

## BRAIN STORMING PROBLEMS

### OBJECTIVE QUESTIONS for IIT ASPIRANTS

The following questions contain single correct option:

1. The average life of a  $W$  gm sample of  $^{200}\text{RaE}$  is  $T$  seconds and average energy of the  $\beta$ -particles emitted is  $E$  MeV. At what rate in watts does the sample emit energy?

$$\begin{array}{ll} (\text{a}) \frac{8WN_0E}{T} \times 10^{-16} & (\text{b}) \frac{8(\ln 2)WN_0E}{T} \times 10^{-13} \\ (\text{c}) \frac{8WN_0E}{T} \times 10^{-13} & (\text{d}) \text{None is correct} \end{array}$$

[Hint: Rate of  $\beta$ -particles emitted per second

$$= \lambda \times \frac{W}{\text{At. wt.}} \times N_0 = \frac{1}{T} \times \frac{W}{200} \times N_0$$

Energy evolved per second

$$\begin{aligned} &= \frac{1}{T} \times \frac{W}{200} \times N_0 \times E \times 1.6 \times 10^{-19} \times 10^6 \text{ J sec}^{-1} \\ &= \frac{8WN_0E}{T} \times 10^{-16} \text{ watt per second} \end{aligned}$$

2. In nuclear fission, 0.01% mass is converted into energy. The energy released by the fission of 100 kg mass will be:

$$(\text{a}) 9 \times 10^{15} \text{ J} \quad (\text{b}) 9 \times 10^{11} \text{ kJ} \quad (\text{c}) 9 \times 10^{17} \text{ J} \quad (\text{d}) 9 \times 10^{13} \text{ kJ}$$

$$\text{Hint: } \Delta m = 100 \times \frac{0.01}{100} = 0.01 \text{ kg}$$

$$\begin{aligned} E &= \Delta m c^2 = 0.01 \times (3 \times 10^8)^2 \text{ J} \\ &= 9 \times 10^{14} \text{ J} = 9 \times 10^{11} \text{ kJ} \end{aligned}$$

3. The activity of a radioactive substance is  $R_1$  at time  $t_1$  and  $R_2$  at time  $t_2$  ( $> t_1$ ). Its decay constant is  $\lambda$ . Then:

$$\begin{array}{ll} (\text{a}) R_1 t_1 = R_2 t_2 & (\text{b}) R_2 = R_1 e^{\lambda(t_2 - t_1)} \\ (\text{c}) R_2 = R_1 e^{\lambda(t_1 - t_2)} & (\text{d}) \frac{R_1 - R_2}{t_2 - t_1} = \text{constant} \end{array}$$

$$\text{Hint: } \frac{R_2}{R_1} = \frac{R_0 e^{-\lambda t_2}}{R_0 e^{-\lambda t_1}}, \quad R_2 = R_1 e^{\lambda(t_1 - t_2)}$$

4. The age of a specimen ' $t$ ' is related to the daughter/parent ratio by the equation:

$$(\text{a}) t = \frac{1}{\lambda} \ln \left( \frac{D}{P} \right) \quad (\text{b}) t = \frac{1}{\lambda} \ln \left( 1 + \frac{P}{D} \right)$$

$$(\text{c}) t = \frac{1}{\lambda} \ln \left( 1 + \frac{D}{P} \right) \quad (\text{d}) t = \frac{1}{\lambda} \ln \left( 2 + \frac{D}{P} \right)$$

5. A radioactive substance is being produced at a constant rate of 200 nuclei/sec. The decay constant of the substance is  $1 \text{ sec}^{-1}$ . After what time will the number of radioactive nuclei become 100? Initially, there are no nuclei present.

$$(\text{a}) 1 \text{ sec} \quad (\text{b}) 2 \text{ sec} \quad (\text{c}) \ln(2) \text{ sec} \quad (\text{d}) \frac{1}{\ln(2)} \text{ sec}$$

$$\text{Hint: } N = N_0 e^{-\lambda t}$$

$$100 = 200e^{-1 \times t}$$

$$\frac{1}{2} = e^{-t}$$

$$t = \ln(2) \text{ sec}$$

6. The rate of decay of a radioactive sample is given by  $R_1$  at time  $t_1$  and  $R_2$  at a later time  $t_2$ . The mean life of this radioactive sample is:

$$\begin{array}{ll} (\text{a}) T = \frac{R_1}{R_2} \times \frac{t_2}{t_1} & (\text{b}) T = \frac{t_1 - t_2}{\ln(R_2/R_1)} \\ (\text{c}) T = \frac{t_2 - t_1}{\ln(R_2/R_1)} & (\text{d}) T = \frac{\ln(R_2/R_1)}{t_1 - t_2} \end{array}$$

$$\text{Hint: } R_2 = R_0 e^{-\lambda t_2}$$

$$R_1 = R_0 e^{-\lambda t_1}$$

On dividing the above equations, we get

$$\frac{R_2}{R_1} = e^{\lambda(t_1 - t_2)}$$

$$\ln \left( \frac{R_2}{R_1} \right) = \lambda(t_1 - t_2)$$

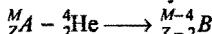
$$\frac{1}{\lambda} = \frac{(t_1 - t_2)}{\ln(R_2/R_1)}$$

$$T = \frac{(t_1 - t_2)}{\ln(R_2/R_1)}$$

7. Isodiapheres are the atoms of two elements having same values of:

$$(\text{a}) p/n \quad (\text{b}) (p-n) \quad (\text{c}) (n-p) \quad (\text{d}) n \times p$$

[Hint: Isodiapheres are formed by  $\alpha$ -decay



$$(n-p) \text{ in } {}_{Z-2}^M A = (M-Z) - Z = (M-2Z)$$

$$(n-p) \text{ in } {}_{Z-2}^{M-4} B = \{(M-4) - (Z-2)\} - (Z-2)$$

$$= \{M - Z - 2\} - Z + 2$$

$$= (M-2Z)$$

$\therefore (n-p)$  of isodiapheres are same.]

8. In a sample of radioactive material, what fraction of the initial number of active nuclei will remain undisintegrated after half of a half life of the sample?

$$(\text{a}) \frac{1}{4} \quad (\text{b}) \frac{1}{2\sqrt{2}} \quad (\text{c}) \frac{1}{\sqrt{2}} \quad (\text{d}) \sqrt{2} - 1$$

$$\text{Hint: } \frac{0.693}{t_{1/2}} = \frac{2.303}{t} \log \left( \frac{N_0}{N} \right)$$

$$\frac{2.303 \times \log 2}{t_{1/2}} = \frac{2.303}{(t_{1/2}/2)} \log_{10} \left( \frac{N_0}{N} \right)$$

$$\log_{10}(2^{1/2}) = \log_{10} \left( \frac{N_0}{N} \right)$$

$$\left( \frac{N}{N_0} \right) = \frac{1}{\sqrt{2}}$$

9. Let  $T$  be the mean life of a radioactive sample. 75% of the active nuclei present in the sample initially will decay in time:

(a)  $2T$       (b)  $\frac{1}{2}(\log_e 2)T$       (c)  $4T$       (d)  $2(\log_e 2)T$

10.  $^{218}_{84}\text{Po}$  ( $t_{1/2} = 183 \text{ sec}$ ) decays to  $^{214}_{82}\text{Pb}$  ( $t_{1/2} = 161 \text{ sec}$ ) by  $\alpha$ -emission, while  $^{214}_{82}\text{Pb}$  decays by  $\beta$ -emission. In how much time the number of nuclei of  $^{214}_{82}\text{Pb}$  will reach to the maximum?

(a) 182 sec      (b) 247.5 sec      (c) 308 sec      (d) 194.8 sec

$$\begin{aligned} \text{Hint: } & ^{218}_{84}\text{Po} \xrightarrow{\lambda_1} ^{214}_{82}\text{Pb} \\ & \lambda_1 = \frac{0.693}{183} = (3.786 \times 10^{-3} \text{ sec}^{-1}) \\ & ^{214}_{82}\text{Pb} \xrightarrow{\lambda_2} \\ & \lambda_2 = \frac{0.693}{161} = 4304 \times 10^{-3} \text{ sec}^{-1} \end{aligned}$$

$$\begin{aligned} t_{\max} &= \frac{2.303}{\lambda_1 - \lambda_2} \log \frac{\lambda_1}{\lambda_2} \\ &= \frac{2.303}{3.786 \times 10^{-3} - 4.304 \times 10^{-3}} \log \frac{3.786 \times 10^{-3}}{4.304 \times 10^{-3}} \\ &= -\frac{2.303}{5.183 \times 10^{-4}} [-0.05569] \\ &= 247.5 \text{ sec} \end{aligned}$$

11. Fusion reaction takes place at high temperature because:

(a) atoms are ionised at high temperature  
 (b) molecules break up at high temperature  
 (c) nuclei break-up at high temperature  
 (d) kinetic energy is high enough to overcome repulsion between nuclei

12. In the radioactive change,



the radiations emitted in sequence are:

(a)  $\alpha, \beta, \gamma$       (b)  $\beta, \alpha, \gamma$       (c)  $\gamma, \alpha, \beta$       (d)  $\beta, \gamma, \alpha$

13. The half life of a radioactive isotope is 3 hours. If the initial mass of the isotope were 256 g, the mass of it remaining undecayed after 18 hours would be:

(a) 12 g      (b) 16 g      (c) 4 g      (d) 8 g

$$\begin{aligned} \text{Hint: } & N = N_0 \left(\frac{1}{2}\right)^n \quad n = \text{number of half lives} = \frac{18}{3} = 6 \\ & = 256 \left(\frac{1}{2}\right)^6 = 4 \text{ g} \end{aligned}$$

14. In an old rock, the mass ratio of  $^{238}_{92}\text{U}$  to  $^{206}_{82}\text{Pb}$  is found to be 595 : 103. The age of the rock is (Mean life of  $^{238}_{92}\text{U}$  is  $T_0$ ):

$$(a) T_0 \ln 1.2 \quad (b) T_0 \ln \frac{698}{595} \quad (c) T_0 \frac{\ln 1.2}{\ln 2} \quad (d) T_0 \frac{\ln \frac{698}{595}}{\ln 2}$$

$$\begin{aligned} \text{Hint: } & \lambda = \frac{2.303}{t} \log \left( \frac{N_0}{N} \right) \\ & \frac{1}{T_0} = \frac{1}{t} \ln \left( \frac{595 + 103}{595} \right) \\ & t = T_0 \ln \left( \frac{698}{595} \right) \end{aligned}$$

15. 80% of the radioactive nuclei present in a sample are found to remain undecayed after one day. The percentage of undecayed nuclei left after two days will be:

(a) 64      (b) 20      (c) 46      (d) 80

$$\text{Hint: } \lambda = \frac{2.303}{t} \log \left( \frac{N_0}{N} \right)$$

$$= \frac{2.303}{1} \log \left( \frac{100}{80} \right) \quad \dots \text{(i)}$$

$$\lambda = \frac{2.303}{2} \log \left( \frac{100}{N} \right) \quad \dots \text{(ii)}$$

$$\frac{2.303}{1} \log \left( \frac{100}{80} \right) = \frac{2.303}{2} \log \left( \frac{100}{N} \right)$$

$$\left( \frac{5}{4} \right)^2 = \frac{100}{N}$$

$$N = 64]$$

16. A sample of radioactive material has mass ' $m$ ', decay constant  $\lambda$  and molecular mass ' $M$ '. If  $N_A$  is Avogadro's number, the initial activity of the sample is:

(a)  $\lambda m$       (b)  $\lambda \frac{m}{M}$       (c)  $\frac{\lambda m N_A}{M}$       (d)  $m M e^\lambda$

17. A radioactive nucleus can decay by two different processes. The mean value period for the first process is  $Z_1$  and that for the second process is  $Z_2$ . The effective mean value period for the two processes is:

$$(a) \frac{Z_1 + Z_2}{2} \quad (b) Z_1 + Z_2 \quad (c) \sqrt{Z_1 Z_2} \quad (d) \frac{Z_1 Z_2}{Z_1 + Z_2}$$

18. The radioactivity of a sample is  $R_1$  at time  $T_1$  and  $R_2$  at time  $T_2$ . If the half life of specimen is  $T$ , the number of atoms that have disintegrated in time  $(T_2 - T_1)$  is proportional to:

$$\begin{aligned} & (a) (R_1 T_1 - R_2 T_2) \quad (b) R_1 - R_2 \\ & (c) \frac{(R_1 - R_2)}{T} \quad (d) (R_2 - R_1) T \end{aligned}$$

**Hint:** Rate =  $\lambda \times$  Number of atoms of element yet not decayed.

$$R_1 = \lambda \times N_1$$

$$R_2 = \lambda \times N_2$$

Number of atoms decayed in time  $(T_2 - T_1)$

$$= \frac{R_2 - R_1}{\lambda} = \frac{(R_2 - R_1)}{\lambda} = \frac{T(R_2 - R_1)}{0.693}$$

$\therefore$  Number of atoms decayed in time  $(T_2 - T_1) \propto T(R_2 - R_1)$

19. Half life period of lead is:

(a) zero      (b) infinite      (c) 1590 years      (d) 1590 days

20. A freshly prepared radioactive sample of half life 2 hours emits radiation of intensity which is 64 times the permissible safe level. The minimum time after which it would be possible to work safely with this source is:

(a) 6 hrs      (b) 12 hrs      (c) 24 hrs      (d) 128 hrs

$$\text{Hint: } N = N_0 \left(\frac{1}{2}\right)^n$$

$$\frac{N}{N_0} = \left(\frac{1}{2}\right)^n$$

$$\frac{1}{64} = \left(\frac{1}{2}\right)^n$$

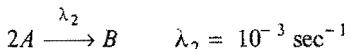
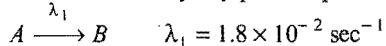
$$n = 6$$

$$\therefore t = 2 \times 6 = 12 \text{ hours}]$$

21. Which of the following is the best nuclear fuel?

(a)  $^{238}\text{U}$  (b)  $^{236}\text{Th}$  (c)  $^{239}\text{Pu}$  (d)  $^{239}\text{Np}$

22. A radioactive element decays by parallel path as given below:



Average life of radio-nuclide  $A$  will be:

- (a) 52.63 sec (b) 500 sec (c) 50 sec (d) 120 sec

[Hint:  $\lambda = \lambda_1 + 2\lambda_2$

$$= 1.8 \times 10^{-2} + 2 \times 10^{-3}$$

$$= 2 \times 10^{-2} \text{ sec}^{-1}$$

$$\tau = \frac{1}{\lambda} = \frac{1}{2 \times 10^{-2}} = 50 \text{ sec}$$

23. Among the following, which has the longest half life?

(a)  $^{232}_{90}\text{Th}$  (b)  $^{237}_{93}\text{Np}$  (c)  $^{238}_{92}\text{U}$  (d)  $^{235}_{92}\text{U}$

24. Which of the following is likely to be least stable?

(SCRA 2007)

- (a)  $^{40}_{20}\text{Ca}$  (b)  $^{55}_{25}\text{Mn}$  (c)  $^{119}_{50}\text{Sn}$  (d)  $^{30}_{13}\text{Al}$

[Hint:  $\frac{n}{p} = \frac{20}{20} = 1$ ,  $\frac{30}{25} = 1.2$ ,  $\frac{69}{50} = 1.38$ ,  $\frac{17}{13} = 1.31$

All are stable according to  $n/p$  rule but experimental observations confirm that  $^{30}\text{Al}$  is radioactive with half life of 3.7 sec]

25.  $^{27}\text{Al}$  is a stable isotope.  $^{29}\text{Al}$  is expected to disintegrate by:

- (a)  $\alpha$ -emission (b)  $\beta$ -emission  
(c) positron emission (d) proton emission

[Hint: Number of neutrons will be reduced by  $\beta$ -decay.

$${}^1_0n \longrightarrow {}^1_1H + {}^0_{-1}e + \text{Antineutrino} + \text{Energy}$$

26. For a radioactive element, a graph of  $\log N$  against time has a slope equal to:

- (a)  $+2.303\lambda$  (b)  $+\frac{\lambda}{2.303}$  (c)  $-\frac{\lambda}{2.303}$  (d)  $-2.303\lambda$

[Hint:  $\log N_0 - \log N = \frac{\lambda t}{2.303}$

$$\log N = \left( \frac{-\lambda}{2.303} \right) t + \log N_0$$

$$Y = Mx + C$$

$$\therefore \text{Slope } (M) = \frac{-\lambda}{2.303}$$

27. Two elements  $P$  and  $Q$  have half lives of 10 and 15 minutes respectively. Freshly prepared samples of each isotope initially contain the same number of atoms as each other. After 30 minutes, the ratio  $\frac{\text{number of } P \text{ atoms}}{\text{number of } Q \text{ atoms}}$  will be:

- (a) 0.5 (b) 2 (c) 1 (d) 3

[Hint: In 30 minutes, there will be 3 half lives of  $P$  and 2 half lives of  $Q$ .

$\therefore$  Number of  $P$  atoms will be  $1/8$  th and number of  $Q$  atoms will be  $1/4$  th of original atoms.

Then,  $\frac{\text{Number of atoms of } P}{\text{Number of atoms of } Q} = \frac{1/8}{1/4} = \frac{1}{2}$ , i.e., 0.5]

28. Select the wrong statement among the following:

- (a) Antineutrino can be detected during  $\beta$ -emission  
(b) Neutrino was predicted to conserve the spin of a nuclear reaction  
(c) Synchrotron can accelerate neutrons  
(d) Area of cross-section of nucleus is about 1 barn  
(1 barn =  $10^{-24} \text{ cm}^2$ )

[Hint: Synchrotron can accelerate only charged particles, not the neutral particles like neutron.]

29. A radioactive atom ' $X$ ' emits a  $\beta$ -particle to produce an atom ' $Y$ ' which then emits an  $\alpha$ -particle to give an atom ' $Z$ :

- (1) The atomic number of ' $X$ ' is less than that of ' $Z$ '

- (2) The atomic number of ' $Y$ ' is less than that of ' $Z$ '

- (3) The mass number of ' $X$ ' is same as that of ' $Y$ '

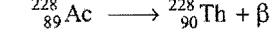
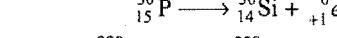
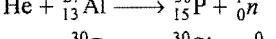
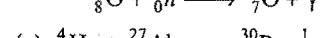
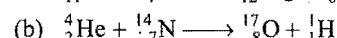
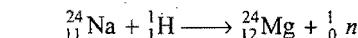
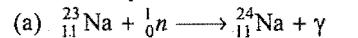
- (a) 1, 2 and 3 are correct

- (b) 1 and 2 are correct

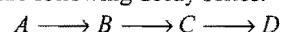
- (c) 2 and 3 are correct

- (d) 3 is correct

30. Which one of the following is an exact example of artificial radioactivity?



31. Consider the following decay series:



Where,  $A$ ,  $B$  and  $C$  are radioactive elements with half lives of 4.5 sec, 15 days and 1 sec respectively and  $D$  is non-radioactive element. Starting with 1 mole of  $A$ , the number of moles of  $A$ ,  $B$ ,  $C$  and  $D$  left after 30 days are:

- (a) one mole of  $D$  and none of  $A$ ,  $B$  or  $C$

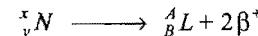
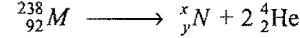
- (b)  $3/4$  mol of  $B$ ,  $1/4$  mol of  $D$  and none of  $A$  or  $C$

- (c)  $1/4$  mol of  $B$ ,  $3/4$  mol of  $D$  and none of  $A$  or  $C$

- (d)  $1/2$  mol of  $B$ ,  $1/4$  mol of  $C$ ,  $1/4$  mol of  $D$  and none of  $A$

- (e)  $1/4$  mol of each  $A$ ,  $B$ ,  $C$  and  $D$

32. Consider the following nuclear reactions:



the number of neutrons present in the element ' $L$ ' is:

- (a) 142 (b) 144

- (c) 140 (d) 146

33. If  $n_t$  is the number of radio-atoms present at time ' $t$ ', the following expression will be a constant:

[JEE (West Bengal) 2009]

- (a)  $\frac{n_t}{t}$  (b)  $\frac{\ln n_t}{t}$

- (c)  $\frac{d \ln n_t}{dt}$  (d)  $t n_t$



8. A radioactive element has atomic number 'Z' and mass number 'A'. Select the correct statements among the following:  
 (a) Both 'A' and 'Z' decrease in  $\alpha$ -decay  
 (b) Both 'A' and 'Z' remain unchanged in  $\gamma$ -decay  
 (c) 'A' remains unchanged and 'Z' decreases by one; the process is called  $\beta^+$  (positron) decay or K-electron capture  
 (d) Both 'A' and 'Z' increase in the nuclear isomerism
9. When nucleus of an electrically neutral atom undergoes a radioactive decay process, it will remain neutral after the decay if the process is:  
 (a) an  $\alpha$ -decay                         (b) a  $\beta$ -decay  
 (c) a  $\gamma$ -decay                                 (d) a K-capture process
10. Which of the following is/are characteristics of nuclear forces?  
 (a) These forces operate within small distances of  $2 \times 10^{-13}$  cm  
 (b) These forces drop to zero rapidly at a distance greater than  $1.4 \times 10^2$  fermi  
 (c) They follow inverse square law  
 (d) They are stronger than electrostatic forces of attraction
11. The correct starting material and end product of different disintegration series are:  
 (a)  $^{232}\text{Th}, ^{208}\text{Pb}$                              (b)  $^{235}\text{U}, ^{206}\text{Pb}$   
 (c)  $^{238}\text{U}, ^{207}\text{Pb}$                              (d)  $^{237}\text{Np}, ^{209}\text{Bi}$
12. Select the wrong statement(s):  
 (a) Nuclear isomers contain the same number of protons and neutrons  
 (b) The decay constant is independent of the amount of the substance taken  
 (c) 1 curie =  $3.7 \times 10^{10}$  dis  
 (d) Actinium series starts with  $^{238}\text{U}$
13. Which of the following are synthetic elements?  
 (a) Tc   (b) Pu                                     (c) Np                                     (d) U
14. Which of the following nuclides belong to actinium ( $\text{U}^{235}$ ) series?  
 (a)  $^{213}\text{Po}$                                      (b)  $^{215}\text{Po}$                                      (c)  $^{222}\text{Rn}$                                      (d)  $^{207}\text{Pb}$
15. In a nuclear reactor, heavy water is used to:  
 (a) transfer the heat from the reactor  
 (b) provide high speed neutrons for the fission reaction  
 (c) reduce the speed of fast moving neutrons  
 (d) increase the speed of neutrons

## Answers

### • Single correct option

- |         |         |         |         |         |         |         |         |
|---------|---------|---------|---------|---------|---------|---------|---------|
| 1. (a)  | 2. (b)  | 3. (c)  | 4. (c)  | 5. (b)  | 6. (b)  | 7. (c)  | 8. (c)  |
| 9. (d)  | 10. (b) | 11. (d) | 12. (b) | 13. (c) | 14. (b) | 15. (a) | 16. (c) |
| 17. (d) | 18. (d) | 19. (b) | 20. (b) | 21. (c) | 22. (c) | 23. (a) | 24. (d) |
| 25. (b) | 26. (c) | 27. (a) | 28. (c) | 29. (d) | 30. (c) | 31. (d) | 32. (b) |
| 33. (c) | 34. (b) | 35. (a) | 36. (a) | 37. (a) | 38. (c) |         |         |

### • One or more than one correct options

- |              |               |              |            |               |            |              |              |
|--------------|---------------|--------------|------------|---------------|------------|--------------|--------------|
| 1. (a, b, c) | 2. (a, b)     | 3. (a, b, c) | 4. (a, c)  | 5. (b, d)     | 6. (a, c)  | 7. (a, b, d) | 8. (a, b, c) |
| 9. (c, d)    | 10. (a, b, d) | 11. (a, d)   | 12. (a, b) | 13. (a, b, c) | 14. (b, d) | 15. (a, c)   |              |

## Integer Answer TYPE QUESTIONS

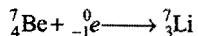
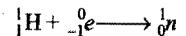
This section contains 7 questions. The answer to each of the questions is a single digit integer, ranging from 0 to 9. If the correct answers to question numbers X, Y, Z and W (say) are 6, 0, 9 and 2 respectively, then the correct darkening of bubbles will look like the given figure :

X	Y	Z	W
○	●	○	○
○	○	○	○
○	○	○	○
○	○	○	●
○	○	○	○
○	○	○	○
○	○	○	○
○	○	○	○
●	○	○	○
○	○	○	○
○	○	○	○
○	○	○	○
○	○	○	○
○	○	○	○
○	○	○	○
○	○	○	○
○	○	○	○
○	○	○	○
○	○	○	○

- The total number of  $\alpha$  and  $\beta$  particles emitted in the nuclear reaction :  $^{238}_{92}\text{U} \longrightarrow ^{214}_{82}\text{Pb}$  is : (IIT 2009)
- The  $t_{1/2}$  of a radionuclide is 8 hours. Starting with 40 g of the isotope, the amount in gm remaining after one day will be:
- If  $\frac{3}{4}$  quantity of a radioactive nuclide disintegrates in two hours, its half-life (in hour) will be:

- $^7_4\text{Be}$  captures a K-electron into its nucleus. What will be the mass number of resulting nuclide?

[Hint : In K-electron capture, a proton of nucleus changes into neutron.



- $^{232}_{90}\text{Th}$  disintegrates to  $^{208}_{82}\text{Pb}$ . How many of  $\beta$ -particles are evolved?
- What mass in milligram of  $^{226}\text{Ra}$ , whose ( $t_{1/2} = 1620$  yr), will be required to yield 1 millicurie of radiation?

- The number of neutrons emitted when  $^{235}_{92}\text{U}$  undergoes controlled nuclear fission to  $^{142}_{54}\text{Xe}$  and  $^{90}_{38}\text{Sr}$  is: (IIT 2010)

[Hint :  $^{235}_{92}\text{U} \longrightarrow ^{142}_{54}\text{Xe} + ^{90}_{38}\text{Sr} + 3 [^1_0n]$ ]

### **Answers**

1. (8)

2. (5)

3. (1)

4. (7)

5. (4)

6. (1)

7. (3)

## ● LINKED COMPREHENSION TYPE QUESTIONS ●

### ● Passage 1

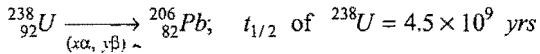
There are four radioactive decay series called thorium ( $4n$ ); uranium ( $4n + 2$ ); actinium ( $4n + 3$ ) and neptunium ( $4n + 1$ ) series. Neptunium series is artificial while other three series are natural. End products of each radioactive decay series have stable nuclei. All natural decay series terminate at lead but neptunium or artificial series terminates at bismuth.

**Answer the following questions:**

1. The end product formed in the disintegration of  $^{222}_{88}\text{Ra}$  is:  
(a)  $^{204}_{81}\text{Ti}$     (b)  $^{206}_{82}\text{Pb}$     (c)  $^{222}_{86}\text{Rn}$     (d)  $^{207}_{83}\text{Bi}$
2. Actinium series begins with an isotope of:  
(a) actinium    (b) radium    (c) uranium    (d) polonium
3.  $^{219}_{86}\text{Rn}$  is a member of actinium series. Another member of same series is:  
(a)  $^{235}_{92}\text{U}$     (b)  $^{222}_{89}\text{Ac}$     (c)  $^{212}_{90}\text{Th}$     (d)  $^{212}_{84}\text{Po}$
4. The end products of uranium and actinium series are respectively:  
(a)  $^{206}\text{Pb}, ^{207}\text{Pb}$                          (b)  $^{206}\text{Pb}, ^{208}\text{Pb}$   
(c)  $^{207}\text{Pb}, ^{208}\text{Pb}$                                (d)  $^{206}\text{Pb}, ^{208}\text{Bi}$
5. The starting isotope and the end product isotope of actinium series are:  
(a)  $^{227}_{88}\text{Ac}$  and  $^{208}_{82}\text{Pb}$                          (b)  $^{235}_{92}\text{U}$  and  $^{207}_{82}\text{Pb}$   
(c)  $^{238}_{92}\text{U}$  and  $^{207}_{82}\text{Pb}$                                (d)  $^{235}_{92}\text{U}$  and  $^{208}_{82}\text{Pb}$

### ● Passage 2

Initially the earth was a fire-ball; slowly it has cooled to form earth crust and its different layers. At the beginning  $^{238}_{92}\text{U}$  was present and no  $^{206}_{82}\text{Pb}$  was there. With the passage of time, uranium decayed to  $^{206}_{82}\text{Pb}$ . The decay process is:



**Answer the following questions:**

1.  $x$  and  $y$  in above decay series are:  
(a) 6, 8    (b) 8, 6    (c) 8, 8    (d) 6, 6
  2. A sample of rock from South America contains equal number of atoms of  $^{238}\text{U}$  and  $^{206}\text{Pb}$ . The age of the rock will be:  
(a)  $4.5 \times 10^9$  years    (b)  $9 \times 10^9$  years  
(c)  $13.5 \times 10^9$  years    (d)  $2.25 \times 10^9$  years
- [Hint:  $\frac{0.693}{t_{1/2}} = \frac{2.303}{t_{\text{age}}} \log \left( \frac{N_0}{N} \right)$
- $$\frac{0.693}{4.5 \times 10^9} = \frac{2.303}{t_{\text{age}}} \log \left( \frac{2}{1} \right)$$
- $$t_{\text{age}} = 4.5 \times 10^9 \text{ yrs.}$$
- $N_0 = 1 + 1 = 2, \quad N = 1]$
3. Atomic mass of  $^{238}\text{U}$  is 238.125 amu. Its packing fraction will be:  
(a) 5.25    (b) 0.125    (c) 12.5    (d) 1.25

4. The analysis of a rock shows the relative number of  $^{238}\text{U}$  and  $^{206}\text{Pb}$  atoms ( $\text{Pb}/\text{U} = 0.25$ ). The age of rock will be:

$$(a) \frac{2.303}{0.693} \times 4.5 \times 10^9 \log 1.25 \quad (b) \frac{2.303}{0.693} \times 4.5 \times 10^9 \log 0.25$$

$$(c) \frac{2.303}{0.693} \times 4.5 \times 10^9 \log 4 \quad (d) \frac{2.303}{4.5 \times 10^9} \times 0.693 \log 4$$

Nathan Thomson, one of the first inhabitants of Lord Howe Island, decided to plant some European deciduous trees in his garden. Unfortunately the exact timing of planting the seeds is not known. Over the years, pollen produced by the trees accumulated at the bottom of the lake near Nathan's house. Very small quantities of radioactive  $^{210}\text{Pb}$  ( $t_{1/2} = 22.3$  years) were deposited at the same time. Note that European deciduous trees pollinate in their first year of growth.

In 1995, a team of researchers sampled a sediment core from the bottom of the lake. The examination of sediment core found that:

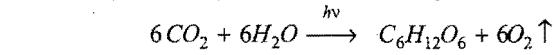
- (a) Pollen of trees first occurs at the depth of 50 cm.
- (b) The activity of  $^{210}\text{Pb}$  at the top of sediment core is 356 Bq / kg and at 50 cm depth 1.40 Bq / kg.

**Answer the following questions:**

5. In what year did Nathan Thomson plant the seeds?  
(a)  $1719 \pm 2$     (b)  $1819 \pm 2$     (c)  $1519 \pm 2$     (d)  $1919 \pm 2$
- [Hint:  $\frac{0.693}{t_{1/2}} = \frac{2.303}{t_{\text{age}}} \log \left( \frac{N_0}{N} \right)$
- $$\frac{0.693}{22.3} = \frac{2.303}{t_{\text{age}}} \log \left( \frac{356}{1.40} \right)$$
- $$t_{\text{age}} = 176 \text{ yrs}]$$
6. Which step in the decay scheme explains how  $^{210}\text{Pb}$  ends up in rain water while its parent  $^{238}\text{U}$  is only present in earth's crust?  
(a)  $^{238}\text{U} \rightarrow ^{234}\text{U}$                                          (b)  $^{234}\text{U} \rightarrow ^{230}\text{Th}$   
(c)  $^{230}\text{Th} \rightarrow ^{226}\text{Ra}$                                          (d)  $^{226}\text{Ra} \rightarrow ^{222}\text{Rn}$

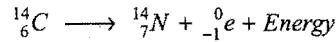
### ● Passage 3

In the atmosphere, carbon dioxide is found in two forms, i.e.,  $^{12}\text{CO}_2$  and  $^{14}\text{CO}_2$ . Plants absorb  $\text{CO}_2$  during photosynthesis. In presence of chlorophyll, plants synthesise glucose.



Half life of  $^{14}\text{C}$  is 5760 years. The analysis of wooden artifacts for  $^{14}\text{C}$  and  $^{12}\text{C}$  gives useful information for determination of its age.

All living organisms, because of their constant exchange of  $\text{CO}_2$  with the surroundings have the same ratio of  $^{14}\text{C}$  to  $^{12}\text{C}$ , i.e.,  $1.3 \times 10^{-12}$ . When an organism dies, the  $^{14}\text{C}$  in it keeps on decaying as follows:



Thus, the ratio  $^{14}\text{C}/^{12}\text{C}$  decreases with the passage of time. We can measure the proportion of  $^{14}\text{C}$  in the remains of a dead organism and determine how long ago it died. The method of carbon dating can be used to date anything made of organic matter; e.g., bone,

skeleton, wood, etc. Using carbon dating, materials have been dated to about 50,000 years with accuracy.

**Answer the following questions:**

1.  $^{14}\text{C}$  exists in atmosphere due to:
  - (a) conversion of  $^{12}\text{C}$  to  $^{14}\text{C}$
  - (b) combustion of fossil fuel
  - (c) bombardment of atmospheric nitrogen by cosmic ray neutrons
  - (d) none of the above
2. A wooden piece is 11520 yrs old. What is the fraction of  $^{14}\text{C}$  activity left in the piece?
  - (a) 0.12
  - (b) 0.25
  - (c) 0.50
  - (d) 0.75

[Hint:  $\frac{0.693}{t_{1/2} \cdot ^{14}\text{C}} = \frac{2.303}{t_{\text{age}}} \log \left( \frac{N_0}{N} \right)$

$$\frac{0.693}{5760} = \frac{2.303}{11520} \log \left( \frac{N_0}{N} \right)$$

$$\frac{N}{N_0} = 0.25]$$
3. In the process of photosynthesis,  $\text{O}_2$  gas is released from:
  - (a)  $\text{CO}_2$
  - (b)  $\text{H}_2\text{O}$
  - (c) both  $\text{H}_2\text{O}$  and  $\text{CO}_2$
  - (d) mechanism is not confirmed
4. A piece of wood from an archeological source shows a  $^{14}\text{C}$  activity which is 60% of the activity found in fresh wood today. The age of archeological sample will be:
  - (a) 4246 yrs
  - (b) 4624 yrs
  - (c) 4628 yrs
  - (d) 6248 yrs
5. A sample of ancient wooden boat is found to undergo 9 dpm  $\text{g}^{-1}$  of  $^{14}\text{C}$ . What is the approximate age of the boat? The rate of disintegration of wood recently cut down is 15 dpm  $\text{g}^{-1}$  of  $^{14}\text{C}$ .
  - (a) 4246.5 yrs
  - (b) 5384 yrs
  - (c) 4628 yrs
  - (d) 2684 yrs

**Passage 4**

The mineral monazite is a rich source of thorium, available in large quantity in Kerala. A typical monazite sample contains 9%  $\text{ThO}_2$  and 0.35%  $\text{U}_3\text{O}_8$ .  $^{208}\text{Pb}$  and  $^{206}\text{Pb}$  are the stable end products in the radioactive decay series of  $^{232}\text{Th}$  and  $^{238}\text{U}$  respectively. All the lead in monazite is of radiogenic origin.

The isotopic ratio of  $^{208}\text{Pb}/^{232}\text{Th}$  was found to be 0.104. The half lives of Th and U are  $1.41 \times 10^{10}$  years and  $4.47 \times 10^9$  years respectively.

