 - x_1 - \frac{x_2}{2} - x_4$

- 36.** Use the given bond enthalpy data to estimate the  $\Delta H^\circ$  (kJ) for the following reaction.

(C - H = 414 kJ, H - Cl = 431 kJ, Cl - Cl = 243 kJ, C - Cl = 331 kJ).



- 37.**  $\Delta H_f^\circ$  of water is  $-285.8 \text{ kJ mol}^{-1}$ . If enthalpy of neutralisation of monoacid strong base is  $-57.3 \text{ kJ mol}^{-1}$ ,  $\Delta H_f^\circ$  of  $\text{OH}^-$  ion will be ?

- (A)  $-228.5 \text{ kJ mol}^{-1}$     (B)  $228.5 \text{ kJ mol}^{-1}$     (C)  $114.25 \text{ kJ mol}^{-1}$     (D)  $-114.25 \text{ kJ mol}^{-1}$

- 38\*.** 4 grams of sodium hydroxide pellets were dissolved in  $100 \text{ cm}^3$  of water. The temperature before adding the sodium hydroxide pellets was 25 degrees C, and after adding the pellets it was 35 degrees C. Calculate the enthalpy change in kJ/mole of the reaction (Specific heat capacity of water =  $4.2 \text{ J/K/g}$ )

- (A) 42 kJ/mole    (B) 4.2 kJ/mole    (C) 4200 kJ/mole    (D) none

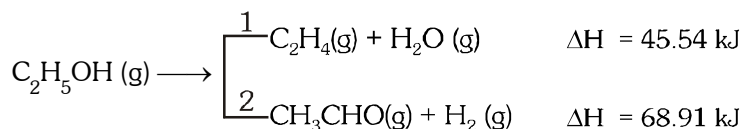
- 39.** 50.0 mL of 0.10 M HCl is mixed with 50.0 mL of 0.10 M NaOH. The solution temperature rises by  $3.0^\circ\text{C}$ . Calculate the enthalpy of neutralization per mol of HCl.

- (A)  $-2.5 \times 10^2 \text{ kJ}$     (B)  $-1.3 \times 10^2 \text{ kJ}$     (C)  $-8.4 \times 10^1 \text{ kJ}$     (D)  $-6.3 \times 10^1 \text{ kJ}$

**40\*.** The standard enthalpies of formation of  $\text{CO}_{2(g)}$  and  $\text{HCOOH(l)}$  are  $-393.7 \text{ kJ/mol}$  and  $-409.2 \text{ kJ/mol}$  respectively:-

- (A)  $-393.7 \text{ kJ/mol}$  is the enthalpy change for the reaction  $\text{C}_{(s)} + \text{O}_{2(g)} \rightarrow \text{CO}_{2(g)}$   
 (B) the enthalpy change for the reaction  $\text{CO}_{2(g)} + \text{H}_{2(g)} \rightarrow \text{HCOOH}_{(l)}$  would be  $+15.5 \text{ kJ/mol}$   
 (C) the enthalpy change for the reaction  $\text{H}_2\text{O} + \text{CO} \rightarrow \text{HCOOH}$  is  $-409.2 \text{ kJ/mol}$   
 (D) the enthalpy change for the reaction  $\text{H}_{2(g)} + \text{CO}_{2(g)} \rightarrow \text{H}_2\text{O}_{(l)} + \text{CO}_{(g)}$  is  $-409.2 \text{ kJ/mol}$

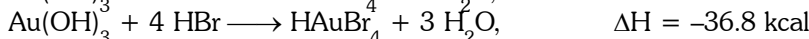
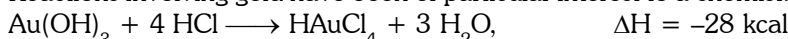
**41\*.** Ethanol can undergoes decomposition to form two sets of products ?



if the molar ratio of  $\text{C}_2\text{H}_4$  to  $\text{CH}_3\text{CHO}$  is 8 : 1 in a set of product gases, then the energy involved in the decomposition of 1 mole of ethanol is ?

- (A) 65.98 kJ (B) 48.137 kJ (C) 48.46 kJ (D) 57.22 kJ

**42.** Reactions involving gold have been of particular interest to a chemist. Consider the following reactions,



In an experiment there was an absorption of 0.44 kcal when one mole of  $\text{HAuBr}_4$  was mixed with 4 moles of HCl. What is the percentage conversion of  $\text{HAuBr}_4$  into  $\text{HAuCl}_4$  ?

- (A) 0.5 % (B) 0.6 % (C) 5 % (D) 50%

**43.** For which of the following change  $\Delta H \neq \Delta E$ ?

- (A)  $\text{H}_2 (\text{g}) + \text{I}_2 (\text{g}) \longrightarrow 2\text{HI} (\text{g})$  (B)  $\text{HCl (aq)} + \text{NaOH(aq)} \longrightarrow \text{NaCl(aq)} + \text{H}_2\text{O(l)}$   
 (C)  $\text{C(s)} + \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g})$  (D)  $\text{N}_2 (\text{g}) + 3\text{H}_2(\text{g}) \longrightarrow 2\text{NH}_3(\text{g})$

**44\*.** The reaction  $\text{CH}_4(\text{g}) + \text{Cl}_2(\text{g}) \longrightarrow \text{CH}_3\text{Cl}(\text{g}) + \text{HCl}(\text{g})$  has  $\Delta H = -25 \text{ kcal}$ .

Bond	Bond Energy kCal
$\text{E}_{\text{C}-\text{Cl}}$	84
$\text{E}_{\text{H}-\text{Cl}}$	103
$\text{E}_{\text{C}-\text{H}}$	x
$\text{E}_{\text{Cl}-\text{Cl}}$	y
x : y = 9 : 5	

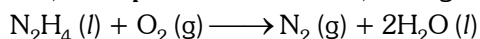
From the given data, what is the bond enthalpy of  $\text{Cl}-\text{Cl}$  bond

- (A) 70 kCal (B) 80 kCal (C) 67.75 kCal (D) 57.75 kCal

**45.** For the allotropic change represented by the equation  $\text{C (graphite)} \longrightarrow \text{C (diamond)}$ ,  $\Delta H = 1.9 \text{ kJ}$ . If 6 g of diamond and 6 g of graphite are separately burnt to yield  $\text{CO}_2$ , the enthalpy liberated in first case is

- (A) less than in the second case by 1.9 kJ (B) more than in the second case by 11.4 kJ  
 (C) more than in the second case by 0.95 kJ (D) less than in the second case by 11.4 kJ

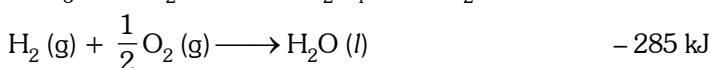
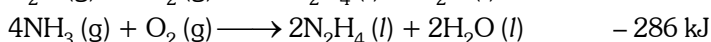
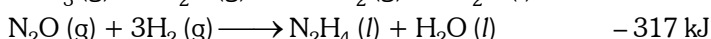
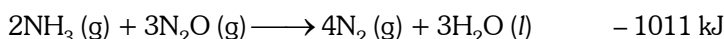
**46\*.** Hydrazine, a component of rocket fuel, undergoes combustion to yield  $\text{N}_2$  and  $\text{H}_2\text{O}$ .



What is the enthalpy combustion of  $\text{N}_2\text{H}_4$  (kJ/mole)

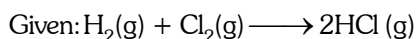
**Given Reaction**

**$\Delta H/\text{kJ}$**

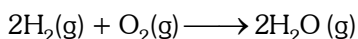


- (A) -620.5 (B) -622.75 (C) 1167.5 (D) +622.75

47. Find  $\Delta_r U^\circ$  for the reaction  $4\text{HCl (g)} + \text{O}_2 \text{ (g)} \rightarrow 2\text{Cl}_2 \text{ (g)} + 2\text{H}_2\text{O (g)}$  at 300 K. Assume all gases are ideal.



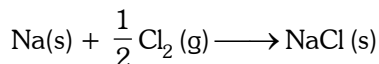
$\Delta_r H_{300}^\circ = -184.5 \text{ kJ/mole}$



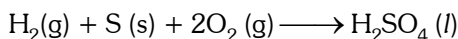
$\Delta_r H_{300}^\circ = -483 \text{ kJ/mole}$  (Use  $R = 8.3 \text{ J/mole}$ )

- (A) 111.5 kJ/mole (B) -109.01 kJ/mole (C) -111.5 kJ/mole (D) None

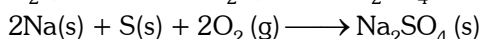
- 48\*. The enthalpy changes of the following reactions at  $27^\circ\text{C}$  are



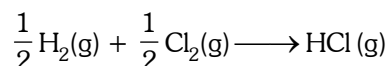
$\Delta_r H = -411 \text{ kJ/mol}$



$\Delta_r H = -811 \text{ kJ/mol}$

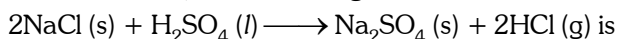


$\Delta_r H = -1382 \text{ kJ/mol}$



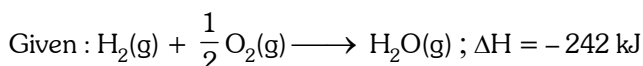
$\Delta_r H = -92 \text{ kJ/mol}; R = 8.3 \text{ J/K-mol}$

from these data, the heat change of reaction at constant volume (in kJ/mol) at  $27^\circ\text{C}$  for the process



- (A) 67 (B) 62.02 (C) 71.98 (D) None

49. What is the ratio of the enthalpy yield on combustion of hydrogen atoms to steam to the yield on combustion of an equal mass of hydrogen molecules to steam?



B.E.  $(\text{H} - \text{H}) = 436 \text{ kJ}$

- (A) 0.80 : 1 (B) 1 : 0.80 (C) 1.80 : 1 (D) 2.80 : 1

50. The molar heat capacities at constant pressure (assume constant with respect to temperature) of A, B and C are in ratio of **1.5 : 3.0 : 2.0**. If enthalpy change for the exothermic reaction  $\text{A} + 2\text{B} \rightarrow 3\text{C}$  at 300 K is -10 kJ/mol &  $C_{p,m}$  (B) is 300 J/mol then enthalpy change at 310 K is:

- (A) -8.5 kJ/mol (B) 8.5 kJ/mol (C) -11.5 kJ/mol (D) none of these

- 51\*. (i) Cis-2-butene  $\rightarrow$  trans-2-butene,  $\Delta H_1$   
(ii) Cis-2-butene  $\rightarrow$  1-butene,  $\Delta H_2$   
(iii) Trans-2-butene is more stable than cis-2-butene.  
(iv) Enthalpy of combustion of 1-butene,  $\Delta H = -649.8 \text{ kCal/mol}$   
(v)  $9\Delta H_1 + 5\Delta H_2 = 0$   
(vi) Enthalpy of combustion of trans 2-butene,  $\Delta H = -647.0 \text{ kCal/mol}$ .