**Answer the following questions:**

1. The time elapsed since the formation of monazite sample will be:
  - (a)  $1.34 \times 10^9$  years
  - (b)  $2.01 \times 10^9$  years
  - (c)  $1.41 \times 10^{10}$  years
  - (d)  $4.47 \times 10^9$  years

[Hint:  $\frac{0.693}{t_{1/2} \cdot \text{Th}} = \frac{2.303}{t_{\text{age}}} \log \left( \frac{N_0}{N} \right)$

$$\frac{0.693}{1.41 \times 10^{10}} = \frac{2.303}{t_{\text{age}}} \log (1.104)$$

$$t_{\text{age}} = 2.01 \times 10^9 \text{ years}]$$
2. Estimated isotopic ratio of  $^{206}\text{Pb}/^{238}\text{U}$  in the monazite sample will be:
  - (a) 0.166
  - (b) 0.266
  - (c) 0.366
  - (d) 0.466

3. Select the incorrect information about  $^{232}\text{Th}$ :
  - (a) It belongs to third group of actinide series
  - (b)  $^{232}\text{Th}$  is fissile material
  - (c) It is a fertile material
  - (d) It belongs to  $4n$  series

**Passage 5**

Geiger-Nuttal proposed that the activity of a nucleus is inversely proportional to its half or average life. Thus, shorter the half life of an element, greater is its radioactivity, i.e., greater the number of atoms disintegrating per second. Half life and average life are related with each other.

$$t_{1/2} = \frac{0.693}{\lambda} = \tau \times 0.693 \quad \text{or} \quad \tau = 1.44 t_{1/2}$$

**Answer the following questions:**

1. The half life periods of four isotopes are given:  
I = 6.7 years; II = 8000 years; III = 5760 years; IV =  $2.35 \times 10^5$  years.  
Which of these is most stable?  
  - (a) I
  - (b) II
  - (c) III
  - (d) IV
2. Mark the incorrect relation:  
  - (a)  $N_0 = Ne^{\lambda t}$
  - (b)  $\tau = 1.44 t_{0.5}$
  - (c)  $N = N_0 \left( \frac{1}{2} \right)^n$
  - (d)  $t_{1/2} = \lambda \ln 2$
3. Half life of a radioactive element is 10 years. What percentage of it will decay in 100 years?  
  - (a) 0.1%
  - (b) 100%
  - (c) 99.9%
  - (d) 10%

**Passage 6**

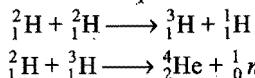
It has been estimated that the total energy radiated by the sun is  $3.8 \times 10^{26}$  J per second. The source of energy of stars is a thermonuclear reaction called nuclear fusion. Fusion reactions are not controlled. It is presumed that the energy of stars is due to two processes called proton-proton cycle and carbon-nitrogen cycle. Fusion cannot take place at ordinary temperature. Thus, hydrogen bomb uses a small fission bomb, which on explosion causes the temperature to rise very high, about  $10^7$  K. We have yet to see how a hydrogen bomb can be used for peaceful life-sustaining purpose. Energy released in the process of fusion is due to mass defect. It is also called Q-value.

$$Q = \Delta mc^2, \quad \Delta m = \text{mass defect}$$

**Answer the following questions:**

1. The binding energy per nucleon of  ${}_1^2\text{H}$  and  ${}_2^4\text{He}$  are 1.1 MeV and 7 MeV respectively. If two deuteron nuclei react to form a single helium nucleus, then the energy released is:  
  - (a) 13.9 MeV
  - (b) 26.9 MeV
  - (c) 23.6 MeV
  - (d) 19.2 MeV
2. Mass equivalent to the energy 931 MeV is:  
  - (a)  $6.02 \times 10^{-27}$  kg
  - (b)  $1.662 \times 10^{-27}$  kg
  - (c)  $16.66 \times 10^{-27}$  kg
  - (d)  $16.02 \times 10^{-27}$  kg
3. Fusion reaction takes place at about:  
  - (a)  $3 \times 10^2$  K
  - (b)  $3 \times 10^3$  K
  - (c)  $3 \times 10^4$  K
  - (d)  $3 \times 10^6$  K

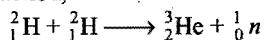
4. A star has  $10^{40}$  deuterons. It produces energy via the process:



If the average power radiated by the star is  $10^{16}$  W, then the deuteron supply of the star is exhausted in a time of the order of:

- (a)  $10^6$  sec (b)  $10^8$  sec (c)  $10^{12}$  sec (d)  $10^{16}$  sec

5. In a nuclear reaction,



if the masses of  ${}_{1,1}^2\text{H}$  and  ${}_{2,1}^3\text{He}$  are 2.014741 amu and 3.016977 amu respectively, then the  $Q$ -value of the reaction is nearly:

- (a) 0.00352 MeV (b) 3.27 MeV  
(c) 0.82 MeV (d) 2.45 MeV

### ● Passage 7

*Moderator is a material which is used to slow down the neutrons produced during nuclear fission. The neutrons from the source are of high speed and energy. Heavy water or graphite moderators slow down the speed of the neutrons. The energy of fast moving neutrons decreases from 2 MeV to 0.02535 eV; it corresponds to the velocity of  $220 \text{ m sec}^{-1}$ . At this velocity, the neutrons are in thermal equilibrium with the moderator. Such neutrons are called 'thermal neutrons'. Thermal neutrons cause further fission reaction. The essential characteristics of moderators are:*

- (i) its molar mass must be low,
- (ii) it should not absorb neutrons,
- (iii) it should undergo elastic collisions with neutrons.

Answer the following questions:

1. The moderator in a reactor:
  - (a) absorbs neutrons
  - (b) accelerates neutrons
  - (c) slows down neutrons
  - (d) absorbs thermal energy produced in the reactors
2. A good moderator should:
  - (a) not be a gas only
  - (b) not have appetite for neutrons only
  - (c) be light in mass number only
  - (d) be all the above three
3. Which of the following is not used as a moderator?
  - (a) Heavy water
  - (b) Graphite
  - (c) Beryllium
  - (d) Sodium
4. Moderator in the reactor yields:
  - (a) fast moving neutrons
  - (b) thermal neutrons
  - (c) magnetic neutrons
  - (d) electric neutrons
5. Which among the following characters make graphite a good moderator?
  - (a) Cross-sectional area of graphite is very high
  - (b) Graphite is a good conductor of electricity
  - (c) There is elastic collision between graphite and neutron
  - (d) Graphite has weak van der Waals' force between two layers

### ● Passage 8

*Radioactive decay follows first order kinetics. The disintegration of radioactive elements does not depend on the temperature. Unlike chemical first order reactions, the nuclear reactions are also independent of catalyst. Mean life and half life of nuclear decay process are  $\tau = \frac{1}{\lambda}$  and  $t_{1/2} = \frac{0.693}{\lambda}$ . There are a number of radioactive elements in nature; their abundance is directly proportional to half life. Amount remaining after  $n$  half lives of radioactive elements can be calculated using the relation:*

$$N = N_0 \left( \frac{1}{2} \right)^n$$

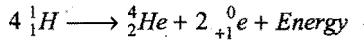
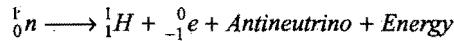
Answer the following questions:

1. Which is/are true about the decay constant?
  - (a) Unit of  $\lambda$  is time $^{-1}$
  - (b)  $\lambda$  is independent of temperature
  - (c)  $\lambda$  depends on initial amount of element taken
  - (d)  $\lambda$  depends on the nature of radioactive element
2. Amount of radioactive element (activity) decreases with passage of time as:
  - (a) linearly
  - (b) exponentially
  - (c) parabolically
  - (d) all of these
3. Half life of  ${}^{60}\text{Co}$  is 5.3 yrs, the time taken for 99.9% decay will be:
  - (a) 0.53 yrs
  - (b) 53 yrs
  - (c) 530 yrs
  - (d) 5300 yrs
4. Rate of radioactive decay is:
  - (a) independent of time
  - (b) independent of temperature
  - (c) dependent on catalyst
  - (d) dependent on the amount of element not yet decayed
5. Select the correct relations:
 

$(a) t_{1/2} = \frac{0.693}{\lambda}$	$(b) \tau = \frac{1}{\lambda}$
$(c) \tau = 1.44 \times t_{1/2}$	$(d) \tau = \frac{t_{1/2}}{0.693}$

### ● Passage 9

*In the disintegration of a radioactive element,  $\alpha$  and  $\beta$ -particles are evolved from the nucleus.*



*Then, emission of these particles changes the nuclear configuration and results into a daughter nuclide. Emission of an  $\alpha$ -particle results into a daughter element having atomic number lowered by 2 and mass number by 4; on the other hand, emission of a  $\beta$ -particle yields an element having atomic number raised by one. Soddy and Fajan proposed that the daughter nuclide may occupy different positions in the periodic table.*

**Answer the following questions:**

1. Which of the following combinations give finally an isotope of the parent element?  
 (a)  $\alpha, \alpha, \beta$     (b)  $\alpha, \gamma, \alpha$     (c)  $\alpha, \beta, \beta$     (d)  $\beta, \gamma, \alpha$
2. A radioactive element belongs to IIIB group; it emits one ' $\alpha$ ' and one  $\beta$ -particle to form a daughter nuclide. The position of daughter nuclide will be in:  
 (a) IIA    (b) IA    (c) IIB    (d) IVB
3. During  $\beta$ -decay, the mass of atomic nucleus:  
 (a) decreases by 1 unit    (b) increases by 1 unit  
 (c) decreases by 2 units    (d) remains unaffected
4. How many  $\alpha$  and  $\beta$ -particles should be emitted from a radioactive nuclide so that an isobar is formed?  
 (a)  $1\alpha, 1\beta$     (b)  $1\alpha, 2\beta$     (c)  $2\alpha, 2\beta$     (d)  $n\beta$
5. Select the correct statements among the following:  
 (a) Emission of a  $\beta$ -particle results into isobar of parent element  
 (b) Emission of a  $\beta$ -particle results into isodisphere of parent element  
 (c) Emission of one  $\alpha$  and two  $\beta$ -particles results into isotope of the parent element  
 (d) Emission of  $\gamma$ -radiations may yield nuclear isomer

## Answers

<b>Passage 1.</b>	1. (b)	2. (c)	3. (a)	4. (a)	5. (b)	
<b>Passage 2.</b>	1. (b)	2. (a)	3. (a)	4. (a)	5. (b)	6. (d)
<b>Passage 3.</b>	1. (c)	2. (b)	3. (b)	4. (a)	5. (a)	
<b>Passage 4.</b>	1. (b)	2. (c)	3. (b)			
<b>Passage 5.</b>	1. (d)	2. (d)	3. (c)			
<b>Passage 6.</b>	1. (c)	2. (b)	3. (d)	4. (c)	5. (b)	
<b>Passage 7.</b>	1. (c, d)	2. (d)	3. (d)	4. (b)	5. (a, c)	
<b>Passage 8.</b>	1. (a, d)	2. (b)	3. (b)	4. (b, d)	5. (a, b, c, d)	
<b>Passage 9.</b>	1. (c)	2. (a)	3. (d)	4. (d)	5. (a, b, c, d)	



## SELF ASSESSMENT

### ASSIGNMENT NO. 3

#### SECTION-I

##### Straight Objective Type Questions

This section contains 10 multiple choice questions. Each question has 4 choices (a), (b), (c) and (d), out of which only one is correct.

1. If  $\frac{3}{4}$  quantity of a radioactive substance decays in 2 hrs, its half life would be:
  - (a) 1 hour
  - (b) 45 minutes
  - (c) 30 minutes
  - (d) 15 minutes
2. Radio carbon dating is done by estimating in a specimen: **(VITEEE 2007)**
  - (a) the amount of ordinary carbon still present
  - (b) the amount of radio carbon still present
  - (c) the ratio of amount of  $^{14}_6\text{C}$  to  $^{12}_6\text{C}$  still present
  - (d) the ratio of amount of  $^{12}_6\text{C}$  to  $^{14}_6\text{C}$  still present
3. Which of the following are correct with respect to the unit of radioactivity?
  - (i) The SI unit of radioactivity is curie (Ci)
  - (ii)  $1\text{ Ci} = 3.7 \times 10^{-10} \text{ dis s}^{-1}$
  - (iii)  $1\text{ Bq} = 3.7 \times 10^{-10} \text{ Ci}$
  - (iv) The SI unit of radioactivity is becquerel (Bq)
  - (v)  $1\text{ Ci} = 3.7 \times 10^{10} \text{ Bq}$
  - (a) (i) and (iii)
  - (b) (iv) and (v)
  - (c) (i) and (ii)
  - (d) (ii) and (iv)
  - (e) (i) and (v)
4. A freshly cut tree and a wooden artifact have 30.4 and 15.2 counts  $\text{g}^{-1} \text{ min}^{-1}$  of  $\text{C}^{14}$  of half life of 5700 years. The age of the artifact in years would be:
  - (a) 2850
  - (b) 5700
  - (c) 570
  - (d) 6930
  - (e) 11400
5. The radioactive isotope of cerium-137 of weight 8g was collected on 1st Feb. 2006 and kept in a sealed tube. On 1st July, 2006, it was found that only 0.25 g of it remained. The half life period of the isotope is: **[PET (Kerala) 2007]**
  - (a) 37.5 days
  - (b) 30 days
  - (c) 25 days
  - (d) 50 days
  - (e) 60 days
6. The number of  $\alpha$  and  $\beta$ -particles emitted in the nuclear reaction  $^{228}_{90}\text{Th} \longrightarrow ^{212}_{83}\text{Bi}$  are: **(DCE 2007)**
  - (a)  $4\alpha$  and  $1\beta$
  - (b)  $3\alpha$  and  $7\beta$
  - (c)  $8\alpha$  and  $1\beta$
  - (d)  $4\alpha$  and  $7\beta$
7. A cyclotron cannot accelerate:
  - (a) protons
  - (b) neutrons
  - (c) electrons
  - (d) deuterons
8. Isotope  $\text{I}^{128}$  has no medicinal importance because:
  - (a) it is non-radioactive
  - (b) it is poisonous
  - (c) it is radioactive
  - (d) none of these

9. The decay of mass during nuclear fission and fusion are:

- (a) 0.1% and 0.231%
- (b) 0.231% and 0.1%
- (c) 0.4% and 0.2%
- (d) 0.3% and 0.3%

[Hint: Greater mass is converted to energy in nuclear fusion as compared to that of fission.]

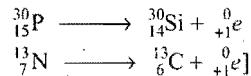
10. On large scale, tritium is produced by which of the following nuclear reactions? **(SCRA 2009)**
  - (a)  $^6_3\text{Li} + {}_0^1n \rightarrow {}_2^4\text{He} + {}_1^3\text{T}$
  - (b)  ${}_1^2\text{D} + {}_1^2\text{D} \rightarrow {}_1^3\text{T} + {}_1^1\text{H}$
  - (c)  ${}_{-1}^{14}\text{N} + {}_0^1n \rightarrow {}_{-1}^{12}\text{C} + {}_1^3\text{T}$
  - (d)  ${}_{-1}^{14}\text{N} + {}_1^1\text{H} \rightarrow {}_1^3\text{T} + \text{Other fragments}$

#### SECTION-II

##### Multiple Answers Type Objective Questions

11. Which of the following will emit positron?
  - (a)  ${}_{15}^{30}\text{P}$
  - (b)  ${}_{7}^{13}\text{N}$
  - (c)  ${}_{1}^{3}\text{H}$
  - (d)  ${}_{6}^{14}\text{C}$

[Hint:  ${}_{15}^{30}\text{P} \left( \frac{n}{p} = 1 \right)$  and  ${}_{7}^{13}\text{N} \left( \frac{n}{p} < 1 \right)$ ; these nuclei emit positron.]



12. If  $\frac{n}{p}$  ratio is less than 1, the nuclide can:
  - (a) K-capture
  - (b) emit positron
  - (c) emit  $\beta$ -particle
  - (d) emit  $\alpha$ -particle

13. For radioactive decay:

- (a)  $t_{3/4} = 2 t_{1/2}$
- (b)  $t_{7/8} = 3 t_{1/2}$
- (c)  $t_{99\%} = 2 t_{90\%}$
- (d)  $t_{90\%} = \frac{10}{3} t_{50\%}$

14. Which of the following statements is/are correct?

- (a) Nuclear fusion produces more energy than nuclear fission
- (b) Nuclear fusion takes place at very high temperature ( $10^6 \text{ K}$ )
- (c) Nuclear fusion yields radioactive product
- (d) Nuclear fusion involves chain reaction

15. Decrease in atomic number is observed during:

- (a)  $\alpha$ -emission
- (b)  $\beta$ -emission
- (c) positron emission
- (d) K-capture

#### SECTION-III

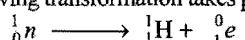
##### Assertion-Reason Type Questions

This section contains 4 questions. Each question contains Statement-1 (Assertion) and Statement-2 (Reason). Each question has following 4 choices (a), (b), (c) and (d), out of which only one is correct.

- (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.
16. Statement-1:  $\beta$ -particles are emitted by nucleus.  
 Because

Statement-2: Following transformation takes place in  $\beta$ -emission.



17. Statement-1: Nuclide  ${}_{20}^{40}\text{Ca}$  is less stable than  ${}_{20}^{40}\text{Ca}$ .  
 Because

Statement-2: Nuclides having even number of nucleons are stable.

18. Statement-1: Energy is released in the nuclear fusion of hydrogen nuclei to form helium nuclei.  
 Because

Statement-2: Binding energy per nucleon of helium is greater than hydrogen.

19. Statement-1:  ${}_{56}^{133}\text{Ba} + e^- \longrightarrow {}_{55}^{133}\text{Cs} + \text{X-ray}$   
 It is an example of  $K$ -electron capture.

Because

Statement-2: Atomic number of daughter nuclide decreases by one unit in  $K$ -electron capture.

[Hint: Nucleus may capture electron from  $K$ -shell and the vacancy is filled by electrons from higher shells; X-ray is released in this process.]

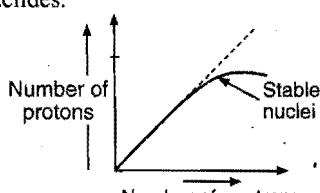
20. Statement-1: The plot of atomic number ( $y$ -axis) versus number of neutrons ( $x$ -axis) for stable nuclei shows a curvature towards  $x$ -axis from the line of  $45^\circ$  slope as atomic number is increased.

Because

Statement-2: Proton-proton electrostatic repulsions begin to overcome attractive forces involving protons and neutrons in heavier nuclides.

(IIT 2008)

[Hint:



In heavier nuclei, attractive forces between proton-neutron overcome proton-proton electrostatic repulsion.]

## SECTION-IV

### Matrix-Matching Type Questions

This section contains 2 questions. Each question contains statements given in two columns which have to be matched. Statements (a, b, c and d) in Column-I have to be matched with statements (p, q, r and s) in Column-II. The answers to these questions have to be appropriately bubbled as illustrated in the following examples:

If the correct matches are (a-p, s), (b-q, r), (c-p, q) and (d-s), then correct bubbled  $4 \times 4$  matrix should be as follows:

	p	q	r	s
a	<input checked="" type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input checked="" type="radio"/>
b	<input type="radio"/>	<input checked="" type="radio"/>	<input checked="" type="radio"/>	<input type="radio"/>
c	<input checked="" type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>
d	<input type="radio"/>	<input type="radio"/>	<input checked="" type="radio"/>	<input checked="" type="radio"/>

21. Match the Column-I with Column-II:

**Column-I**

(a)  ${}^1_1\text{D} + {}^3_1\text{T} \longrightarrow {}^4_2\text{He} + {}^1_0n + \text{Energy}$  (p)  $\beta$ -emission

(b)  ${}^9_4\text{Be} + {}^4_2\text{He} \longrightarrow {}^{12}_6\text{C} + {}^1_0n$  (q) Artificial transmutation

(c)  ${}^{24}_{12}\text{Mg} + {}^4_2\text{He} \longrightarrow {}^{27}_{14}\text{Si} + {}^1_0n$  (r) Discovery of neutrons

(d)  ${}^1_0n \longrightarrow {}^1_1\text{H} + {}^0_{-1}e$  (s) Hydrogen bomb

22. Match the Column-I with Column-II:

**Column-I**

(a)  $n \longrightarrow p^+ + \dots$

(p) Positron emission

(b)  $p^+ \longrightarrow n + \dots$

(q)  $\beta$ -emission

(c) X-ray emission

(r)  $K$ -electron capture

(d)  $4[{}^1_1\text{H}] \longrightarrow \dots + 2\beta^+ + \text{Energy}$

(s)  $\alpha$ -emission

## SECTION-V

### Linked Comprehension Type Questions

Nucleus of an atom resembles with a drop of liquid. Density of nucleus is very high, i.e.,  $10^8$  tonne/cc or 130 trillion tonnes  $\text{m}^{-3}$ . This density is about a trillion times greater than that of water. Density of nuclei of all elements are same, it is independent of atomic number or atomic mass. However, the radius of nucleus depends on the mass number. Surface tension of nucleus is also very high, i.e., about  $1.24 \times 10^{18}$  times, the surface tension of water.

#### Answer the following questions:

23. The radius of  ${}^6_6\text{C}$  nucleus is:

(a)  $5 \times 10^{-15}$  m (b)  $1.4 \times 10^{-15}$  m

(c)  $3.5 \times 10^{-15}$  m (d)  $6 \times 10^{-15}$  m

[Hint:  $r = r_0 \times A^{1/3}$  where  $A$  = Mass number

$r_0 = 1.4 \times 10^{-15}$  m]

24. Ratio of volume of atom and nucleus is:

(a)  $10^8 : 1$  (b)  $10^{15} : 1$  (c)  $10^{13} : 1$  (d)  $10^{12} : 1$

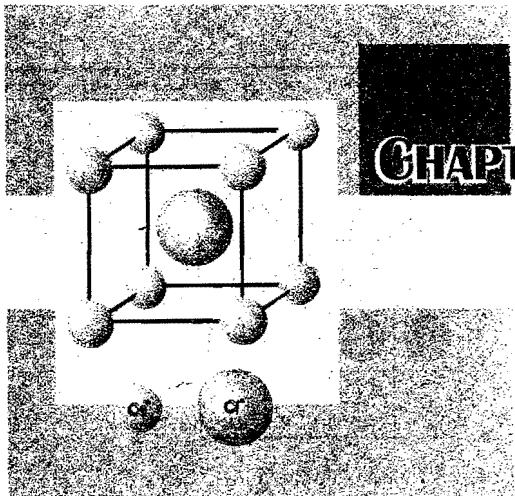
25. Radius of nucleus is directly proportional to:

(a)  $A^2$  (b)  $A^{1/3}$  (c)  $[A]^3$  (d)  $A$

## Answers

1. (c) 2. (c) 3. (b) 4. (b)  
 9. (a) 10. (b) 11. (a, b) 12. (a, b)  
 17. (d) 18. (a) 19. (b) 20. (c)  
 22. (a - q) (b - p) (c - r) (d - s) 23. (c) 24. (b)

5. (b) 6. (a) 7. (c) 8. (a)  
 13. (a, b, c, d) 14. (a, b, c) 15. (a, c, d) 16. (a)  
 21. (a - s) (b - q, r) (c - q) (d - p)  
 25. (c)



## CHAPTER

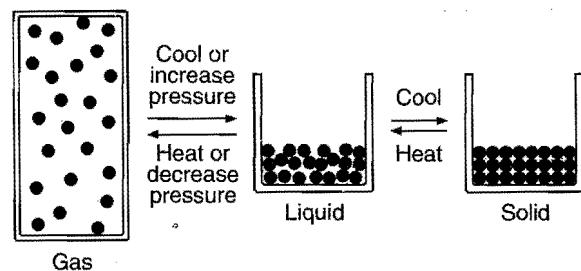
# 4

# STATES OF MATTER

### 4.1 INTRODUCTION

Matter is capable of existing in three physical states: solid, liquid and gas. Matter is anything which has mass and occupies space. Any substance can exist in either of three states depending on temperature and pressure. Liquid and solid states are condensed states as they have much higher densities. Both liquids and gases are termed as fluids as they have flowing ability.

The three states of a substance are interconvertible by variation of temperature and pressure. A liquid state is intermediate between the gaseous state (complete molecular randomness) and the solid state (orderly arrangement of molecules).



**Fig. 4.1 Schematic representation of states of matter**

Some common characteristics of three forms of matter are summarised below:

S.No.	Gases	Liquids	Solids
1.	No definite shape; can fill uniformly any volume available; have indefinite volume.	No definite shape, i.e., assume the shape of the container; have definite volume.	Have definite shape and definite volume.
2.	Extremely disordered particles; much empty space; particles have random motion; intermolecular attraction very small but high kinetic energies (particles are free to move in all directions).	Disordered clusters of particles; quite close to each other; random motion; considerable intermolecular attraction; kinetic energy is less (particles free to move but always remain in contact with each other).	Ordered arrangement of particles; distances between the particles are very small and fixed. Intermolecular forces are high; vibrational motion only.
3.	Low density.	Intermediate density.	High density.
4.	Compressible.	Slightly compressible.	Nearly incompressible.
5.	Fluid, diffuse rapidly.	Fluid; diffuse through other liquids.	Not fluid; diffuse very slowly only through solids.

### SECTION 1 : GASEOUS STATE

#### 4.2 THE GASEOUS STATE

Of the three states of matter, the gaseous state is the simplest and shows greatest uniformity in behaviour. Gases have the following general characteristics:

(i) Gases are highly compressible. These can be compressed into smaller volumes, i.e., increasing their densities by applying increased pressure.

(ii) Gases expand without limit. A gas sample can occupy completely and uniformly the volume of any container.

(iii) Gases exert pressure on the walls of the container uniformly in all directions.

(iv) Gases diffuse rapidly through each other to form a homogeneous mixture. Conversely, different gases in a mixture like air do not separate on standing.

(v) The characteristics of gases are described fully in terms of four parameters (measurable properties):

- (a) the volume,  $V$ , of the gas
- (b) its pressure,  $P$
- (c) its temperature,  $T$
- (d) the amount of the gas (*i.e.*, mass or number of moles).

(a) The volume of the container is the volume of the gas sample. Volume is expressed in litre (L), millilitre (mL) or cubic centimetre ( $\text{cm}^3$ ) or cubic metre ( $\text{m}^3$ ).

$$1 \text{ L} = 1000 \text{ mL}; 1 \text{ mL} = 10^{-3} \text{ L}$$

$$1 \text{ L} = 1 \text{ dm}^3; 1 \text{ dm}^3 = 10^3 \text{ cm}^3$$

$$1 \text{ m}^3 = 10^3 \text{ dm}^3 = 10^6 \text{ cm}^3 = 10^6 \text{ mL} = 10^3 \text{ L}$$

(b) The pressure of the gas is the force exerted by the gas per unit area of the walls of the container. The pressure of gases is measured by a device known as manometer. Two types of manometers, open-end manometer and closed-end manometer, are commonly used to measure gaseous pressure.

**Pressure of one atmosphere** (1 atm) is defined as the pressure that can support a column of mercury of 76 cm height at  $0^\circ\text{C}$  (density of mercury =  $13.5951 \text{ g cm}^{-3}$ ) and at standard gravity =  $980.665 \text{ cm s}^{-2}$ . One atmosphere is also referred to as 760 torr.

$$1 \text{ atm} = 76.0 \text{ cm of mercury} = 760 \text{ mm of mercury}$$

$$= 760 \text{ torr}$$

SI unit of pressure is pascal (Pa) which is defined as the pressure exerted when a force of 1 newton acts on a  $1 \text{ m}^2$  area.

$$1 \text{ atm} = 101.325 \times 10^3 \text{ N m}^{-2} = 101.325 \text{ kPa}$$

An older unit of pressure is 'bar' which is equal to  $10^5 \text{ Pa}$ .

(c) The temperature of the gas is measured in centigrade degree ( ${}^\circ\text{C}$ ) or celsius degree with the help of thermometers.

SI unit of temperature is Kelvin (K) or absolute degree.

$$K = {}^\circ\text{C} + 273$$

(d) Mass of gas is expressed in gram or kilogram.

$$1 \text{ kg} = 10^3 \text{ g}$$

The mass of the gas is also expressed in number of moles.

$$\text{moles of gas (n)} = \frac{\text{Mass in grams}}{\text{Molar mass}} = \frac{m}{M}$$

(vi) All gases obey certain laws called **gas laws**.

### 4.3 GAS LAWS

(i) **Boyle's law:** It relates the volume and the pressure of a given mass of a gas at constant temperature.

The relationship between the volume and the pressure of a gas was studied by **Robert Boyle** in 1662. He found that increasing the pressure at constant temperature on a sample of a gas causes the volume of the gas to decrease proportionately, *i.e.*, if the pressure is doubled, the volume becomes half and so on. Boyle's law states that **at constant temperature, the volume of a sample of a gas varies inversely with the pressure**.

$$V \propto \frac{1}{P} \quad (\text{when temperature is kept constant})$$

The proportionality can be changed into an equality by introducing a constant,  $k$ , *i.e.*,

$$V = \frac{k}{P} \quad \text{or} \quad PV = k$$

Alternatively, Boyle's law can also be stated as follows:

**Temperature remaining constant, the product of pressure and volume of a given mass of a gas is constant.**

The value of the constant depends upon the amount of a gas and the temperature.

Mathematically, it can be written as,

$$P_1 V_1 = P_2 V_2 = P_3 V_3 = \dots$$

Boyle's law can be verified by any one of the following three ways graphically (Fig. 4.2):

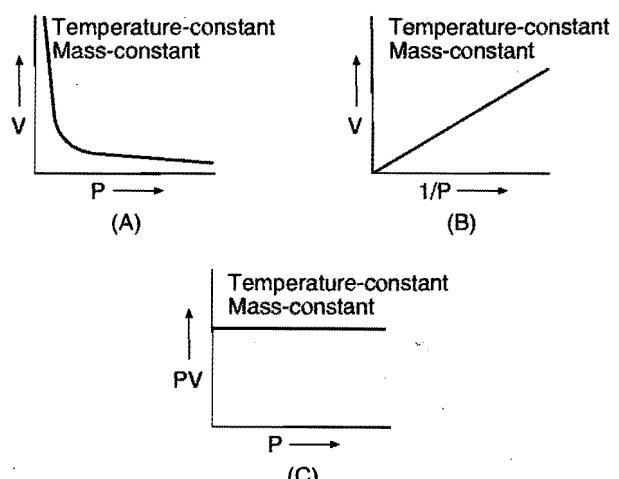


Fig. 4.2

The first curve shows the variation of volume of a given mass of gas with pressure at constant temperature. The shape of the curve is rectangular hyperbola. This curve is also called **isotherm**.

The second curve showing the relationship between volume and reciprocal of pressure is a straight line. It confirms the statement that at constant temperature, volume of a given mass of gas is inversely proportional to the pressure. The third curve shows a straight line parallel to pressure-axis. This confirms that the product of pressure and volume of a given mass of a gas at constant temperature is constant.

Location of straight line and curve changes with temperature in the isotherm.

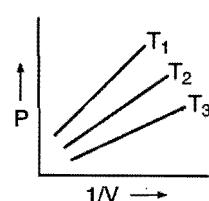


Fig. 4.2(D)

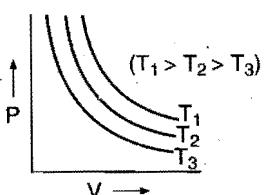


Fig. 4.2(E)

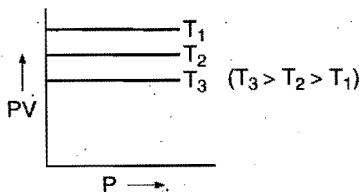


Fig. 4.2(F)

According to Boyle's law,  $PV = \text{constant}$  at constant temperature

$$\therefore \log P + \log V = \text{constant}$$

$$\log P = -\log V + \text{constant}$$

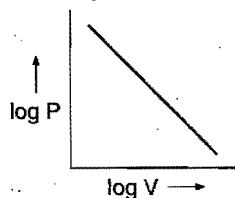


Fig. 4.2(G)

(ii) **Charles' law:** It relates the volume and temperature of a given mass of a gas at constant pressure.

Experiments have shown that when 273 mL sample of a gas at  $0^\circ\text{C}$  is heated to  $1^\circ\text{C}$ , its volume increases by 1 mL, i.e., it becomes 274 mL. At  $10^\circ\text{C}$ , the volume increases to 283 mL if the pressure remains constant in both cases. Similarly, when 273 mL sample of gas at  $0^\circ\text{C}$  is cooled to  $-1^\circ\text{C}$ , its volume decreases to 272 mL while at  $-10^\circ\text{C}$ , the volume decreases to 263 mL if the pressure remains constant.

Thus, all gases expand or contract by the same fraction of their volumes at  $0^\circ\text{C}$  per degree change of temperature, i.e., for each degree change of temperature, the volume of a sample of a gas changes by the fraction  $\frac{1}{273}$  of its volume at  $0^\circ\text{C}$ .

Let the volume of a given amount of a gas be  $V_0$  at  $0^\circ\text{C}$ . The temperature is increased by  $t^\circ\text{C}$  and the new volume becomes  $V_t$ .

$$\text{Thus, } V_t = V_0 + \frac{V_0}{273} \times t = V_0 \left(1 + \frac{t}{273}\right)$$

$$\text{or } V_t = V_0 \left(\frac{273+t}{273}\right) \quad \dots (\text{i})$$

A new temperature scale was introduced known as **Kelvin scale** or **absolute scale** named after the British physicist and mathematician **Lord Kelvin**. The lower limit of the scale is

called **absolute zero** which corresponds to  $-273^\circ\text{C}$ . At absolute zero or  $-273^\circ\text{C}$ , all molecular motions would stop and the volume of the gas would become zero. The gas would become a liquid or solid. Thus, **absolute zero is that temperature at which no substance exists in the gaseous state**. The temperature in absolute is always obtained by adding 273 to the temperature expressed in  $^\circ\text{C}$ .

$$K = (^\circ\text{C} + 273)$$

This new temperature scale may be used for deducing Charles' law.

By substituting  $T$  for  $273 + t$  and  $T_0$  for 273 in Eq. (i),

$$V_t = \frac{V_0 \times T}{T_0}$$

$$\text{or } \frac{V_t}{T} = \frac{V_0}{T_0}$$

$$\text{or } \frac{V}{T} = \text{constant (if pressure is kept constant)}$$

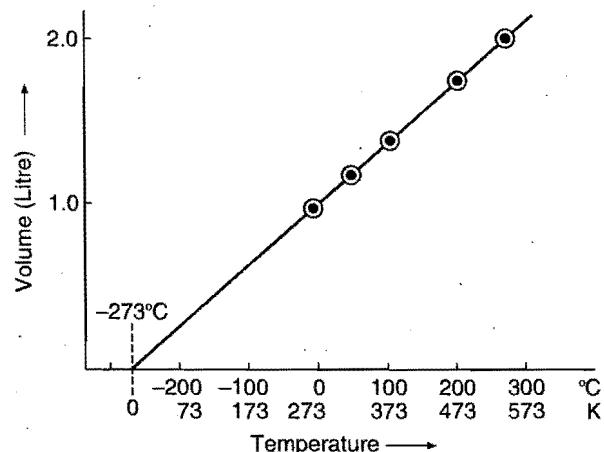


Fig. 4.3

This is Charles' law. It can be stated as follows:

The volume of a given amount of a gas at constant pressure varies directly as its absolute temperature.

$$V \propto T \quad (\text{if pressure is kept constant})$$

Charles' law can be verified experimentally by plotting the values of volumes of a given amount of a gas under respective absolute temperatures at constant pressure. The straight line confirms the above statement.

(iii) **Pressure-temperature law:** It relates the pressure and absolute temperature of a given mass of a gas at constant volume.

Volume remaining constant, the pressure of a given mass of a gas increases or decreases by  $\frac{1}{273}$  of its pressure at  $0^\circ\text{C}$  per degree change of temperature.

$$P_t = P_0 + \frac{P_0 \times t}{273}$$

$$\text{or } P_t = P_0 \left(1 + \frac{t}{273}\right)$$

$$\text{or } P_t = P_0 \left( \frac{273 + t}{273} \right) = P_0 \frac{T}{T_0}$$

$$\text{or } R = \frac{P \times V}{T} = \frac{\text{Pressure} \times \text{Volume}}{\text{Temperature}}$$

$$\text{or } \frac{P_t}{T} = \frac{P_0}{T_0}$$

$$\text{or } P \propto T \text{ (if volume is kept constant)}$$

**At constant volume, the pressure of a given amount of a gas is directly proportional to its absolute temperature.**

#### 4.4 IDEAL GAS EQUATION

This equation is obtained by combining Boyle's and Charles' laws.

$$V \propto \frac{1}{P} \quad \dots (\text{i}) \text{ (at constant temperature and definite mass)}$$

$$V \propto T \quad \dots (\text{ii}) \text{ (at constant pressure and definite mass)}$$

Combining eqs. (i) and (ii), we get

$$V \propto \frac{T}{P} \quad \text{(for definite mass)}$$

$$\frac{PV}{T} = \text{constant} \quad \dots (\text{iii})$$

From the above relation, we have

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \quad \dots (\text{iv})$$

From eq. (iii),

$$\frac{PV}{T} = R$$

$$\text{or } PV = RT \text{ for 1 mole gas}$$

$$PV = nRT \text{ for } n \text{ mole gas} \quad \dots (\text{v})$$

When mass of the gas is taken in grams, the value of  $n$  will be given by:

$$n = \frac{\text{Mass of the gas in gram}}{\text{Mol. mass of the gas in gram}}$$

Let  $w$  and  $M$  be the mass and molecular mass of a gas; then

$$n = \frac{w}{M}$$

Hence, eq. (v) becomes

$$PV = \frac{w}{M} RT \quad \dots (\text{vi})$$

$$\text{or } P = \frac{w}{M} \cdot \frac{RT}{V} \quad \left[ \frac{w}{V} = \frac{\text{Mass}}{\text{Volume}} = \text{Density } (d) \right]$$

$$\text{or } P = \frac{d}{M} RT \quad \dots (\text{vii})$$

Eqs. (vi) and (vii) are modified forms of gas equation. The above equations are strictly followed by ideal gases.

#### Nature of Molar Gas Constant $R$

Gas equation for one gram mole,

$$PV = RT$$

$$\text{Pressure} = \frac{\text{Force}}{\text{Area}} = \frac{\text{Force}}{(\text{Length})^2}$$

$$\text{Volume} = (\text{Length})^3$$

$$\begin{aligned} \text{So, } R &= \frac{\frac{\text{Force}}{(\text{Length})^2} \times (\text{Length})^3}{\text{Temperature}} \\ &= \frac{\text{Force} \times \text{Length}}{\text{Temperature}} \\ &= \frac{\text{Work}}{\text{Temperature}} \end{aligned}$$

Thus, the value of  $R$  should always be expressed in units of work per degree kelvin per mole.

#### Numerical Values of $R$

$$R = \frac{PV}{T}$$

One gram mole of a gas at one atmospheric pressure and 0°C (273 K) occupies a volume 22.4 litre.

$$P = 1 \text{ atmosphere}, \quad T = 273 \text{ K}, \quad V = 22.4 \text{ litre}$$

$$\begin{aligned} \text{So, } R &= \frac{1 \times 22.4}{273} \\ &= 0.0821 \text{ litre-atm K}^{-1} \text{ mol}^{-1} \end{aligned}$$

If pressure is taken in dyne/cm<sup>2</sup> and volume in mL,  
 $P = 76 \times 13.67 \times 981 \text{ dyne/cm}^2$ ,  $V = 22400 \text{ mL}$  for 1 mole,  
 $T = 273 \text{ K}$

$$\begin{aligned} \text{So, } R &= \frac{76 \times 13.67 \times 981 \times 22400}{273} \\ &= 8.314 \times 10^7 \text{ erg K}^{-1} \text{ mol}^{-1} \end{aligned}$$

Since, 1 joule =  $10^7$  erg, so

$$R = 8.314 \text{ joule K}^{-1} \text{ mol}^{-1}$$

Since, 1 calorie =  $4.184 \times 10^7$  erg, so

$$\begin{aligned} R &= \frac{8.314 \times 10^7}{4.184 \times 10^7} \\ &= 1.987 \approx 2 \text{ calorie K}^{-1} \text{ mol}^{-1} \end{aligned}$$

**Note:** Although,  $R$  can be expressed in different units, but for pressure-volume calculations,  $R$  must be taken in the same units of pressure and volume.

#### Barometric Distribution

In the case of ordinary gases, pressure in the container is unaffected by the gravitational field. But in high molecular mass polymeric gases, pressure varies with height.

Let  $P_0$  be the pressure at ground level and  $P$  be the pressure at height ' $h$ '; then

$$2.303 \log_{10} \left( \frac{P}{P_0} \right) = - \left\{ \frac{Mgh}{R} \right\}$$

Similarly for density and number of moles the equation may be given as:

$$2.303 \log_{10} \left( \frac{d}{d_0} \right) = - \left\{ \frac{Mgh}{R} \right\}$$

$$2.303 \log_{10} \left( \frac{n}{n_0} \right) = - \left\{ \frac{Mgh}{R} \right\}$$

These relations are valid under isothermal conditions for density, pressure and number of moles.

If temperature is not constant then the relations of barometric distribution may be given as,

$$2.303 \log_{10} \left( \frac{P}{P_0} \right) = - \frac{Mgh}{RT}$$

$$2.303 \log_{10} \left( \frac{n}{n_0} \right) = - \frac{Mgh}{RT}$$

**Open vessel concept:** In open vessel of a gas, pressure and volume are always constant.

$$\therefore PV = n_1 RT_1 \quad \dots (1)$$

$$PV = n_2 RT_2 \quad \dots (2)$$

Here,  $n_1$  and  $n_2$  are number of moles at temperatures  $T_1$  and  $T_2$ .

Dividing eq. (1) by (2), we get

$$n_1 T_1 = n_2 T_2$$

**Dry and moist gas:** If volume under moist condition is given then volume of dry gas can be determined.

$$P_{\text{moist}} V_{\text{moist}} = P_{\text{dry}} V_{\text{dry}}$$

$P_{\text{dry}} = P_{\text{moist}} - \text{Aqueous tension or vapour pressure of water}$

$$\text{Relative humidity} = \frac{\text{Partial pressure of water in air}}{\text{Vapour pressure of water}}$$

### Payload (Lifting Capacity of Balloon)

When a balloon is filled with lighter gas like  $H_2$  and He (lighter than air) then it rises up due to the difference in the density of air and the gas. Payload or lifting capacity of balloon may be calculated as:

$$\text{Pay Load} = \left[ \text{Mass of air filled in the balloon} \right] - \left[ \begin{array}{l} \text{Mass of gas filled in the} \\ \text{balloon at same temperature and pressure} \end{array} \right] - \left[ \text{Mass of balloon} \right]$$

### SOME SOLVED EXAMPLES

**Example 1.** A sample of a gas occupies 10 litre under a pressure of 1 atmosphere. What will be its volume if the pressure is increased to 2 atmosphere? Assume that the temperature of the gas sample does not change.

**Solution:**  $V_1 = 10 \text{ litre}$   $V_2 = ?$

$$P_1 = 1 \text{ atm}$$
  $P_2 = 2 \text{ atm}$

Applying Boyle's law,

$$P_1 V_1 = P_2 V_2$$

$$\text{So, } V_2 = \frac{P_1 V_1}{P_2} = \frac{1 \times 10}{2} = 5 \text{ litre}$$

**Example 2.** A sample of a gas occupies 600 mL at  $27^\circ C$  and 1 atm. What will be the volume at  $127^\circ C$  if the pressure is kept constant?

**Solution:**  $V_1 = 600 \text{ mL}$   $T_1 = 27 + 273 = 300 \text{ K}$

$$V_2 = ? \quad T_2 = 127 + 273 = 400 \text{ K}$$

Applying Charles' law,  $\frac{V_1}{T_1} = \frac{V_2}{T_2}$

$$V_2 = \frac{V_1}{T_1} \times T_2$$

$$= \frac{600 \times 400}{300}$$

$$= 800 \text{ mL}$$

**Example 3.** A gas cylinder containing cooking gas can withstand a pressure of 14.9 atmosphere. The pressure gauge of the cylinder indicates 12 atmosphere at  $27^\circ C$ . Due to a sudden fire in the building, the temperature starts rising. At what temperature will the cylinder explode?

**Solution:** Since, the gas is confined in a cylinder, its volume will remain constant.

Initial conditions

$$P_1 = 12 \text{ atm}$$

$$T_1 = 27 + 273 = 300 \text{ K}$$

Final conditions

$$P_2 = 14.9 \text{ atm}$$

$$T_2 = ?$$

Applying pressure-temperature law,

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

$$\text{So, } T_2 = \frac{P_2 \times T_1}{P_1}$$

$$= \frac{14.9 \times 300}{12} = 372.5 \text{ K}$$

$$\text{Temperature in } {}^\circ \text{C} = (372.5 - 273) = 99.5 \text{ } {}^\circ \text{C}$$

**Example 4.** A 1000 mL sample of a gas at  $-73^\circ C$  and 2 atmosphere is heated to  $123^\circ C$  and the pressure is reduced to 0.5 atmosphere. What will be the final volume?

**Solution:**

Initial conditions

$$P_1 = 2 \text{ atm}$$

$$V_1 = 1000 \text{ mL}$$

$$T_1 = -73^\circ C = (-73 + 273)$$

$$= 200 \text{ K}$$

Final conditions

$$P_2 = 0.5 \text{ atm}$$

$$V_2 = ?$$

$$T_2 = 123^\circ C = (123 + 273)$$

$$= 400 \text{ K}$$

We know that,

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

So,

$$\frac{2 \times 1000}{200} = \frac{0.5 \times V_2}{400}$$

or

$$P = \frac{w}{V} \times \frac{RT}{M}$$

$$= d \times \frac{RT}{M}$$

$\left( \frac{w}{V} = \text{density} = d \right)$

Given,  $d = 8.0 \text{ kg m}^{-3}$ ;  $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ ;

$$T = -40 + 273 = 233 \text{ K}$$

$$\text{and } M = 36.5 \text{ g mol}^{-1} = 36.5 \times 10^{-3} \text{ kg mol}^{-1}$$

Substituting the values in the above equation,

$$P = \frac{8.0 \times 8.314 \times 233}{36.5 \times 10^{-3}} = 424.58 \times 10^3 \text{ Pa}$$

**Example 5.** A sample of a gas occupies a volume of 512 mL at 20°C and 74 cm of Hg as pressure. What volume would this gas occupy at STP?

**Solution:**

Initial conditions

$$P_1 = 74 \text{ cm}$$

$$T_1 = 20^\circ \text{C} = (20 + 273) = 293 \text{ K},$$

$$V_1 = 512 \text{ mL}$$

Final conditions (STP)

$$P_2 = 76 \text{ cm}$$

$$T_2 = 0^\circ \text{C} = 273 \text{ K}$$

$$V_2 = ?$$

We know that,

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$\frac{74 \times 512}{293} = \frac{76 \times V_2}{273}$$

So,

$$V_2 = \frac{74 \times 512 \times 273}{293 \times 76}$$

$$= 464.5 \text{ mL}$$

**Example 6.** 3.7 g of a gas at 25°C occupied the same volume as 0.184 g of hydrogen at 17°C and at the same pressure. What is the molecular mass of the gas?

**Solution:** For hydrogen,

$$w = 0.184 \text{ g}; T = 17 + 273 = 290 \text{ K}; M = 2$$

$$\text{We know that, } PV = \frac{w}{M} RT$$

$$= \frac{0.184}{2} \times R \times 290 \quad \dots (\text{i})$$

For unknown gas,

$$w = 3.7 \text{ g}; T = 25 + 273 = 298 \text{ K}; M = ?$$

$$PV = \frac{3.7}{M} \times R \times 298 \quad \dots (\text{ii})$$

Equating both the equations,

$$\frac{3.7}{M} \times R \times 298 = \frac{0.184}{2} \times R \times 290$$

$$\text{or } M = \frac{3.7 \times 298 \times 2}{0.184 \times 290} = 41.33$$

**Example 7.** What is the pressure of HCl gas at -40°C if its density is 8.0 kg m<sup>-3</sup>? ( $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ )

**Solution:** Equation for ideal gas,

$$PV = \frac{w}{M} RT$$

**Example 8.** A certain quantity of a gas occupies 100 mL when collected over water at 15°C and 750 mm pressure. It occupies 91.9 mL in dry state at NTP. Find the aqueous vapour pressure at 15°C.

**Solution:** Let the aqueous vapour pressure be  $p$  mm.

Initial conditions

$$P_1 (\text{dry gas}) = (750 - p) \text{ mm}$$

$$V_1 = 100 \text{ mL}$$

$$T_1 = 15 + 273 = 288 \text{ K}$$

NTP conditions

$$P_2 = 760 \text{ mm}$$

$$V_2 = 91.9 \text{ mL}$$

$$T_2 = 273 \text{ K}$$

Applying gas equation,

$$\frac{(750 - p) \times 100}{288} = \frac{760 \times 91.9}{273}$$

$$\text{or } 750 - p = \frac{760 \times 91.9 \times 288}{100 \times 273}$$

$$= 736.8 \text{ mm}$$

$$p = 750 - 736.8$$

$$= 13.2 \text{ mm}$$

**Example 9.** A balloon of diameter 20 m weighs 100 kg. Calculate its payload if it is filled with helium at 1.0 atm and 27°C. Density of air is 1.2 kg m<sup>-3</sup>.

$$(R = 0.082 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1})$$

(IIT 1994)

**Solution:**

$$\text{Volume of balloon} = \frac{4}{3} \pi r^3 = \frac{4}{3} \times \frac{22}{7} \times (10)^3 = 4190.47 \text{ m}^3$$

$$\text{Mass of the air displaced} = 4190.47 \times 1.2 = 5028.56 \text{ kg}$$

$$\text{No. of moles of helium in the balloon} = \frac{PV}{RT}$$

$$= \frac{1 \times 4190.47 \times 10^3}{0.082 \times 300} = 170344$$

$$\text{Mass of helium} = 4 \times 170.344 \times 10^3 \text{ g} = 681.376 \text{ kg}$$

$$\text{Mass of filled balloon} = 681.376 + 100 = 781.376 \text{ kg}$$

$$\text{Payload} = \text{Mass of air displaced} - \text{Mass of filled balloon}$$

$$= 5028.56 - 781.376 = 4247.184 \text{ kg}$$

**Example 10.** The density of a gas is  $0.259 \text{ g L}^{-1}$  at  $400 \text{ K}$  and  $190 \text{ torr}$ . Find its molar mass.

**Solution:**  $760 \text{ torr} = 1 \text{ atm}$

So,  $190 \text{ torr} = \frac{190}{760} \text{ atm}$

We know that,  $P = \frac{d}{M} RT$

or  $M = \frac{d}{P} RT$

Given,  $d = 0.259 \text{ g L}^{-1}$ ;  $P = \frac{190}{760} \text{ atm};$

$$R = 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}; \quad T = 400 \text{ K}$$

$$M = \frac{0.259 \times 0.0821 \times 400 \times 760}{190} = 34.02 \text{ g mol}^{-1}$$

**Example 11.** The density of phosphorus vapour at  $310^\circ\text{C}$  and  $775 \text{ torr}$  is  $2.64 \text{ g dm}^{-3}$ . What is the molecular formula of phosphorus?

**Solution:** We know that,  $P = \frac{d}{M} RT$  or  $M = \frac{d}{P} RT$

Given,  $d = 2.64 \text{ g dm}^{-3}$ ;  $P = \frac{775}{760} \text{ atm};$

$$R = 0.0821 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$$

and  $T = 310 + 273 = 583 \text{ K}$

So,  $M = \frac{2.64 \times 0.0821 \times 583 \times 760}{775} = 123.9 \text{ g mol}^{-1}$

Atomic mass of P =  $31 \text{ g mol}^{-1}$

No. of P atoms in a molecule =  $\frac{123.9}{31} = 3.997 \approx 4$

Hence, molecular formula of phosphorus =  $P_4$

**Example 12.** What percentage of a sample of nitrogen must be allowed to escape if its temperature, pressure and volume are changed from  $220^\circ\text{C}$ ,  $3.0 \text{ atm}$  and  $1.65 \text{ L}$  to  $110^\circ\text{C}$ ,  $0.7 \text{ atm}$  and  $1.0 \text{ L}$  respectively?

**Solution:** Applying the formula,  $m$  (mass of the gas)  $= \frac{PV \times M}{RT}$ , under both the conditions,

$$\text{Mass of gas before escaping} = \frac{3.0 \times 1.65 \times 28}{0.0821 \times 493} = 3.42 \text{ g}$$

$$\text{Mass of gas after escaping} = \frac{0.7 \times 1.0 \times 28}{0.0821 \times 383} = 0.62 \text{ g}$$

Percentage of nitrogen allowed to escape

$$= \frac{(3.42 - 0.62)}{3.42} \times 100 = 81.87$$

**Example 13.** The density of oxygen is  $1.43 \text{ g L}^{-1}$  at STP. Determine the density of oxygen at  $17^\circ\text{C}$  and  $800 \text{ torr}$ .

**Solution:** Applying the formula  $d = \frac{MP}{RT}$

At STP,  $d_1 = \frac{MP_1}{RT_1}$

$$[P_1 = 760 \text{ torr}; T_1 = 273 \text{ K}; d_1 = 1.43 \text{ g L}^{-1}]$$

At given conditions,  $d_2 = \frac{MP_2}{RT_2}$

$$[P_2 = 800 \text{ torr}; T_2 = 290 \text{ K}; d_2 = ?]$$

So,  $\frac{d_2}{d_1} = \frac{P_2}{T_2} \times \frac{T_1}{P_1}$

or  $d_2 = \frac{P_2}{P_1} \times \frac{T_1}{T_2} \times d_1$

$$= \frac{800}{760} \times \frac{273}{290} \times 1.43$$

$$= 1.417 \text{ g L}^{-1}$$

**Example 14.** A car tyre has a volume of  $10 \text{ litre}$  when inflated. The tyre is inflated to a pressure of  $3 \text{ atm}$  at  $17^\circ\text{C}$  with air. Due to driving the temperature of the tyre increases to  $47^\circ\text{C}$ . (a) What would be the pressure at this temperature? (b) How many litres of air measured at  $47^\circ\text{C}$  and pressure of  $1 \text{ atm}$  should be let out to restore the tyre to  $3 \text{ atm}$  at  $47^\circ\text{C}$ ?

**Solution:** (a) At constant volume,

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

or  $\frac{3}{290} = \frac{P_2}{320}$

or  $P_2 = \frac{320 \times 3}{290} = 3.31 \text{ atm}$

(b) Pressure to be decreased in tyre

$$= 3.31 - 3.0 = 0.31 \text{ atm}$$

Let the volume of the gas to be taken out at  $1 \text{ atmospheric pressure}$  be  $V$ . As the temperature remains constant, i.e.,  $47^\circ\text{C}$ , Boyle's law can be applied to determine  $V$ .

$$1 \times V = 0.31 \times 10$$

or  $V = 3.1 \text{ litre}$

**Example 15.** Oxygen is present in a one litre flask at a pressure of  $7.6 \times 10^{-10} \text{ mm of Hg}$ . Calculate the number of oxygen molecules in the flask at  $0^\circ\text{C}$ .

**Solution:**  $n = \frac{PV}{RT}$  ... (i)

$$P = \frac{7.6 \times 10^{-10}}{760} = 10^{-12} \text{ atm}$$

$$V = 1 \text{ L}, T = 273 \text{ K}, R = 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}$$

$$\text{From eq. (i)} \quad n = \frac{10^{-12} \times 1}{0.0821 \times 273}$$

$$\text{Number of molecules} = n \times 6.023 \times 10^{23}$$

$$= \frac{10^{-12}}{0.0821 \times 273} \times 6.023 \times 10^{23}$$

$$= 2.68 \times 10^{10}$$

**Example 16.** An open flask contains air at 27°C. Calculate the temperature at which it should be heated so that 1/3rd of air measured at 27°C escapes out.

**Solution:** Let the initial number of moles of air at 27°C (300 K) be =  $n$

Number of moles of air left when the air is heated to

$$\text{the temperature } T \text{ K} = n - \frac{n}{3} = \frac{2n}{3}$$

At constant pressure and constant volume,

$$n_1 T_1 = n_2 T_2$$

$$\text{or} \quad n \times 300 = \frac{2n}{3} \times T$$

$$\text{or} \quad T = 450 \text{ K} = (450 - 273) = 177^\circ \text{C}$$

**Example 17.** A mixture of CO and CO<sub>2</sub> is found to have a density of 1.5 g L<sup>-1</sup> at 30°C and 730 torr. What is the composition of the mixture?

**Solution:** Let the average molecular mass be  $M$ .

$$M = \frac{dRT}{P} = \frac{1.5 \times 0.0821 \times 303 \times 760}{730} = 38.85$$

Let  $x$  mole of CO and  $(1-x)$  mole of CO<sub>2</sub> be present.

$$x \times 28 + (1-x) \times 44 = 38.85$$

$$x = 0.3218$$

$$\text{mole \% of CO} = 32.18 \text{ and mole \% of CO}_2 = 67.82$$

**Example 18.** Calculate the value of molar gas constant, 'R' in (i) cc atm K<sup>-1</sup> mol<sup>-1</sup> (ii) torr cc K<sup>-1</sup> mol<sup>-1</sup> (iii) kPa litre K<sup>-1</sup> mol<sup>-1</sup>.

**Solution:** (i) When the pressure is expressed in atmosphere and volume in cc.

$$P = 1 \text{ atm}; V = 22400 \text{ cc}$$

$$R = \frac{PV}{nT} = \frac{1 \times 22400}{1 \times 273} = 82.1 \text{ cc atm K}^{-1} \text{ mol}^{-1}$$

(ii) When the pressure is expressed in torr and volume in cc.

$$P = 760 \text{ torr}; V = 22400 \text{ cc}$$

$$R = \frac{760 \times 22400}{1 \times 273} = 62360 \text{ torr cc K}^{-1} \text{ mol}^{-1}$$

(iii) When the pressure is expressed in k Pascal and volume in litre.

$$P = 101.3 \text{ kPa}; V = 22.4 \text{ litre}$$

$$R = \frac{PV}{nT} = \frac{101.3 \times 22.4}{1 \times 273} = 8.31 \text{ kPa litre K}^{-1} \text{ mol}^{-1}$$

**Example 19.** The pressure exerted by 12 g of an ideal gas at temperature  $t^\circ \text{C}$  in a vessel of  $V$  litre is one atmosphere. When

the temperature is increased by  $10^\circ \text{C}$  at the same volume, the pressure increases by 10%. Calculate the temperature  $t$  and volume  $V$  (Molecular mass of the gas = 120). (IIT 1999)

**Solution:** As the volume is constant, pressure law can be applied, i.e.,

$$\frac{P_1}{P_2} = \frac{T_1}{T_2}$$

$$\text{or} \quad \frac{1}{1.1} = \frac{t + 273}{t + 283}$$

$$\text{or} \quad t = -173^\circ \text{C} = 100 \text{ K}$$

Now, applying gas equation,

$$PV = nRT$$

$$\text{or} \quad V = \frac{n}{P} RT = \frac{12 \times 0.082 \times 100}{120 \times 1} = 0.82 \text{ litre}$$

### ILLUSTRATIONS OF OBJECTIVE QUESTIONS

1. 2.5 L of a sample of a gas at 27°C and 1 bar pressure is compressed to a volume of 500 mL keeping the temperature constant, the percentage increase in the pressure is:

(a) 100% (b) 400% (c) 500% (d) 80%

[Ans. (b)]

[Hint:  $P_1 V_1 = P_2 V_2$

$$1 \times 2.5 = P_2 \times \frac{1}{2}$$

$$P_2 = 5 \text{ bar}$$

$$\begin{aligned} \text{\% Increase} &= \frac{\text{Increase in pressure}}{\text{Initial pressure}} \times 100 \\ &= \frac{4}{1} \times 100 = 400\% \end{aligned}$$

2. Which of the following gases will have density of 1.8 g L<sup>-1</sup> at 760 torr pressure and 27°C?

(a) O<sub>2</sub> (b) CO<sub>2</sub> (c) NH<sub>3</sub> (d) SO<sub>2</sub>

[Ans. (b)]

[Hint:  $Pm = dRT$

$$m = \frac{dRT}{P} = \frac{1.8 \times 0.0821 \times 300}{1} = 44$$

∴ The gas will be CO<sub>2</sub>.]

3. 10 g C<sub>2</sub>H<sub>6</sub> is filled in a bulb of 1 litre capacity which can withstand a maximum pressure of 10 atm. At what temperature will the pressure of gas reach the bursting limit?

(a) 76°C (b) 361.4°C (c) 92.4°C (d) 120°C

[Ans. (c)]

$$[\text{Hint: } T = \frac{PV}{nR} = \frac{10 \times 1}{(10/30) \times 0.0821} = 365.4 \text{ K} = 92.4^\circ \text{C}]$$

4. The vapour of phosphine gas at 27°C and 3 bar pressure has density:

(a) 4.09 g mL<sup>-1</sup> (b) 4.14 g L<sup>-1</sup>  
(c) 2.04 kg L<sup>-1</sup> (d) 2.04 g L<sup>-1</sup>

[Ans. (b)]

[Hint:  $d = \frac{Pm}{RT} = \frac{3 \times 34}{0.0821 \times 300} = 4.14 \text{ g L}^{-1}$ ]

5. Coefficient of volume expansion of a gas is:

(a)  $\frac{1}{273}$       (b)  $\frac{2}{273}$   
 (c)  $\frac{3}{273}$       (d)  $\frac{4}{273}$

[Ans. (a)]

[Hint: According to Charles' law,

$$V_t = V_0 \left(1 + \frac{t}{273}\right)$$

$$V_t = V_0 (1 + \alpha t)$$

$$\alpha = \frac{1}{273} = \text{Coefficient of volume expansion}$$

Here,  $V_0$  = Volume at  $0^\circ\text{C}$  and  $V_t$  = Volume at  $t^\circ\text{C}$

6. A gas has a vapour density 11.2. The volume occupied by 1 gram of the gas at STP will be:

(a) 11.2 L    (b) 22.4 L    (c) 1 L    (d) 10 L

[Ans. (c)]

[Hint: Number of moles =  $\frac{\text{Mass}}{\text{Molar mass}}$   
 $= \frac{\text{Mass}}{2 \times \text{Vapour density}}$   
 $= \frac{1}{2 \times 11.2} = \frac{1}{22.4}$

$$\text{Volume of gas} = n \times 22.4 \text{ L}$$

$$= \frac{1}{22.4} \times 22.4 \text{ L} = 1 \text{ L}$$

7. When a gas is heated from  $25^\circ\text{C}$  to  $50^\circ\text{C}$  at constant pressure of 1 bar, its volume:

- (a) increases from  $V$  to  $2V$   
 (b) increases from  $V$  to  $1.5V$   
 (c) increases from  $V$  to  $1.084V$   
 (d) increases from  $V$  to  $1.8V$

[Ans. (c)]

[Hint:  $\frac{V_1}{T_1} = \frac{V_2}{T_2}$   
 $\frac{V}{298} = \frac{V_2}{323}$

$$V_2 = V \times \frac{323}{298} = 1.084 V$$

8. The molecular weights of two ideal gases  $A$  and  $B$  are respectively 100 and 200. One gram of  $A$  occupies  $V$  litre of volume at STP. What is the volume (in litre) occupied by one gram of  $B$  at STP? (EAMCET 2006)

- (a)  $\frac{V}{2}$     (b)  $V$     (c)  $V^2$     (d)  $2V$

[Ans. (a)]

[Hint: Under identical conditions of temperature and pressure:

$$\frac{V_A}{V_B} = \frac{n_A}{n_B}$$

$$\frac{V}{V_B} = \frac{1/100}{1/200}$$

$$V_B = \frac{V}{2}$$

9. A bubble of volume  $V_1$  is at the bottom of a pond at  $15^\circ\text{C}$  and 1.5 atm pressure. When it comes at the surface, it observes a pressure of 1 atm at  $25^\circ\text{C}$  and has volume  $V_2$ ; give  $\left(\frac{V_2}{V_1}\right)$ : (DCE 2006)

- (a) 15.5    (b) 0.155    (c) 155.0    (d) 1.55

[Ans. (d)]

[Hint:  $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$   
 $\frac{V_2}{V_1} = \frac{P_1 T_2}{P_2 T_1}$   
 $= \frac{1.5 \times 288}{1 \times 298} = 1.5$

## 4.5 DALTON'S LAW OF PARTIAL PRESSURES

When different gases that do not react chemically with each other are enclosed in the same container, they intermix rapidly and exert a definite pressure. Again, each of the gas in the mixture exerts its own individual pressure if it is present only in the same container at the same temperature. John Dalton, in 1801, established the relation between the pressure of the mixture of gases and individual pressures of the constituent gases. This relationship is known as Dalton's law of partial pressures. It states that,

*At a given temperature, the total pressure exerted by two or more non-reacting gases occupying a definite volume is equal to the sum of the partial pressures of the component gases.* Mathematically,

$$P = p_A + p_B + p_C + \dots$$

when  $P$  is the total pressure and  $p_A, p_B, p_C, \dots$  are the partial pressures of the component gases  $A, B, C, \dots$  respectively. The pressure that a component gas of the gaseous mixture would exert if it were only present in the volume under consideration at a given temperature, is the partial pressure of the component.

### Derivation of Dalton's Law

Let  $n_1$  and  $n_2$  be the no. of moles of two non-reacting gases 'A' and 'B' filled in a vessel of volume ' $V$ ' at temperature  $T$ .

Total pressure in the vessel ' $P$ ' may be calculated as,

$$PV = (n_1 + n_2)RT \quad \dots \text{(i)}$$

Individual or partial pressure may be calculated as,

$$p_A V = n_1 RT \quad \dots \text{(ii)}$$

$$p_B V = n_2 RT \quad \dots \text{(iii)}$$

Adding eqs. (ii) and (iii), we get

$$(p_A + p_B)V = (n_1 + n_2)RT \quad \dots \text{(iv)}$$

Comparing equations (i) and (iv), we get

$$P = p_A + p_B \quad (\text{Dalton's expression})$$

Dividing eq. (ii) by (i), we get

$$\frac{P_A}{P} = \frac{n_1}{n_1 + n_2} = x_A$$

$$P_A = x_A \times P$$

where,  $x_A$  = mole fraction of 'A'.

Similarly, dividing eq. (iii) by (i), we get

$$P_B = x_B \times P$$

i.e., Partial pressure of a component

$$= \text{Mole fraction} \times \text{Total pressure}$$

### Relationship between Total Pressure and Individual Pressure (before Mixing) of the Constituent Gases at Constant Temperature

At constant temperature, let  $V_1$  volume of a gas A at a pressure  $p_1$  be mixed with  $V_2$  volume of gas B at a pressure  $p_2$ . Both these gases do not react chemically.

$$\text{Total volume} = V_1 + V_2$$

Let the total pressure be  $P$  and partial pressures of A and B be  $p_A$  and  $p_B$  respectively. Applying Boyle's law,

$$p_A (V_1 + V_2) = p_1 V_1 \quad \dots (i)$$

and

$$p_B (V_1 + V_2) = p_2 V_2 \quad \dots (ii)$$

Adding eqs. (i) and (ii),

$$p_A + p_B = \frac{p_1 V_1}{V_1 + V_2} + \frac{p_2 V_2}{V_1 + V_2} = \frac{p_1 V_1 + p_2 V_2}{V_1 + V_2}$$

or

$$P = \frac{p_1 V_1 + p_2 V_2}{V_1 + V_2}$$

In the laboratory, it is often convenient to collect a gas over water. When a gas is collected over water, the observed pressure of the gas is equal to the sum of the pressure of dry gas and the pressure of water vapour.

Therefore, the pressure of dry gas

$$\begin{aligned} &= \text{pressure of moist gas} - \text{pressure of water vapour} \\ &= \text{pressure of moist gas} - \text{aqueous tension} \end{aligned}$$

### Amagat Law of Partial Volume

Total volume of a mixture of gases which does not react at constant temperature and pressure is equal to sum of individual volumes (partial volumes) of constituent gases.

$$V = \sum V_i = V_1 + V_2 + V_3 + \dots + V_n$$

## 4.6 DIFFUSION OF GASES AND GRAHAM'S LAW OF DIFFUSION

When two or more non-reacting gases are kept side by side, they have the tendency to mix with one another spontaneously and form a homogeneous mixture. This can occur also if two gases have different densities. The heavier gas moves up and the lighter one comes down even against the action of gravity. Such a phenomenon is due to the fact that gas particles are moving at random with very high velocities and there is much intermolecular empty space in the volume of any gas. When two gases are brought together, they mix with each other in no time.

This ability of a gas to mix spontaneously and to form a homogeneous mixture is known as diffusion. It is due to this phenomenon that we can readily detect the fragrance of a flower or a perfume or bad smell of hydrogen sulphide, sulphur dioxide, chlorine, etc., when these are evolved or used in any work in laboratory or in industry.

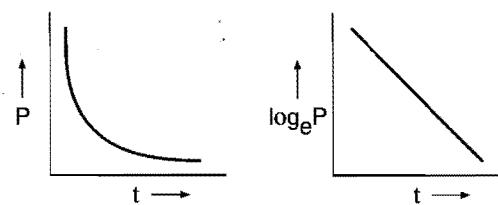
### Effusion

It is a process in which a gas is allowed to escape under pressure through a fine orifice or a small aperture made in the wall of a closed container. The difference between diffusion and effusion is that in the former case, the gas spontaneously streams through a porous partition while in the case of effusion, the gas is forced out through a small hole by applying some external pressure. However, both the processes are essentially the same.

Instantaneous rate of effusion is directly proportional to the instantaneous gas pressure and inversely proportional to the square root of molar mass.

$$\begin{aligned} -\frac{dP}{dt} &= \frac{KP}{\sqrt{M}} \\ -\int_{P_1}^{P_2} \frac{dP}{P} &= \frac{K}{\sqrt{M}} \int_0^t dt \\ \ln\left(\frac{P_1}{P_2}\right) &= \frac{Kt}{\sqrt{M}} \\ \ln P_2 &= \ln P_1 - \frac{Kt}{\sqrt{M}} \\ P_2 &= P_1 e^{-Kt/\sqrt{M}} \end{aligned}$$

Hence, partial pressure decreases exponentially with time as



**Fig. 4.4 Variation of partial pressure of gas with time, in the process of effusion.**

### Graham's Law of Diffusion or Effusion

This law was presented by Thomas Graham in 1833. The law states that "At constant pressure and temperature, the rate of diffusion or effusion of a gas is inversely proportional to the square root of its density."

$$\text{Rate of diffusion} \propto \frac{1}{\sqrt{d}}$$

If  $r_1$  and  $r_2$  represent the rates of diffusion of two gases and  $d_1$  and  $d_2$  are their respective densities, then

$$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}}$$

This equation can be written as:

$$\frac{r_1}{r_2} = \sqrt{\frac{\text{density of gas II}}{\text{density of hydrogen}}} \times \sqrt{\frac{\text{VD gas II}}{\text{VD gas I}}} = \sqrt{\frac{\text{Mol. mass gas II}}{\text{Mol. mass gas I}}} = \sqrt{\frac{M_2}{M_1}}$$

$$= \sqrt{\frac{2 \text{VD gas II}}{2 \text{VD gas I}}} = \sqrt{\frac{\text{Volume of gas diffused}}{\text{Time taken for diffusion}}}$$

$$\text{Rate of diffusion} = \frac{\text{Volume of gas diffused}}{\text{Time taken for diffusion}}$$

i.e., the volume which diffuses in unit time.