The value of  $\Delta H_1$  &  $\Delta H_2$  in KCal/mole are

- (A) -1.0, 1.8 (B) 1.8, -1.0 (C) -5, 9 (D) -2, 3.6

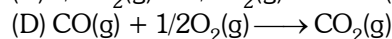
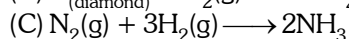
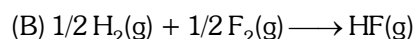
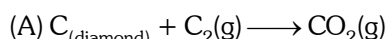
- 52\*. The lattice enthalpy of solid NaCl is  $772 \text{ kJmol}^{-1}$  and enthalpy of solution is  $2 \text{ kJmol}^{-1}$ . If the hydration enthalpy of  $\text{Na}^+$  &  $\text{Cl}^-$  ions are in the ratio of 3:2.5, what is the enthalpy of hydration of chloride ion?

- (A) -140 kJmol<sup>-1</sup> (B) -350 kJmol<sup>-1</sup> (C) -351.81 kJmol<sup>-1</sup> (D) None

53.  $\Delta_f H^\circ$  of water is  $-285.8 \text{ kJ mol}^{-1}$ . If enthalpy of neutralisation of monoacid strong base is  $-57.3 \text{ kJ mol}^{-1}$ ,  $\Delta_f H^\circ$  of  $\text{OH}^-$  ion will be

- (A) -228.5 kJ mol<sup>-1</sup> (B) 228.5 kJ mol<sup>-1</sup> (C) 114.25 kJ mol<sup>-1</sup> (D) -114.25 kJ mol<sup>-1</sup>

54. Which of the following reactions defines  $\Delta_f H^\circ$ ?



55\*. Standard molar enthalpy of formation of  $\text{CO}_2$  is equal to :-

[IIT-JEE-1997]

- (A) Zero  
 (B) Standard molar enthalpy of combustion of carbon (graphite)  
 (C) Standard molar enthalpy of combustion of gaseous carbon  
 (D) Sum of molar enthalpies of formation of CO and  $\text{O}_2$

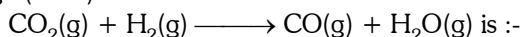
56. Which of the following is not an endothermic reaction :-

[IIT-JEE-1999]

- (A) Combustion of methane (B) Decomposition of water  
 (C) Dehydrogenation of ethene to ethylene (D) Conversion of graphite to diamond

57\*.  $\Delta H_f^\circ$  for  $\text{CO}_2(\text{g})$ ,  $\text{CO}(\text{g})$  and  $\text{H}_2\text{O}(\text{g})$  are  $-393.5$ ,  $-110.5$  and  $-241.8 \text{ kJ mol}^{-1}$  respectively. The standard enthalpy change (in kJ) for the relation :

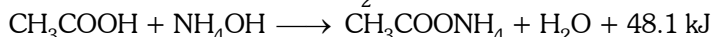
[IIT-JEE-2000]



- (A) 524.1 (B) 41.2 (C) -262.5 (D) -41.2

### Multiple Choice Correct

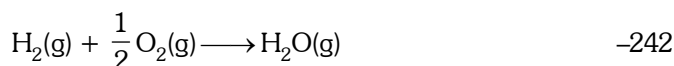
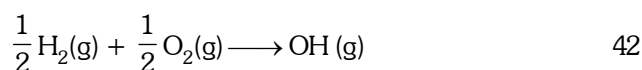
58. 100 ml 0.5 N  $\text{H}_2\text{SO}_4$  (strong acid) is neutralised with 200 ml 0.2M  $\text{NH}_4\text{OH}$  in a constant pressure Calorimeter which results in temperature rise of  $1.4^\circ\text{C}$ . If heat capacity of Calorimeter content is  $1.5 \text{ kJ/}^\circ\text{C}$ . Which statement is/are correct



- (A) Enthalpy of neutralisation of HCl v/s  $\text{NH}_4\text{OH}$  is  $-52.5 \text{ kJ/mol}$   
 (B) Enthalpy of dissociation (ionization) of  $\text{NH}_4\text{OH}$  is  $4.5 \text{ kJ/mol}$   
 (C) Enthalpy of dissociation of  $\text{CH}_3\text{COOH}$  is  $4.6 \text{ kJ/mol}$   
 (D)  $\Delta H$  for  $2\text{H}_2\text{O}(\text{l}) \longrightarrow 2\text{H}^+(\text{aq.}) + 2\text{OH}^-(\text{aq.})$  is  $114 \text{ kJ}$

59\*. From the following data at  $25^\circ\text{C}$

**Reaction**  **$\Delta_f H^\circ \text{ kJ/mol}$**



Which of the following statement(s) is/are correct:

- (A)  $\Delta_f H^\circ$  for the reaction  $\text{H}_2\text{O}(\text{g}) \longrightarrow 2\text{H}(\text{g}) + \text{O}(\text{g})$  is  $925.5 \text{ kJ/mol}$   
 (B)  $\Delta_f H^\circ$  for the reaction  $\text{OH}(\text{g}) \longrightarrow \text{H}(\text{g}) + \text{O}(\text{g})$  is  $502 \text{ kJ/mol}$   
 (C) Enthalpy of formation of  $\text{H}(\text{g})$  is  $-218 \text{ kJ/mol}$   
 (D) Enthalpy of formation of  $\text{OH}(\text{g})$  is  $42 \text{ kJ/mol}$

60\*. Which of the following statement(s) is/are **true**?

- (A) When  $(\Delta G_{\text{system}})_{T,P} < 0$ ; the reaction must be exothermic  
 (B)  $\Delta_f H^\circ$  (S, monoclinic)  $\neq 0$   
 (C) If dissociation enthalpy of  $\text{CH}_4(\text{g})$  is  $1656 \text{ kJ/mole}$  and  $\text{C}_2\text{H}_6(\text{g})$  is  $2812 \text{ kJ/mole}$ , then value of C-C bond enthalpy will be  $328 \text{ kJ/mole}$   
 (D) If  $\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \longrightarrow \text{H}_2\text{O}(\text{l})$   $\Delta_f H^\circ = -56 \text{ kJ/mol}$   
 $\Delta_f H^\circ(\text{H}_2\text{O}, \text{g}) = -242 \text{ kJ/mole}$ ; Enthalpy of vaporization of liquid water =  $44 \text{ kJ/mol}$   
 then,  $\Delta_f H^\circ(\text{OH}^-, \text{aq})$  will be  $-142 \text{ kJ/mole}$

61. Select the option in which heat evolved is maximum.

**Given :**  $\Delta_f H^\circ(\text{CO}_2, \text{g}) = -75 \text{ kCal/mol}$ ;  $\Delta_f H^\circ(\text{CO}, \text{g}) = -25 \text{ kCal/mol}$

The product will be CO if excess amount of carbon is present and  $\text{CO}_2$  if excess  $\text{O}_2$  is present

- (A) 10 moles of carbon and 4.5 moles of  $\text{O}_2$  (B) 24 gm of carbon and 64 gm of  $\text{O}_2$   
 (C) 4 moles of carbon and 3.5 moles of  $\text{O}_2$  (D) 30 gm of carbon and 80 gm of  $\text{O}_2$



**62\*.** For the process:  $\text{H}_2\text{O} (l, \text{TK}, P \text{ bar}) \rightarrow \text{H}_2\text{O} (g, \text{TK}, P \text{ bar})$

- (A)  $\Delta G = 0$ , If  $P =$  vapour pressure of  $\text{H}_2\text{O}(l)$  at TK  
 (B)  $\Delta G = +ve$ , If  $P =$  vapour pressure of  $\text{H}_2\text{O}(l)$  at a temperature above TK  
 (C)  $\Delta G = +ve$ ; If  $P >$  vapour pressure of  $\text{H}_2\text{O}(l)$  at TK  
 (D)  $\Delta G = -ve$ ; If  $P <$  vapour pressure of  $\text{H}_2\text{O}(l)$  at TK

### Match the Column

**63.** List equation/law (in Column I) with statement (in Column II) :

#### Column-I

- (A) Arrhenius equation  
 (B) Kirchhoff equation  
 (C) Second law of thermodynamics  
 (D) Hess's law of constant heat summation

#### Column-II

- (p) Variation of enthalpy of a reaction with temperature  
 (q) Variation of rate constant with temperature  
 (r) Entropy of an isolated system tends to increase and reach a maximum value  
 (s) Enthalpy change in a reaction is always constant and independent of the manner in which the reaction occurs.

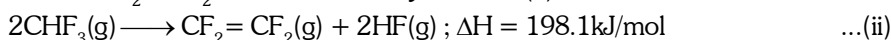
### Comprehension

#### Comprehension-1

The industrial preparation of a polymer, PTFE, is based on the synthesis of the monomer  $\text{CF}_2 = \text{CF}_2$ , which is produced according to reaction (i) below :



The monomer  $\text{CF}_2 = \text{CF}_2$  is also obtained by reaction (ii) below :



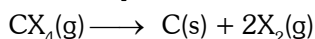
Consider the information below to answer the questions:

Compound	$\Delta H_f$	Molecule X-X	$\Delta(X-X)$
$\text{HCl}(g)$	-92.3	F-F	154.7
$\text{CHClF}_2(g)$	-485.2	Cl-Cl	246.7
$\text{CF}_2 = \text{CF}_2(g)$	-658.3		
$\text{CF}_4$	-679.6		
$\text{CCl}_4$	-106.6		

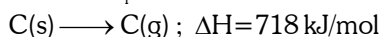
**64.** The enthalpy change for reaction (i).

- (A) 100.23 kJ/mol (B) 127.5 kJ/mol (C) -127.5 kJ/mol (D) -100.23 kJ/mol

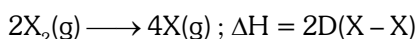
**65. (i)** Use the expressions



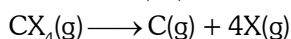
$$\Delta H = -\Delta H_f$$



and



where  $X = \text{F}, \text{Cl}$ , to the enthalpy change for the two processes



What is the average C-X bond energies for the species  $\text{CX}_4(g)$  (where  $X = \text{F}, \text{Cl}$ ).