**(i) Comparison of times taken for the same volume of two gases:** Let the times of diffusion for the same volume of two gases be  $t_1$  and  $t_2$  respectively; then

$$\frac{r_1}{r_2} = \frac{t_1}{t_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}}$$

$$\text{or } \frac{t_2}{t_1} = \sqrt{\frac{d_1}{d_2}} = \sqrt{\frac{M_1}{M_2}}$$

**(ii) Comparison of the volumes of the gases that diffuse in same time:** Let  $V_1$  and  $V_2$  be the volumes of two gases that diffuse in the same time  $t$ . Then

$$\frac{V_1}{V_2} = \frac{r_1}{r_2} = \frac{t_1}{t_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}}$$

**(iii) Effect of pressure on rate of diffusion:** When pressure is not constant then rate of effusion may be taken proportional to pressure.

$$r \propto \frac{1}{\sqrt{M}} \quad r \propto P$$

Combination of these equations gives:

$$r \propto \frac{P}{\sqrt{M}}$$

$$\frac{r_1}{r_2} = \frac{P_1}{P_2} \sqrt{\frac{M_2}{M_1}}$$

### How to Determine Rate of Diffusion?

- Rate of diffusion is equal to distance travelled by gas per unit time through a tube of uniform cross-section.
- Number of moles effusing per unit time is also called rate of diffusion.
- Decrease in pressure of a cylinder per unit time is called rate of effusion of gas.

### Application of Graham's Law of Diffusion

According to Graham's law of diffusion, the ratio of rate of diffusion of two gases may be given as:

$$\frac{r_1}{r_2} = \left( \frac{M_2}{M_1} \right)^{1/2}$$

where,  $M_1$  and  $M_2$  are respective molar masses of the gases.

The factor  $\left( \frac{M_2}{M_1} \right)^{1/2}$  is called enrichment factor; this tells

about the preferential effusion of lighter species relative to the heavier ones. This enrichment can be applied to separate isotopes. For example, the isotope  $U^{235}$ , the active component in atomic weapons and in nuclear power generation, has a natural abundance of only 0.7% while  $U^{238}$  is far more abundant. By reaction of the isotopic mixture with fluorine, gaseous  $UF_6$  is produced and can be enriched by passing it through a porous barrier. The process of diffusion through the porous barrier is repeated many times to achieve sufficient enrichment.

$$\text{Separation factor } f' = \frac{n'_1 / n'_2}{n_1 / n_2}$$

where,  $n_1 n_2$  and  $n'_1 n'_2$  are the concentration of two isotopes before and after diffusion.

$$\text{Theoretical separation factor for single step } f' = \sqrt{\frac{M_2}{M_1}}$$

Let enrichment of species '1' is achieved after 'n' times then

$$(f')^n = \frac{n'_1 / n'_2}{n_1 / n_2} = f$$

$$n \log f' = \log \left( \frac{n'_1 / n'_2}{n_1 / n_2} \right)$$

$$n \log \sqrt{\frac{M_2}{M_1}} = \log \left( \frac{n'_1 / n'_2}{n_1 / n_2} \right)$$

$$\frac{n}{2} \log \left( \frac{M_2}{M_1} \right) = \log \left( \frac{n'_1 / n'_2}{n_1 / n_2} \right)$$

$$n = \frac{2 \log \left( \frac{n'_1 / n'_2}{n_1 / n_2} \right)}{\log (M_2 / M_1)} = \frac{2 \log (f)}{\log \left( \frac{M_2}{M_1} \right)}$$

### SOME SOLVED EXAMPLES

**Example 20.** A 10 litre flask contains 0.2 mole of methane, 0.3 mole of hydrogen and 0.4 mole of nitrogen at 25°C. What is the partial pressure of each component and what is the pressure inside the flask?

**Solution:**

$$P = \frac{nRT}{V}$$

$$\text{Partial pressure of methane} = \frac{0.2 \times 0.0821 \times 298}{10} = 0.489 \text{ atm}$$

$$\text{Partial pressure of hydrogen} = \frac{0.3 \times 0.0821 \times 298}{10} = 0.734 \text{ atm}$$

$$\text{Partial pressure of nitrogen} = \frac{0.4 \times 0.0821 \times 298}{10} = 0.979 \text{ atm}$$

$$\begin{aligned}\text{Total pressure} &= (0.489 + 0.734 + 0.979) \text{ atm} \\ &= 2.202 \text{ atm}\end{aligned}$$

**Alternative solution:** Total number of moles  
 $= 0.2 + 0.3 + 0.4 = 0.9$

Let the total pressure be  $P$ .

We know that,

$$P = \frac{\text{total number of moles}}{V} \cdot RT$$

$$V = 10 \text{ litre}, R = 0.0821 \text{ L atm K}^{-1}, T = (25 + 273) = 298 \text{ K}$$

$$P = \frac{0.9}{10} \times 0.0821 \times 298 = 2.20 \text{ atm}$$

$$\begin{aligned}\text{Partial pressure of CH}_4 &= \text{Mole fraction of methane} \times \text{total pressure} \\ &= \frac{0.2}{0.9} \times 2.20 = 0.489 \text{ atm}\end{aligned}$$

$$\begin{aligned}\text{Partial pressure of H}_2 &= \text{Mole fraction of H}_2 \times \text{total pressure} \\ &= \frac{0.3}{0.9} \times 2.20 = 0.733 \text{ atm}\end{aligned}$$

$$\begin{aligned}\text{Partial pressure of N}_2 &= \text{Mole fraction of N}_2 \times \text{total pressure} \\ &= \frac{0.4}{0.9} \times 2.20 = 0.978 \text{ atm}\end{aligned}$$

**Example 21.** If 200 mL of  $N_2$  at 25°C and a pressure of 250 mm are mixed with 350 mL of  $O_2$  at 25°C and a pressure of 300 mm so that, the volume of resulting mixture is 300 mL, what would be the final pressure of the mixture at 25°C?

**Solution:** In the case of nitrogen, volume increases, its pressure must decrease. Let the new pressure be  $P_{N_2}$ .

$$P_{N_2} = \frac{250 \times 200}{300} = 166.6 \text{ mm} \quad (\text{Applying Boyle's law})$$

In the case of oxygen, volume decreases, its pressure must increase. Let the new pressure be  $P_{O_2}$ .

$$P_{O_2} = \frac{300 \times 350}{300} = 350 \text{ mm} \quad (\text{Applying Boyle's law})$$

$$\text{Total pressure} = P_{N_2} + P_{O_2} = (166.6 + 350) = 516.6 \text{ mm}$$

**Example 22.** 1.22 g of a gas measured over water at 15°C and a pressure of 775 mm of mercury occupied 900 mL. Calculate the volume of dry gas at NTP. Vapour pressure of water at 15°C is 14 mm.

**Solution:** Pressure of dry gas = Pressure of moist gas  
 $-$  Aqueous tension  
 $= 775 - 14$   
 $= 761 \text{ mm}$

Initial conditions

$$V_1 = 900 \text{ mL}$$

$$P_1 = 761 \text{ mm}$$

$$T_1 = (273 + 15) = 288 \text{ K} \quad T_2 = 273 \text{ K}$$

Since,

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

So,

$$V_2 = \frac{P_1 V_1 T_2}{T_1 P_2}$$

$$\begin{aligned}&= \frac{761 \times 900 \times 273}{288 \times 760} \\ &= 854.2 \text{ mL}\end{aligned}$$

**Example 23.** When 2 g of a gaseous substance A is introduced into an initially evacuated flask at 25°C, the pressure is found to be 1-atmosphere. 3 g of another gaseous substance B is then added to it at the same temperature and pressure. The final pressure is found to be 1.5 atmosphere. Calculate the ratio of molecular masses of A and B assuming ideal gas behaviour.

**Solution:** Let the molecular masses of A and B be  $M_A$  and  $M_B$  respectively.

Pressure exerted by the gas B =  $(1.5 - 1.0) = 0.5 \text{ atm}$ . Volume and temperature are same in both the gases.

$$\text{For gas A: } P = 1 \text{ atm}, w = 2 \text{ g}, M = M_A$$

$$\text{We know that, } PV = \frac{w}{M} RT$$

$$1 \times V = \frac{2}{M_A} \cdot RT \quad \text{or} \quad M_A = \frac{2RT}{V} \quad \dots \text{(i)}$$

$$\text{For gas B: } P = 0.5 \text{ atm}, w = 3 \text{ g}, M = M_B$$

$$0.5 \times V = \frac{3}{M_B} \cdot RT \quad \text{or} \quad M_B = \frac{3RT}{0.5 \times V} \quad \dots \text{(ii)}$$

Dividing Eq. (i) by Eq. (ii),

$$\begin{aligned}\frac{M_A}{M_B} &= \frac{2RT}{V} \times \frac{0.5 \times V}{3RT} \\ &= \frac{2 \times 0.5}{3} = \frac{1}{3}\end{aligned}$$

$$\text{Thus, } M_A : M_B = 1 : 3$$

**Example 24.** Find the total pressure exerted by 1.6 g methane and 2.2 g  $CO_2$  contained in a four litre flask at 27°C.

$$\text{Solution: } PV = (n_1 + n_2)RT$$

$$P \times 4 = \left( \frac{1.6}{16} + \frac{2.2}{44} \right) \times 0.0821 \times 300$$

$$P = 0.9236 \text{ atm}$$

**Example 25.** 1500 mL flask contains 400 mg  $O_2$  and 60 mg  $H_2$  at 100°C.

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

(b) If the mixture is permitted to react to form water vapour at 100°C, what will be left and what will be their partial pressures?

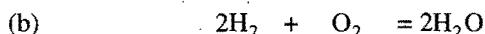
$$\text{Solution: (a) No. of moles of } O_2 = \frac{400}{1000 \times 32} = 0.0125$$

$$\text{No. of moles of } H_2 = \frac{60}{1000 \times 2} = 0.03$$

$$\text{Partial pressure of } O_2 = \frac{0.0125 \times 0.0821 \times 373}{1.5} = 0.255 \text{ atm}$$

$$\text{Partial pressure of } H_2 = \frac{0.03 \times 0.0821 \times 373}{1.5} = 0.612 \text{ atm}$$

$$\text{Total pressure} = 0.255 + 0.612 = 0.867 \text{ atm}$$



Initial      0.03      0.0125      0

After reaction    0.005      0      0.025

$$\text{Partial pressure of H}_2 = \frac{0.005 \times 0.0821 \times 373}{1.5} = 0.102 \text{ atm}$$

$$\text{Partial pressure of H}_2\text{O} = \frac{0.025 \times 0.0821 \times 373}{1.5} = 0.51 \text{ atm}$$

**Example 26.**  $20 \text{ dm}^3$  of  $\text{SO}_2$  diffuse through a porous partition in 60 s. What volume of  $\text{O}_2$  will diffuse under similar conditions in 30 s? (IIT 1996)

**Solution:** Rate of diffusion of  $\text{SO}_2 = \frac{20}{60} \text{ dm}^3 \text{ s}^{-1}$

$$\text{Rate of diffusion of O}_2 = \frac{V}{30} \text{ dm}^3 \text{ s}^{-1}$$

According to Graham's law of diffusion,

$$\frac{(V/30)}{(20/60)} = \sqrt{\frac{M_{\text{SO}_2}}{M_{\text{O}_2}}} = \sqrt{\frac{64}{32}}$$

$$V = 14.1 \text{ dm}^3$$

**Example 27.** 50 volume of hydrogen take 20 minute to diffuse out of a vessel. How long will 40 volume of oxygen take to diffuse out from the same vessel under the same conditions?

**Solution:** Rate of diffusion for hydrogen,  $r_1 = \frac{50}{20}$

Rate of diffusion for oxygen,  $r_2 = \frac{40}{t}$

Mol. mass of hydrogen = 2

Mol. mass of oxygen = 32

$$\text{So, } \frac{50/20}{40/t} = \sqrt{\frac{32}{2}}$$

$$\text{or, } \frac{50}{20} \times \frac{t}{40} = 4$$

$$t = 64 \text{ minute}$$

**Example 28.** Calculate the relative rates of diffusion of  $^{235}\text{UF}_6$  and  $^{238}\text{UF}_6$  in the gaseous state (At. mass of F = 19).

**Solution:** Mol. mass  $^{235}\text{UF}_6 = 235 + 6 \times 19 = 349$

Mol. mass  $^{238}\text{UF}_6 = 238 + 6 \times 19 = 352$

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}} = \sqrt{\frac{352}{349}} = 1.0043$$

$$r_1 : r_2 :: 1.0043 : 1.0000$$

**Example 29.** 180 mL of a hydrocarbon diffuses through a porous membrane in 15 minutes while 120 mL of  $\text{SO}_2$  under identical conditions diffuses in 20 minutes. What is the molecular mass of the hydrocarbon?

**Solution:**

$$r_1 = \text{rate of diffusion of hydrocarbon} = \frac{180}{15} \text{ mL min}^{-1}$$

$$r_2 = \text{rate of diffusion of SO}_2 = \frac{120}{20} \text{ mL min}^{-1}$$

$$\frac{r_1}{r_2} = \frac{M_{\text{SO}_2}}{M}$$

Thus,

$$\frac{180/15}{120/20} = \sqrt{\frac{64}{M}}$$

$$2 = \sqrt{\frac{64}{M}}$$

So,

$$M = 16$$

**Example 30.** The reaction between gaseous  $\text{NH}_3$  and  $\text{HBr}$  produces a white solid  $\text{NH}_4\text{Br}$ . Suppose a small quantity of gaseous  $\text{NH}_3$  and gaseous  $\text{HBr}$  are introduced simultaneously into opposite ends of an open tube which is one metre long. Calculate the distance of white solid formed from the end which was used to introduce  $\text{NH}_3$ .

**Solution:** Let the distance of white solid from  $\text{NH}_3$  end =  $x$  cm.

The distance of white solid from  $\text{HBr}$  end =  $(100 - x)$  cm.

Rates of diffusion shall be proportional to these distances.

$$\frac{r_1}{r_2} = \frac{x}{(100-x)} = \sqrt{\frac{M_{\text{HBr}}}{M_{\text{NH}_3}}}$$

$$\text{Mol. mass of HBr} = 1 + 80 = 81$$

$$\text{Mol. mass of NH}_3 = 14 + 3 = 17$$

$$\text{So, } \frac{x}{(100-x)} = \sqrt{\frac{81}{17}}$$

$$\text{or, } \frac{x}{(100-x)} = 2.18$$

$$\text{So, } x = 100 \times 2.18 - 2.18x$$

$$\text{or, } 3.18x = 100 \times 2.18$$

$$\text{So, } x = \frac{100 \times 2.18}{3.18} = 68.55 \text{ cm}$$

**Example 31.** At  $27^\circ\text{C}$ , hydrogen is leaked through a tiny hole into a vessel for 20 minute. Another unknown gas at the same temperature and pressure as that of hydrogen leaked through the same hole for 20 minute. After the effusion of the gases the mixture exerts a pressure of 6 atmosphere. The hydrogen content of the mixture is 0.7 mole. If the volume of the container is 3 litre, what is the molecular mass of the unknown gas? (IIT 1992)

**Solution:** Let  $p_{\text{H}_2}$  and  $p_{\text{un}}$  be the partial pressures of hydrogen and unknown gas respectively and  $w$  be the number of moles of unknown gas.

$$p_{\text{H}_2} = \frac{0.7}{3} \times 0.0821 \times 300$$

$$p_{\text{un}} = \frac{w}{3} \times 0.0821 \times 300$$

Adding both,

$$p_{\text{H}_2} + p_{\text{un}} = 6 = (1/3) \times 0.0821 \times 300(0.7 + w)$$

$$w = 0.0308 \text{ mole}$$

Applying law of diffusion,

$$\frac{0.7/20}{0.0308/20} = \sqrt{\frac{M}{2}} \text{ or } M = 1033$$

**Example 32.** The ratio of velocities of diffusion of gases A and B is 1:4. If the ratio of their masses present in the mixture is 2:3, calculate the ratio of their mole fractions. [OEE (Bihar) 1990]

**Solution:**

$$\frac{r_A}{r_B} = \sqrt{\frac{M_B}{M_A}} = \frac{1}{4}$$

or

$$\frac{M_B}{M_A} = \frac{1}{16}$$

Let masses  $W_A$  and  $W_B$  of A and B be present respectively.

$$\text{Mole fraction of } A = \frac{\frac{W_A}{M_A}}{\frac{W_A}{M_A} + \frac{W_B}{M_B}}$$

$$\text{Mole fraction of } B = \frac{\frac{W_B}{M_B}}{\frac{W_A}{M_A} + \frac{W_B}{M_B}}$$

$$\text{Ratio} = \frac{W_A}{M_A} \times \frac{M_B}{W_B}$$

$$\text{or } \frac{W_A}{W_B} \times \frac{M_B}{M_A} = \frac{2}{3} \times \frac{1}{16} = \frac{1}{24}$$

**Example 33.** A space capsule is filled with neon gas at 1.00 atm and 290 K. The gas effuses through a pin hole into outer space at such a rate that pressure drops by 0.30 torr per second.

(a) If the capsule is filled with ammonia at the same temperature and pressure, what would be rate of pressure drop?

(b) If the capsule is filled with 30.0 mol % helium, 20.0 mol % oxygen and 50.0 mol % nitrogen at a total pressure of 1.0 atm and a temperature of 290 K, what would be the corresponding rate of pressure drop?

**Solution:** (a) The rate of pressure drop is directly proportional to rate of effusion.

$$\frac{r_{\text{Ne}}}{r_{\text{NH}_3}} = \sqrt{\frac{M_{\text{NH}_3}}{M_{\text{Ne}}}} = \sqrt{\frac{17.0}{20}} = 0.92$$

$$r_{\text{NH}_3} = \frac{r_{\text{Ne}}}{0.92} = \frac{0.30}{0.92} = 0.326 \text{ torr / second}$$

(b) The average molecular mass of the gaseous mixture is

$$0.3 \times 4 + 0.2 \times 32 + 0.5 \times 28 = 21.6$$

$$\text{Rate of drop of pressure} = \sqrt{\frac{20}{21.6}} \times 0.30 \\ = 0.29 \text{ torr / second}$$

**Example 34.** One mole of nitrogen gas at 0.8 atm takes 38 second to diffuse through a pin hole whereas one mole of an unknown compound of xenon with fluorine at 1.6 atm takes 57 second to diffuse through the same hole. Calculate the molecular formula of the compound. (IIT-JEE 1999)

**Solution:**

$$\frac{r_{N_2}}{r_{\text{XeF}_n}} = \frac{P_{N_2}}{P_{\text{XeF}_n}} \sqrt{\frac{M_{\text{XeF}_n}}{M_{N_2}}}$$

Molar volume

$$\frac{r_{N_2}}{r_{\text{XeF}_n}} = \frac{t_{N_2}}{\text{Molar volume}} = \frac{t_{\text{XeF}_n}}{t_{N_2}} = \frac{57}{38}$$

$t_{\text{XeF}_n}$

$$\frac{57}{38} = \frac{0.8}{1.6} \sqrt{\frac{M_{\text{XeF}_n}}{28}}$$

$$M_{\text{XeF}_n} = \left(\frac{57}{38}\right)^2 \times \left(\frac{1.6}{0.8}\right)^2 \times 28 \\ = 252$$

$$\text{Xe} + n\text{F} = 252$$

$$131 + n \times 19 = 252$$

$$n = 6$$

Molecular formula =  $\text{XeF}_6$

**Example 35.**  $100 \text{ cm}^3$  of  $\text{NH}_3$  diffuses through a pin hole in 32.5 second. How much time will 60 cc of  $\text{N}_2$  take to diffuse under the same conditions?

$$\frac{r_{\text{NH}_3}}{r_{\text{N}_2}} = \sqrt{\frac{M_{\text{N}_2}}{M_{\text{NH}_3}}}$$

$$\frac{100/32.5}{60/t} = \sqrt{\frac{28}{17}}$$

$$\frac{100 \times t}{60 \times 32.5} = \sqrt{\frac{28}{17}}$$

$$t = 25 \text{ second}$$

### ILLUSTRATIONS OF OBJECTIVE QUESTIONS

10. A gas with molecular formula  $\text{C}_n\text{H}_{2n+2}$  diffuses through a porous plug at a rate 1/6th of the rate of diffusion of hydrogen gas under similar conditions. The formula of the gas is:

- (a)  $\text{C}_2\text{H}_6$       (b)  $\text{C}_{10}\text{H}_{22}$       (c)  $\text{C}_5\text{H}_{12}$       (d)  $\text{C}_6\text{H}_{14}$

[Ans. (c)]

$$[\text{Hint: } \frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}]$$

$$\frac{r_1}{r_1/6} = \sqrt{\frac{M_2}{2}}$$

$$M_2 = 72$$

∴ The formula of gas will be  $\text{C}_5\text{H}_{12}$ .]

11. Under similar conditions which of the following gases will diffuse four times as quickly as oxygen?

- (a) He      (b)  $\text{H}_2$       (c)  $\text{N}_2$       (d)  $\text{D}_2$

[Ans. (b)]

$$[\text{Hint: } \frac{r_{\text{gas}}}{r_{\text{O}_2}} = \sqrt{\frac{M_{\text{O}_2}}{M_{\text{gas}}}}]$$

$$4 = \sqrt{\frac{32}{M_{\text{gas}}}} \text{ or } 16 = \frac{32}{M_{\text{gas}}}$$

$$\text{or } M_{\text{gas}} = \frac{32}{16} = 2, \text{ i.e., } [\text{H}_2]$$

12. The rates of diffusion of hydrogen and deuterium are in the ratio:

$$(a) 1:1 \quad (b) \sqrt{2}:1 \quad (c) 4:1 \quad (d) 1:4$$

[Ans. (b)]

$$[\text{Hint: } \frac{r_{\text{H}_2}}{r_{\text{D}_2}} = \sqrt{\frac{M_{\text{D}_2}}{M_{\text{H}_2}}}]$$

$$\frac{r_{\text{H}_2}}{r_{\text{D}_2}} = \sqrt{\frac{4}{2}}$$

$$r_{\text{H}_2} = \sqrt{2} r_{\text{D}_2}]$$

13. The time taken for effusion of 64 mL of oxygen will be same as the time taken for the effusion of which of the following gases under identical conditions?

$$(a) 64 \text{ mL of H}_2 \quad (b) 100 \text{ mL of N}_2$$

$$(c) 64 \text{ mL of CO}_2 \quad (d) 45.24 \text{ mL of SO}_2$$

[Ans. (d)]

$$[\text{Hint: } \frac{r_{\text{O}_2}}{r_{\text{gas}}} = \sqrt{\frac{M_{\text{gas}}}{M_{\text{O}_2}}}]$$

$$\frac{64}{V} = \sqrt{\frac{64}{32}} \text{ or } V = \frac{64}{\sqrt{2}} = 45.25 \text{ mL}$$

14. Which of the following pairs of gases will have identical rate of effusion under similar conditions?

$$(a) Diprotium and dideuterium  
(b) Carbon dioxide and ethane  
(c) Dideuterium and helium  
(d) Ethene and ethane$$

[Ans. (c)]

[Hint: Dideuterium and helium have same molar mass; hence they will diffuse with identical rate under identical conditions.]

15. Two gas bulbs A and B are connected by a tube having a stopcock. Bulb A has a volume of 100 mL and contains hydrogen. After opening the gas from A to the evacuated bulb B, the pressure falls down to 40%. The volume (mL) of B must be:

$$(a) 75 \quad (b) 150 \quad (c) 125 \quad (d) 200$$

$$(e) 250$$

[Ans. (b)]

$$[\text{Hint: } P_1 V_1 (A) + P_2 V_2 (B) = P_R (V_1 + V_2)]$$

$$100 \times 100 + 0 \times V_2 = 40(100 + V_2)$$

$$V_2 = 250 - 100 = 150 \text{ mL}$$

#### 4.7 KINETIC THEORY OF GASES

This theory was a generalization for about ideal gases. It was presented by Bernoulli in 1738 and developed in 1860 by Clausius, Maxwell, Kroning and Boltzmann. Postulates of kinetic theory of gases are:

(1) Gases are made up of small structural units called atoms or molecules. Volume of individual atom or molecule is considered negligible.

(2) Gas molecules are always in rapid random motion colliding with each other and with the wall of container.

(3) Collision among gas molecules is perfectly elastic, i.e., there is no loss in kinetic energy and moment during such collision.

(4) Gas molecules neither attract nor repel each other.

(5) Pressure exerted by gas is due to collisions of gas molecules with the wall of the container.

Pressure  $\propto$  Number of collisions per unit time per unit area by the molecules on the wall of the container

(6) Kinetic energy of gas molecules depends only on absolute temperature.

Kinetic energy  $\propto$  absolute temperature

(7) The force of gravity has no effect on the speed of gas molecules.

#### Derivation of Kinetic Gas Equation

On the basis of the postulates of kinetic theory of gases, it is possible to derive the mathematical expression, commonly known as kinetic gas equation, i.e.,

$$PV = \frac{1}{3} mn c^2$$

where,  $P$  = pressure of the gas,  $V$  = volume of the gas,  $m$  = mass of a molecule,  $n$  = number of molecules present in the given amount of a gas and  $c$  = root mean square speed.

The root mean square speed (rms speed) may be defined as the square root of the mean of squares of the individual speed of all the molecules.

$$\text{rms speed} = \sqrt{\frac{c_1^2 + c_2^2 + c_3^2 + \dots + c_n^2}{n}}$$

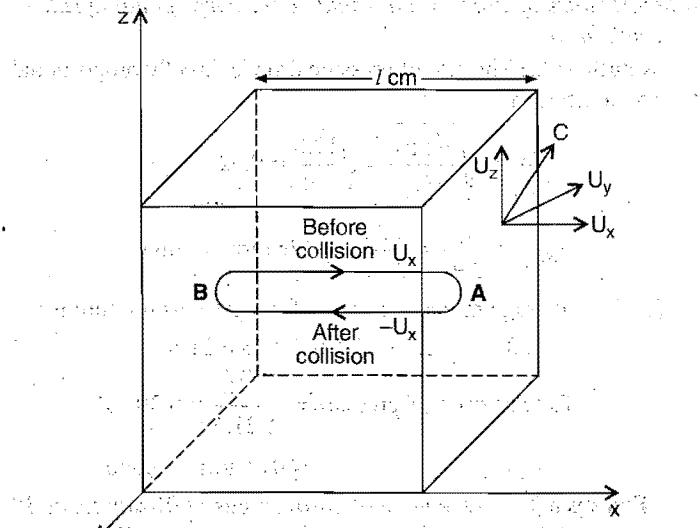


Fig. 4.5

Consider a certain mass of a gas enclosed in a cubical vessel of side ' $l$ ' cm. Let the total number of gas molecules be ' $n$ ' and mass of each molecule be ' $m$ '. Let  $c$  be the root mean square speed. Speed can be resolved into three components, i.e.,  $U_x$ ,  $U_y$  and  $U_z$  parallel to the edges of the container (i.e., parallel to three axes  $x$ ,  $y$  and  $z$ ).

$$c^2 = U_x^2 + U_y^2 + U_z^2$$

Consider the movement of a single molecule between opposite faces  $A$  and  $B$  parallel to  $x$ -axis. When the molecule strikes with one wall of the container, it bounces back with the same speed and subsequently strikes the opposite wall.

The momentum of the molecule before collision with face  $A = mU_x$ .

The momentum of the molecule after collision =  $-mU_x$   
The change in momentum in one collision =  $mU_x - (-mU_x)$

$$= 2mU_x$$

After collision, the molecule must move a distance  $2l$  cm along  $x$ -axis before making another impact on this wall. Since the velocity ' $U_x$ ' remains unchanged, the time taken to travel a distance  $2l$  cm =  $\frac{2l}{U_x}$  second.

So, the number of collisions by the gas molecule in one second  
 $= \frac{1}{2l} = \frac{U_x}{2l}$

$$\text{Change of momentum per second} = 2mU_x \times \frac{U_x}{2l} = m \frac{U_x^2}{l}$$

The change of momentum on both the opposite faces  $A$  and  $B$  along  $x$ -axis per second would be double, i.e.,  $\frac{2mU_x^2}{l}$

Similarly,

$$\text{Change in momentum per second along } y\text{-axis} = \frac{2mU_y^2}{l}$$

and change in momentum per second along  $z$ -axis =  $\frac{2mU_z^2}{l}$

Hence, total change of momentum per second on all faces will be

$$\begin{aligned} &= \frac{2mU_x^2}{l} + \frac{2mU_y^2}{l} + \frac{2mU_z^2}{l} \\ &= \frac{2m}{l} (U_x^2 + U_y^2 + U_z^2) \\ &= \frac{2m}{l} c^2 \end{aligned}$$

Change of momentum per second = Force

$$\text{Pressure} = \frac{\text{Force}}{\text{Area}}$$

$$\text{Pressure created by one molecule} = \frac{2m}{l} \frac{c^2}{6l^2}$$

$$\text{Pressure created by } n \text{ molecules} = \frac{2mnc^2}{6l^3}$$

$$P = \frac{1}{3} \frac{mnc^2}{V} \quad [l^3 = V]$$

$$\text{or } PV = \frac{1}{3} mnc^2$$

This equation is called kinetic gas equation.

For one gram mole of the gas,

$$n = N \quad (\text{Avogadro's number})$$

$$= 6.02 \times 10^{23}$$

$$m \times N = M = \text{molecular mass of the gas}$$

The above kinetic equation can be written as:

$$PV = \frac{1}{3} Mc^2$$

or

$$c^2 = \frac{3PV}{M}$$

$$c = \sqrt{\frac{3PV}{M}}$$

$$= \sqrt{\frac{3P}{d}} \quad [d = \text{density}]$$

$$= \sqrt{\frac{3RT}{M}}$$

Thus,

$$c = \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3P}{d}}$$

The value of  $R$  should be taken in erg K<sup>-1</sup> mol<sup>-1</sup>, e.g.,

$$R = 8.314 \times 10^7 \text{ erg K}^{-1} \text{ mol}^{-1}$$

$$c = \sqrt{\frac{3 \times 8.314 \times 10^7 \times T}{M}} = 1.58 \sqrt{\frac{T}{M}} \times 10^4 \text{ cm/sec}$$

### Calculation of Kinetic Energy

$$PV = \frac{1}{3} mnc^2$$

For one gram mole of the gas,

$$PV = RT \quad \text{and } n = N$$

$$\frac{1}{3} mnc^2 = RT$$

$$\text{or } \frac{2}{3} \cdot \frac{1}{2} mnc^2 = RT \quad \left( \frac{1}{2} mnc^2 = \text{KE per mol} \right)$$

$$\frac{2}{3} \cdot \text{KE} = RT$$

$$\text{or } \text{KE} = \frac{3}{2} RT$$

Average kinetic energy per mol does not depend on the nature of the gas but depends only on temperature. Thus, when two gases are mixed at the same temperature, there will be no rise or decrease in temperature unless both react chemically.

$$\text{Average kinetic energy per molecule} = \frac{\text{Average KE per mole}}{N}$$

$$= \frac{3}{2} \frac{RT}{N} = \frac{3}{2} kT$$

$$k = \text{Boltzmann constant}$$

The ratio  $R/N$  is constant and is known as Boltzmann constant. Its numerical value is  $1.38 \times 10^{-16}$  erg K<sup>-1</sup> molecule<sup>-1</sup>.

#### 4.8 MAXWELL-BOLTZMANN DISTRIBUTION OF MOLECULAR SPEEDS

The gas molecules are moving in all possible directions. They collide with one another and also with the walls of the container. As a result of collisions, the speed and direction of the gas molecules are ever changing, i.e., all the molecules in a given sample of gas do not have the same speed.

The distribution of gas molecules among different possible speeds was studied by Maxwell and Boltzmann using the theory of probability. The results are mathematically expressed as,

$$dN_u = 4\pi N \left[ \frac{M}{2\pi RT} \right]^{3/2} e^{-\frac{Mu^2}{2RT}} u^2 du$$

$$= 4\pi N \left[ \frac{m}{2\pi kT} \right]^{3/2} e^{-\frac{mu^2}{2RT}} u^2 du$$

Here,  $N$  = Total number of molecules,  $M$  = molar mass of gas

This expression gives the number of molecules ( $dN_u$ ) having speed between  $u$  and  $(u+du)$  at temperature ( $T$ ).

A plot of fraction of molecules in the speed range ( $u+du$ ),  $\frac{1}{N} \left( \frac{dN_u}{du} \right)$  against speed  $u$  is:

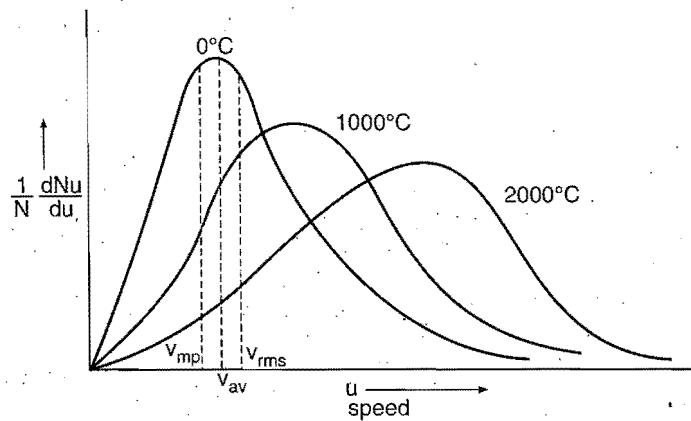


Fig. 4.6

$v_{mp}$  = most probable speed

$v_{av}$  = average speed

$v_{rms}$  = root mean square speed

#### Kinds of Molecular Speeds

Molecular speeds are of three types:

- (i) The rms speed,
- (ii) The average speed and
- (iii) The most probable speed

**Note:** Root mean square speed explained the non-existence of gases in the atmosphere of moon. Root mean square speed of gases exceeds the escape velocity of moon and hence gases escape from atmosphere of moon against the gravitational barrier of moon.

**(i) The root mean square speed:** The speed in kinetic gas equation,  $PV = \frac{1}{3} mnc^2$ , is the hypothetical speed possessed by

all the gas molecules when the total kinetic energy is equally distributed amongst them. The total kinetic energy of the  $n$  molecules of the gas is sum of the kinetic energies of the individual molecules.

Total kinetic energy

$$= \frac{1}{2} mc_1^2 + \frac{1}{2} mc_2^2 + \frac{1}{2} mc_3^2 + \dots + \frac{1}{2} mc_n^2 \quad \dots (i)$$

Let  $c$  be the velocity possessed by each of the  $n$  molecules; then,

$$\text{total kinetic energy} = n \times \frac{1}{2} mc^2 \quad \dots (ii)$$

Equating both the equations,

$$n \times \frac{1}{2} mc^2 = \frac{1}{2} mc_1^2 + \frac{1}{2} mc_2^2 + \frac{1}{2} mc_3^2 + \dots + \frac{1}{2} mc_n^2$$

$$\text{or } c^2 = \frac{c_1^2 + c_2^2 + c_3^2 + c_4^2 + \dots + c_n^2}{n}$$

$$\text{or } c = \sqrt{\frac{c_1^2 + c_2^2 + c_3^2 + \dots + c_n^2}{n}}$$

Thus, rms speed is defined as the square root of the mean of the squares of the speed of all the molecules present in the given sample of the gas. The value of  $c$  is determined by using the following expressions:

$$c = \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3P}{d}}$$

In SI units, the values of  $R$ ,  $P$ ,  $V$ ,  $M$  and  $d$  used are given below:

(i)  $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$  or  $R = 8.314 \text{ kPa dm}^3 \text{ K}^{-1} \text{ mol}^{-1}$

(ii)  $V$  of the gas always in litre

(iii)  $P$  of the gas in kilopascal (kPa). 1 atm = 101.3 kPa and 1 torr = 0.133 kPa

(iv)  $M$  in kg mol<sup>-1</sup>

(v)  $d$  in kg m<sup>-3</sup>

**(ii) Average speed:** It is the arithmetic mean of the various speeds of the molecules.

$$\text{Average speed} = \frac{c_1 + c_2 + c_3 + \dots + c_n}{n}$$

$$\text{It is equal to } \sqrt{\frac{8RT}{\pi M}}$$

It is related to rms speed by the following relationship:

$$\text{Average speed} = 0.9213 \times \text{rms speed}$$

$$\text{rms speed} = 1.085 \times \text{average speed}$$

**(iii) Most probable speed:** This is defined as the speed possessed by maximum number of molecules of a gas at a given temperature.

$$\text{It is equal to } \sqrt{\frac{2RT}{M}}$$

This is related to rms speed by the following relationship:

$$\text{Most probable speed} = \sqrt{\frac{2}{\sqrt{3}}} \text{ rms} = 0.816 \text{ rms}$$

or

$$\text{rms} = 1.224 \text{ most probable speed}$$

The three kinds of molecular speeds are related to each other as:

$$\text{Most probable speed : Average speed : rms speed}$$

$$\begin{aligned} &= \sqrt{\frac{2RT}{M}} : \sqrt{\frac{8RT}{\pi M}} : \sqrt{\frac{3RT}{M}} \\ &= \sqrt{2} : \sqrt{\frac{8}{\pi}} : \sqrt{3} \\ &= 1 : 1.128 : 1.224 \end{aligned}$$

rms speed at any temperature  $t^\circ \text{C}$  may be related to its value at STP as:

$$c_t = c_0 \sqrt{\frac{(273+t)}{273}} \quad \dots (i)$$

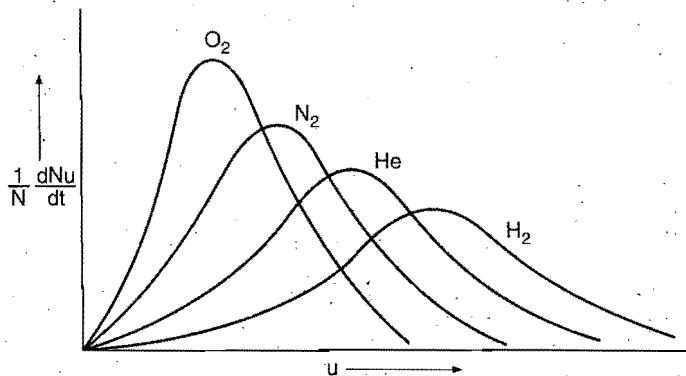
$$c_0 = \sqrt{\frac{3P}{d}} \quad \dots (ii)$$

From eqs. (i) and (ii), we get

$$\begin{aligned} c_t &= \sqrt{\frac{3P}{d}} \sqrt{\frac{(273+t)}{273}} \\ &= \sqrt{\frac{3P(273+t)}{273d}} \end{aligned}$$

### Some Essential Points for Distribution of Molecular Speed

(i) The fraction of molecules with very low or very high speeds is very small. Maximum fraction of molecules have speed near to the most probable speed  $v_{mp}$ .



**Fig. 4.7** Distribution of molecular speeds of various gases at a constant temperature

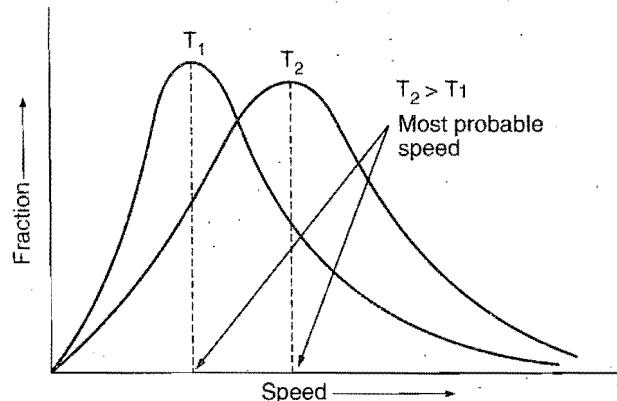
(ii) Total area under the curve is a measure of total number of molecules in the collection. Thus, area under the curve remains constant at different temperatures.

(iii) Distribution of molecular speed also depends upon the molecular mass of the gas. At similar temperature a heavier gas molecule has a narrow distribution of speed than those of lighter gas molecules.

(iv) The fraction of molecules having speeds greater than minimum goes on increasing with increase in speed. It reaches to a maximum value and then begins to decrease.

(v) As long as temperature of the gas is constant, the fraction having a particular speed remains the same inspite of the fact that the molecules change their speeds due to collisions.

The increase in the temperature of the gas increases the molecular speed. As a result, the most probable speed increases with the increase of temperature and the distribution curve shifts towards right. The general shape of the curve remains the same but the maxima of the curve becomes somewhat flat at a higher temperature, i.e., there is a wider distribution of molecular speeds and the fraction of the molecules having high speeds increases. However, the fraction of molecules possessing most probable speeds decreases with increase in temperature.



**Fig. 4.8**

### SOME SOLVED EXAMPLES

**Example 36.** Calculate the kinetic energy in joule of 8.00 g of methane at  $27^\circ \text{C}$ .

**Solution:** Number of gram moles of methane =  $\frac{3}{16} = \frac{1}{2}$

$$T = (27 + 273) = 300 \text{ K}$$

$$R = 8.32 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\text{Kinetic energy for one gram mole} = \frac{3}{2} RT$$

$$= \frac{3}{2} \times 8.32 \times 300 \text{ J}$$

Thus,

$$\text{kinetic energy for } \frac{1}{2} \text{ gram mole} = \frac{1}{2} \times \frac{3}{2} \times 8.32 \times 300 = 1872 \text{ J}$$

**Example 37.** Calculate the average and total kinetic energy of 0.5 mole of an ideal gas at  $0^\circ \text{C}$ .

**Solution:** Average kinetic energy per molecule of the gas

$$\begin{aligned} &= \frac{3}{2} \frac{R}{N} T \\ &= \frac{3}{2} \times \frac{8.314 \times 10^7}{6.023 \times 10^{23}} \times 273 \\ &= 5.65 \times 10^{-14} \text{ erg} = 5.65 \times 10^{-21} \text{ J} \end{aligned}$$

Total kinetic energy of 0.5 mole of the gas

$$\begin{aligned} &= \frac{3}{2} RT \times 0.5 \\ &= \frac{3}{2} \times 8.314 \times 10^7 \times 273 \times 0.5 \\ &= 1.702 \times 10^{10} \text{ erg} = 1.702 \text{ kJ} \end{aligned}$$

**Example 38.** Calculate the pressure exerted by  $10^{23}$  gas molecules each of mass  $10^{-22}$  g in a container of volume 1 litre, the rms speed is  $10^5 \text{ cm s}^{-1}$ .

**Solution:** Using kinetic gas equation,

$$P = \frac{1}{3} \frac{mnC^2}{V}$$

Given,  $V = 1 \text{ litre} = 1000 \text{ mL} = 1000 \text{ cm}^3$ ;  $n = 10^{23}$ ;  $m = 10^{-22} \text{ g}$  and  $c = 10^5 \text{ cm s}^{-1}$

Substituting the values in the above equation,

$$P = \frac{1}{3} \frac{10^{-22} \times 10^{23} \times 10^{10}}{1000} = 3.33 \times 10^7 \text{ dyne cm}^{-2}$$

**Example 39.** Calculate the root mean square speed of an oxygen molecule at 288 K in SI units.

**Solution:**  $c = \sqrt{\frac{3RT}{M}}$

$$R = 8.314 \text{ kPa dm}^3 \text{ K}^{-1} \text{ mol}^{-1}, T = 288 \text{ K}$$

and  $M = 0.032 \text{ kg mol}^{-1}$

Substituting the values in above equation

$$c = \sqrt{\frac{3 \times 8.314 \times 288}{0.032}} = 473.79 \text{ ms}^{-1}$$

**Example 40.** Calculate the root mean square speed of hydrogen molecule at STP.

**Solution:**  $c = \sqrt{\frac{3PV}{M}}$

$$P = 1 \text{ atm} = 101.3 \text{ kPa}$$

$$V = 22.4 \text{ dm}^3$$

$$M = 2 \text{ g mol}^{-1} = 0.002 \text{ kg mol}^{-1}$$

Substituting the values,

$$c = \sqrt{\frac{3 \times 101.3 \times 22.4}{0.002}} = 1844.91 \text{ ms}^{-1}$$

**Alternative method:**

$$c = \sqrt{\frac{3RT}{M}}$$

$$R = 8.314 \text{ kPa dm}^3 \text{ K}^{-1} \text{ mol}^{-1}, T = 273 \text{ K},$$

$$M = 0.002 \text{ kg mol}^{-1}$$

Substituting the values,

$$c = \sqrt{\frac{3 \times 8.314 \times 273}{0.002}} = 1845.15 \text{ ms}^{-1}$$

**Example 41.** Oxygen at 1 atmosphere and  $0^\circ\text{C}$  has a density of  $1.4290 \text{ g L}^{-1}$ . Find the rms speed of oxygen molecule.

**Solution:**  $P = 1 \text{ atm} = 101.3 \times 10^3 \text{ Pa}$

$$d = 1.4290 \text{ g L}^{-1} = 1.4290 \text{ kg m}^{-3}$$

We know that,

$$c = \sqrt{\frac{3P}{d}} = \sqrt{\frac{3 \times 101.3 \times 10^3}{1.4290}} = 461.15 \text{ ms}^{-1}$$

**Example 42.** At what temperature will hydrogen molecules have the same root mean square speed as nitrogen molecules at  $27^\circ\text{C}$ ?

**Solution :**  $\sqrt{\frac{3RT}{M_H}} = \sqrt{\frac{3R \times 300}{M_N}}$

or  $\frac{T}{M_H} = \frac{300}{M_N}$  or  $T = \frac{300}{28} \times 2 = 21.43 \text{ K}$

**Example 43.** Calculate the root mean square, average and most probable speed of oxygen at  $27^\circ\text{C}$ .

**Solution:**  $27^\circ\text{C} = 300 \text{ K}$

$$\text{Root mean square speed} = \sqrt{\frac{3RT}{M}}$$

$$R = 8.314 \times 10^7 \text{ erg K}^{-1} \text{ mol}^{-1}; M = 32 \text{ g mol}^{-1}; T = 300 \text{ K}$$

Substituting the values,

$$= \sqrt{\frac{3 \times 8.314 \times 10^7 \times 300}{32}}$$

$$= 48356 \text{ cm/sec}$$

$$= 483.56 \text{ m/sec}$$

$$\text{Average speed} = \sqrt{\frac{8RT}{\pi M}}$$

$$= \sqrt{\frac{8 \times 8.314 \times 10^7 \times 300 \times 7}{22 \times 32}}$$

$$= 44542 \text{ cm/sec}$$

$$= 445.42 \text{ m/sec}$$

$$\text{Most probable speed} = \sqrt{\frac{2 \times R \times T}{M}}$$

$$= \sqrt{\frac{2 \times 8.314 \times 10^7 \times 300}{32}}$$

$$= 39483 \text{ cm/sec}$$

$$= 394.83 \text{ m/sec}$$

**Example 44.** Calculate the average kinetic energy per mole of  $\text{CO}_2$  gas at  $27^\circ\text{C}$  in different units.

**Solution:**  $KE = \frac{3}{2} nRT$

$$= \frac{3}{2} \times 1 \times 1.987 \times 300 = 894.15 \text{ cal}$$

$$KE = \frac{3}{2} nRT$$

$$= \frac{3}{2} \times 1 \times 8.314 \times 300 = 3741 \text{ J}$$

$$= 3.741 \times 10^{10} \text{ erg}$$

**Example 45.** A gas bulb of 1 litre capacity contains  $2.0 \times 10^{21}$  molecules of nitrogen exerting a pressure of  $7.57 \times 10^3 \text{ N m}^{-2}$ . Calculate the root mean square speed and temperature of the gas molecules. If the ratio of most probable speed to the root mean square speed is 0.82, calculate the most probable speed of these molecules at this temperature. (IIT 1993)

**Solution:** Amount of the gas =  $\frac{2.0 \times 10^{21}}{6.023 \times 10^{23}}$  mole

Given,  $V = 1 \text{ litre} = 10^{-3} \text{ m}^3$ ;  $P = 7.57 \times 10^3 \text{ N m}^{-2}$ ,  $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ .

Applying  $PV = nRT$  or  $T = \frac{PV}{nR}$

$$T = \frac{10^{-3} \times 7.57 \times 10^3}{\frac{2.0 \times 10^{21}}{6.023 \times 10^{23}} \times 8.314} = 274.2 \text{ K}$$

$$\text{rms speed} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.314 \times 274.2}{28 \times 10^{-3}}} = 494.22 \text{ ms}^{-1}$$

Most probable speed =  $0.8 \times \text{rms}$

$$= 0.8 \times 494.22 \text{ ms}^{-1} = 395.376 \text{ ms}^{-1}$$

### ILLUSTRATIONS OF OBJECTIVE QUESTIONS

16. At what temperature is the root mean square speed of  $\text{N}_2$  gas equal to that of propane gas at STP?

- (a)  $173.7^\circ\text{C}$  (b)  $173.7 \text{ K}$  (c)  $273 \text{ K}$  (d)  $-40^\circ\text{C}$

[Ans. (b)]

[Hint:  $v_{\text{rms}}(\text{N}_2) = v_{\text{rms}}(\text{C}_3\text{H}_8)$

$$\sqrt{\frac{3RT}{M}} = \sqrt{\frac{3R \cdot 273}{44}}$$

$$T = 173.7 \text{ K}$$

17. At what temperature is the kinetic energy of a gas molecule half of its value at  $327^\circ\text{C}$ ?

- (a)  $13.5^\circ\text{C}$  (b)  $150^\circ\text{C}$  (c)  $27^\circ\text{C}$  (d)  $-123^\circ\text{C}$

[Ans. (c)]

[Hint:  $KE = \frac{3}{2} RT$

$$\frac{E_1}{E_2} = \frac{\frac{3}{2} RT_1}{\frac{3}{2} RT_2}$$

$$\frac{1}{2} = \frac{600}{T_2}$$

$$T_2 = 300 \text{ K}$$

$$t = 27^\circ\text{C}$$

18. The root mean square speed of molecules of nitrogen gas is  $v$  at a certain temperature. When the temperature is doubled, the molecules dissociate into individual atoms. The new rms speed of the atom is:

- (a)  $\sqrt{2}v$  (b)  $2v$  (c)  $v$  (d)  $4v$

[Ans. (b)]

[Hint:  $v_1 = \sqrt{\frac{3RT}{M}}$

$$T_2 = 2T, M_2 = M/2$$

$$v_2 = \sqrt{\frac{3R \times 2T}{M/2}} = 2v_1$$

19. The translational kinetic energy of an ideal gas depends only on its:

- (a) pressure (b) force  
(c) temperature (d) molar mass

[Ans. (c)]

[Hint:  $KE = \frac{3}{2} RT$  : Kinetic energy depends on temperature.]

20. At what temperature is the rms speed of  $\text{H}_2$  molecules the same as that of oxygen molecules at  $1327^\circ\text{C}$ ?

- (a)  $173 \text{ K}$  (b)  $100 \text{ K}$  (c)  $400 \text{ K}$  (d)  $523 \text{ K}$

[Ans. (b)]

[Hint:  $\left( \sqrt{\frac{3RT_1}{M_1}} \right)_{\text{H}_2} = \left( \sqrt{\frac{3RT_2}{M_2}} \right)_{\text{O}_2}$

$$\sqrt{\frac{T_1}{2}} = \sqrt{\frac{1600}{32}}$$

$$T_1 = 100 \text{ K}$$

21. If the temperature of 1 mole of a gas is increased by  $50^\circ\text{C}$ , calculate the change in kinetic energy of the system. (DCE 2006)

- (a)  $62.32 \text{ J}$  (b)  $6.235 \text{ J}$  (c)  $623.5 \text{ J}$  (d)  $6235.0 \text{ J}$

[Ans. (c)]

[Hint:  $E = \frac{3}{2} RT$  (Kinetic energy of 1 mole gas)]

$$\begin{aligned} \Delta E &= \frac{3}{2} R(T + 50) - \frac{3}{2} RT \\ &= \frac{3}{2} R \times 50 = \frac{3}{2} \times 8.314 \times 50 \\ &= 623.55 \text{ J} \end{aligned}$$

22. At same temperature, calculate the ratio of average velocity of  $\text{SO}_2$  to  $\text{CH}_4$ : (DCE 2006)

- (a)  $2:3$  (b)  $3:4$  (c)  $1:2$  (d)  $6:1$

[Ans. (c)]

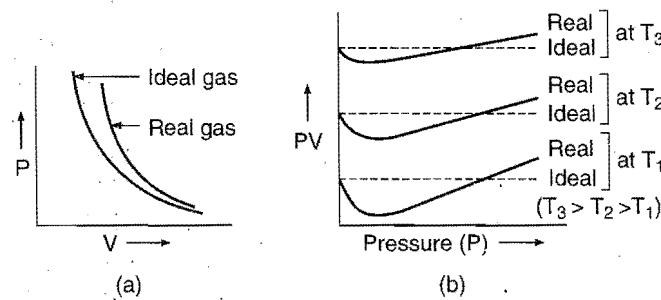
[Hint:  $v_{\text{av}} = \sqrt{\frac{8RT}{\pi m}}$

$$\begin{aligned}\frac{v_{\text{SO}_2}}{v_{\text{CH}_4}} &= \sqrt{\frac{m_{\text{CH}_4}}{m_{\text{SO}_2}}} \\ &= \sqrt{\frac{16}{64}} = \frac{1}{2}\end{aligned}$$

#### 4.9 VAN DER WAALS' EQUATION

The gas which conforms to all of the postulates of kinetic theory or which obeys Boyle's law and Charles' law rigidly for all values of temperature and pressure or which strictly follows the general gas equation ( $PV = nRT$ ) is called **ideal** or **perfect gas**. Actually no gas is ideal or perfect in nature. Under ordinary conditions, only those gases nearly behave as ideal or perfect which have very low boiling points such as nitrogen, hydrogen, etc.

At low pressure and moderately high temperature, the real gases approach ideal behaviour (see fig.).



**Fig. 4.9 (a) Ideal and real gas, (b) Ideal and real gas (real gas is approaching ideal behaviour with rise in temperature)**

It is observed that deviations from gas laws are high under high pressure and low temperature. van der Waals suggested that these deviations are due to the following two faulty assumptions in the kinetic theory of gases:

(i) Actual volume of the gas molecules is negligible as compared to the total volume of the gas.

(ii) Intermolecular attractions are not present in gases.

van der Waals pointed out that in the case of real gases, molecules do have a volume and also exert intermolecular attractions especially when the pressure is high and temperature is low. He applied two corrections:

**(a) Volume correction:** van der Waals assumed that molecules of a real gas are rigid spherical particles which possess a definite volume. Thus, the volume of a real gas, i.e., volume available for compression or movement is, therefore, actual volume minus the volume occupied by gas molecules. If  $b$  is the effective volume of the molecules per mol of the gas, the ideal volume for the gas equation is  $(V - b)$  and not  $V$ , i.e.,

corrected volume ' $V_i$ ' =  $V - b$  for one mole of the gas

and for  $n$  mole of the gas, ' $V_i$ ' =  $V - nb$ .

$b$  is termed the excluded volume which is constant and characteristic for each gas. The excluded volume ' $b$ ' is actually four times the actual volume of the gas molecules.

$$b = \left[ \frac{4}{3} \pi r^3 \right] \times 4N$$

where ' $r$ ' = radius of gas molecule

$N$  = Avogadro's number

**(b) Pressure correction:** A molecule in the interior of the gas is attracted by other molecules on all sides. These forces, thus, are not effective, as equal and opposite forces cancel each other. However, a gas molecule which is just going to strike the wall of the vessel experiences an inward pull due to unbalanced attractive forces. Therefore, it strikes the wall with less momentum and the observed pressure will be less than the ideal pressure.

$$P_{\text{ideal}} = P_{\text{obs}} + P'$$

where  $P'$  is the pressure correction.

#### Pressure Correction Depends upon Two Factors

(i) The attractive force exerted on a single molecule about to strike the wall is proportional to the number of molecules per unit volume in the bulk of the gas.

(ii) The number of molecules striking the wall which is also proportional to the number of molecules per unit volume of the gas.

Both these factors are proportional to the density of the gas. Therefore, the attractive force is proportional to the square of the density of the gas.

$$P' \propto \text{total attractive force}$$

$$\propto d^2$$

$$\propto \frac{1}{V^2}$$

or

$$P' = \frac{a}{V^2}$$

where ' $a$ ' is a constant depending upon the nature of the gas and  $V$  is the volume of 1 mole of the gas.

$$\text{Thus, corrected pressure, } P_{\text{ideal}} = P_{\text{obs}} + \frac{a}{V^2}$$

Making both the corrections, the general gas equation  $PV = RT$  may be written as:

$$\left( P + \frac{a}{V^2} \right) (V - b) = RT$$

The equation is called van der Waals' equation. van der Waals' equation for  $n$  moles of the gas is:

$$\left( P + \frac{n^2 a}{V^2} \right) (V - nb) = nRT$$

van der Waals' equation is obeyed by real gases over a wide range of temperature and pressure and hence this equation is called equation of state for the real gases. The constants ' $a$ ' and ' $b$ ' are called van der Waals' constants and they are characteristic of each gas.

### Unit of van der Waals' Constants

$a$  and  $b$  are expressed in terms of the units of  $P$  and  $V$ .

$$\text{Pressure correction } P' = \frac{n^2 a}{V^2}$$

$$a = \frac{P' V^2}{n^2} = \frac{\text{Pressure correction} \times (\text{Volume})^2}{(\text{Mole})^2}$$

Thus, if pressure and volume are expressed in atmosphere and litre respectively, the units of constant ' $a$ ' will be atmosphere litre<sup>2</sup> mol<sup>-2</sup>.

$$\text{SI unit, } 'a' = \text{N m}^4 \text{ mol}^{-2}$$

' $b$ ' is the effective volume of the gas molecules in one gram mole of the gas. Thus, the unit of ' $b$ ' is the same as for the volume, i.e., litre mol<sup>-1</sup>.

$$\text{SI unit, } 'b' = \text{m}^3 \text{ mol}^{-1}$$

**Boyle temperature:** The temperature at which real gas behaves like ideal gas and obeys the gas laws over a wide range of pressure is called Boyle temperature ' $T_b$ '. At this temperature,  $PV$  remains constant for an appreciable range of pressure

$$T_b = \frac{a}{Rb} = \frac{1}{2T_i}$$

where,  $T_i$  = inversion temperature

$a, b$  = van der Waals' constants

At Boyle temperature,  $\frac{\partial PV}{\partial P} \approx 0$  when  $P$  approaches zero.

### 4.10 CRITICAL PHENOMENON AND LIQUEFACTION OF GASES

During the early part of nineteenth century, a number of gases such as carbon dioxide, sulphur dioxide, ammonia, etc. were liquefied by subjecting the gas to low temperature and high pressure. On cooling, the kinetic energy of the gas molecules decreases. The slow moving molecules come nearer to each other due to forces of attraction and, thus, aggregate and are converted into liquid. The increase of pressure can also bring the gas molecules closer to each other and, thus, is helpful in converting a gas into liquid. The effect of temperature is rather more important than that of pressure. The essential conditions for liquefaction of gases were discovered by Andrews in 1869 as a result of his study of Pressure-Volume-Temperature ( $P-V-T$ ) relationship for carbon dioxide. It was found that above a certain temperature, it was impossible to liquefy a gas whatever the pressure was applied. The temperature below which the gas can be liquefied by the application of pressure alone is called critical temperature ( $T_c$ ). The pressure required to liquefy a gas at this temperature is called the critical pressure ( $P_c$ ). The volume occupied by one mole of the substance at the critical temperature and pressure is called critical volume ( $V_c$ ).

The results of Andrews experiments are shown in the following Figure. 4.10(a) in which the pressure is plotted against volume at various temperatures for carbon dioxide. Each pressure-volume plot is called isotherm.

Let us consider an isotherm at 13.1°C. At low pressure, carbon dioxide is entirely gaseous and is represented by the point (A) in the isotherm. On increasing pressure, volume decreases as shown by the portion AX of the isotherm, approximately in accordance with Boyle's law. At X, deviations from Boyle's law begin to appear and the volume decreases rapidly as the gas is converted into liquid. At point Y, carbon dioxide has been completely liquefied. Between X and Y, pressure remains constant and both the gas and liquid phases are in equilibrium. The pressure corresponding to the horizontal portion XY of the isotherm is the vapour pressure of the liquid at the temperature of the isotherm.

The isotherm at 21.5°C shows a similar behaviour except that liquefaction starts at higher pressure and the horizontal portion MN is shorter. As the temperature is raised, the horizontal portion

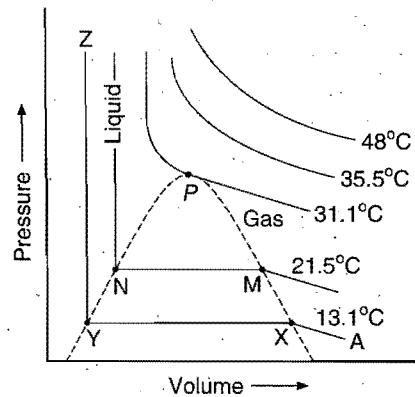


Fig. 4.10 (a) Isotherms of carbon dioxide showing critical region

of the isotherm becomes smaller and smaller until at 31.1°C at which it reduces to a point P. Point P is called **critical point**; at this point the boundary between liquid and gas phase (meniscus) disappears indicating that both the phases have identical characteristics. Above 31.1°C, there is no indication of liquefaction. The isotherm at critical temperature 31.1°C is called **critical isotherm**. The tangent at critical point P is horizontal, so that,  $\frac{dP}{dV}$  at critical point will be zero. Thus, the point 'P' is also called the **point of inflection**.

It may be concluded from this explanation that in the area to the left of the dotted line below the critical isotherm, only liquid carbon dioxide exists. To the right of the dotted line, only gaseous carbon dioxide exists. The horizontal portion, within the dotted line shows the equilibrium between gas and liquid phase.

### The van der Waals' Equation and the Critical Constants

The van der Waals' equation for 1 mole of a gas is given by:

$$\left( P + \frac{a}{V^2} \right) (V - b) = RT$$

This equation may be written as,

$$PV + \frac{a}{V} - Pb - \frac{ab}{V^2} = RT$$

$$\text{or } PV^3 + aV - PbV^2 - ab - RTV^2 = 0 \quad \dots (i)$$

Dividing above equation by 'P', we get

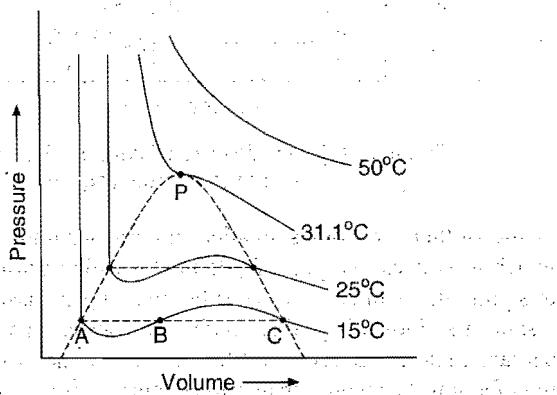
$$V^3 + \frac{aV}{P} - bV^2 - \frac{ab}{P} - \frac{RTV^2}{P} = 0$$

Arranging in descending powers of V, we get

$$V^3 - \left( b + \frac{RT}{P} \right) V^2 + \frac{aV}{P} - \frac{ab}{P} = 0 \quad \dots (i)$$

Equation (i) is a cubic equation in  $V^2$  and therefore, for any value of P and T, it will have three values of V, all of which may be real or one may be real and the other two imaginary. When pressure *versus* volume plots are constructed using equation (i) we get the curves as shown in Fig. 4.10(b).

It is evident from the Fig. 4.10 (b) that the curves at and above the critical temperature are similar to those in Fig. 4.10 (a). However, below critical temperature, the horizontal portion determining the coexistence of gas and liquid is replaced by a (~) shaped curve ABC in Fig. 4.10(b). Thus, this curve predicts that there are three values of V corresponding to the points A, B and C. At the critical point 'P', the three roots of van der Waals' equation are not only real and positive but also identical and equal to the critical value  $V_c$ . This condition may be expressed as,



**Fig. 4.10 (b) Isotherms of carbon dioxide according to van der Waals' equation**

$$V = V_c$$

$$\text{or } V - V_c = 0 \quad \dots (ii)$$

$$(V - V_c)^3 = 0$$

$$\therefore V^3 - 3V_cV^2 + 3V_c^2V - V_c^3 = 0 \quad \dots (iii)$$

At critical point, equations (i) and (ii) must be identical. Comparing and equating the coefficients of like powers of V gives:

$$3V_c = b + \frac{RT_c}{P_c} \quad \dots (iii)$$

$$3V_c^2 = \frac{a}{P_c} \quad \dots (iv)$$

$$V_c^3 = \frac{ab}{P_c} \quad \dots (v)$$

In above equations,  $T = T_c$ ,  $P = P_c$  at critical state.

Dividing equation (v) by (iv), we get,

$$\frac{V_c}{3} = b$$

i.e.,

$$V_c = 3b \quad \dots (vi)$$

Substituting the value of  $V_c$  from eq. (vi) in (v), we get

$$(3b)^3 = \frac{ab}{P_c}$$

$$\therefore P_c = \frac{a}{27b^2} \quad \dots (vii)$$

Finally, substituting the values of  $P_c$  and  $V_c$  in eq. (iii), we get

$$T_c = \frac{8a}{27Rb} \quad \dots (viii)$$

We can express the constants  $a$ ,  $b$  and  $R$  in terms of critical constants as:

$$b = \frac{V_c}{3}$$

$$a = 3P_c V_c^2$$

$$R = \frac{8P_c V_c}{3T_c}$$

$$P_c V_c = \frac{3}{8} R T_c \quad \dots (ix)$$

Equation (ix) is called equation of critical state. Critical compressibility factor of a gas may be calculated as,

$$Z_c = \frac{P_c V_c}{R T_c} = \frac{\left( \frac{a}{27b^2} \right) (3b)}{R \left( \frac{8a}{27Rb} \right)} = 0.375$$

#### Critical constants of gases

Gas	$P_c$ (atm)	$V_c$ ( $\text{cm}^3 \text{ mol}^{-1}$ )	$T_c$ (K)
He	2.3	57.8	5.3
H <sub>2</sub>	12.8	65	33.2
Ne	26.9	41.7	44.4
N <sub>2</sub>	33.6	90.1	126.1
O <sub>2</sub>	50.3	74.4	154.5
CO <sub>2</sub>	72.7	95.0	304.2
H <sub>2</sub> O	218.0	55.6	647.3
NH <sub>3</sub>	112.0	72.0	405.5
CH <sub>4</sub>	45.8	99.0	191.0
C <sub>2</sub> H <sub>6</sub>	48.2	139.0	305.5
C <sub>2</sub> H <sub>4</sub>	50.5	124.0	417.2

#### 4.10.1 EXPERIMENTAL METHODS FOR LIQUEFACTION OF GASES

Discovery of critical phenomenon by Andrews in 1869 showed that gases cannot be liquefied by the application of pressure alone; they must first be cooled below their critical temperatures and then subjected to adequate pressure to cause liquefaction.

Principles involved in liquefaction are:

(1) A gas must be at or below its critical temperature. Lower the temperature below the critical value, easier would be the liquefaction.

(2) The gas is cooled either by doing external work or by expanding against the internal forces of molecular attraction.

Low temperature for liquefaction of gases can be achieved by the following techniques:

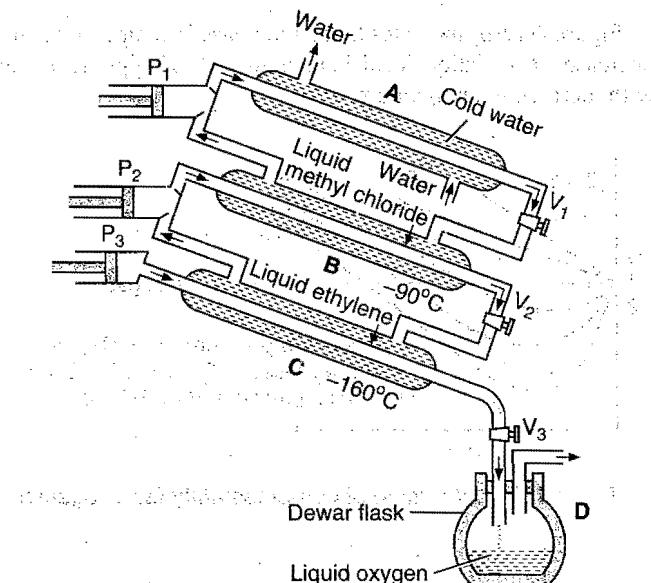
(a) Cooling by rapid evaporation of a volatile liquid.

(b) Cooling by Joule-Thomson effect.

(c) Cooling by adiabatic expansion involving mechanical work.

#### (a) Cooling by Rapid Evaporation of a Volatile Liquid

This method was first employed by Pictet and Cailletet. An easily volatile liquid is rapidly evaporated to cool and liquefy a less volatile liquid. This is the principle underlying the cascade process [Fig. 4.11(a)] for liquefaction of O<sub>2</sub>.



**Fig. 4.11 (a) Cascade process for the liquefaction of oxygen**

The apparatus consists of three compression pumps  $P_1$ ,  $P_2$  and  $P_3$  and three compression chambers  $A$ ,  $B$  and  $C$ . The compression pumps are joined in series. The pump  $P_1$  compresses methyl chloride gas which is cooled by cold water circulating in outer jacket of  $A$ . As the critical temperature of methyl chloride is 143°C, it is liquefied at room temperature. The liquid methyl chloride passes through valve  $V_1$  into the outer jacket of  $B$  which is connected to the suction side of  $P_1$ . As a result of reduced pressure, the liquid methyl chloride evaporates and the temperature in  $B$  reaches -90°C.

The inner tube of  $B$  is filled with ethylene gas which is cooled to -90°C. As the critical temperature of ethylene is 10°C, it gets liquefied and passes through valve  $V_2$  into the outer jacket of  $C$ . Ethylene liquid is allowed to evaporate under reduced pressure with the help of pump  $P_2$  resulting in a sharp fall in the

temperature of oxygen (-118°C) which is filled in the inner tube of  $C$ . Oxygen gets liquefied during the compression stroke of pumps  $P_3$  and is collected in the Dewar flask  $D$ .

#### (b) Cooling by Joule-Thomson Effect

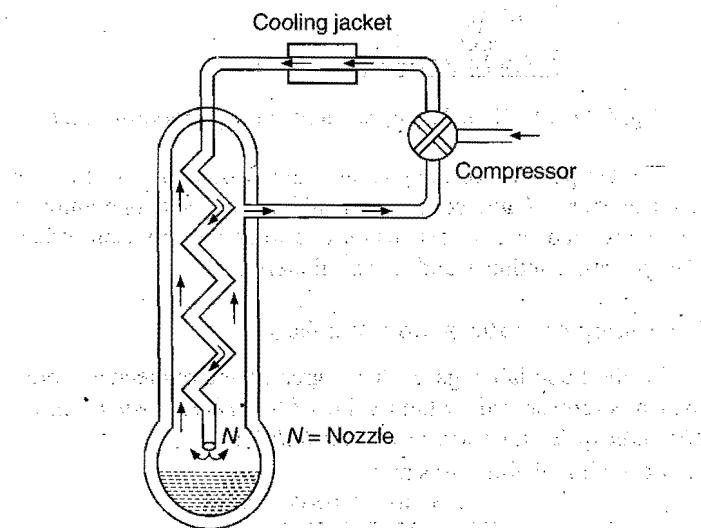
##### (Linde's process for liquefaction of air)

When a compressed gas is allowed to expand into a low pressure or vacuum under adiabatic conditions, a lowering of temperature is observed. This is known as Joule-Thomson effect. In the expansion, molecules of the gas move far apart from one another. Work is done by the gas molecules to overcome intermolecular forces. Work is done at the cost of the kinetic energy of gas molecules. Consequently a cooling effect is observed. For each gas, there is a characteristic temperature above which a gas on expansion shows a heating effect while below it the gas cools on expansion. This temperature is known as **inversion temperature** of the gas. This temperature is related to van der Waals' constant  $a$  and  $b$  by the expression:

$$T_i = \frac{2a}{Rb}$$

where,  $T_i$  is the inversion temperature of the gas.

Gases like H<sub>2</sub> and He have low inversion temperatures ( $T_{iH_2} = 193$  K and  $T_{iHe} = 33$  K) and they show heating effects in Joule-Thomson expansion under ordinary temperature. If these gases are cooled below their inversion temperatures, they also show cooling effects.