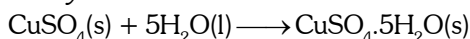
- (A) 329.5 kJ/mol, 426.75 kJ/mol (B) 426.75 kJ/mol, 329.5 kJ/mol  
 (C) -329.5 kJ/mol, -426.75 kJ/mol (D) -426.75 kJ/mol, -329.5 kJ/mol

**(ii)** Given that the C-H bond energy is 416.1 kJ/mol, the order of relative chemical reactivities of C-H, C-F, and C-Cl bonds.

- (A)  $\text{C-H} > \text{C-Cl} > \text{C-F}$  (B)  $\text{C-F} > \text{C-Cl} > \text{C-H}$   
 (C)  $\text{C-Cl} > \text{C-H} > \text{C-F}$  (D)  $\text{C-Cl} > \text{C-F} > \text{C-H}$

**Comprehension-2**

The hydration enthalpy of anhydrous copper (II) sulphate is defined as the heat absorbed or evolved when one mole of anhydrous solid is converted to one mole of crystalline hydrated solid.



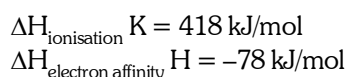
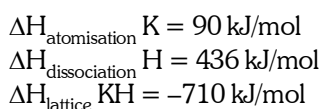
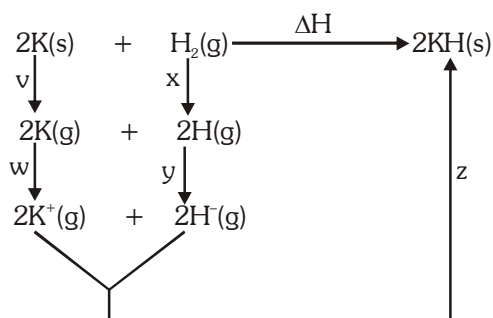
It cannot be measured directly.

In an experiment to determine the hydration enthalpy indirectly, 4 g of the anhydrous solid were added to 50 g of water and the rise in temperature was 8 degrees. When 4 g of the hydrated solid was added to 50 g of water the fall in temperature was 1.3 degrees.

- 66\*.** What is the heat produced when 4 g of anhydrous solid is added to 50 g of water.  
 (A) 400 kJ (B) 1672 J (C) 200 kJ (D) 836 kJ
- 67\*.** What is the enthalpy of solution of anhydrous copper (II) sulphate in kJ/mol.  
 (A) 68.88 kJ/mol (B) 4054.375 kJ/mol (C) 139.8948 kJ/mol (D) 8108.750 kJ/mol
- 68\*.** Given that the enthalpy of solution of the hydrated copper (II) sulphate is +11.3 kJ/mol, what is the enthalpy of hydration of the anhydrous solid.  
 (A) 97.321 kJ/mol (B) -97.321 kJ/mol (C) -77.971 kJ/mol (D) 77.971 kJ/mol

**Comprehension-3**

The Born Haber cycle below represents the energy changes occurring at 298K when KH is formed from its elements



- 69.** In terms of the letters v to z write down expressions for  
 (i)  $\Delta H$  for the reaction  $2\text{K}(\text{s}) + \text{H}_2(\text{g}) \longrightarrow 2\text{KH}(\text{s})$   
 (ii)  $\Delta H_f$  of K  
 (iii)  $\Delta H_{\text{electron affinity}}$  of H  
 (iv)  $\Delta H_{\text{lattice}}$  of KH(s)
- 70.** Calculate the value of  $\Delta H$  showing all your working.
- 71.** Calculate the  $\Delta H_f$  of KH(s).
- 72.** Write a balanced equation for the reaction of KH with water.
- 73.** On complete reaction with water, 0.1 g of KH gave a solution requiring  $25 \text{ cm}^3$  of 0.1M HCl for neutralisation. Calculate the relative atomic mass of potassium from this information.

**Subjective Questions**

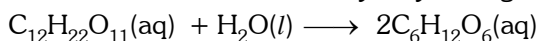
- 74\*.** Two mole of ideal diatomic gas ( $C_{v,m} = 5/2 R$ ) at 300 K and 5 atm expanded irreversibly & adiabatically to a final pressure of 2 atm against a constant pressure of 1 atm. Calculate q, w,  $\Delta H$  &  $\Delta U$ .

- 75.** A bomb containing 5.4g of Al and 15.97g of  $\text{Fe}_2\text{O}_3$  is placed in an ice calorimeter containing initially 8 kg of ice and 8 kg of water. The reaction  $2\text{Al(s)} + \text{Fe}_2\text{O}_3\text{(s)} \rightarrow \text{Al}_2\text{O}_3\text{(s)} + 2\text{Fe(s)}$  is set off by remote control and it is then observed that the calorimeter contains 7.746 kg of ice and 8.254 kg of water. Find the  $\Delta H$  for the above reaction.

$$\Delta H_{\text{fusion}}(\text{ice}) = 1.436 \text{ kcal/mole}$$

- 76\*.** A sample of the sugar D-ribose ( $\text{C}_5\text{H}_{10}\text{O}_5$ ) of mass 0.727g was placed in a calorimeter and then ignited in the presence of excess oxygen. The temperature raise by 0.910 K. In a separate experiment in the same calorimeter, the combustion of 0.825 g of benzoic acid, for which the internal energy of combustion is  $-3251 \text{ kJ mol}^{-1}$ , gave a temperature rise of 1.940K. Calculate the internal energy of combustion of D-ribose and its enthalpy of formation.
- 77.** The heat of combustion of formaldehyde<sub>(g)</sub> is  $-134 \text{ kcal mole}^{-1}$  and the heat of combustion of paraformaldehyde<sub>(s)</sub> is  $-122 \text{ kcal per } (1/n) (\text{CH}_2\text{O})_n$ . Calculate the heat of polymerization of formaldehyde to paraformaldehyde.

- 78\*.** The disaccharide  $\alpha$  - maltose can be hydrolysed to glucose according to the equation



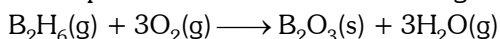
Using the following values, calculate the standard enthalpy change in this reaction:

$$\Delta_f H^\circ(\text{H}_2\text{O}, \text{l}) = -285.85 \text{ kJ}\cdot\text{mol}^{-1}$$

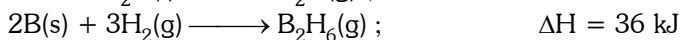
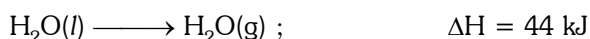
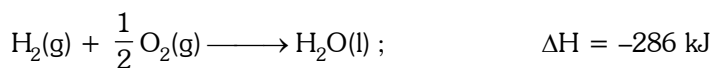
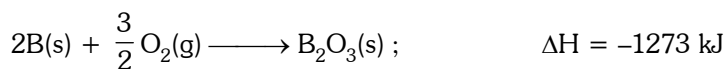
$$\Delta_f H^\circ(\text{C}_6\text{H}_{12}\text{O}_6, \text{aq}) = -1263.1 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_f H^\circ(\text{C}_{12}\text{H}_{22}\text{O}_{11}, \text{aq}) = -2238.3 \text{ kJ}\cdot\text{mol}^{-1}$$

- 79\*.** Diborane is a potential rocket fuel which undergoes combustion according to the reaction, [IIT-JEE-2000]



From the following data, calculate the enthalpy change for the combustion of diborane :



- 80\*.** For the reaction  $\text{cis-2-butene} \rightarrow \text{trans-2-butene}$  and  $\text{cis-2-butene} \rightarrow 1\text{-butene}$ ,  $\Delta H = -950$  and  $+1771 \text{ cal/mol}$  respectively. The heat of combustion of 1-butene is  $-649.8 \text{ kcal/mol}$ . Determine the heat of combustion of trans-2-butene. Also calculate the bond energy of C=C bond in trans-2-butene. Given B.E of C = O = 196, O—H = 110, O = O = 118, C—C = 80 and C—H = 98 kcal/mol respectively.  $\Delta H_v(\text{H}_2\text{O}) = 11 \text{ kcal/mol}$ .

- 81.** Using the data (all values are in kJ/mol at 25°C) given below :

(i) Enthalpy of polymerization of ethylene =  $-72$ .

(ii) Enthalpy of formation of benzene ( $\ell$ ) =  $49$

(iii) Enthalpy of vaporization of benzene ( $\ell$ ) =  $30$

(iv) Resonance energy of benzene ( $\ell$ ) =  $-152$

(v) Heat of formation of gaseous atoms from the elements in their standard states H = 218, C = 715. Average bond energy of C—H = 415. Calculate the B.E. of C—C and C=C. [A : 331 and 590 kJ/mol]

- 82\*.** Determine resonance energy of benzene [ $\text{C}_6\text{H}_6(\ell)$ ] from the following information :

$$\Delta H_f^\circ \text{ of } \text{C}_6\text{H}_6(\ell) = +49 \text{ kJ} ;$$

$$\Delta H_f^\circ \text{ of } \text{C}_2\text{H}_2(\text{g}) = +75 \text{ kJ} \quad \Delta H_v^\circ \text{ of } \text{C}_6\text{H}_6(\ell) = +45 \text{ kJ}$$

$$\text{B.E. } \text{C} \equiv \text{C} = 930 \text{ kJ/mol} ; \text{C} = \text{C} = 615 \text{ kJ/mol} ; \text{C} - \text{C} = 348 \text{ kJ/mol}$$