**Fig. 4.11 (b) Linde's process for liquefaction of air**

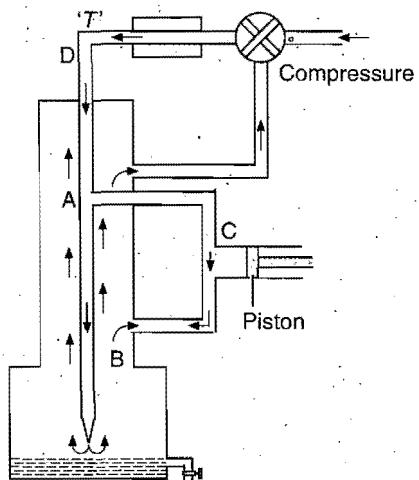
Joule-Thomson effect is the basis for liquefaction of air by Linde's process. The apparatus is shown in Fig. 4.11 (b).

Pure and dry air is compressed to a pressure of about 200 atm. Any heat produced during the compression is removed by passing the gas through a cooling jacket. Compressed air is allowed to expand suddenly through a nozzle ( $N$ ) to a large chamber, where it gets cooled and the pressure reduced to about 1 atmosphere. The cooled air is made to pass through the outer tube and is sent back to the compressor. The incoming air further cools on expansion. The process is continued until air liquefies and is collected at the bottom.

### (c) Cooling by Adiabatic Expansion Involving Mechanical Work

When a gas is allowed to expand adiabatically against a pressure, it does some external work at the cost of its kinetic energy, due to which its temperature falls. This principle is used in Claude's process for liquefaction of air. The apparatus is shown in Fig. 4.11 (c).

Pure and dry air is compressed to about 200 atmospheric pressure and then passed through the tube *T*. Compressed air divides itself into two parts at '*A*' and a portion enters through '*C*' fitted with an airtight piston. There, it expands, pushing the piston outward and performs some external work.



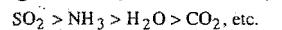
**Fig. 4.11 (c) Claude's apparatus for liquefaction of air**

The temperature of the gas thus falls. Cooled air then enters the chamber at *B* and cools the incoming air. The temperature of air is also reduced on expansion due to Joule-Thomson effect. The process continues until the air liquefies.

### Tendency of Liquefaction of a Gas

Easily liquefiable gases have greater intermolecular force which is represented by high value of '*a*'. Thus, greater will be the value of '*a*' more will be its liquefiability.

Easily liquefiable gases are:



Decreasing value of constant '*a*'  
(Decreasing tendency of liquefiability)

Above gases have higher value of '*a*' as compared to the permanent gases  $\text{O}_2$ ,  $\text{N}_2$ ,  $\text{H}_2$ , He, Ne, etc.

### Incompressibility of a Gas

van der Waals' constant '*b*' represents the excluded volume, i.e., four times the volume occupied by the gas per mole. Value of '*b*' remains constant over a wide range of temperature and pressure which implies that gas molecules are incompressible.

**Compressibility factor:** Mathematically, it may be defined as,

$$Z = \frac{PV}{nRT}$$

The extent to which a real gas departs from ideal behaviour is expressed in terms of compressibility factor.

$$Z = \frac{\text{Molar volume of real gas } (V_m)}{\text{Molar volume of ideal gas } (V_m)} = \frac{PV_m}{RT}$$

When  $Z > 1$ ,  $V_m > 22.4 \text{ L}$  at STP and when  $Z < 1$ ,  $V_m < 22.4 \text{ L}$  at STP.

(i)  $Z = 1$  for ideal gas. Deviation from the unity indicates extent of imperfection or non-ideality.

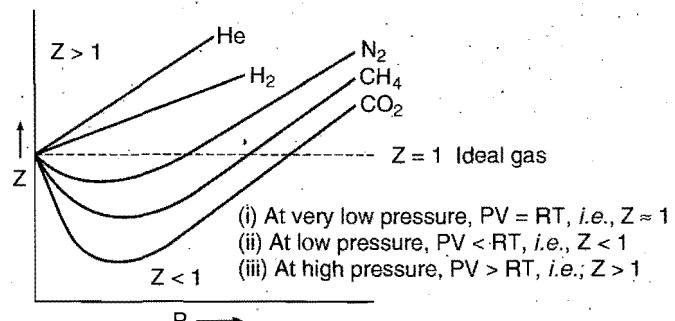
(ii) Real gases have  $Z \approx 1$  at low pressure and high temperature. In this case, the real gas behaves like ideal gas.

(iii)  $Z > 1$  shows that it is difficult to compress the gas as compared to ideal gas. It is possible at high pressure. In this case, repulsive forces dominate.

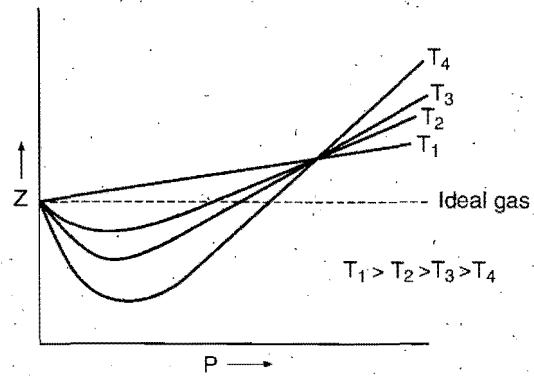
(iv)  $Z < 1$  shows that the gas is easily compressible as compared to ideal gas. It is possible at intermediate pressure. In this case, attractive forces are dominant.

### Plots of Compressibility Factor against Pressure

Figure 4.12(b) indicates that an increase in temperature shows decrease in deviation ideal behaviour, i.e.,  $Z$  approaches unity with increase in temperature.



**Fig. 4.12(a) Variation of compressibility factor against**



**Fig. 4.12(b) Variation of compressibility factor against pressure at different temperature**

**Note:** (i) In case of  $\text{H}_2$ ,  $Z > 1$  at  $273 \text{ K}$  and  $Z$  increases with the pressure. When temperature is less than  $273 \text{ K}$ ,  $\text{H}_2$  has  $Z < 1$ .

(ii) For gases other than hydrogen, at  $273 \text{ K}$  there is decrease in '*Z*' at initial stage, with increase in pressure, value of '*Z*' approaches a minimum, with increase in pressure.

(iii) In case of easily liquefiable gas like  $\text{CO}_2$ ,  $Z$  dips largely below ideal line in low pressure region, see Fig. 4.12 (a).

### Specific Heat of Gases

*Amount of heat required to raise the temperature of 1 g of a substance through  $1^\circ\text{C}$  is called its specific heat. It can be measured at constant pressure and at constant volume.*

Molar specific heat, i.e., heat required to raise 1 gram mole of a substance through  $1^\circ\text{C}$  is called heat capacity.

### Heat Capacity at Constant Volume

*It is denoted by  $C_V$ . It may be the heat supplied to one mole of a substance to increase the temperature through  $1^\circ\text{C}$  at constant volume.*

We know from kinetic theory that,

$$PV = \frac{1}{3} mnc^2 \quad \text{or} \quad \frac{1}{2} mnc^2 = \frac{3}{2} RT$$

Thus, kinetic energy  $E = \frac{3}{2} RT$

When temperature is raised through  $1^\circ\text{C}$  then the increase in kinetic energy may be given as:

$$\text{Increase in kinetic energy} = \frac{3}{2} R(T+1) - \frac{3}{2} RT = \frac{3}{2} R$$

Now,  $C_V = \frac{3}{2} R$  since at constant volume, heat supplied to raise the temperature is used up to increase the kinetic energy only.

$$C_V = \frac{3}{2} R \quad [\text{for monoatomic gases only, since monoatomic gases undergo translational motion only}]$$

$$C_V = \frac{3}{2} R + x \quad [\text{for di and polyatomic molecules; vibrational and rotational motions also contribute to the total kinetic energy}]$$

where factor 'x' varies from gas to gas and its value is zero for monoatomic gases.

### Heat Capacity at Constant Pressure

It is denoted by  $C_P$ ; it may be defined as heat supplied to 1 mole of a substance in order to increase the temperature through  $1^\circ\text{C}$  at constant pressure.

Heat supplied at constant pressure will be used in:

(i) Increasing kinetic energy, which is equal to  $\frac{3}{2} R + x$ . For monoatomic gas increase in kinetic energy is equal to  $\frac{3}{2} R$  when temperature is raised through  $1^\circ\text{C}$ .

(ii) Doing work due to volume expansion.

We know that,  $PV = RT$  for 1 mole of gas ... (i)

When temperature changes to  $(T+1)$ , then

$$P(V + \Delta V) = R(T+1) \quad \dots \text{(ii)}$$

Subtracting eq. (i) from eq. (ii), we have

$P\Delta V = R$  = Work done due to volume expansion

$$\text{Thus, } C_P = \frac{3}{2} R + R = \frac{5}{2} R \text{ for monoatomic gases}$$

$$C_P = C_V + R \quad \text{or} \quad C_P - C_V = R \quad (\text{general equation})$$

### Ratio of Molar Heat Capacity

It is denoted as  $\gamma$  and it represents atomicity of the gas.

$$\text{For monoatomic gas, } (\gamma) = \frac{C_P}{C_V} = \frac{\frac{5}{2} R}{\frac{3}{2} R} = 1.66$$

$$\text{For diatomic gas, } (\gamma) = \frac{C_P}{C_V} = \frac{\frac{7}{2} R}{\frac{5}{2} R} = 1.40$$

$$\text{For triatomic gas, } (\gamma) = \frac{C_P}{C_V} = \frac{4R}{3R} = 1.33$$

Name	$C_P$	$C_V$	$C_P + C_V$	$C_P/C_V$	Atomicity
He	5	3.01	1.99	1.661	1
$\text{N}_2$	6.95	4.96	1.99	1.4	2
$\text{O}_2$	6.82	4.83	1.99	1.4	2
$\text{CO}_2$	8.75	6.71	2.04	1.30	3
$\text{H}_2\text{S}$	8.62	6.53	2.09	1.32	3

**Example 46.** Specific heat of a monoatomic gas at constant volume is  $315 \text{ J kg}^{-1} \text{ K}^{-1}$  and at a constant pressure is  $525 \text{ J kg}^{-1} \text{ K}^{-1}$ . Calculate the molar mass of the gas.

**Solution:**  $C_P = M \times 525$  and  $C_V = M \times 315$

where,  $M$  is the molecular mass.

$$C_P - C_V = R \quad (R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1})$$

$$M \times 525 - M \times 315 = 8.314$$

$$M(525 - 315) = 8.314$$

$$M = \frac{8.314}{210} = 0.0396 \text{ kg mol}^{-1} = 39.6 \text{ g mol}^{-1}$$

**Example 47.** Calculate the pressure exerted by 16 g of methane in a 250 mL container at 300 K using van der Waals' equation. What pressure will be predicted by ideal gas equation?

$$a = 2.253 \text{ atm L}^2 \text{ mol}^{-2}, b = 0.0428 \text{ L mol}^{-1},$$

$$R = 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}$$

**Solution:** Given, 16 g  $\text{CH}_4 = \frac{16}{16} = 1 \text{ mole}$

Applying van der Waals' equation,

$$\left( P + \frac{n^2 a}{V^2} \right) (V - nb) = nRT$$

$$P = \frac{nRT}{(V - nb)} - \frac{n^2 a}{V^2}$$

Substituting  $n = 1$ ,

$$P = 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}; T = 300 \text{ K}; V = 0.250 \text{ L};$$

$$a = 2.253 \text{ atm L}^2 \text{ mol}^{-2}; b = 0.0428 \text{ L mol}^{-1}$$



**Hint:**  $\left( P + \frac{a}{V^2} \right) (V - nb) = nRT$

$$\left( P + \frac{a}{V^2} \right) (V - b) = RT \text{ for 1 mol gas}$$

At high pressure,  $\left( P + \frac{a}{V^2} \right) \approx P$

$$P(V - b) = RT$$

$$PV = RT + Pb$$

**SOME SOLVED EXAMPLES**

**Example 49.** Calculate the total pressure in a 10 litre cylinder which contains 0.4 g of helium, 1.6 g of oxygen and 1.4 g of nitrogen at 27°C. Also calculate the partial pressure of helium gas in the cylinder. Assume ideal behaviour of gases.

Given that,  $R = 0.082 \text{ litre-atm K}^{-1} \text{ mol}^{-1}$ . (IIT 1997)

**Solution:**

$$n_{\text{He}} = \frac{0.4}{4} = 0.1, n_{\text{O}_2} = \frac{1.6}{32} = 0.05, n_{\text{N}_2} = \frac{1.4}{28} = 0.05$$

$$P_{\text{He}} \times V = n_{\text{He}} \times R \times T$$

$$P_{\text{He}} \times 10 = 0.1 \times 0.0821 \times 300$$

$$P_{\text{He}} = 0.2463 \text{ atm}$$

$$P \times V = (n_{\text{He}} + n_{\text{O}_2} + n_{\text{N}_2}) RT$$

$$P \times 10 = (0.1 + 0.05 + 0.05) \times 0.0821 \times 300$$

$$P = 0.4926 \text{ atm}$$

**Example 50.** An evacuated glass vessel weighs 50.0 g when empty, 148.0 g when filled with a liquid of density 0.98 g/mL<sup>-1</sup> and 50.5 g when filled with an ideal gas at 760 mm Hg at 300 K. Determine the molecular weight of the gas. (IIT 1998)

**Solution:** Mass of liquid = 148 - 50 = 98 g

$$\text{Volume of liquid} = \frac{\text{mass}}{\text{density}} = \frac{98}{0.98} = 100 \text{ mL}$$

Volume of vessel = Volume of liquid

Mass of gas = 50.5 - 50 = 0.5 g

On applying ideal gas equation, we have,

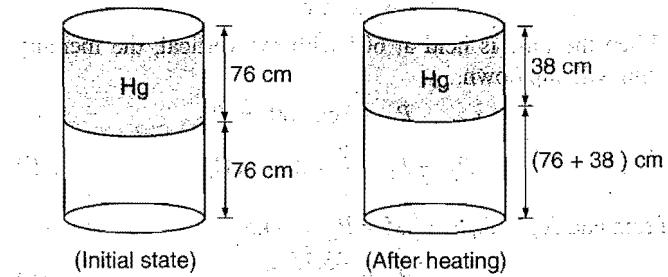
$$PV = \frac{w}{m} RT$$

$$\frac{760}{760} \times \frac{100}{1000} = \frac{0.5}{m} \times 0.0821 \times 300$$

$$m = 123$$

**Example 51.** A vertical hollow cylinder of height 1.52 m is fitted with a movable piston of negligible mass and thickness. The lower half of the cylinder contains an ideal gas and the upper half is filled with mercury. The cylinder is initially at 300 K. When the temperature is raised half of the mercury comes out of the cylinder. Find the temperature assuming the thermal expansion of mercury to be negligible.

**Solution:**



At initial stage:

$$\begin{aligned} \text{Pressure of gas} &= \text{Pressure of Hg} + \text{Pressure of atmospheric air} \\ &= 76 + 76 = 152 \text{ cm} \\ T &= 300 \text{ K} \end{aligned}$$

$$V = V_1 / 2, \text{ where } V_1 \text{ is volume of cylinder.}$$

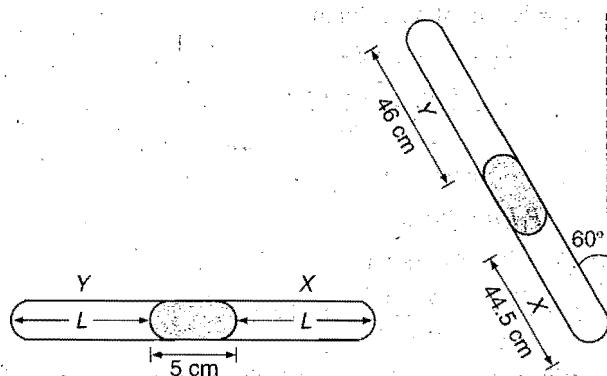
At final stage after heating:

$$\begin{aligned} \text{Pressure of gas} &= \text{Pressure of Hg} + \text{Pressure of atmospheric air} \\ &= 38 + 76 = 114 \text{ cm} \\ V &= \frac{3V_1}{4}, T = ? \end{aligned}$$

Applying gas equation, we have

$$\begin{aligned} \frac{152 \times V_1}{2 \times 300} &= \frac{114 \times (3V_1/4)}{T} \\ T &= \frac{114 \times 3 \times 2 \times 300}{4 \times 152} \\ &= 337.5 \text{ K} \end{aligned}$$

**Example 52.** A thin tube of uniform cross-section is sealed at both ends. It lies horizontally, the middle 5 cm containing Hg and the two equal ends containing air at the same pressure  $P_0$ . When the tube is held at an angle 60° with the vertical, the lengths of the air column above and below the mercury are 46 and 44.5 cm respectively. Calculate pressure  $P_0$  in cm of Hg. (The temperature of the system is kept at 30°C).



**Solution:** At horizontal position, let the length of air column in tube be  $L$  cm.

$$2L + 5 = 46 + 5 + 44.5 \text{ cm}$$

$$L = 45.25 \text{ cm}$$

When the tube is held at  $60^\circ$  with the vertical, the mercury column will slip down.

$$P_Y + 5 \cos 60^\circ = P_X$$

$$P_X - P_Y = \frac{5}{2} = 2.5 \text{ cm Hg} \quad \dots (\text{i})$$

$$\text{From end } X, \quad P_0 \times 45.25 = P_X \times 44.5$$

$$P_X = \frac{45.25}{44.5} P_0 \quad \dots (\text{ii})$$

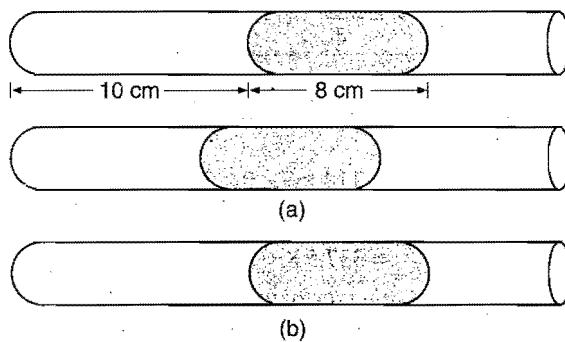
$$\text{From end } Y, \quad P_0 \times 45.25 = P_Y \times 46$$

$$P_Y = \frac{45.25}{46} P_0 \quad \dots (\text{iii})$$

Substituting the values of  $P_X$  and  $P_Y$  in equation (i) we get

$$P_0 = 75.4$$

**Example 53.** A 10 cm column of air is trapped by a column of Hg, 8 cm long, in a capillary tube horizontally fixed as shown below, at 1 atm pressure. Calculate the length of air column when the tube is fixed at the same temperature (a) vertically with open end up (b) vertically with open end down (c) at  $45^\circ$  with the horizontal with open end up.



$$\text{Solution: (a)} \quad P_1 V_1 = P_2 V_2$$

$$\text{or} \quad P_1 l_1 a = P_2 l_2 a$$

where,  $a$  = area of cross section of tube

$l_1, l_2$  = length of air column

$$P_2 = 76 + 8 = 84 \text{ cm}$$

$$l_2 = \frac{P_1 l_1}{P_2} = \frac{76 \times 10}{84}$$

$$= 9.04 \text{ cm}$$

$$P_1 l_1 a = P_2 l_2 a$$

$$(b) \quad P_2 = 76 - 8 = 68 \text{ cm}$$

$$\therefore l_2 = \frac{P_1 l_1}{P_2} = \frac{76 \times 10}{68} = 11.17 \text{ cm}$$

(c) When the tube is held at  $45^\circ$  with open end up, the weight of Hg is borne partially by the gas and partially by the Hg. Vertical height of Hg is a measure of additional pressure on gas, i.e.,

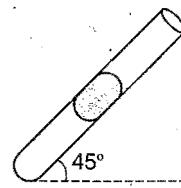
$$l = \frac{8}{\sqrt{2}}$$

$$\text{Also} \quad P_2 l_2 a = P_1 l_1 a$$

$$l_2 = \frac{P_1 l_1}{P_2}$$

$$= \frac{76 \times 10}{84} = 9.3 \text{ cm}$$

(c)



**Example 54.** The stop cock connecting two bulbs of volume 5 litre and 10 litre containing an ideal gas at 9 atm and 6 atm respectively, is opened. What is the final pressure in the two bulbs if the temperature remains the same?

$$\text{Solution:} \quad P_1 V_1 + P_2 V_2 = P_R (V_1 + V_2)$$

$$9 \times 5 + 6 \times 10 = P_R (15)$$

$$P_R = 7 \text{ atm}$$

where,  $P_R$  = resultant pressure after mixing.

**Example 55.** At what temperature is the average velocity of  $O_2$  molecule equal to the root mean square velocity at  $27^\circ C$ ?

(CBSE PMT 2009/5)

**Solution:**

$$v_{av} = v_{rms}$$

$$\sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{3RT}{M}}$$

$$\frac{8RT}{\pi M} = \frac{3R \times 300}{M}$$

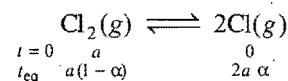
$$T = 353.57 \text{ K}$$

$$t = 80.57^\circ C$$

**Example 56.** The composition of the equilibrium mixture for the equilibrium  $Cl_2 \rightleftharpoons 2Cl$  at  $1400 \text{ K}$  may be determined by the rate of diffusion of mixture through a pin hole. It is found that at  $1400 \text{ K}$ , the mixture diffuses 1.16 times as fast as krypton diffuses under the same conditions. Find the degree of dissociation of  $Cl_2$  equilibrium.

(IITJEE 1995)

**Solution:** Equilibrium of dissociation of  $Cl_2$  may be represented as:



$$\text{Total moles} = a(1-\alpha) + 2a\alpha = a(1+\alpha)$$

$$M_{\text{mix}} = \frac{aM_{Cl_2}}{a(1+\alpha)} = \frac{M_{Cl_2}}{(1+\alpha)}$$

$$\frac{R_{\text{mix}}}{R_{Kr}} = \sqrt{\frac{M_{Kr}}{M_{\text{mix}}}}$$

$$1.16 = \frac{84(1+\alpha)}{M_{Cl_2}}$$

$$\frac{(1.16)^2 \times 71}{84} - 1 = \alpha; \quad \alpha = 0.1374$$

**Example 57.** A gaseous mixture of helium and oxygen is found to have a density of  $0.518 \text{ g dm}^{-3}$  at  $25^\circ\text{C}$  and 720 torr. What is the per cent by mass of helium in this mixture?

**Solution:** We know that,  $Pm = dRT$

$$\frac{720}{760} \times m = 0.518 \times 0.0821 \times 298$$

$$m = 13.37 \text{ g/mol}$$

Let mole fraction of He in mixture be  $\alpha$ .

$$x_{\text{He}} = \alpha, x_{\text{O}_2} = (1 - \alpha)$$

$$\text{Average mw} = \alpha \times M_{\text{He}} + (1 - \alpha)M_{\text{O}_2}$$

$$13.37 = \alpha \times 4 + (1 - \alpha)32$$

$$\alpha = 0.666$$

$$\% \text{ by mass of He} = 0.666 \times \frac{4}{0.666 \times 4 + 0.334 \times 32} \times 100$$

$$= 19.95\%$$

**Example 58.** Find the temperature at which 3 moles of  $\text{SO}_2$  will occupy a volume of 10 litre at a pressure of 15 atm.

$$a = 6.71 \text{ atm litre}^2 \text{ mol}^{-2}; b = 0.0564 \text{ litre mol}^{-1}$$

$$\text{Solution: } \left( P + \frac{an^2}{V^2} \right) (V - nb) = nRT$$

$$\left( 15 + \frac{6.71 \times 9}{100} \right) (10 - 3 \times 0.0564) = 3 \times 0.082 \times T$$

$$T = 624 \text{ K}$$

**Example 59.** van der Waals' constant 'b' of Ar is  $3.22 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$ . Calculate the molecular diameter of Ar.

**Solution:** We know that,

$$b = 4 \times \text{volume occupied by the molecules in one mole of a gas}$$

$$= 4 \times N_0 \times \left( \frac{4}{3} \pi r^3 \right)$$

$$3.22 \times 10^{-5} = 4 \times 6.02 \times 10^{23} \times \frac{4}{3} \times \frac{22}{7} \times r^3$$

$$\text{or } r = \left( \frac{3.22 \times 10^{-5} \times 3 \times 7}{4 \times 6.02 \times 10^{23} \times 4 \times 22} \right)^{1/3}$$

$$= 0.1472 \times 10^{-9} \text{ m}$$

$$\therefore \text{Diameter} = 2r = 2 \times 0.1472 \times 10^{-9}$$

$$= 0.2944 \times 10^{-9} \text{ m}$$

**Example 60.** The compression factor (compressibility factor) for 1 mole of a van der Waals' gas at  $0^\circ\text{C}$  and 100 atmospheric pressure is found to be 0.5. Assuming that the volume of a gas molecule is negligible, calculate the van der Waals' constant 'a'.

(IIT 2001)

**Solution:** We know that,

$$Z = \frac{PV}{RT}$$

$$0.5 = \frac{100 \times V}{0.0821 \times 273}$$

$$V = 0.112 \text{ litre}$$

According to van der Waals' equation,

$$\left( P + \frac{a}{V^2} \right) (V - b) = RT \quad \text{for 1 mole}$$

$$\left[ 100 + \frac{a}{(0.112)^2} \right] [0.112 - 0] = 0.0821 \times 273$$

On solving, we get  $a = 1.253 \text{ L}^2 \text{ mol}^{-2} \text{ atm}$

**Example 61.** The density of the vapours of a substance at 1 atm pressure and  $500 \text{ K}$  is  $0.36 \text{ kg m}^{-3}$ . The vapours effuse through a small hole at a rate of 1.33 times faster than oxygen under the same conditions:

(a) Determine: (i) molecular weight, (ii) molar volume, (iii) compressibility factor ( $Z$ ) of the vapours, (iv) Which forces among gas molecules are dominating, the attractive or the repulsive?

(b) If the vapours behave ideally at  $1000 \text{ K}$ , determine the average translational kinetic energy of a molecule. (IIT 2002)

$$\text{Solution: (a) (i)} \quad \frac{r_{\text{vapour}}}{r_{\text{O}_2}} = \sqrt{\frac{M_{\text{O}_2}}{M_{\text{vapour}}}}$$

$$1.33 = \sqrt{\frac{32}{M_{\text{vapour}}}}$$

$$M_{\text{vapour}} = 18.1$$

$$\text{(ii) Molar volume} = \frac{\text{Molar mass}}{\text{Density}}$$

$$= \frac{18.1}{0.36} = 50.25 \times 10^{-3} \text{ m}^{-3}$$

$$\text{(iii) Compressibility factor, } Z = \frac{PV}{RT} = \frac{101325 \times 50.25 \times 10^{-3}}{8.314 \times 500}$$

$$= 1.225$$

(iv)  $Z > 1$  shows that repulsive forces are dominant.

(b) Translational KE per molecule

$$= \frac{3}{2} \times \frac{R}{N} \times T$$

$$= \frac{3}{2} \times \frac{8.314}{6.023 \times 10^{23}} \times 1000$$

$$= 2.07 \times 10^{-20} \text{ J}$$

**Example 62.** The ratio of rate of diffusion of helium and methane under identical conditions of pressure and temperature will be:

[IIT (S) 2005]

- (a) 4      (b) 2      (c) 1      (d) 0.5

$$\text{Solution: } \frac{r_{\text{CH}_4}}{r_{\text{He}}} = \sqrt{\frac{m_{\text{He}}}{m_{\text{CH}_4}}} = \sqrt{\frac{4}{16}} = \frac{1}{2}$$

$$r_{\text{He}} = 2r_{\text{CH}_4}$$

## SECTION 2 : LIQUID STATE

### 4.11 THE LIQUID STATE

Liquid state is intermediate between gaseous and solid states. The liquids possess fluidity like gases but incompressibility like solids.

The behaviour of liquids explained above gives some characteristic properties to the liquids such as definite volume but no definite shape, incompressibility, diffusion, fluidity (or viscosity), evaporation (or vapour pressure), surface tension, etc.

Properties of liquids can be explained on the basis of kinetic molecular theory which has the following postulates:

- (i) A liquid is made up of molecules; atoms in rare cases, e.g., Hg (mercury).
- (ii) The molecules of the liquid are quite close together.
- (iii) The intermolecular forces of attraction in a liquid are quite large.
- (iv) The molecules of liquids are in a state of constant rapid motion.
- (v) The average kinetic energy of the molecules of a liquid is directly proportional to their absolute temperature.

A liquid state is regarded as a condensed gas or a molten solid. Liquid state, however, has much more in common with solid state than with gaseous state. The following general characteristics are exhibited by liquids:

#### (i) Shape

Liquids have no shape of their own but assume the shape of the container in which they are kept. No doubt, liquids are mobile but they do not expand like gases as to fill up all the space offered to them but remain confined to the lower part of the container.

#### (ii) Volume

Liquids have definite volume as the molecules of a liquid are closely packed and the cohesive forces are strong. The molecules are not quite free to occupy any space.

#### (iii) Density

As the molecules in liquids are closely packed, the densities of liquids are much higher than in gaseous state. For example, density of water at 100°C and 1 atmospheric pressure is 0.958 g mL<sup>-1</sup> while that of water vapour under similar conditions as calculated from ideal gas law ( $d = \frac{MP}{RT}$ ) is 0.000588 g mL<sup>-1</sup>.

#### (iv) Compressibility

The molecules in a liquid are held in such close contact by their mutual attractive forces (cohesive forces) that the volume of any liquid decreases very little with increased pressure. Thus, liquids are relatively incompressible compared to gases.

#### (v) Diffusion

When two miscible liquids are put together, there is slow mixing as the molecules of one liquid move into the other liquid. As the space available for movement of molecules in liquids is

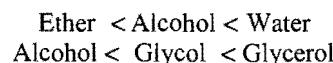
much less and their velocities are small, liquids diffuse slowly in comparison to gases.

#### (vi) Evaporation

The process of change of liquid into vapour state on standing is termed **evaporation**. Evaporation may be explained in terms of motion of molecules. At any given temperature, all the molecules do not possess the same kinetic energy (average kinetic energy is, however, same). Some molecules move slowly, some at intermediate rates and some move very fast. A rapidly moving molecule near the surface of the liquid may possess sufficient kinetic energy to overcome the attraction of its neighbours and escape. Evaporation is accompanied by cooling as average kinetic energy of remaining molecules decreases.

Evaporation depends on the following factors:

**(a) Nature of the liquid:** The evaporation depends on the strength of intermolecular forces (cohesive forces). The liquids having low intermolecular forces evaporate faster in comparison to the liquids having high intermolecular forces. For example, ether evaporates more quickly than alcohol, and alcohol evaporates more quickly than water, as the intermolecular forces in these liquids are in the order:



Increasing extent of hydrogen bonding →

**(b) Surface area:** Evaporation is a surface phenomenon. Larger the surface area, greater is the opportunity of the molecules to escape. Thus, rate of evaporation increases with increase of surface area.

$$\text{Rate of evaporation} \propto \text{Surface area}$$

**(c) Temperature:** Rate of evaporation increases with the increase of temperature as the kinetic energy of the molecules increases with the rise of temperature.

$$\text{Rate of evaporation} \propto \text{Temperature}$$

**(d) Flow of air current over the surface:** Flow of air helps the molecules to go away from the surface of liquid and, therefore, increases the evaporation.

#### (vii) Heat of vaporisation

The quantity of heat required to evaporate a unit mass of a given liquid at constant temperature is known as heat of vaporisation or heat of evaporation. The heat of vaporisation depends on the strength of the intermolecular forces within the liquid. The value of heat of vaporisation generally decreases with increase in temperature. It becomes zero at the critical temperature. When the vapour is condensed into a liquid, heat is evolved. This is called **heat of condensation**. It is numerically equal to the heat of vaporisation at the same temperature.

#### (viii) Vapour pressure

When the space above the liquid is closed, the molecules cannot escape into open but strike the walls of the container, rebound and may strike the surface of the liquid, where they are

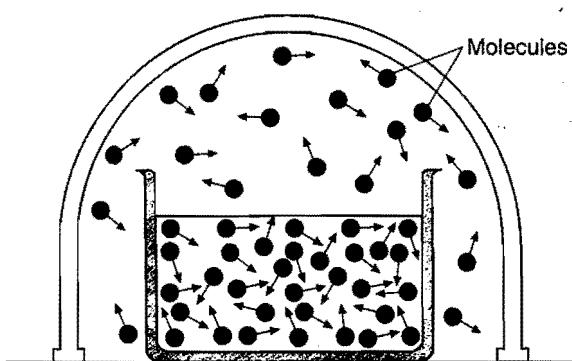


Fig. 4.13 (a) Evaporation in a closed vessel

trapped. The return of the molecules from the vapour state to the liquid state is known as **condensation**. As evaporation proceeds, the number of molecules in the vapour state increases and, in turn, the rate of condensation increases.

The rate of condensation soon becomes equal to the rate of the evaporation, i.e., the vapour in the closed container is in equilibrium with the liquid.

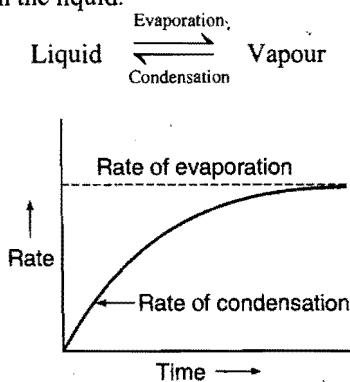


Fig. 4.13 (b)

At equilibrium, the concentration of molecules in the vapour phase remains unchanged. The pressure exerted by the vapour in equilibrium with liquid, at a given temperature, is called the **vapour pressure**. Mathematically, it is given by the gas equation:

$$P = \frac{n}{V} RT = CRT$$

where,  $C$  is the concentration of vapour, in mol/litre.

In closed vessel,

$$\text{Rate of evaporation} \propto e^{-E/RT}$$
 (Boltzmann factor)

Thus, rate of evaporation remains constant at constant temperature.

Since, the rate of evaporation increases and rate of condensation decreases with increasing temperature, vapour pressure of liquids always increases as temperature increases. At any given temperature, the vapour pressures of different liquids are different because their cohesive forces are different. Easily vaporised liquids are called **volatile liquids** and they have relatively high vapour pressures. Vapour pressure values (in mm

**Note : Vapour and gas:** A gas can be liquefied only below critical temperature, by applying pressure. There is no characteristic critical temperature for vapours.

of Hg) for water, alcohol and ether at different temperatures are given in the following table:

Substance	Temperatures				
	0°C	20°C	40°C	80°C	100°C
Water	4.6	17.5	55.0	355.5	760.3
Ethyl alcohol	12.2	43.9	135.3	812.6	1693.3
Diethyl ether	185.3	442.2	921.1	2993.6	4859.4

It is observed that non-polar or less polar liquids such as diethyl ether and ethyl alcohol possess fairly high vapour pressures on account of weak intermolecular forces (cohesive forces) whereas polar molecules such as water which have stronger intermolecular forces possess relatively lower vapour pressures.

The simplest method for measuring vapour pressure is the **barometric method**. It consists of two barometer tubes as shown in Fig. 4.14. A small quantity of the liquid is introduced into one of the tubes. It changes into vapour and rises into vacuum above

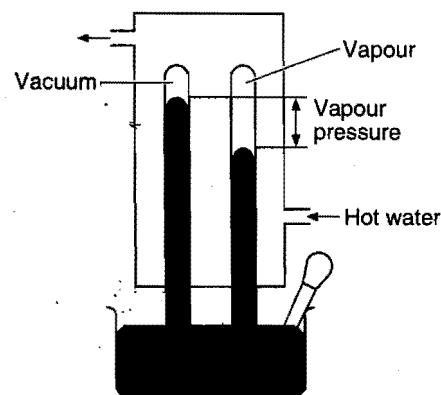


Fig. 4.14 The barometric method for measurement of vapour pressure

the mercury. Some more of the liquid is introduced and the process is continued till a small amount of the liquid is visible on the surface of mercury. The difference in the levels of mercury in the two tubes is noted and this measures the vapour pressure of the liquid at atmospheric temperature. The measurement can also be made at any desired temperature by surrounding the tubes with a jacket maintained at that temperature.