- 83.** Consider the following thermodynamic data :  
 Enthalpy of formation of  $\text{CaC}_2(\text{s}) = -60 \text{ kJ/mol}$  ;  
 Enthalpy of sublimation of  $\text{Ca}(\text{s}) = 179 \text{ kJ/mol}$  ;  
 Enthalpy of sublimation of  $\text{C}(\text{s}) = 718 \text{ kJ/mol}$  ;  
 First ionization energy of  $\text{Ca}(\text{g}) = 590 \text{ kJ/mol}$  ;  
 Second ionization energy of  $\text{Ca}(\text{g}) = 1143 \text{ kJ/mol}$  ;  
 Bond energy of  $\text{C}_2(\text{g}) = 614 \text{ kJ/mol}$  ;  
 First electron affinity of  $\text{C}_2(\text{g}) = -315 \text{ kJ/mol}$  ;  
 Second electron affinity of  $\text{C}_2(\text{g}) = +410 \text{ kJ/mol}$  ;  
 Draw a clear Born-Haber cycle and determine lattice energy of  $\text{CaC}_2(\text{s})$ .
- 84\*.** A swimmer breaths 20 times in one minute when swimming and inhale 200 mL of air in one breath. Inhaled air contain 20%  $\text{O}_2$  by volume and exhaled air contain 10%  $\text{O}_2$  by volume. If all oxygen are consumed in combustion of glucose in the body and 25% of energy obtained from combustion is available for muscular work. Determine the maximum distance this swimmer can swim in one hour if 100 kJ energy is required for 1.0 km swimming. Standard molar enthalpy of combustion of glucose is  $-2880 \text{ kJ/mol}$  and body temperature is  $37^\circ\text{C}$ .
- 85\*.** Given the following standard molar enthalpies :  
 $\Delta H_f^\circ$  of  $\text{CH}_3\text{CN}(\text{g}) = 88 \text{ kJ/mol}$ ,  $\Delta H_f^\circ$  of  $\text{C}_2\text{H}_6 = -84 \text{ kJ/mol}$ ,  $\Delta H_{\text{Sublimation}}^\circ$  of  $\text{C}(\text{gr}) = 717 \text{ kJ/mol}$ , bond dissociation energy of  $\text{N}_2(\text{g})$  and  $\text{H}_2(\text{g})$  are 946 and 436 kJ/mole respectively, B.E. ( $\text{C}-\text{H}$ ) = 410 kJ/mol. Determine  $\text{C}-\text{C}$  and  $\text{C}\equiv\text{N}$  bond energies.
- 86.** By using the following data draw an appropriate energy cycle & calculate the enthalpy change of hydration of (i) the chloride ion ; (ii) the iodide ion.  
 Comment on the difference in their values.  
 Enthalpy change of solution of  $\text{NaCl}(\text{s}) = -2 \text{ kJ/mol}$ .  
 Enthalpy change of solution of  $\text{NaI}(\text{s}) = +2 \text{ kJ/mol}$ .  
 Enthalpy change of hydration of  $\text{Na}^+(\text{g}) = -390 \text{ kJ/mol}$ .  
 Lattice energy of  $\text{NaCl} = -772 \text{ kJ/mol}$ .  
 Lattice energy of  $\text{NaI} = -699 \text{ kJ/mol}$ .
- 87\*.** Use the following enthalpies of combustion in the calculations that follow.
- | Element/Compound                           | Enthalpy of Combustion |
|--|------------------------|
| $\text{C}(\text{s})$                       | -394                   |
| $\text{H}_2(\text{g})$                     | -286                   |
| $\text{CH}_3\text{CO}_2\text{H}(\text{l})$ | -876                   |
| $\text{C}_4\text{H}_6(\text{g})$           | -2542                  |
| $\text{C}_2\text{H}_6(\text{g})$           | -1561                  |
| $\text{C}_2\text{H}_4(\text{g})$           | -1393                  |
- (i) Calculate the enthalpy change for the reaction :  
 $2\text{C}(\text{s}) + 2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \longrightarrow \text{CH}_3\text{CO}_2\text{H}(\text{l})$
- (ii) Calculate the enthalpy of formation of buta-1, 3- diene  $\text{C}_4\text{H}_6$ .
- (iii) Calculate the enthalpy of formation of ethene  $\text{C}_2\text{H}_4$ .
- (iv) Calculate the enthalpy change for the conversion of ethene  $\text{C}_2\text{H}_4$  to ethane  $\text{C}_2\text{H}_6$ .
- 88.** Cesium chloride is formed according to the following equation :  
 $\text{Cs}(\text{s}) + 0.5\text{Cl}_2(\text{g}) \longrightarrow \text{CsCl}(\text{s})$ .  
 The enthalpy of sublimation of Cs, enthalpy of dissociation of chlorine, ionization energy of Cs & electron affinity of chlorine are 81.2, 243.0, 375.7 and  $-348.3 \text{ kJ mol}^{-1}$ . The energy change involved in the formation of  $\text{CsCl}$  is  $-388.6 \text{ kJ mol}^{-1}$ . Calculate the lattice energy of  $\text{CsCl}$ .
- 89\*.** The enthalpy of formation of ethane, ethylene and benzene from the gaseous atom are  $-2839.2$ ,  $-2275.2$  and  $-5506 \text{ kJ mol}^{-1}$  respectively. Calculate the resonance energy of benzene. The bond enthalpy of  $\text{C}-\text{H}$  bond is given as equal to  $+410.87 \text{ kJ/mol}$ .

# ANSWERS

## • True and False

1. True      2. False      3. False      4. False      5. False  
 6. False      7. True      8. True      9. True

## • Fill in the Blanks

10. Exothermic      11. Endothermic  
 12. heat of transition      13.  $+33 \text{ kJ mol}^{-1}$   
 14.  $-18 \text{ kcal mol}^{-1}$       15.  $-57.2$   
 16.  $-110.5$       17.  $-RT$

## • Assertion-Reason

18. (A)      19. (C)      20. (C)      21. (A)      22. (D)  
 23. (A)      24. (D)      25. (B)

## • Single Choice Correct

26. (C)      27. (C)      28. (A)      29. (A)      30. (B)  
 31. (A)      32. (B)      33\*. (A)      34. (B)      35\*. (B)  
 36. (C)      37. (A)      38\*. (A)      39. (A)      40\*. (B)  
 41\*. (B)      42. (C)      43. (D)      44\*. (D)      45. (C)  
 46\*. (A)      47. (C)      48\*. (B)      49. (D)      50. (C)  
 51\*. (A)      52\*. (C)      53. (A)      54. (B)      55\*. (B)  
 56. (A)      57\*. (B)

## • Multiple Choice Correct

58. (ABD)      59. (AD)      60. (BC)      61. (C)      62. (ABCD)

## • Match the Column

63. (A) - (q), (B) - (p), (C) - (r), (D) - (s)

## • Comprehension

**Comprehension 1 :**

**Comprehension 2 :**

**Comprehension 3 :**

64. (B)      65.(i) (B)      (ii) (C)

66\*. (B)      67\*. (A)      68\*. (C)

69. (i)  $\Delta H = (v + w + x + y + z)$

(ii)  $(\Delta H)_f K^+ = \frac{w}{2}$       (iii)  $(\Delta H)_{EA}$  for H =  $\frac{y}{2}$

(iv)  $(\Delta H)_{lattice}$  for KH =  $\frac{z}{2}$

70.  $-124 \text{ kJ/mol}$       71.  $-62 \text{ kJ/mol}$

72.  $\text{KH} + \text{H}_2\text{O} \longrightarrow \text{KOH} + \text{H}_2$       73. 39

## • Subjective Questions

74\*.  $q = 0$        $\Delta U = w$

$$n C_v \Delta T = P_{\text{avg.}} \left( \frac{nRT_f}{P_f} - \frac{nRT_i}{P_i} \right) \quad n \times \frac{5}{2} R \Delta T = -P_{\text{avg.}} \left( \frac{nRT_f}{P_f} - \frac{nRT_i}{P_i} \right)$$

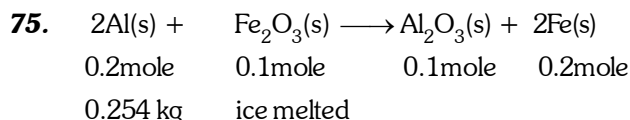
$$5/2 (T - 300) = - \left( \frac{T_f}{2} - \frac{300}{5} \right)$$

$$5/2 T - 750 - \frac{T_f}{2} + 60$$

$$3T = 810 \quad T = 270 \text{ K}$$

$$\Delta U = w = 2 \times \frac{5}{2} R(-300) = -150R = -1247.1 \text{ J}$$

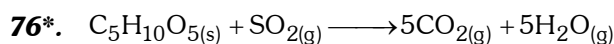
$$\Delta H = -150 R + 2 R(-30) = -210R = -1745.9 \text{ J}$$



$$\Delta H = \frac{-254 \times 1.436}{18} = 20.26 \text{ kcal}$$

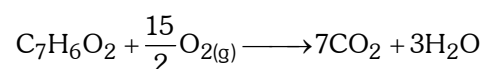
Heat liberated for 0.1 mole = 20.26 kcal

Heat liberated for 1 mole = -202.6 kcal



$$\text{C}_5\text{H}_{10}\text{O}_5 = 150$$

$$\text{C}_6\text{H}_5\text{COOH} = -2.13 - 5 \times 8.314$$



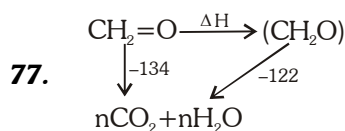
$$mS\Delta T = \frac{0.825}{122} \times 0.3251 = mS(1.940)$$

$$mS = 11.33$$

$$11.33 \times 0.910 \rightarrow 0.727$$

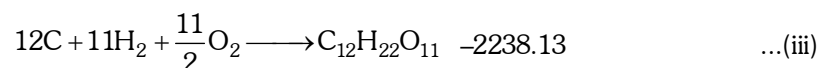
$$x \rightarrow 150 \text{ y}$$

$$\Delta H = -2.13 \text{ MS}$$



applying Hess law

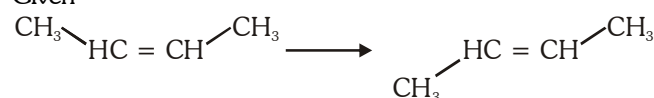
$$\Delta H - 122 = -134 \quad \Delta H = 12 \text{ Kcal}$$



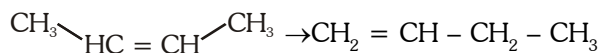
$$-(iii) + 2(ii) - (i) = 2238.3 + 285.85 + 2(-1263.1) = -2.05 \text{ kJmol}^{-1}$$

**79\*.**  $-2035 \text{ kJ mol}^{-1}$

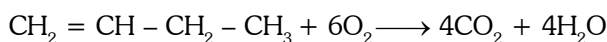
**80\*.** Given



$$\Delta H_1 = -950 \frac{\text{cal}}{\text{mole}} = -0.95 \frac{\text{kcal}}{\text{mole}} \quad \dots(i)$$

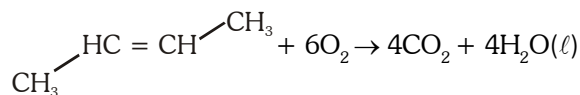


$$\Delta H_2 = +1771 \frac{\text{cal}}{\text{mole}} = 1.771 \frac{\text{kcal}}{\text{mole}} \quad \dots(\text{ii})$$

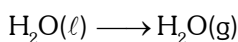


$$\Delta H_3 = -649.8 \frac{\text{kcal}}{\text{mole}} \quad \dots(\text{iii})$$

$$(\text{ii}) + (\text{iii}) - (\text{i})$$

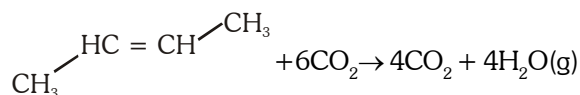


$$\Delta H = -647.079 \frac{\text{kcal}}{\text{mole}} \quad \dots(\text{iv})$$



$$\Delta H_4 = 11 \frac{\text{kcal}}{\text{mole}} \quad \dots(\text{v})$$

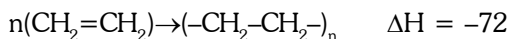
$$(\text{iv}) + 4 \times (\text{v})$$



$$\Delta H = -603.079$$

$$\begin{aligned}
 &[2 B_{\text{C}-\text{C}} + B_{\text{C}=\text{C}} + 8 B_{\text{C}-\text{H}}] \\
 &+ 6B_{\text{O}=\text{O}} - 8 B_{\text{C}=\text{O}} - 8B_{\text{O}-\text{H}} = -603.079 \\
 &B_{\text{C}=\text{C}} = 192.921 \text{ kcal/mole}
 \end{aligned}$$

**81.** Given



$$\text{i.e., } B_{\text{C}=\text{C}} - 2 B_{\text{C}-\text{C}} = -72 \quad \dots(\text{i})$$



$$\text{R.E. of } \text{C}_6\text{H}_6 = -152$$



$$B_{\text{C}-\text{H}} = 415 \quad \text{for equation (2)}$$

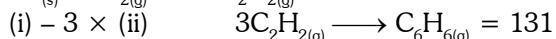
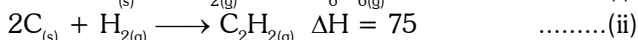
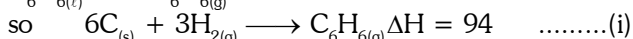
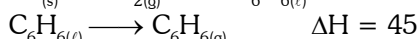
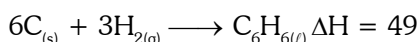
$$(6 \times 715 + 6 \times 218) - (3B_{\text{C}-\text{C}} + 3B_{\text{C}=\text{C}} + 6 \times 415 - \text{RE}) = 79$$

$$B_{\text{C}-\text{C}} + B_{\text{C}=\text{C}} = 959 \quad \dots(\text{iii})$$

$$\text{from equation (i) and (iii)}$$

$$B_{\text{C}-\text{C}} = 343.66 \quad B_{\text{C}=\text{C}} = 615.33$$

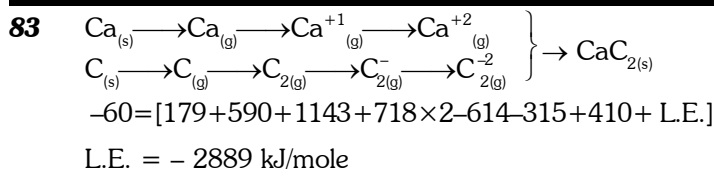
**82\*.** Given



$$3[B_{\text{C}=\text{C}} + 2B_{\text{C}-\text{H}}] - [3B_{\text{C}-\text{C}} + 3B_{\text{C}=\text{C}} + 6B_{\text{C}-\text{H}} - \text{RE}] = -131$$

$$3[B_{\text{C}=\text{C}} - B_{\text{C}-\text{C}} - B_{\text{C}=\text{C}}] + \text{RE} = -131$$

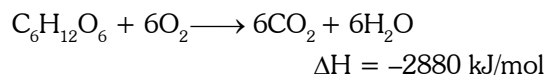
$$\text{RE} = -131 + 99 = -32$$



84\*.  $\text{O}_2$  consumed by body in 1 hr. =  $20 \times 60 \times 200 (0.2 - 0.1) = 24000 \text{ mL}$ .

so volume of  $\text{O}_2$  at 273K is let V then  $\frac{V}{273} = \frac{24000}{310}$

$V = 21135.48 \text{ mL}$  moles of  $\text{O}_2 = 0.9435$

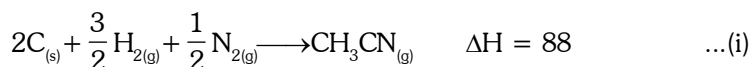


moles of glucose  $\longrightarrow \frac{0.9435}{6}$

Heat released =  $\frac{2880 \times 0.9435}{6} = 452.9 \text{ kJ}$

Heat used for muscular work  
 =  $452.9 \times 0.25 = 113.22 \text{ kJ}$   
 so distance = 1.132 km

85\*. Given :



$B_{\text{C-H}} = 410$

from equation (i)

$(2 \times 717 + 1.5 \times 436 + 0.5 \times 946) - (3 \times 410 + B_{\text{C-C}} + B_{\text{C=N}}) = 88$

$B_{\text{C-C}} + B_{\text{C=N}} = 1243$

$\dots(iii)$

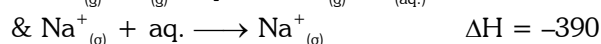
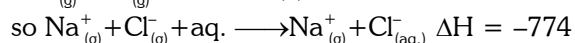
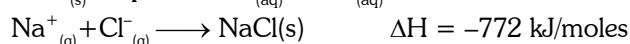
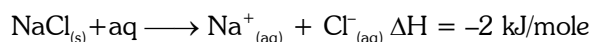
from equation (ii)

$(2 \times 717 + 3 \times 436) - (B_{\text{C-C}} + 6 \times 410) = -84$

$B_{\text{C-C}} = 366 \text{ kJ/mole}$  from equation (iii)

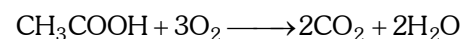
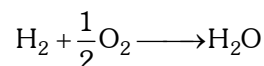
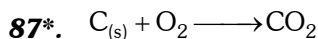
$B_{\text{C=N}} = 877 \text{ kJ/mole}$

86. Given :

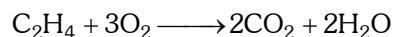
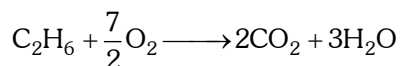
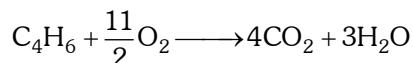


so enthalpy of hydration of  $\text{Cl}^{-} = -384$

similarly enthalpy of hydration of  $\text{I}^{-} = -307$





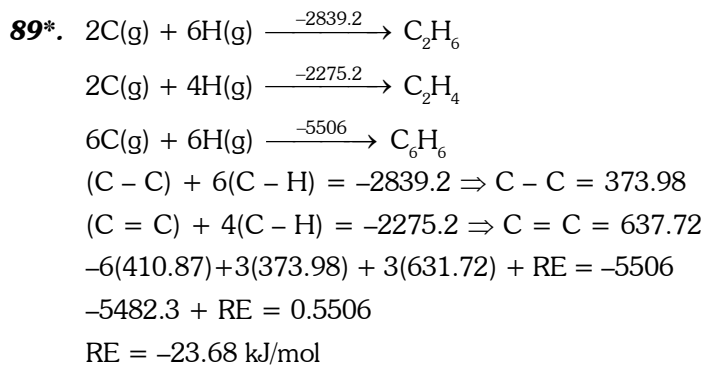
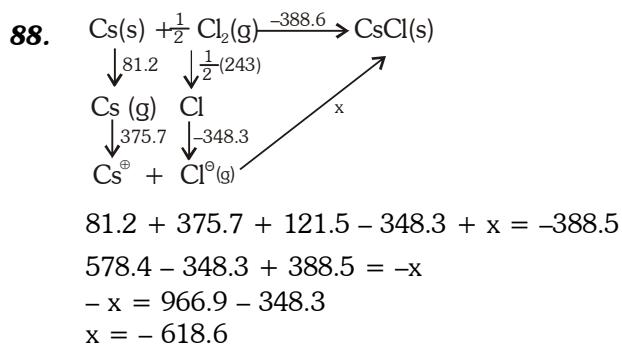


$$\begin{aligned}
 \text{(i)} \quad & 2\text{(i)} + 2\text{(ii)} - \text{(iii)} \\
 & = 2(-394 - 286) + 876 \\
 & = -1360 + 876 = -484 \text{ kJ/mol}
 \end{aligned}$$

$$\begin{aligned}
 \text{(ii)} \quad & 4\text{C}_{(\text{s})} + 3\text{H}_{2(\text{g})} \longrightarrow \text{C}_4\text{H}_{6(\text{g})} \\
 & = 4\text{C}(-394) + 3(-286) + 2542 \\
 & = -1576 - 858 + 2542 \\
 & = 108
 \end{aligned}$$

$$\begin{aligned}
 \text{(iii)} \quad & 2\text{C} + 2\text{H}_2 \longrightarrow \text{C}_2\text{H}_4 \\
 & = 2(-394) + 2(-286) + 1393 \\
 & = -1360 + 1393 = 33
 \end{aligned}$$

$$\begin{aligned}
 \text{(iv)} \quad & \text{C}_2\text{H}_4 + \text{H}_2 \longrightarrow \text{C}_2\text{H}_6 \\
 & \text{(vi)} - \text{(v)} + \text{(ii)} \\
 & = -1393 - 286 + 1561 = -118
 \end{aligned}$$



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**CHEMICAL BONDING**


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**Assertion-Reason**

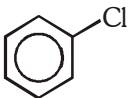
These questions contains, Statement-I (assertion) and Statement-II (reason).

- (A) Statement-I is True, Statement-II is True ; Statement-II is a correct explanation for Statement-I  
 (B) Statement-I is True, Statement-II is True ; Statement-II is NOT a correct explanation for Statement-I  
 (C) Statement-I is True, Statement-II is False.  
 (D) Statement-I is False, Statement-II is True.

1. **Statement-I** :  $\text{CO}_2$  and  $\text{SiO}_2$  has same physical state at room temp.

**Because**

**Statement-II** : Carbon has more electronegativity than silicon atom.

2. **Statement-I** : Dipole moment of  is similar as bromo benzene.