The vapour pressure of a given liquid at two different temperatures can be compared with the help of **Clausius-Clapeyron equation**.

$$\log \frac{P_2}{P_1} = \frac{\Delta H}{2.303R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

where,  $\Delta H$  is the latent heat of vaporisation and  $R$  is the molar gas constant.

The actual form of Clausius-Clapeyron equation is:

$$\log_{10} P = \frac{-\Delta H_{\text{vap}}}{2.303RT} + A$$

When  $\Delta H_{\text{vap}}$  = Latent heat of vaporisation and 'A' is constant. A graph between  $\log_{10} P$  and  $\frac{1}{T}$  will be a straight line with negative slope.

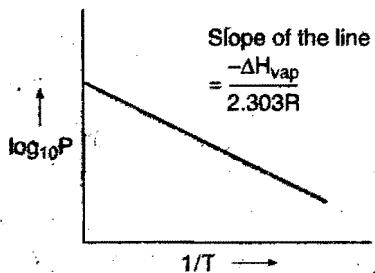


Fig. 4.15 Variation of vapour pressure with temperature

#### (ix) Boiling point

The temperature at which the vapour pressure of the liquid becomes equal to the atmospheric pressure is called the **boiling point** of the liquid. When a liquid is heated under a given applied pressure, bubbles of vapour begin to form below the surface of the liquid. They rise to the surface and burst releasing the vapour into the air. This process is called **boiling**. The normal boiling point is the temperature at which the vapour pressure of a liquid is equal to exactly one standard atmospheric pressure (760 mm of Hg). Fig. 4.16 shows that normal boiling points of diethyl ether, ethyl alcohol and water are 34.6°C, 78.5°C and 100°C respectively.

The temperature of the boiling liquid remains constant until all the liquid has been vaporised. Heat must be added to the boiling liquid to maintain the temperature because in the boiling process, the high energy molecules are lost by the liquid. The higher rate at which heat is added to the boiling liquid, the faster it boils.

The boiling point of a liquid changes with the change in external pressure. A liquid may boil at temperature higher than normal under external pressure greater than one atmosphere; conversely, the boiling point of a liquid may be lowered than normal below one atmosphere. Thus, at high altitudes where the atmospheric pressure is less than 760 mm, water boils at temperature below its normal boiling point of 100°C. Food cooks more slowly at higher altitudes because the temperature of boiling water is lower than it would be nearer the sea level. The temperature of boiling water in a pressure cooker is higher than the normal, thus making it possible to cook foods faster than in open vessels.

If a liquid decomposes when heated, it can be made to boil at lower temperature by reducing the pressure. This is the principle of vacuum distillation. Unwanted water is removed from many food products by boiling it away under reduced pressure.

Boiling and evaporation are similar processes (conversion of liquid into vapour) but differ in the following respects:

(a) Evaporation takes place spontaneously at all temperatures but boiling occurs only at a particular temperature at which the vapour pressure is equal to the atmospheric pressure.

(b) Evaporation is a surface phenomenon. It occurs only at the surface of the liquid whereas boiling involves formation of bubbles below the surface of the liquid.

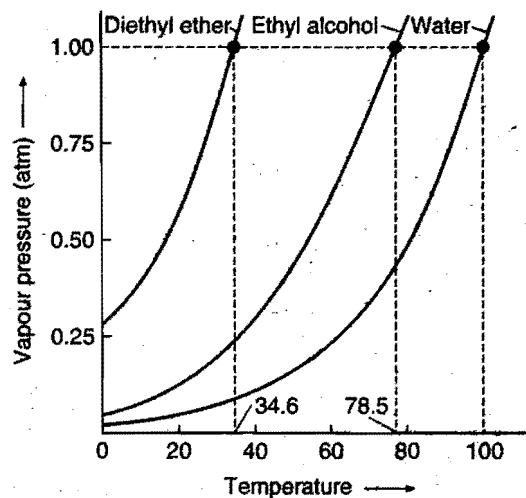


Fig. 4.16 Vapour pressure curves for diethyl ether, ethyl alcohol and water

(c) In vaporisation, the vapour molecules diffuse from the liquid into the atmosphere but in boiling, molecules escape with sufficient pressure into the space over the surface of liquid.

#### (x) Freezing point

When a liquid is cooled, the kinetic energy of the molecules goes on decreasing. A stage comes when the intermolecular forces become stronger and the translational motion is reduced to minimum. At this stage, the formation of solid begins and the liquid is seen to freeze out. The point (temperature) at which the vapour pressure of solid and liquid forms of a substance become equal is termed as **freezing point**.

**Normal freezing point** of a liquid is the temperature at which its liquid and solid forms are in equilibrium with each other under a pressure of one atmosphere. The freezing point of a liquid is the same as the melting point of its solid form. At the freezing point the temperature of the solid-liquid system remains constant until all the liquid is frozen. The amount of heat that must be removed to freeze a unit mass of the liquid at the freezing point is called the **heat of fusion**.

The freezing point of a liquid is affected by the change of external pressure. With increased external pressure, the freezing point of some liquids rises while of others falls.

#### (xi) Surface tension

It is the property of liquids caused by the intermolecular attractive forces. A molecule within the bulk of the liquid is attracted equally in all the directions by the neighbouring molecules. The resultant force on any one molecule in the centre of the liquid is, therefore, zero. However, the molecules on the surface of the liquid are attracted only inward and sideways. This unbalanced molecular attraction pulls some of the molecules into the bulk of the liquid, i.e., are pulled inward and the surface area is minimized. **Surface tension is a measure of this inward force on the surface of the liquid.** It acts downwards perpendicular to the plane of the surface. The unit of surface tension is dyne  $\text{cm}^{-1}$  or Newton metre  $^{-1}$  ( $\text{N m}^{-1}$ ). It is a scalar quantity. Surface

tension is, thus, defined as the force acting on unit length of a line imagined to be drawn tangentially anywhere on the free surface of a liquid at rest. It acts at right angles on both sides of the line and along the tangent to the liquid surface. Surface tension depends on the area, not on the length, like elastic properties.

As the intermolecular forces of attraction decrease with the rise of temperature, the surface tension of a liquid, thus, decreases with increase in temperature. Similarly, addition of chemicals to a liquid reduces its surface tension. For example, addition of chemicals like soaps, detergents, alcohol, camphor, etc., lowers the surface tension of water.

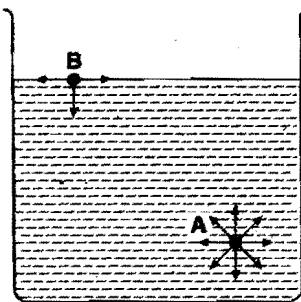


Fig. 4.17 (a) Molecules at the surface are under unequal tension

Many common phenomena can be explained with the help of surface tension. Some are described here:

(a) **Small droplets are spherical in shape:** The surface tension acting on the surface of the liquid tries to minimise the surface area of a given mass of a liquid. It is known that for a given volume, a sphere has the minimum surface area. On account of this, drops of liquids acquire a spherical shape.

(b) **Insects can walk on the surface of water:** Many insects can walk on the surface of water without drowning. This is due to the existence of surface tension. The surface tension makes the water surface to behave like an elastic membrane and prevents the insects from drowning.

(c) **Cleaning action of soap and detergents:** Soap and detergent solutions due to their lower surface tensions penetrate into the fibre and surround the greasy substances and wash them away.

(d) **Capillary action:** The tendency of a liquid to rise into narrow pores and tiny openings is called capillary action. The liquids rise in the capillary tubes due to the surface tension. The force of adhesion between the molecules of water and the molecules of glass of the capillary tube is greater than the force of cohesion between water molecules. Due to this, surface of water in a glass capillary tube curves upwards in convex shape and then the force of surface tension of water pulls the water up into the tube. The water rises into a capillary tube to such a height that the weight of resulting water column is just balanced by the force of surface tension.

The rise of oil in a lamp wick and flow of water from the roots of a tree to upper parts are also the examples of capillary action.

**Note:** At the critical temperature, surface tension of liquid becomes zero (where the meniscus between the liquid and the vapour disappears). Surface tension is scalar quantity.

In general, the liquids which wet the material show capillary rise. Those liquids which do not wet the material of a capillary always show depression, e.g., glycerine, honey, mercury, etc.

When a liquid rises in a column, its upper surface becomes concave and when the liquid goes down in a capillary, its upper surface becomes convex.

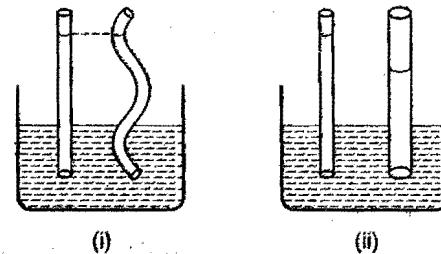


Fig. 4.17 (b) Effect of shape and radius on capillary rise

(i) Height of liquid in the column of capillary is independent of shape of capillary if its radius is same.

(ii) Thinner is the capillary, greater is the height of liquid in the column.

(e) **Surface energy:** The work in erg required to be done to increase or extend surface area by 1 sq. cm is called surface energy. The units of surface energy are, therefore, erg per sq. cm (or joule per sq. metre, i.e.,  $J m^{-2}$  in SI system). Surface tension of liquid is numerically equal to the surface energy.

Surface energy,

$$\gamma = \text{Work done to increase the surface area by one unit}$$

$$= \frac{\text{Work}}{\text{Change in area}}$$

$$= \frac{\text{force} \times \text{displacement in the direction of force}}{\text{area}}$$

$$= \frac{\text{Force}}{\text{Length}}$$

The unit of surface tension is therefore  $\text{dyne cm}^{-1}$  (force per unit length).

**Measurement of surface tension:** The surface tension of a liquid is measured by the drop count method using a stalagmometer.

Let  $\gamma_1$  and  $d_1$  be the surface tension and density of water and  $\gamma_2$  and  $d_2$  be surface tension and density of the liquid whose surface tension is to be determined. Using a stalagmometer the number of drops formed by the same volume of water and liquid is determined.

$$\frac{\gamma_1}{\gamma_2} = \frac{n_1 d_2}{n_2 d_1}$$

Using the above relation, the surface tension of the liquid,  $\gamma_2$ , can be calculated.

Note: At the critical temperature, surface tension of liquid becomes zero (where the meniscus between the liquid and the vapour disappears).

Surface tension of the liquid can also be measured by capillary rise method.

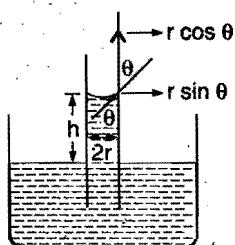


Fig. 4.18 Capillary rise

When liquid rises in a capillary, upward force due to surface tension is balanced by gravitational force.

$$2\pi r \gamma \cos \theta = mg$$

where,  $m$  = mass of liquid in column  
 $r$  = radius of capillary  
 $h$  = capillary rise  
 $g$  = gravitational force

Mass of liquid in column ( $m$ ) =  $V \times \rho$

$$= \pi r^2 h \times \rho$$

$$\therefore 2\pi r \gamma \cos \theta = \pi r^2 h \rho g$$

$$\gamma = \frac{r \rho g}{2 \cos \theta} \quad (\rho = \text{density of liquid})$$

If angle of contact between glass and liquid is zero, i.e.,  $\cos \theta = 1$ , then

$$\gamma = \frac{r \rho g}{2}$$

**Effect of temperature on surface tension :** Surface tension decreases with rise in temperature because the intermolecular force also decreases with rise in temperature. The decrease in surface tension with rise in temperature continues till critical temperature at which the surface tension of liquid becomes zero, i.e., meniscus between liquid and vapour disappears.

According to Eötvos equation,

$$\gamma = \left( \frac{M}{\rho} \right)^{2/3} = K (t_c - t)$$

∴ As  $t$  increases,  $\gamma$  decreases linearly, when  $t = t_c$ ,  $\gamma = 0$ , here  $t_c$  is the critical temperature.

### (xii) Viscosity

All liquids have a characteristic property of flow. Some liquids like water, alcohol, ether, etc., flow quickly while glycerine, castor oil, molasses, etc., flow very slowly. The property of the liquids which determines their resistance to flow, is called viscosity.

When a liquid flows through a pipe, all parts of it do not move at the same rate. The thin layer in immediate contact with the wall of the pipe is almost stationary. The velocity of flow of each successive layer of liquid increases progressively as we proceed inward towards the centre. At the centre, the flow becomes fastest. Each layer of liquid moving with greater velocity over the

one having lower velocity will experience a retarding effect due to the internal friction between the two layers. This internal friction or resistance is called viscosity.

Imagine a liquid to be made up of a large number of thin cylindrical coaxial layers.

It has been found that force of friction ' $f$ ' between two cylindrical layers each having area ' $A$ ' sq. cm separated by a distance ' $x$ ' cm and having a velocity difference  $v$  cm/sec is given by:

$$f \propto A \frac{v}{x}$$

$$f = \eta A \frac{v}{x}$$

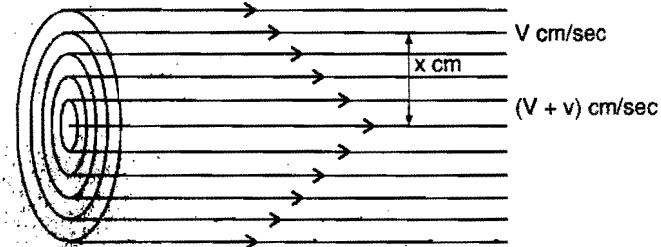


Fig. 4.19

Here,  $\eta$  is a constant known as coefficient of viscosity. If  $x = 1$  cm,  $A = 1 \text{ cm}^2$  and  $v = 1 \text{ cm/sec.}$ , then  $f = \eta$ .

Thus, coefficient of viscosity can be defined as the force per unit area needed to maintain unit difference of velocity between two consecutive parallel layers of the liquid which are one centimetre apart.

Coefficient of viscosity is expressed in dyne  $\text{cm}^{-2}$  sec. It is more commonly expressed as poise, centipoise ( $10^{-2}$  poise) and millipoise ( $10^{-3}$  poise), after the name of Poiseuille who derived the formula and gave the method for its determination. 1 poise is equal to a force of 1 dyne per unit area which maintains a velocity difference of 1 cm per second between two parallel consecutive layers of the liquid 1 cm apart.

The reciprocal of the coefficient of viscosity is called Fluidity ( $\phi$ ).

$$\phi = \text{Fluidity} = \frac{1}{\eta}$$

Liquids with low viscosity are termed mobile and others with high viscosity are called viscous.

Viscosity depends on the following factors:

(a) **Intermolecular forces:** The liquids with high intermolecular attractive forces offer greater resistance to the flow of molecules and thus possess high viscosity.

(b) **Molecular mass:** The flow of molecules is inversely proportional to its mass. Liquids having high molecular mass possess greater viscosity.

(c) **The structure and shape of molecules:** Viscosity generally increases as the branching in the chain increases. Symmetrical molecules have low viscosity.

(d) **Temperature:** Intermolecular forces decrease with rise in temperature. Thus, viscosity decreases with the increase of temperature. This property is used to select the lubricant for a machine and engine. The variation of viscosity with temperature can be expressed by the following relationship:

$$\eta = Ae^{-E_a/RT} \quad \dots(i)$$

where,  $A$  = Pre-exponential factor (constant)

$E_a$  = Activation energy

Taking logarithm of equation (i) we get :

$$\log_{10} \eta = \log_{10} A - \frac{E_a}{2.303R} \times \frac{1}{T} \quad \dots(ii)$$

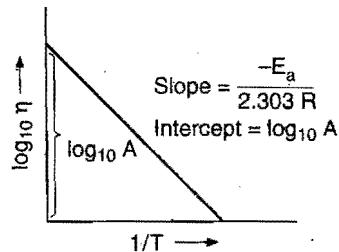


Fig. 4.20

This equation represents straight line with formula  $y = mx + C$ . Equation (ii) may also be given as

$$\log_{10} \frac{\eta_2}{\eta_1} = \frac{E_a}{2.303R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]$$

where  $\eta_2$  is the coefficient of viscosity at temperature  $T_2$  and  $\eta_1$  is the coefficient of viscosity at temperature  $T_1$ .

(e) **Pressure:** The increase of pressure increases the intermolecular forces. Thus, the viscosity of a given liquid increases with increase of pressure.

(f) **Density :** Viscosity of a liquid increases with increase in density while that of gas decreases.

**Measurement of viscosity:** Viscosity is generally determined by Ostwald's method. It involves the comparison of time of flow of equal volumes of two liquids through the same capillary using an apparatus called viscometer.

$$\frac{\eta}{\eta_w} = \frac{d \times t}{d_w \times t_w}$$

where,  $\eta_w, \eta$  = coefficients of viscosity of water and liquid respectively;  $d$  = density of liquid;  $d_w$  = density of water;  $t$  = time of flow of liquid;  $t_w$  = time of flow of water.

**Note:** Viscosity of gases increases with increase in temperature.

#### Comparison between viscous force and solid friction

##### Points of differences :

Viscous force	Solid friction
1. It is directly proportional to the area of layers in contact.	It is independent of the area of the surfaces in contact.
2. It is directly proportional to the relative velocity between the two liquid layers.	It is independent of the relative velocity between two solid surfaces.

##### Point of similarities:

- (i) Both viscous force and solid friction come into action where ever there is relative motion.
- (ii) Both these forces oppose the motion.
- (iii) Both are due to molecular attraction.

## SECTION 3 : SOLID STATE

### 4.12 THE SOLID STATE

In solid state, the particles (molecules, ions or atoms) are closely packed. These are held together by strong intermolecular attractive forces (cohesive forces) and cannot move at random. These are held at fixed positions and surrounded by other particles. There is only one form of molecular motion in solids, namely vibrational motion by virtue of which the particles move about fixed positions and cannot easily leave the solid surface. The following general characteristics are exhibited by solids:

(i) **Definite shape and volume:** Unlike gases and liquids, solids have definite shape and rigidity. This is due to the fact that constituent particles do not possess enough energy to move about to take-up different positions. Solids are characterised by their definite volume which does not depend on the size and shape of

the container. This is due to close packing of molecules and strong short range intermolecular forces between them.

(ii) **High density and low compressibility:** Solids have generally high density and low compressibility due to close packing of molecules which eliminates free space between molecules.

(iii) **Very slow diffusion:** The diffusion of solid is negligible or rather very slow as the particles have permanent positions from which they do not move easily.

(iv) **Vapour pressure:** The vapour pressure of solids is generally much less than the vapour pressure of liquids at a definite temperature. Some particles near the surface may have high energies (kinetic) as to move away and enter the vapour state.

(v) **Melting point:** The temperature at which the solid and the liquid forms of a substance exist at equilibrium or both the forms have same vapour pressure, is called the **melting point**. On supplying heat energy, the particles acquire sufficient energy and move away from their fixed positions in space. This results in the formation of liquid state. The solids have definite melting points depending on the strength of binding energy. However, in some solids (amorphous solids)\* the melting point is not sharp.

### 4.13 FORMS OF SOLIDS

Solids are divided into two classes on the basis of haphazard and regular arrangement of the building constituents.

(i) **Amorphous solids:** The term 'amorphous' has been derived from a Greek word '*Omorphe*' meaning shapeless. In amorphous solids the arrangement of building constituents is not regular but haphazard. Although these solids possess some of the mechanical properties such as rigidity, incompressibility, refractive index, etc., but do not have characteristic shapes or geometrical forms. Amorphous solids in many respects resemble liquids which flow very slowly at room temperature and regarded as supercooled liquids in which the cohesive forces holding the molecules together are so great that the material is rigid but there is no regularity of the structure. Glass, rubber, plastics, etc., are some of the examples of amorphous solids.

Amorphous solids do not have sharp melting points. For example, when glass is heated, it softens and then starts flowing without undergoing any abrupt change from solid to liquid state.

Thus, amorphous substances are not true solids but can be regarded as intermediate between liquids and solids.

(ii) **Crystalline solids:** In crystalline solids, the building constituents arrange themselves in regular manner throughout the entire three-dimensional network. The ordered arrangement of building constituents (molecules, atoms or ions) extends over a large distance. Thus, crystalline solids have long range order. A crystalline solid consists of a large number of units, called crystals. A crystal is defined as a solid figure which has a definite geometrical shape, with flat faces and sharp edges.

A crystalline substance has a sharp melting point, i.e., it changes abruptly into liquid state. Strictly speaking 'a solid state refers to crystalline state' or 'only a crystalline substance can be considered to be a true solid'.

### 4.14 ISOTROPY AND ANISOTROPY

The substances which show same properties in all directions are said to be isotropic and the substances exhibiting directional differences in properties are termed **anisotropic**.

Amorphous solids like liquids and gases are said to be isotropic as arrangement of building constituents is random and disordered. Hence, all directions are equal and therefore, properties are same in all the directions.

Crystalline solids are anisotropic. Magnitude of some of the physical properties of crystalline solids such as refractive index, coefficient of thermal expansion, electrical and thermal conductivities, etc., is different in different directions, within the crystal. For example, in the crystal of silver iodide ( $\text{AgI}$ ), the coefficient of thermal expansion is positive in one direction and negative in the other direction.

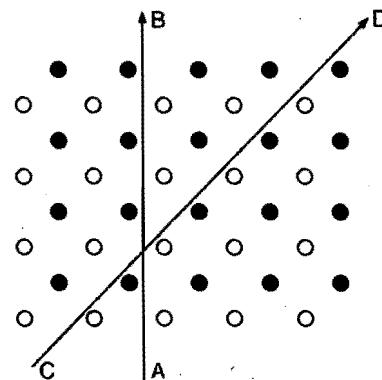


Fig. 4.21 Anisotropic behaviour of crystals

The phenomenon of anisotropy provides a strong evidence for the presence of ordered molecular arrangement in crystals. This can be explained with the help of Fig. 4.21 in which a simple two dimensional arrangement of two different kinds of atoms has been depicted. When a physical property is measured along the slanting line  $CD$ , it will be different from that measured in the direction of vertical line  $AB$ , as line  $CD$  contains alternate types of atoms while line  $AB$  contains one type of atoms only.

### 4.15 DIFFERENCES BETWEEN CRYSTALLINE AND AMORPHOUS SOLIDS

Crystalline Solids	Amorphous Solids
1. They have definite and regular geometry due to definite and orderly arrangement of atoms, ions or molecules in three dimensional space.	They do not have any pattern of arrangement of atoms, ions or molecules and, thus, do not have any definite geometrical shape.
2. They have sharp melting points and change abruptly into liquids.	Amorphous solids do not have sharp melting points and do not change abruptly into liquids.
3. Crystalline solids are anisotropic. Some of their physical properties are different in different directions.	Amorphous solids are isotropic. Their physical properties are same in all directions.
4. These are considered as true solids.	These are considered pseudo-solids or supercooled liquids.
5. Crystalline solids are rigid and their shape is not distorted by mild distorting forces.	Amorphous solids are not very rigid. These can be distorted by bending or compressing forces.

\* Melting point of a solid depends on the structure of the solid. It is used for the identification of solids whether it is crystalline or amorphous.

Crystalline solids	Amorphous solids
<p>6. Crystals are bound by plane faces. The angle between any two faces is called interfacial angle. For a given crystalline solid, it is a definite angle and remains always constant no matter how the faces develop.</p> <p>When a crystalline solid is hammered, it breaks up into smaller crystals of the same geometrical shape.</p>	<p>Amorphous solids do not have well defined planes. When an amorphous solid is broken, the surfaces of the broken pieces are generally not flat and intersect at random angles.</p>
<p>7. An important property of crystals is their symmetry. There are:</p> <ul style="list-style-type: none"> <li>(i) plane of symmetry, (ii) axis of symmetry and (iii) centre of symmetry.</li> </ul>	<p>Amorphous solids do not have any symmetry.</p>

#### 4.16 TYPES OF SYMMETRY IN CRYSTALS

(i) **Centre of symmetry:** It is such an imaginary point within the crystal that any line drawn through it intersects the surface of the crystal at equal distances in both directions. A crystal always possesses only one centre of symmetry [Fig. 4.22 (f)].

(ii) **Plane of symmetry:** It is an imaginary plane which passes through the centre of a crystal and divides it into two equal portions such that one part is exactly the mirror image of the other.

A cubical crystal like NaCl possesses, in all, nine planes of symmetry; three rectangular planes of symmetry and six diagonal planes of symmetry. One plane of symmetry of each of the above is shown in Fig. 4.22 (a) and (b).

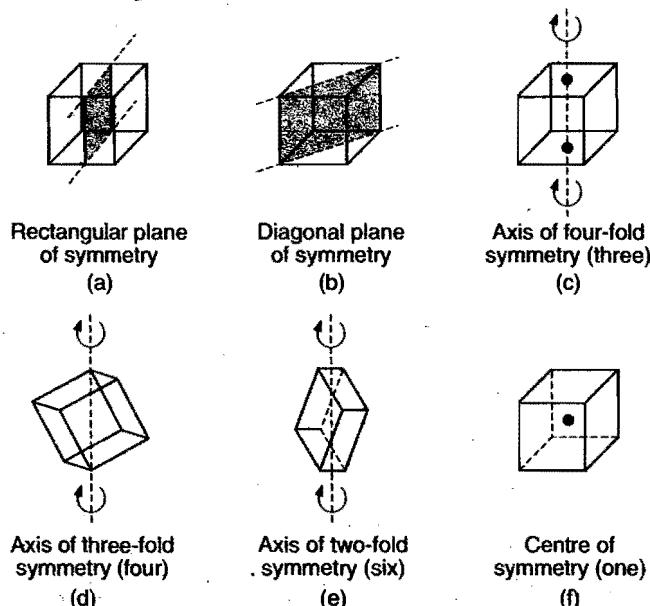


Fig. 4.22 Various elements of symmetry in a cubic crystal

(iii) **Axis of symmetry:** It is an imaginary straight line about which, if the crystal is rotated, it will present the same appearance more than once during the complete revolution. The

axes of symmetry are called diad, triad, tetrad and hexad, respectively, if the original appearance is repeated twice (after an angle of  $180^\circ$ ), thrice (after an angle of  $120^\circ$ ), four times (after an angle of  $90^\circ$ ) and six times (after an angle of  $60^\circ$ ) in one rotation. These axes of symmetry are also called two-fold, three-fold, four-fold and six-fold, respectively.

In general, if the same appearance of a crystal is repeated on rotating through an angle of  $\frac{360^\circ}{n}$ , around an imaginary axis, the axis is called an  $n$ -fold axis.

In all, there are 13 axes of symmetry possessed by a cubical crystal like NaCl as shown in Fig. 4.22 (c), (d) and (e).

(iv) **Elements of symmetry:** The total number of planes, axes and centre of symmetry possessed by a crystal are termed as elements of symmetry. A cubic crystal possesses a total of 23 elements of symmetry.

$$\text{Planes of symmetry} = (3 + 6) = 9 \quad [\text{Fig. 4.22 (a) and (b)}]$$

$$\text{Axes of symmetry} = (3 + 4 + 6) = 13 \quad [\text{Fig. 4.22 (c), (d) and (e)}]$$

$$\text{Centre of symmetry} = 1 \quad [\text{Fig. 4.22 (f)}]$$

$$\text{Total number of symmetry elements} = 23$$

#### 4.17 SPACE LATTICE AND UNIT CELL

All crystals are polyhedra consisting of regularly repeating arrays of atoms, molecules or ions which are the structural units. A crystal is a homogeneous portion of a solid substance made of regular pattern of structural units bonded by plane surfaces making definite angles with each other. The geometrical form consisting only of a regular array of points in space is called a lattice or space lattice or it can be defined as an array of points showing how molecules, atoms or ions are arranged in different sites, in three-dimensional space. Fig. 4.23 shows a space lattice. A space lattice can be subdivided into a number of small cells known as unit cells. It can be defined as the smallest repeating unit in space lattice which, when repeated over and over again, results in a crystal of the given substance or it is the smallest block or geometrical figure from which entire crystal can be built up by its translational repetition in three-dimensions. A unit cell of a crystal possesses all the structural properties of the given crystal. For example, if a crystal is a cube, the unit cell must also have its atoms, molecules or ions arranged so as to give a cube.

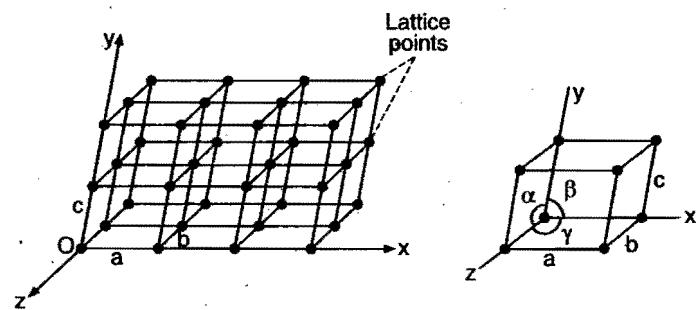


Fig. 4.23 Space lattice and unit cell

System	Edges	Angles	Maximum symmetry elements	Examples
1. Cubic $a = b = c, \alpha = \beta = \gamma = 90^\circ$	All the three equal	All right angles	Nine planes, thirteen axes	NaCl, KCl, ZnS, diamond, alums
2. Orthorhombic $a \neq b \neq c, \alpha = \beta = \gamma = 90^\circ$	All unequal	All right angles	Three planes, three axes	KNO <sub>3</sub> , BaSO <sub>4</sub> , K <sub>2</sub> SO <sub>4</sub> , rhombic sulphur.
3. Tetragonal $a = b \neq c, \alpha = \beta = \gamma = 90^\circ$	Two equal	All right angles	Five planes, five axes	TiO <sub>2</sub> , PbWO <sub>4</sub> , SnO <sub>2</sub> , NH <sub>4</sub> Br
4. Monoclinic $a \neq b \neq c, \alpha = \gamma = 90^\circ, \beta \neq 90^\circ$	All unequal	Two right angles	One plane, one axis	Monoclinic sulphur, KClO <sub>3</sub> , CaSO <sub>4</sub> · 2H <sub>2</sub> O, Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> · 10H <sub>2</sub> O
5. Triclinic $a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90^\circ$	All unequal	None right angles	No planes, no axis	CuSO <sub>4</sub> · 5H <sub>2</sub> O, H <sub>3</sub> BO <sub>3</sub> , K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>
6. Hexagonal $a = b \neq c, \alpha = \beta = 90^\circ, \gamma = 120^\circ$	Two equal	Angle between equal edges = 120°	Seven planes, seven axes	ZnO, CdS, HgS, SiC, AgI
7. Rhombohedral $a = b = c, \alpha = \beta = \gamma \neq 90^\circ$	All three equal	All equal but none 90°	Seven planes, seven axes	NaNO <sub>3</sub> , ICl, quartz (CaCO <sub>3</sub> )

Each unit cell has three vectors  $a$ ,  $b$  and  $c$  as shown in Fig. 4.23. The distances  $a$ ,  $b$  and  $c$  are the lengths of the edges of the unit cell and angles  $\alpha$ ,  $\beta$  and  $\gamma$  are the angles between three imaginary axes  $OX$ ,  $OY$  and  $OZ$ , respectively.

For example: For a crystal system,  $a = b = c$  and  $\alpha = \beta = \gamma \neq 90^\circ$ :

- |                  |                |
|------------------|----------------|
| (a) tetragonal   | (b) hexagonal  |
| (c) rhombohedral | (d) monoclinic |
- [Ans. (c)]

[Hint: From the table  $a = b = c$  for rhombohedral and cubic system both but  $\alpha = \beta = \gamma \neq 90^\circ$  for rhombohedral only.]

#### 4.18 CRYSTAL SYSTEMS

On the basis of geometrical considerations, theoretically there can be 32 different combinations of elements of symmetry of a crystal. These are called 32 systems. Some of the systems have been grouped together. In all, seven types of **basic or primitive unit cells** have been recognised among crystals. These are cubic, orthorhombic, tetragonal, monoclinic, triclinic, hexagonal and rhombohedral. These are shown in Fig. 4.24 and their characteristics are summarised in the following table.

All crystals do not have simple lattices. Some are more complex. Bravais pointed out that there can be 14 different ways in which similar points can be arranged in a three-dimensional space. Thus, the total number of space lattices belonging to all the seven crystal systems are 14.

The crystals belonging to cubic system have three kinds of Bravais lattices. These are:

(i) **Simple cubic lattice:** There are points only at the corners of each unit.

(ii) **Face-centred cubic lattice:** There are points at the corners as well as at the centre of each of the six faces of the cube.

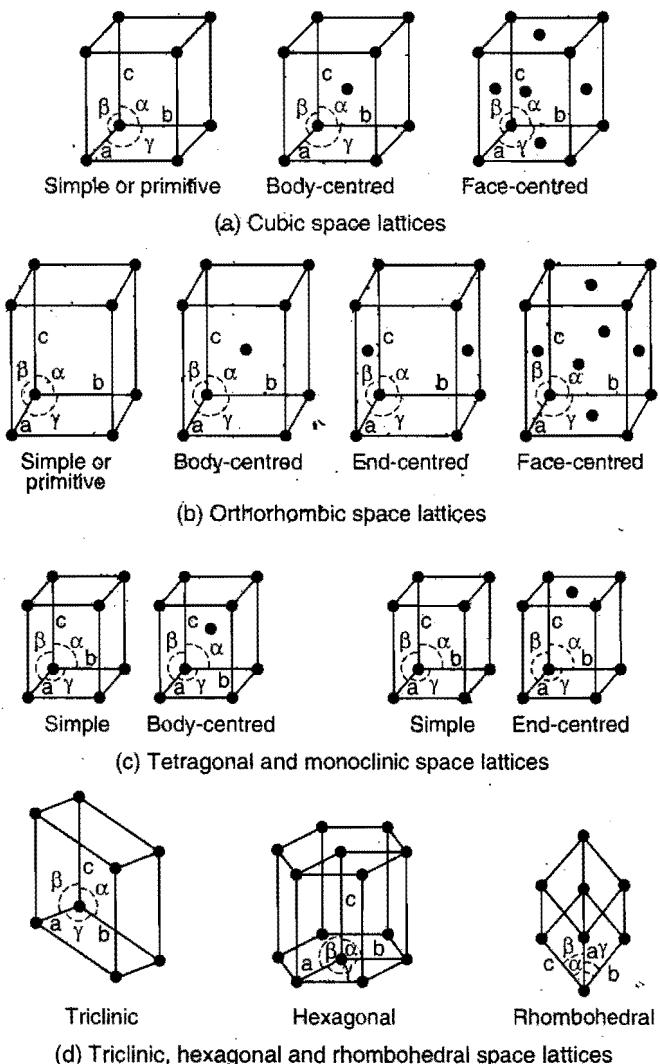


Fig. 4.24 Bravais lattices

(iii) **Body-centred cubic lattice:** There are points at the corners as well as in the body-centre of each cube.

The number of Bravais space lattices in a given system is listed in the following table and shown in Fig. 4.24.

Crystal system	No. of space lattices	Lattice type
1. Cubic	3	Simple, face-centred and body-centred.
2. Orthorhombic	4	Rectangular and body-centred rectangular prism; rhombic and body-centred rhombic prism.
3. Tetragonal	2	Simple and body-centred tetragonal prism.
4. Monoclinic	2	Monoclinic parallelopiped, monoclinic face-centred parallelopiped.
5. Triclinic	1	Triclinic parallelopiped.
6. Hexagonal	1	Hexagonal prism.
7. Rhombohedral	1	Rhombohedron.

In various unit cells, there are three kinds of lattice points: points located at the corners, points in the face-centres and points that lie entirely within the unit cell. In a crystal, atoms located at the corner and face-centre of a unit cell are shared by other cells and only a portion of such an atom actually lies within a given unit cell.

(i) A point that lies at the corner of a unit cell is shared among eight unit cells and, therefore, only one-eighth of each such point lies within the given unit cell.

(ii) A point along an edge is shared by four unit cells and only one-fourth of it lies within any one cell.

(iii) A face-centred point is shared by two unit cells and only one half of it is present in a given unit cell.

(iv) A body-centred point lies entirely within the unit cell and contributes one complete point to the cell.