**Because**

**Statement-II** : Dipole moment of Cl - C bond is greater than Br - C bond.

3. **Statement-I** : The stability of peroxides and superoxides increases in passing from Li to Cs.

**Because**

**Statement-II** : The electropositive character of the elements in the periodic table increases on moving down a group.

4. **Statement-I** : Borazole is aromatic in nature.

**Because**

**Statement-II** : Nitrogen contributes  $\pi$ -electrons to the system.

5. **Statement-1** :  $\text{CH}_4$  and  $\text{CH}_2\text{F}_2$  are having regular tetrahedron geometry.

**Statement-2** : Both are having same hybridization.

- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.

6. **Statement-1** : Dipole moment of  $\text{H}_2\text{O}$  is more than that of  $\text{OF}_2$ .

**Statement-2** : In  $\text{H}_2\text{O}$ , the resultant bond dipole of O - H bond and the resultant lone pair moment are in opposite direction.

- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.

7. **Statement-1** : Allene is a non polar molecule.

**Statement-2** : Allene is non planar molecule.

- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.

**Single Choice Correct**

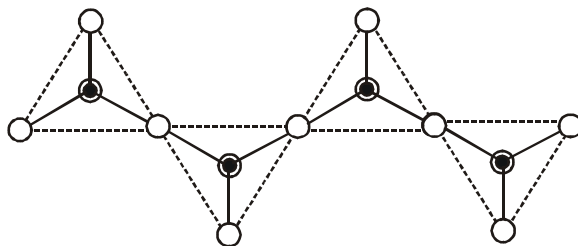
8. The bond angle and hybridization in ether ( $\text{CH}_3\text{OCH}_3$ ) is :  
 (A)  $106^\circ 51'$ ,  $sp^3$  (B)  $104^\circ 31'$ ,  $sp^3$  (C)  $> 109^\circ 28'$ ,  $sp^3$  (D) None of these
9. The types of bonds present in  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  are  
 (A) electrovalent and covalent (B) electrovalent, coordinate covalent & H-bond  
 (C) covalent, coordinate covalent & H-bonds (D) electrovalent, covalent, coordinate covalent & H-bond
10. Amongst  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{S}$ ,  $\text{H}_2\text{Se}$  and  $\text{H}_2\text{Te}$ , the one with the highest boiling point is [JEE 2000]  
 (A)  $\text{H}_2\text{O}$  because of hydrogen bonding (B)  $\text{H}_2\text{Te}$  because of higher molecular weight  
 (C)  $\text{H}_2\text{S}$  because of hydrogen bonding (D)  $\text{H}_2\text{Se}$  because of lower molecular weight
11. The correct order of hybridization of the central atom in the following species  $\text{NH}_3$ ,  $\text{PtCl}_4^{-2}$ ,  $\text{PCl}_5$  and  $\text{BCl}_3$  is [JEE 2001]  
 (A)  $dsp^2$ ,  $sp^3d$ ,  $sp^2$  and  $sp^3$  (B)  $sp^3$ ,  $dsp^2$ ,  $sp^3d$ ,  $sp^2$  (C)  $dsp^2$ ,  $sp^2$ ,  $sp^3$ ,  $sp^3d$  (D)  $dsp^2$ ,  $sp^3$ ,  $sp^2$ ,  $sp^3d$
12. All possible bond angles in anionic part of  $\text{PCl}_5$  are.  
 (A)  $109^\circ 28'$  only (B)  $90^\circ$ ,  $180^\circ$  (C)  $90^\circ$ ,  $120^\circ$ ,  $180^\circ$  (D)  $72^\circ$ ,  $90^\circ$ ,  $180^\circ$
13. Which of following pair of species is having different hybridisation but same shape.  
 (A)  $\text{BeCl}_2$  and  $\text{CO}_2$  (B)  $\text{CO}_2$  and  $\text{SO}_2$  (C)  $\text{SO}_2$  and  $\text{I}_3^+$  (D)  $\text{ICl}_2^-$  and  $\text{BeH}_2$
14. Which of the following statements is correct in the context of the allene molecule,  $\text{C}_3\text{H}_4$ ?  
 (A) The central carbon is  $sp$  hybridized  
 (B) The terminal carbon atoms are  $sp^2$  hybridized  
 (C) The planes containing the  $\text{CH}_2$  groups are mutually perpendicular to permit the formation of two separate  $\pi$ -bonds.  
 (D) All correct
15. Structure of  $\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 8\text{H}_2\text{O}$  contains  
 (A) Two triangular and two tetrahedral units (B) Three triangular and one tetrahedral units.  
 (C) All tetrahedral units. (D) All triangular units.
16. A : tetracyanomethane B : carbondioxide C : benzene D : 1,3-buta-di-ene  
 Ratio of  $\sigma$  and  $\pi$  bonds is in order :  
 (A)  $A = B < C < D$  (B)  $A = B < D < C$  (C)  $A = B = C = D$  (D)  $C < D < A < B$
17. The geometry of ammonia molecule can be best described as  
 (A) nitrogen at one vertex of a regular tetrahedron, the other three vertices being occupied by the three hydrogens  
 (B) nitrogen at the centre of the tetrahedron, three of the vertices being occupied by three hydrogens  
 (C) nitrogen at the centre of an equilateral triangle, three corners being occupied by three hydrogens  
 (D) nitrogen at the junction of a T, three open ends being occupied by three hydrogens.
18. Find the molecule which is planar and polar.  
 (A)  $\text{B}_3\text{N}_3\text{H}_6$  (B)  $\text{F}_2\text{C} = \text{C} = \text{C} = \text{CF}_2$  (C)  $\text{BrF}_2\text{Cl}$  (D)  $\text{F}_2\text{C} = \text{C} = \text{CF}_2$
19. Find out the **incorrect** order of the dipole moment among the following pair of compound  
 (A)  $\text{NH}_3 > \text{NF}_3$  (B) p-dichloro benzene > o-dichloro benzene  
 (C)  $\text{CH}_3\text{Cl} > \text{CH}_2\text{Cl}_2$  (D)  $\text{SiF}_4 < \text{SF}_4$

- 20.** Select the correct order of B.P.  
 (A)  $\text{BF}_3 > \text{BMe}_3$  (B)  $\text{BF}_3 < \text{BMe}_3$  (C)  $\text{BF}_3 = \text{BMe}_3$  (D) None of these
- 21.** In a change from  $\text{PCl}_3 \longrightarrow \text{PCl}_5$ , the hybrid state of P changes from  
 (A)  $\text{sp}^2$  to  $\text{sp}^3$  (B)  $\text{sp}^3$  to  $\text{sp}^2$  (C)  $\text{sp}^3$  to  $\text{sp}^3\text{d}$  (D)  $\text{sp}^3$  to  $\text{dsp}^2$
- 22.** Select correct statement about hydrolysis of  $\text{BCl}_3$  and  $\text{NCl}_3$   
 (A)  $\text{NCl}_3$  is hydrolysed and gives  $\text{HOCl}$  but  $\text{BCl}_3$  is not hydrolysed.  
 (B) Both  $\text{NCl}_3$  and  $\text{BCl}_3$  on hydrolysis gives  $\text{HCl}$   
 (C)  $\text{NCl}_3$  on hydrolysis gives  $\text{HOCl}$  but  $\text{BCl}_3$  gives  $\text{HCl}$   
 (D) Both  $\text{NCl}_3$  and  $\text{BCl}_3$  on hydrolysis gives  $\text{HOCl}$
- 23.** Number of corner/oxygen atoms shared per tetrahedron in pyroxene chain silicate and sheet silicate are .....and.....respectively–  
 (A) 2.5, 3 (B) 2, 3 (C) 3, 2 (D) 2, 2
- 24.** Which of the following order is correct of the given property.  
 (A)  $\text{LiCl} > \text{NaCl} > \text{KCl} > \text{RbCl} > \text{CsCl}$  : Thermal stability order  
 (B)  $\text{BeF}_2 < \text{MgF}_2 < \text{CaF}_2 < \text{SrF}_2 < \text{BaF}_2$  : solubility order  
 (C)  $\text{NO}_2^- > \text{NO}^- > \text{NO} = \text{NO}_2^+ > \text{NO}^+$  : bond length order  
 (D)  $\text{BaO} > \text{SrO} > \text{CaO} > \text{BeO} > \text{MgO}$  : basic character order
- 25.** In which of the following cases, the strength of back bonding is maximum :-  
 (A)  $\text{PF}_3$  (B)  $\text{BF}_3$  (C)  $(\text{H}_3\text{Si})_3\text{N}$  (D)  $(\text{SiH}_3)_2\text{O}$

### Multiple Choice Correct

- 26\*.** Which of the following have a three dimensional network structure ?  
 (A)  $\text{SiO}_2$  (B) Diamond (C)  $\text{P}_4(\text{white})$  (D)  $\text{CCl}_4$
- 27\*.** Which of the following oxyacids of sulphur contain  $\text{S} - \text{S}$  bonds ?  
 (A)  $\text{H}_2\text{S}_2\text{O}_8$  (B)  $\text{H}_2\text{S}_2\text{O}_6$  (C)  $\text{H}_2\text{S}_2\text{O}_4$  (D)  $\text{H}_2\text{S}_2\text{O}_5$
- 28.** London force works in  
 (A) Polar molecule (B) Non-polar molecule  
 (C) All polar and non-polar molecule (D) Only in polar molecule
- 29.** London forces depends upon  
 (A) Molecular weight (B) Number of polarisable electron  
 (C) Molecular size (D) None of these
- 30.** Select the correct order of following property.  
 (A) % s-character :  $\text{sp}^3 > \text{sp}^2 > \text{sp}$   
 (B)  $\text{ONO}$  bond angle :  $\text{NO}_3^- > \text{NO}_2^+ > \text{NO}_2$   
 (C) Second ionisation energy :  $\text{O} > \text{F} > \text{N} > \text{C}$   
 (D) C – H bond length :  $\text{CH}_3\text{F} > \text{CH}_2\text{F}_2 > \text{CF}_3\text{H}$
- 31.** In which of the molecule on hydrolysis proton donor oxyacid is not formed from their central atom-  
 (A)  $\text{NCl}_3$  (B)  $\text{BCl}_3$  (C)  $\text{SF}_4$  (D)  $\text{P}_4\text{O}_{10}$

32. A mineral contain following tetrameric anion in which  $\bullet$  = Si,  $\bigcirc$  = oxygen



Select **correct** option (s) about anion in mineral –

- (A) Formula of anion is  $(\text{SiO}_3)_n^{2n-}$  (where  $n = 4$ ) .  
 (B) The total 10 negative charges are present in this anion.  
 (C) It has three shared oxygen/corners and ten unshared oxygen/corners.  
 (D) It is non planar
33. Choose the **correct** statements.  
 (A)  $\text{CH}_3\text{NCS}$  molecule is linear  
 (B)  $\text{SiH}_3\text{NCS}$  molecule is linear  
 (C)  $\text{GeH}_3\text{NCS}$  molecule is bent  
 (D)  $\text{P}(\text{SiH}_3)_3$  molecule is pyramidal
34. The molecule is/are having N – N bond.  
 (A)  $\text{N}_2\text{O}$  (B)  $\text{N}_2\text{O}_3$  (unsymm.) (C)  $\text{N}_2\text{O}_5$  (D)  $\text{N}_2\text{O}_4$
35. Which of the following statement is/are correct for  $\text{CCl}_3^-$  and  $\text{:CCl}_2$   
 (A) Back bonding in both cases from Cl to C-atom  
 (B) Back bonding in both cases from C to Cl-atom  
 (C) Back bonding in  $\text{CCl}_3^-$  from C to Cl but reverse in  $\text{:CCl}_2$   
 (D) Direction of back bonding is just opposite in two cases.
36. Which of the following molecule(s) is/are having  $p\pi-p\pi$  back bonding  
 (A)  $\text{BF}_3$  (B)  $\text{BeF}_2$  (C)  $\text{B}_3\text{N}_3\text{H}_6$  (D)  $\text{BCl}_3$

### Match the Column

#### 37\*. Column-I

- (A)  $\text{B}_3\text{N}_3\text{H}_6$   
 (B)  $\text{H}_2\text{O}_2$   
 (C)  $\text{B}_2\text{H}_6$   
 (D)  $\text{I}_2\text{Cl}_6$

#### Column-II

- (p) planar geometry  
 (q) non planar geometry  
 (r) no lone pair  
 (s) non polar molecule

38. Match the column:

#### Column -I (Type of orbital)

- (A)  $d_{z^2}$  -orbital  
 (B)  $d_{xy}$  - orbital  
 (C)  $p_y$  - orbital  
 (D)  $d_{x^2-y^2}$  -orbital

#### Column-II (Orbitals involved in hybridisation)

- (P)  $sp^3$  (Tetrahedral)  
 (Q)  $sp^3d^2$  (Octahedral)  
 (R)  $sp^3d$  (TBP)  
 (S)  $sp^3d^3$  (PBP)

### Comprehension

Cation and anion attract each other by electrostatic force of attraction to give a molecule  $A^+ B^-$ . Since the electrostatic field of a charged particle extends in all directions, a positive ion is surrounded by a number of negatively charged ions while each negative ion is similarly surrounded by a number of positive ions. These cations and anions arrange systematically in an alternating cation-anion pattern. This is called a crystal lattice. This process of clustering ions increases the force of attraction and thus potential energy decreases. The energy released when the requisite number of positive and negative ions are condensed into crystal to form one mole of the compound is called lattice energy. Higher the lattice energy, greater will be the ease of forming an ionic compound.

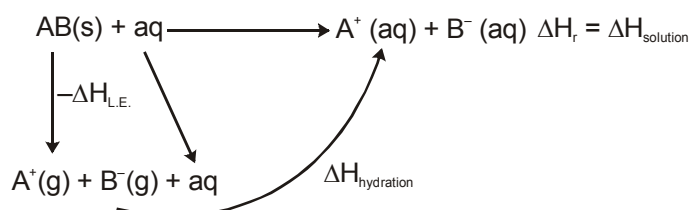
$$L.E. \propto \frac{1}{r_+ + r_-}$$

$$\propto |z^+| |z^-|$$

$r_+$  – radius of cation,  $r_-$  – radius of anion  $z^+$  and  $z^-$  are the charge on cation and anion respectively.

Lattice energy can be indirectly calculated using Born Haber cycle.

Solubility of an ionic solid AB can be explained



$$\Rightarrow \Delta H_{\text{solution}} = \Delta H_{\text{hyd.}} - \Delta H_{\text{L.E.}}$$

Lattice energy (L.E.)  $\propto \frac{1}{r_+ + r_-}$  and hydration energy (H.E.)  $\propto \frac{1}{r_+} + \frac{1}{r_-}$  practically it is found, if  $r_+ \simeq r_-$  then

L.E. dominates over H.E. But if  $r_+ \ll r_-$  or  $r_+ \gg r_-$  then H.E. dominates over L.E. more the lattice energy compared to hydration energy less will be the solubility but if less is the lattice energy & more is the hydration energy more will be the solubility.

- 39\*.** A hypothetical compound  $MX_2(s)$  has lattice energy  $1200 \text{ kJ mol}^{-1}$  and  $\Delta H_{\text{hydration}}$  for  $M^{2+}(g)$  is  $1000 \text{ kJ mol}^{-1}$  and  $\Delta H_{\text{hydration}}$  for  $X^-(g)$  is  $150 \text{ kJ mol}^{-1}$  then if one mole of  $MX_2(s)$  is dissolved in sufficient amount of water then calculate the value of  $\Delta H$  for this process in  $\text{kJ mol}^{-1}$
- (A) – 100                      (B) + 100                      (C) 200                      (D) + 50
- 40\*.** When one mole of  $CsF(s)$  is dissolved in sufficient amount of water then it releases  $40 \text{ kJ}$  energy. If lattice energy of  $CsF$  is  $750 \text{ kJ mol}^{-1}$  then the summation of heat of hydration of  $Cs^+$  &  $F^-$  ion is (magnitude wise)
- (A) –  $750 \text{ kJ mol}^{-1}$                       (B) –  $790 \text{ kJ mol}^{-1}$                       (C) –  $710 \text{ kJ mol}^{-1}$                       (D) –  $830 \text{ kJ mol}^{-1}$
- 41\*.** True order of solubility is :
- (A)  $MgCO_3 > CaCO_3 > SrCO_3 > BaCO_3$                       (B)  $BaCO_3 > SrCO_3 > CaCO_3 > MgCO_3$   
 (C)  $MgCO_3 > CaCO_3 > BaCO_3 > SrCO_3$                       (D)  $SrCO_3 > BaCO_3 > CaCO_3 > MgCO_3$
- 42\*.** The correct order of Lattice energy will be :
- (A)  $Na_2S > MgCl_2$                       (B)  $MgCl_2 > Na_2S$                       (C)  $MgCl_2 \simeq Na_2S$                       (D) Can't be predicted

### Subjective Questions

Draw structures of following:

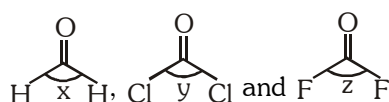
1.  $\text{H}_2\text{SO}_4$
2.  $\text{C}_3\text{O}_2$
3.  $(\text{CN})_2$
4.  $\text{Na}_2\text{S}_4\text{O}_6$
5.  $\text{Cl}_2\text{O}_7$
6.  $\text{P}_4$
7.  $\text{P}_4\text{O}_6$
8.  $\text{P}_4\text{O}_{10}$
9.  $\text{O}_2\text{F}_2$  (dimer form of OF)
10.  $\text{S}_3\text{O}_9$
11.  $\text{N}_2\text{O}_5$
12.  $\text{S}_2\text{O}_7^{2-}$
13.  $\text{N}_2\text{F}_4$
14.  $\text{N}_2\text{O}_3$
15.  $\text{SiO}_2$
16.  $\text{HClO}_4$
17.  $\text{CaCN}_2$
18.  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
19.  $\text{P}_4\text{S}_{10}$
20.  $\text{RbIO}_2$
21.  $\text{CsH}_2\text{PO}_2$
22.  $\text{NaIO}_3$
23.  $\text{NH}_4\text{OCN}$
24.  $\text{H}_2\text{S}_2\text{O}_4$
25.  $\text{NaHSO}_3$
26.  $\text{H}_2\text{PO}_3^-$
27.  $\text{H}_2\text{P}_2\text{O}_5^{2-}$
28. Dithionate ion ( $\text{S}_2\text{O}_6^{2-}$ )
29. Trithionate ion ( $\text{S}_3\text{O}_6^{2-}$ )
30. Thionyl chloride ( $\text{SOCl}_2$ )
31. Sulphury chloride ( $\text{SO}_2\text{Cl}_2$ )
32. Pyrophosphoric acid ( $\text{H}_4\text{P}_2\text{O}_7$ )
33. Meta phosphoric acid ( $\text{HPO}_3$ )
34. Peroxy phosphoric acid ( $\text{H}_3\text{PO}_5$ )
35. Ammonium phosphite
36. Sodium hydrogen phosphate
37. Sodium dihydrogen phosphate
38. Sodium dihydrogen pyrophosphate
39. Potassium bicarbonate ( $\text{KHCO}_3$ )
40. Calcium carbide ( $\text{CaC}_2$ )
41. Peroxy diphosphoric acid ( $\text{H}_4\text{P}_2\text{O}_8$ )
42. Hyponitrous acid ( $\text{H}_2\text{N}_2\text{O}_2$ )
43. Oleum ( $\text{H}_2\text{S}_2\text{O}_7$ )
44. Marshall's acid ( $\text{H}_2\text{S}_2\text{O}_8$ )
45. Caro's acid ( $\text{H}_2\text{SO}_5$ )

**43.** In what hybridization state is the beryllium atom in  $\text{BeCl}_2$  molecule? How will the type of hybridization change when  $\text{BeCl}_2$  transform to the solid state.

**44\*.** (a) What type of bonding holds the layer in graphite? Why will graphite conduct electricity well in a direction parallel to the planes of hexagons, but not at all well in a direction perpendicular to the planes?

(b)  $\text{PCl}_5$  exists as solid in the form of  $[\text{PCl}_4]^+ [\text{PCl}_6]^-$ , yet it is a non conductor of electricity. Why?

**45.** What is the increasing order of the bond angle for the following compounds?



**46\*.** How many S – S linkage present in  $\text{H}_2\text{S}_n\text{O}_6$ .

**47\*.** Draw the structure of following compound

- |  |   |
|--|---|
| (i) $\text{Na}[\text{B}_3\text{O}_3(\text{OH})_4]$ | (ii) $\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 8\text{H}_2\text{O}$ |
| (iii) $\text{Na}_6\text{P}_6\text{O}_{18}$         | (iv) $\text{S}_3\text{O}_6^{-2}$  |
| (v) $\text{S}_3\text{O}_9$                         | (vi) $(\text{CN})_2$  |

- 48.** Draw the geometry of following three molecules and explain with proper reasoning :  
(i)  $\text{N}(\text{CH}_3)_3$                       (ii)  $\text{N}(\text{SiH}_3)_3$                       (iii)  $\text{P}(\text{SiH}_3)_3$
- 49\*.** Find out total number of  $\text{p}\pi\text{-d}\pi$  bonds present in any one of its structures in case of  $\text{PO}_4^{3-}$
- 50\*.** Find out total number of  $\text{p}\pi\text{-p}\pi$  bonds present in  $\text{ClO}_3^-$ .
- 51\*.** How many number of atomic orbitals are required, so that their mixing produces hybrid orbitals each having % of s-character equal to 17%.
- 52.**  $\text{AgNO}_3$  gives a white precipitate with  $\text{NaCl}$  but not with  $\text{CCl}_4$ . Why ?
- 53.** Give reasons for the following :  
(a)  $\text{KHF}_2$  is known whereas  $\text{KHC}_2$  is unknown.  
(b)  $(\text{CH}_3)_3\text{N}$  is pyramidal but  $(\text{SiH}_3)_3\text{N}$  is trigonal planar.  
(c)  $\text{CO}_2$  is a gas but  $\text{SiO}_2$  is a solid.
- 54\*.** (a)  $\text{BF}_3$  has less lewis acidic property than  $\text{BBr}_3$ . Why ?  
(b)  $(\text{CH}_3)_3\text{C-OH}$  is less acid than  $(\text{CH}_3)_3\text{Si-OH}$ . Why ?  
(c) Why in the presence of ethyne HF exhibit more acidic character.  
(d) Why  $\text{SF}_4$  can be hydrolysed easily but  $\text{SF}_6$  can not ?
- 55\*.** Give a suitable reason for the high mobility of  $\text{H}^+$  ions through the ice than through liquid water.
- 56.** HBr has dipole moment  $2.6 \times 10^{-30} \text{ CM}$ . If the ionic character of the bond is 11.5 %, calculate the interatomic spacing.
- 57.** Maleic acid is more acidic than fumaric acid. Why?
- 58.** Molar entropy change of vapourization of acetic acid is less than that of water. Explain
- 59.** Heat of vapourization of water is higher than HF, however strength of H-bond in HF is higher than water. Explain



## ANSWERS

### Assertion-Reason

1. (D)      2. (D)      3. (A)      4. (B)      5. (D)  
 6. (C)      7. (B)

### Single Choice Correct

8. (C)      9. (D)      10. (A)      11. (B)      12. (B)  
 13. (C)      14. (D)      15. (A)      16. (A)      17. (A)  
 18. (C)      19. (B)      20. (B)      21. (C)      22. (C)  
 23. (A)      24. (A)      25. (B)

### Multiple Choice Correct

26. (AB)      27. (BCD)      28. (C)      29. (ABC)      30. (CD)  
 31. (AB)      32. (BCD)      33. (BCD)      34. (ABD)      35. (B)

### Match the Column

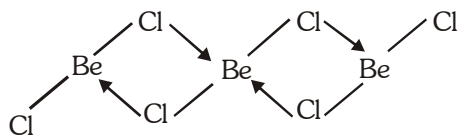
37. A - (p, r, s), B - (q), C - (q, r, s), D - (p, s)  
 38. A - (q, r, s), B - (s), C - (p, q, r, s), D - (q, s)

### Comprehension

39. (A)      40. (B)      41. (A)      42. (B)

### Subjective Questions

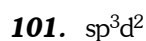
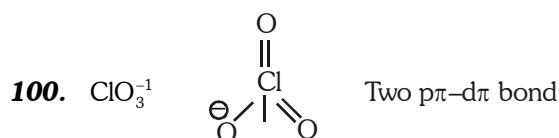
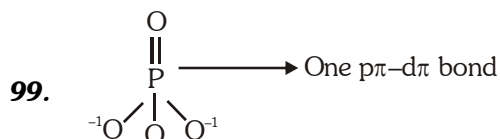
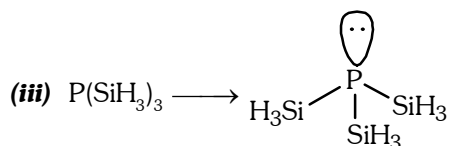
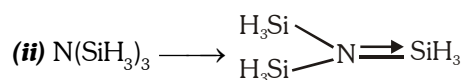
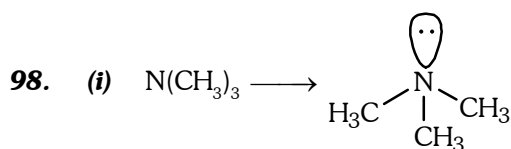
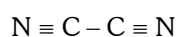
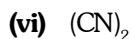
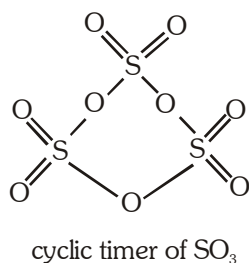
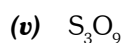
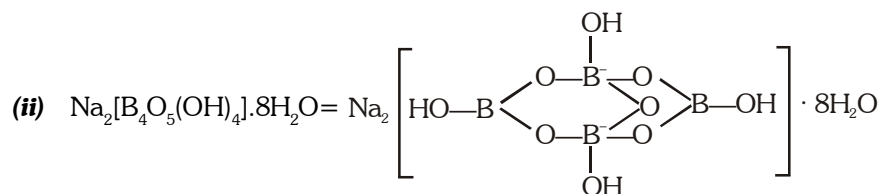
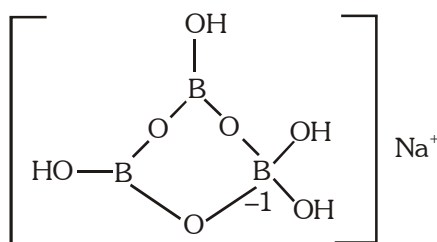
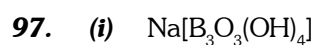
44.  $\longrightarrow \text{Cl} - \text{Be} - \text{Cl} \longrightarrow$  sp hybridization  
 in solid state  $\text{BeCl}_2$  gets polymerized.



45. (a) In graphite layers are held together through weak Vander Waal's forces in graphite each  $\text{C}^-$  atom has one unpaired electron which can move through. The plane from one end to another but between planes due to larger distance electron can't move between planes.  
 (b) In solid state ions are not free to move, so inspite of being ionic it does not conduct electricity.

95.  $\text{F}-\overset{\text{O}}{\parallel}{\text{C}}-\text{F} < \text{Cl}-\overset{\text{O}}{\parallel}{\text{C}}-\text{Cl} < \text{H}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$

96.  $\text{H}_2\text{S}_n\text{O}_6 (n-1) \longrightarrow \text{S}-\text{S} \text{ bond.}$

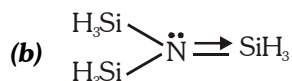


$$\% \text{ s-character} = \frac{\text{no. of s-orbital}}{\text{total no. of orbital}} \times 100$$

$$= \frac{1}{6} \times 100 = 17\%$$

**102.** NaCl is an ionic compound so gives  $\text{Cl}^-$  due to which AgCl is formed while  $\text{CCl}_4$  is a covalent molecule. So it does not give  $\text{Cl}^-$  ion so AgCl is not formed.

**103. (a)**  $\text{F}^-$  due to smaller size and greater EN can form inter molecular H-bond but  $\text{Cl}^-$  can't form due to its larger size and lesser EN.



due to back bonding between N and Si hybridisation state of N becomes  $\text{sp}^2$  and shape becomes planar.

while  $(\text{CH}_3)_3\text{N} \longrightarrow$  no such back bonding takes place.

so hybridisation state  $\longrightarrow \text{sp}^3$

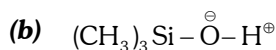
shape  $\longrightarrow$  pyramidal

**(c)** In  $\text{CO}_2$  due to smaller size of C atom stable  $\text{p}\pi\text{-p}\pi$  bond is formed between C and O so in  $\text{CO}_2$  all four valencies of C is completed.

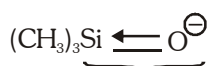
While in  $\text{SiO}_2$  due to larger size of Si it can't form stable  $\text{p}\pi\text{-p}\pi$  bond so  $\text{SiO}_2$  form 3D network structure due to which  $\text{SiO}_2$  exist in solid state.

While in  $\text{CO}_2$  molecules are hold together through weak vander waal's forces.

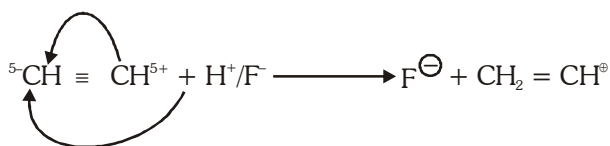
**104. (a)**  $\text{BF}_3$  due to back bonding between F and B electron deficiency of B is completed so it is a weaker Lewis Acid.



The anion of  $(\text{CH}_3)_3\text{Si}-\text{OH}$  is stabilized due to back bonding.



**(c)** because the proton given by HF is accepted by  $\text{CH}\equiv\text{CH}$  so equilibrium shifted towards right.



**(d)** In  $\text{SF}_6$  due to symmetrical shape it is inert while  $\text{SF}_4$  due to unsymmetrical. See-saw shape is easily hydrolyzed.

**105.** In ice due to open cage like structure  $\text{H}_2\text{O}$  molecules are held at fixed positions so  $\text{H}^+$  can move easily while in  $\text{H}_2\text{O}(l)$ .  $\text{H}_2\text{O}$  molecules are not fixed so  $\text{H}^+$  ions are hindered by  $\text{H}_2\text{O}$  molecules in water.

**106.** % ionic character =  $\frac{\mu_{\text{obs}}}{\mu_{\text{cal}}} \times 100$

$$11.5 = \frac{2.6 \times 10^{-30} \times 100}{1.6 \times 10^{-19} \times d}$$

$$d = \frac{2.6 \times 10^{-30} \times 100}{1.6 \times 10^{-19} \times 11.5} = \frac{260}{1.6 \times 11.5} \times 10^{-11} = 14.1 \times 10^{-11} \text{ M}$$

## This image shows a single sheet of white paper with horizontal ruling lines. The lines are evenly spaced and run across the width of the page. There are no margins, text, or other markings on the paper.