Type of lattice point	Contribution to one unit cell
Corner	1/8
Edge	1/4
Face-centre	1/2
Body-centre	1

Total number of constituent units per unit cell

$$= \frac{1}{8} \times \text{occupied corners} + \frac{1}{4} \times \text{occupied edge-centres} \\ + \frac{1}{2} \times \text{occupied face-centres} + \text{occupied body-centre.}$$

Determination of Number of Constituent units per unit cell:

Let edge length of cube =  $a$  cm

Density of substance =  $d$  g cm<sup>-3</sup>

Volume of unit cell =  $a^3$  cm<sup>3</sup>

Mass of unit cell = volume × density = ( $a^3 \times d$ ) g

$$\text{Number of mol per unit cell} = \frac{a^3 \times d}{M};$$

where,  $M$  = molar mass

$$\text{Number of molecules per unit cell} = \text{Number of mole} \times \text{Avogadro's number}$$

$$Z = \frac{a^3 \times d}{M} \times N = \frac{a^3 \times d \times N}{M}$$

#### Calculation of number of constituent units in hexagonal unit cell

(i) Constituent units at each corner of unit cell is common among six unit cells hence contribute 1/6th to each unit cell.

(ii) Constituent unit at edge is common to three unit cells hence contribute 1/3rd to each unit cell.

(iii) Constituent units present at the body centre is considered in single unit cell.

(iv) Constituent unit at face centre is common between two unit cells hence contribute 1/2 to each unit cell.

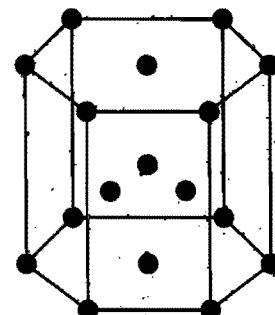


Fig. 4.25 Hexagonal unit cell

In the hexagonal unit cell (Fig. 4.25), 12 corners, 2 face centres and 3 constituent units within the unit cells are occupied, hence effective number of constituent units present in the unit cell may be calculated as

$$z = \frac{1}{6} \times \text{occupied corners} + \frac{1}{2} \times \text{occupied face centres} + \text{Central constituent units} \\ = \frac{1}{6} \times 12 + \frac{1}{2} \times 2 + 3 \\ = 6$$

#### 4.19 DESIGNATION OF PLANES IN CRYSTALS—MILLER INDICES

Planes in crystals are described by a set of integers ( $h, k$  and  $l$ ) known as Miller indices. Miller indices of a plane are the reciprocals of the fractional intercepts of that plane on the various crystallographic axes. For calculating Miller indices, a reference plane, known as parametral plane, is selected having intercepts  $a, b$  and  $c$  along  $x, y$  and  $z$ -axes, respectively (Fig. 4.26). Then, the intercepts of the unknown plane are given with respect to  $a, b$  and  $c$  of the parametral plane.

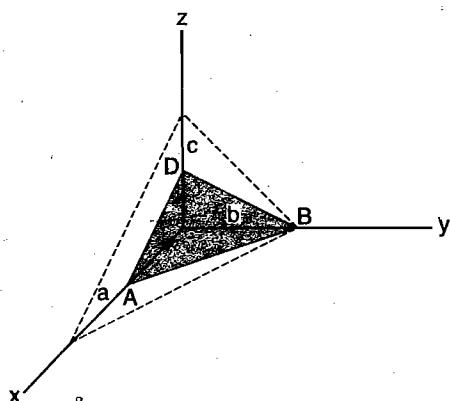


Fig. 4.26 Parametral (intercepts  $a, b, c$  along  $x, y$  and  $z$ -axes)

Thus, the Miller indices are:

$$h = \frac{a}{\text{intercept of the plane along } x\text{-axis}}$$

$$k = \frac{b}{\text{intercept of the plane along } y\text{-axis}}$$

$$l = \frac{c}{\text{intercept of the plane along } z\text{-axis}}$$

Consider the shaded plane  $ABD$  in Fig. 4.26. The intercepts of the shaded plane along  $X, Y$  and  $Z$ -axes are  $a/2$ ,  $b$  and  $c/2$ , respectively. Thus,

$$h = \frac{a}{a/2} = 2;$$

$$k = \frac{b}{b} = 1;$$

$$l = \frac{c}{c/2} = 2$$

The plane is, therefore, designed as (212) plane.

Note: (i) If a plane is parallel to an axis, its intercept with that axis is taken as infinite and the Miller indices will be zero.

(ii) While defining Miller indices for orthogonal crystal,  $X, Y$  and  $Z$ -axes are considered crystallographic axes.

Some of the important planes of cubic crystals are shown in Fig. 4.27.

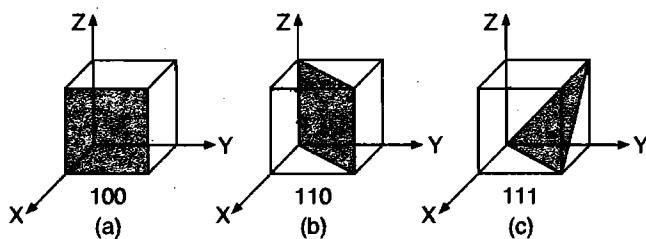


Fig. 4.27 Miller indices of planes in cubic lattice

In (a) intercepts are	1	$\infty$	$\infty$
So, Miller indices are	1	0	0
The plane is designated (100)			
In (b) intercepts are	1	1	$\infty$
So, Miller indices are	1	1	0
The plane is designated (110)			
In (c) intercepts are	1	1	1
So, Miller indices are	1	1	1
The plane is designated (111)			

The distances between the parallel planes in crystals are designated as  $d_{(hkl)}$ . For different cubic lattices these interplanar spacings are given by the general formula,

$$d_{(hkl)} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

where,  $a$  is the length of the cube side while  $h, k$  and  $l$  are the Miller indices of the plane.

The spacings of the three planes (100), (110) and (111) of simple cubic lattice can be calculated.

$$d_{(100)} = \frac{a}{\sqrt{1^2 + 0 + 0}} = a$$

$$d_{(110)} = \frac{a}{\sqrt{1^2 + 1^2 + 0}} = \frac{a}{\sqrt{2}}$$

$$d_{(111)} = \frac{a}{\sqrt{1^2 + 1^2 + 1^2}} = \frac{a}{\sqrt{3}}$$

The ratio is,

$$d_{(100)} : d_{(110)} : d_{(111)} = 1 : \frac{1}{\sqrt{2}} : \frac{1}{\sqrt{3}} = 1 : 0.707 : 0.577$$

Similarly,  $d_{(hkl)}$  ratios for face-centred cubic and body-centred cubic can be calculated. For face-centred cubic,

$$d_{(100)} : d_{(110)} : d_{(111)} = 1 : \frac{1}{2} : \frac{2}{\sqrt{2}} = 1 : 0.707 : 1.154$$

For body-centred cubic,

$$\begin{aligned} d_{(100)} : d_{(110)} : d_{(111)} &= \frac{1}{2} : \frac{1}{\sqrt{2}} : \frac{1}{2\sqrt{3}} \\ &= 1 : \sqrt{2} : \frac{1}{\sqrt{3}} \\ &= 1 : 1.414 : 0.577 \end{aligned}$$

#### 4.20 CRYSTALLOGRAPHY AND X-RAY DIFFRACTION

Crystallography is the branch of science which deals with the geometry, properties and structure of crystals and crystalline substances. Geometric crystallography is concerned with the external spatial arrangement of crystal planes and geometric shapes of crystals.

Atoms, molecules or ions are too small to be seen with naked eye. The arrangement of particles in crystalline solids is determined indirectly by X-ray diffraction. In 1912, Von Laue showed that any crystal could serve as a three-dimensional grating to the incident electromagnetic radiation with wavelength approximately equal to the internuclear separations ( $\approx 10^{-8}$  cm) of atoms in the crystal. Such radiation is in the X-ray region of the electromagnetic spectrum.

The apparatus used is shown in Fig. 4.28. A monochromatic X-ray beam is directed towards the surface of a slowly rotated crystal so as to vary the angle of incidence  $\theta$ . At various angles, strong beams of deflected X-rays strike the photographic plate. The photographic plate after developing shows a central spot due to primary beam and a set of symmetrically disposed spots due to deflected X-rays. Different kinds of crystals produce different arrangements of spots.

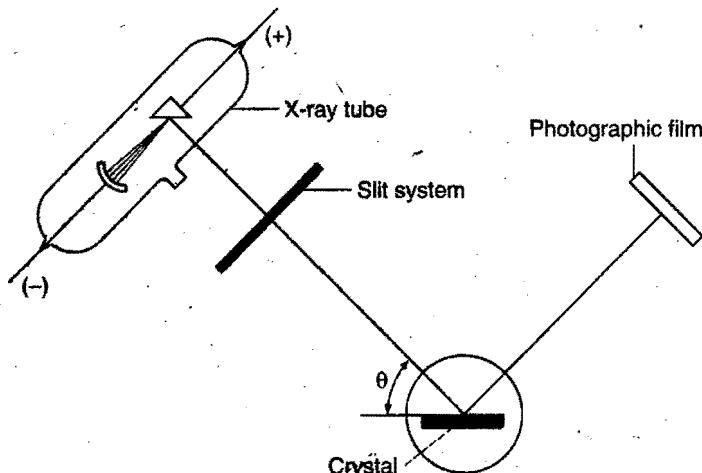


Fig. 4.28 X-ray diffraction of crystals

In 1913, Bragg found that Laue photographs are more easily interpreted by treating the crystals as a reflection grating rather than a diffraction grating. Fig. 4.29 illustrates the way by which the crystal spacings can be determined by use of X-rays of a single wavelength,  $\lambda$ . The rays strike the parallel planes of the crystal at angle  $\theta$ . Some of the rays are reflected from the upper plane, some from the second and some from the lower planes. A strong reflected beam will result only if all the reflected rays are in phase. The waves reflected by different layer planes will be in

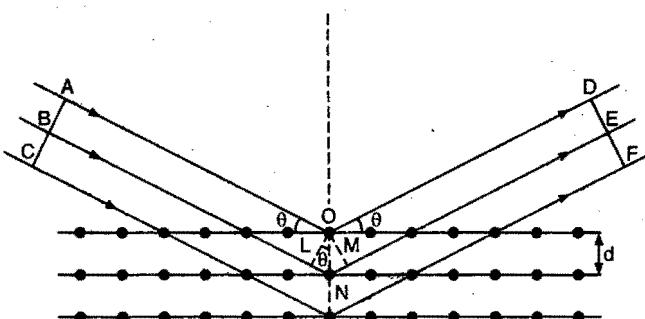


Fig. 4.29 X-ray reflection from crystals

phase with one another only if the difference in the path length of the waves reflected from the successive planes is equal to an integral number of wavelengths.  $OL$  and  $OM$  are the perpendiculars drawn to the incident and reflected beams. The difference in path lengths of waves deflected from the first two planes is given by:

$$LN + NM = n\lambda \quad (n = 1, 2, 3, \dots)$$

Since, the triangles  $OLN$  and  $OMN$  are congruent, hence  $LN = NM$ .

$$\text{So,} \quad \text{Path difference} = 2LN$$

as  $LN = d \sin \theta$  where,  $d$  is the distance between two planes.

$$\text{So,} \quad \text{Path difference} = 2d \sin \theta$$

When two reflected waves reinforce each other (maximum reflection), the path difference should be  $= n\lambda$  (where,  $n = 1, 2, 3, \dots$ ).

So, for maximum reflection,

$$n\lambda = 2d \sin \theta$$

This relation is called Bragg's equation. Distance between two successive planes  $d$  can be calculated from this equation. With X-rays of definite wavelength, reflections at various angles will be observed for a given set of planes separated by a distance  $d$ . These reflections correspond to  $n = 1, 2, 3$  and so on and are spoken of as first order, second order, third order and so on. With each successive order, the angle  $\theta$  increases and the intensity of the reflected beam weakens.

The values of  $\theta$  for the first order reflection from the three faces of sodium chloride crystal were found to be  $5.9^\circ$ ,  $8.4^\circ$  and  $5.2^\circ$  respectively. As  $n$  and  $a$  are same in each case, the distance  $d$  between successive planes in three faces will be in the ratio of

$$\begin{aligned} \frac{1}{\sin 5.9^\circ} : \frac{1}{\sin 8.4^\circ} : \frac{1}{\sin 5.2^\circ} &= 9.61 : 6.84 : 11.04 \\ &= 1 : 0.70 : 1.14 \\ &= 1 : \frac{1}{\sqrt{2}} : \frac{2}{\sqrt{3}} \end{aligned}$$

This ratio corresponds to spacings along the three planes of a face-centred cubic structure. Thus, the NaCl crystal has face-centred cubic structure.

**Example 63.** X-rays of wavelength  $1.54 \text{ \AA}$  strike a crystal and are observed to be deflected at an angle of  $22.5^\circ$ . Assuming that  $n = 1$ , calculate the spacing between the planes of atoms that are responsible for this reflection.

**Solution:** Applying Bragg's equation,

$$n\lambda = 2d \sin \theta$$

$$\text{Given, } n = 1, \lambda = 1.54 \text{ \AA}, \theta = 22.5^\circ.$$

$$\text{Using relation } n\lambda = 2d \sin \theta,$$

$$d = \frac{1.54}{2 \sin 22.5^\circ} = \frac{1.54}{2 \times 0.383} = 2.01 \text{ \AA}$$

**Example 64.** The first order reflection of a beam of X-rays of wavelength  $1.54 \text{ \AA}$  from the (100) face of a crystal of the simple

cubic type occurs at an angle of  $11.29^\circ$ . Calculate the length of the unit cell.

**Solution:** Applying Bragg's equation,

$$2d \sin \theta = n\lambda$$

Given,  $\theta = 11.29^\circ$ ,  $n = 1$ ,  $\lambda = 1.54 \text{ \AA} = 1.54 \times 10^{-8} \text{ cm}$

$$d = \frac{1.54 \times 10^{-8}}{2 \times \sin 11.29^\circ} = \frac{1.54 \times 10^{-8}}{2 \times 0.1957} = 3.93 \times 10^{-8} \text{ cm}$$

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} = a$$

$$a = 3.93 \times 10^{-8} \text{ cm} = \text{length of the unit cell}$$

**Example 65.** When an electron in an excited state of Mo atom falls from L to K-shell, an X-ray is emitted. These X-rays are diffracted at angle of  $7.75^\circ$  by planes with a separation of  $2.64 \text{ \AA}$ . What is the difference in energy between K-shell and L-shell in Mo, assuming a first order diffraction ( $\sin 7.75^\circ = 0.1349$ )?

**Solution:** According to Bragg's equation:

$$n\lambda = 2d \sin \theta$$

$$1 \times \lambda = 2 \times 2.64 \sin 7.75^\circ = 2 \times 2.64 \times 0.1349$$

$$\lambda = 0.712 \text{ \AA}$$

Energy difference between K and L-shell of Mo

$$= \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{0.712 \times 10^{-10}} = 2.791 \times 10^{-15} \text{ J}$$

## 4.21 ANALYSIS OF CUBIC SYSTEMS

The following characteristics are reflected by cubic systems when analysed mathematically:

### (i) Atomic Radius

It is defined as half the distance between nearest neighbouring atoms in a crystal. It is expressed in terms of length of the edge 'a' of the unit cell of the crystal.

**(a) Simple cubic unit cell :** In a simple cubic unit cell, atoms at the corners touch each other along the edge.

Distance between the nearest neighbours,

$$d = AB = a = 2r$$

(where  $r$  = radius of the atom)

or Atomic radius,

$$r = \frac{a}{2} = 0.5a$$

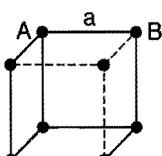


Fig. 4.30  
Simple cubic unit cell

**(b) Body-centred cubic unit cell :** The distance between the two nearest neighbours is represented by length  $AE$  or  $ED$ , i.e., half of the body diagonal,  $AD$ .

$$d = AE = ED = \frac{AD}{2}$$

In  $\Delta ABC$ ,

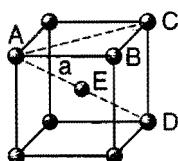


Fig. 4.31  
Body-centred cubic unit cell

$$AC^2 = AB^2 + BC^2 = a^2 + a^2 = 2a^2$$

$$\text{or } AC = \sqrt{2}a$$

Now, in  $\Delta ADC$ ,

$$AD^2 = AC^2 + CD^2$$

$$= (\sqrt{2}a)^2 + a^2 = 3a^2$$

or

$$AD = \sqrt{3}a$$

$\therefore$

$$d = \frac{\sqrt{3}}{2}a$$

$$d = 2r = \frac{\sqrt{3}}{2}a$$

$$\text{or Atomic radius, } r = \frac{\sqrt{3}}{4}a$$

### (c) Face-centred cubic unit cell

The distance between the two nearest neighbours is represented by length  $AB$  or  $BC$ , i.e., half of the face diagonal,  $AC$ .

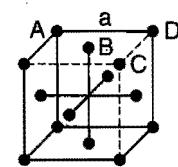


Fig. 4.32  
Face-centred cubic unit cell

$$d = AB = BC = \frac{AC}{2}$$

$$\text{In } \Delta ACD, AC^2 = CD^2 + AD^2$$

$$= a^2 + a^2 = 2a^2$$

$$AC = \sqrt{2}a$$

$$\text{or } d = \frac{AC}{2} = \frac{\sqrt{2}}{2}a = \frac{1}{\sqrt{2}}a$$

$$d = 2r = \frac{1}{\sqrt{2}}a$$

$$\text{or Atomic radius, } r = \frac{1}{2\sqrt{2}}a$$

### (ii) No. of Atoms Per Unit Cell

Different types of cubic unit cells are given in following figure:

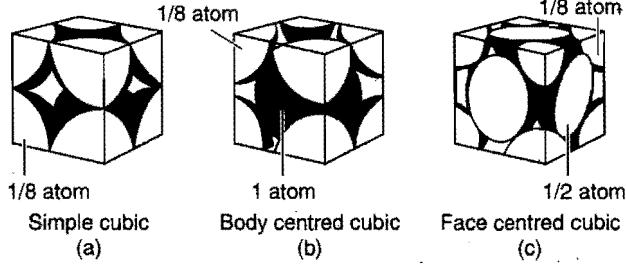
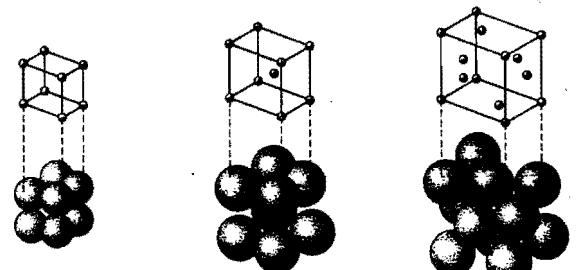


Fig. 4.33 (a) Simple or primitive cubic lattice;  
(b) Body-centred cubic lattice; (c) Face-centred cubic lattice

**(a) Simple cubic structure:** Since, each corner atom is shared by eight surrounding cubes, therefore, it contributes for  $\frac{1}{8}$  of an atom.

$$\text{Thus, for simple cube} = 8 \times \frac{1}{8} = 1 \text{ atom per unit cell}$$

**(b) Face-centred cubic structure:** Since, the structure possesses 8 corner atoms and six at the centre of each face, the contribution will be

$$\begin{aligned} &= 8 \times \frac{1}{8} + 6 \times \frac{1}{2} \quad (\text{Face atom is shared by two cubes}) \\ &= 1 + 3 = 4 \text{ atoms per unit cell} \end{aligned}$$

**(c) Body-centred cubic structure:** Since, the structure possesses 8 corner atoms and one body-centre, the contribution will be  $= 8 \times \frac{1}{8} + 1 = 2$  atoms per unit cell.

### (iii) Coordination Number

It is defined as the number of nearest neighbours that an atom has in a unit cell. It depends upon structure.

**(a) Simple cubic structure:** Coordination number = 6

**(b) Face-centred cubic structure:** Coordination number = 12

**(c) Body-centred cubic structure:** Coordination number = 8

### (iv) Density of Lattice Matter

Knowing the unit cell dimensions, the theoretical density of a crystal can be calculated as:

$$\text{Density of the unit cell} = \frac{\text{Mass of unit cell}}{\text{Volume of the unit cell}}$$

$$\text{Mass of the unit cell} = \frac{\text{number of atoms in the unit cell} \times \text{mass of each atom}}{\text{Atomic mass}}$$

$$\text{Mass of each atom} = \frac{\text{Atomic mass}}{\text{Avogadro's number}} = \frac{M}{N_0}$$

$$\text{So, density of a unit cell} = \frac{Z \times M}{N_0 \times V} = \frac{n \times M}{N_0 \times a^3} \quad (\text{For a cube})$$

where,  $Z$  is the number of atoms in a unit cell and  $V$  is the volume of unit cell.

For a cube  $V = a^3$  where,  $a$  is the edge length of the cubic unit cell.

### (v) Packing Fraction or Density of Packing

It is defined as the ratio of volumes occupied by atoms in unit cell to the total volume of the unit cell.

$$\text{Packing fraction} = \frac{\text{Volume occupied by atoms in unit cell}}{\text{Total volume of the unit cell}} = \frac{v}{V}$$

**(a) Simple cubic structure:** Let  $a$  be the cube edge and  $r$  the atomic radius.

$$V = \text{volume of the unit cell} = a^3$$

Since, one atom is present in a unit cell, its

$$\begin{aligned} \text{Volume, } v &= \frac{4}{3} \pi r^3 & (r = a/2) \\ &= \frac{4}{3} \pi \left(\frac{a}{2}\right)^3 = \frac{\pi a^3}{6} \end{aligned}$$

$$\text{Packing fraction} = \frac{v}{V} = \frac{\pi a^3 / 6}{a^3} = \frac{\pi}{6} = 0.52$$

i.e., 52% of the unit cell is occupied by atoms and 48% is empty.

**(b) Face-centred cubic structure:** Since, four atoms are present in a unit cell, their volume is

$$v = 4 \times \left(\frac{4}{3} \pi r^3\right)$$

$$\text{Putting the value of } r = \frac{a}{2\sqrt{2}},$$

$$v = \frac{16}{3} \pi \left(\frac{a}{2\sqrt{2}}\right)^3 = \frac{\pi}{3\sqrt{2}} a^3$$

$$\text{Volume of unit cell, } V = a^3$$

$$\text{Packing fraction} = \frac{\pi a^3}{3\sqrt{2} a^3} = \frac{\pi}{3\sqrt{2}} = 0.74$$

i.e., 74% of unit cell is occupied by atoms and 26% is empty.

**(c) Body-centred cubic structure:** Since, two atoms are present in a unit cell, their volume is

$$v = 2 \times \left(\frac{4}{3} \pi r^3\right)$$

$$\begin{aligned} \text{Putting the value of } r = \frac{\sqrt{3}}{4} a, 'v' &= 2 \times \frac{4}{3} \pi \times \left(\frac{\sqrt{3}}{4} a\right)^3 \\ &= \frac{\sqrt{3}\pi a^3}{8} \end{aligned}$$

$$\text{Volume of unit cell, } V = a^3$$

$$\text{Packing fraction} = \frac{\sqrt{3}\pi a^3}{8a^3} = \frac{\sqrt{3}}{8} \pi = 0.68$$

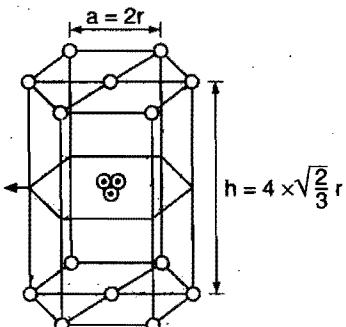
i.e., 68% of the unit cell is occupied by atoms and 32% is empty.

Characteristics of cubic unit cells are summarised in following tables :

	Simple	Body-centered	Face-centered
Volume, conventional cell	$a^3$	$a^3$	$a^3$
Lattice points per cell	1	2	4
Volume, primitive cell	$a^3$	$\frac{1}{2} a^3$	$\frac{1}{4} a^3$
Lattice points per unit volume	$1/a^3$	$2/a^3$	$4/a^3$
Number of nearest neighbors	6	8	12
Nearest-neighbor distance	$a$	$3^{1/2} a/2$ = 0.866a	$a/2^{1/2}$ = 0.707a
Number of second neighbors	12	6	6
Second neighbor distance	$2^{1/2} a$	$a$	$a$
Packing fraction	$\frac{1}{6} \pi$ = 0.524	$\frac{1}{3} \pi \sqrt{3}$ = 0.680	$\frac{1}{6} \pi \sqrt{2}$ = 0.740

**Hexagonal Unit Cell**

Let us consider hexagonal unit cell of height 'h'; its constituent units are spherical having radius 'r'.

**Fig. 4.34 Hexagonal unit cell**

Number of constituent units in the hexagonal unit cell = 6

$$\text{Thus, occupied volume in the unit cell} = 6 \times \frac{4}{3} \pi r^3$$

Volume of unit cell = Area of base  $\times$  height

$$\begin{aligned} &= 6 \times \text{Area of equilateral triangle} \times \text{height} \\ &= 6 \times \frac{\sqrt{3}}{4} a^2 \times 4r \sqrt{\frac{2}{3}} \\ &= 6 \times \frac{\sqrt{3}}{4} (2r)^2 \times 4r \sqrt{\frac{2}{3}} \end{aligned}$$

(Height of the unit cell can be calculated geometrically)

$$\begin{aligned} \text{Percentage occupied space} &= \frac{\text{occupied volume}}{\text{volume of unit cell}} \times 100 \\ &= \frac{6 \times \frac{4}{3} \pi r^3}{6 \frac{\sqrt{3}}{4} (2r)^2 \times 4r \sqrt{\frac{2}{3}}} \times 100 = 74.06\% \end{aligned}$$

**SOME SOLVED EXAMPLES**

**Example 66.** A compound formed by elements A and B crystallises in cubic structure where A atoms are at the corners of a cube and B atoms are at the face-centre. What is the formula of the compound?

**Solution:** An atom at the corner of the cube contributes  $\frac{1}{8}$  to the unit cell. Hence, number of atoms of A in the unit cell =  $8 \times \frac{1}{8} = 1$ .

An atom at the face of the cube contributes  $\frac{1}{2}$  to the unit cell. Hence, number of atoms of B in the unit cell =  $6 \times \frac{1}{2} = 3$ .

Thus, the formula is  $AB_3$ .

**Example 67.** At room temperature, sodium crystallises in body-centred cubic lattice with  $a = 4.24 \text{ \AA}$ . Calculate the theoretical density of sodium (At. mass of Na = 23.0).

**Solution:** A body-centred cubic unit cell contains 8 atoms at the 8 corners and 1 in the centre.

Hence,

$$\text{Total number of atoms in a unit cell} = 8 \times \frac{1}{8} + 1 = 2$$

$$\text{Volume of unit cell} = a^3 = (4.24 \times 10^{-8})^3 \text{ cm}^3$$

$$\text{So, Density} = \frac{Z \times M}{N_0 \times V} = \frac{2 \times 23}{(6.023 \times 10^{23})(4.24 \times 10^{-8})^3} = 1.002 \text{ g cm}^{-3}$$

**Example 68.** The density of KCl is  $1.9893 \text{ g cm}^{-3}$  and the length of a side of unit cell is  $6.29082 \text{ \AA}$  as determined by X-ray diffraction. Calculate the value of Avogadro's number.

**Solution:** KCl has face-centred cubic structure,

i.e.,

$$Z = 4$$

$$\text{Avogadro's number} = \frac{Z \times M}{d \times V}$$

$$\text{Given that, } d = 1.9893; M = 74.5; V = (6.29082 \times 10^{-8})^3 \text{ cm}^3$$

$$\begin{aligned} \text{Avogadro's number} &= \frac{4 \times 74.5}{1.9893 \times (6.29082 \times 10^{-8})^3} \\ &= 6.017 \times 10^{23} \end{aligned}$$

**Example 69.** Silver crystallises in a face-centred cubic unit cell. The density of Ag is  $10.5 \text{ g cm}^{-3}$ . Calculate the edge length of the unit cell.

**Solution:** For face-centred cubic unit,  $Z = 4$ .

$$\begin{aligned} \text{We know that, } V &= \frac{Z \times M}{N_0 \times d} \\ &= \frac{4 \times 108}{(6.023 \times 10^{23}) \times 10.5} = 6.83 \times 10^{-23} \\ &= 68.3 \times 10^{-24} \end{aligned}$$

Let  $a$  be the edge length of the unit cell.

$$\text{So, } V = a^3$$

$$\text{or } a^3 = 68.3 \times 10^{-24}$$

$$a = (68.3 \times 10^{-24})^{1/3} \text{ cm}$$

$$= 4.09 \times 10^{-8} \text{ cm}$$

$$= 409 \text{ pm}$$

**Example 70.** An element occurs in bcc structure with a cell edge of 288 pm. The density of metal is  $7.2 \text{ g cm}^{-3}$ . How many atoms does 208 g of the element contain?

$$\begin{aligned} \text{Solution: Volume of the unit cell} &= (288 \times 10^{-10})^3 \\ &= 23.9 \times 10^{-24} \text{ cm}^3 \end{aligned}$$

$$\text{Volume of 208 g of the element} = \frac{208}{7.2} = 28.88 \text{ cm}^3$$

$$\text{Number of unit cells in } 28.88 \text{ cm}^3 = \frac{28.88}{23.9 \times 10^{-24}}$$

$$= 12.08 \times 10^{23} \text{ unit cells}$$

Each bcc structure contains 2 atoms.

$$\begin{aligned} \text{So, Total atoms in } & 12.08 \times 10^{23} \text{ unit cells} \\ & = 2 \times 12.08 \times 10^{23} \\ & = 24.16 \times 10^{23} \end{aligned}$$

**Example 71.** Lithium forms body-centred cubic crystals. Calculate the atomic radius of lithium if the length of the side of a unit cell of lithium is 351 pm.

**Solution:** In body-centred cubic crystals,

$$\begin{aligned} r &= \frac{\sqrt{3}}{4} a \\ &= \frac{\sqrt{3}}{4} \times 351 \text{ pm} = 151.98 \text{ pm} \end{aligned}$$

**Example 72.** Ammonium chloride crystallises in a body-centred cubic lattice with a unit distance of 387 pm. Calculate (a) the distance between oppositely charged ions in the lattice and (b) the radius of the  $\text{NH}_4^+$  ion if the radius of  $\text{Cl}^-$  ion is 181 pm.

**Solution:** (a) In a body-centred cubic lattice, oppositely charged ions touch each other along the cross-diagonal of the cube.

$$\text{So, } 2r_c + 2r_a = \sqrt{3}a$$

$$\begin{aligned} \text{or } r_c + r_a &= \frac{\sqrt{3}}{2} a \\ &= \frac{\sqrt{3}}{2} \times 387 = 335.15 \text{ pm} \end{aligned}$$

(b) Given that,

$$\begin{aligned} r_a &= 181 \text{ pm} \\ r_c &= 335.15 - 181.0 = 154.15 \text{ pm} \end{aligned}$$

**Example 73.** The unit cell cube length for  $\text{LiCl}$  ( $\text{NaCl}$  structure) is 5.14 Å. Assuming anion-anion contact, calculate the ionic radius for chloride ion.

**Solution:** In a face-centred cubic lattice, anions touch each other along the face diagonal of the cube.

$$\begin{aligned} 4r_{\text{Cl}^-} &= \sqrt{2}a \\ r_{\text{Cl}^-} &= \frac{\sqrt{2}}{4} a \\ &= \frac{\sqrt{2}}{4} \times 5.14 = 1.82 \text{ Å} \end{aligned}$$

**Alternative:** Distance between  $\text{Li}^+$  and  $\text{Cl}^-$  ion

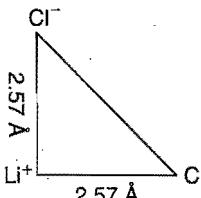
$$= \frac{5.14}{2} = 2.57 \text{ Å}$$

Thus, distance between two chloride ions

$$\begin{aligned} &= \sqrt{(2.57)^2 + (2.57)^2} \\ &= 3.63 \text{ Å} \end{aligned}$$

Hence,

$$\text{radius of } \text{Cl}^- = \frac{3.63}{2} = 1.82 \text{ Å}$$



**Example 74.** The density of crystalline sodium chloride is  $2.165 \text{ g cm}^{-3}$ . What is the edge length of the unit cell. What would be the dimensions of cube containing one mole of  $\text{NaCl}$ ?

**Solution:** We know that,

$$\rho = \frac{N}{a^3} \left( \frac{M}{N_A} \right)$$

where;

$$\rho = \text{density} = 2.165 \text{ g cm}^{-3}$$

$$M = \text{molar mass} = 58.5$$

$$N_A = \text{Avogadro's number} = 6.023 \times 10^{23}$$

$$N = \text{number of formula unit per unit cell}$$

$$= 4 \text{ (for fcc)}$$

$$a^3 = \frac{N}{\rho} \left( \frac{M}{N_A} \right) = \frac{4}{2.165} \left[ \frac{58.5}{6.023 \times 10^{23}} \right] = 1.794 \times 10^{-22}$$

$$a = 5.64 \times 10^{-8} \text{ cm}$$

$$\text{Molar volume} = \frac{\text{Molar mass}}{\text{Density}} = \frac{58.8}{2.165}$$

$$\text{Edge length (} a \text{)} = \left[ \frac{58.8}{2.165} \right]^{1/3} = 3 \text{ cm}$$

**Example 75.** The density of potassium bromide crystal is  $2.75 \text{ g cm}^{-3}$  and the length of an edge of a unit cell is 654 pm. The unit cell of  $\text{KBr}$  is one of three types of cubic unit cells. How many formula units of  $\text{KBr}$  are there in a unit cell? Does the unit cell have a  $\text{NaCl}$  or  $\text{CsCl}$  structure?

**Solution:** We know that,

$$\rho = \frac{N}{a^3} \left( \frac{M}{N_A} \right)$$

$$N = \frac{\rho \times a^3 \times N_A}{M}$$

$$= \frac{2.75 \times (654 \times 10^{-10})^3 \times 6.023 \times 10^{23}}{119} = 3.89 \approx 4$$

Number of mass points per unit cell = 4

It is  $\text{NaCl}$  type crystal, i.e., fcc structure.

**Example 76.** A unit cell of sodium chloride has four formula units. The edge length of unit cell is 0.564 nm. What is the density of sodium chloride? (IIT May 1997)

$$\begin{aligned} \text{Solution: } \rho &= \frac{ZM}{a^3 N} = \frac{4 \times 58.5}{(5.64 \times 10^{-8})^3 \times 6.023 \times 10^{23}} \\ &= 2.16 \text{ g cm}^{-3} \end{aligned}$$

**Example 77.** Chromium metal crystallises with a body-centred cubic lattice. The length of the unit cell edge is found to be 287 pm. Calculate the atomic radius. What would be the density of chromium in  $\text{g/cm}^3$ ? (IIT July 1997)

**Solution:** In body-centred cubic unit cell,

$$a\sqrt{3} = 4r$$

where,  $a$  = edge length,  $r$  = radius of atom

$$r = \frac{a\sqrt{3}}{4} = \frac{\sqrt{3} \times 4.29}{4} = 1.8574 \text{ \AA}$$

**Example 78.** When heated above  $916^\circ\text{C}$ , iron changes its crystal structure from body-centred cubic to cubic closed packed structure. Assuming that the metallic radius of the atom does not change, calculate the ratio of density of the bcc crystal to that of the ccp crystal.

**Solution:** In body-centred packing, the efficiency of packing is 67.92%. In the cubic closed packing, the packing efficiency is 74.02%.

Let  $d_1$  be the density when packing efficiency is 74.02% and  $d_2$  is the density when packing efficiency is 67.92%.

$$\frac{d_2}{d_1} = \frac{67.92}{74.02} = 0.918$$

### ILLUSTRATIONS OF OBJECTIVE QUESTIONS

30. An element 'A' has face-centred cubic structure with edge length equal to 361 pm. The apparent radius of atom 'A' is:

- (a) 127.6 pm      (b) 180.5 pm  
 (c) 160.5 pm      (d) 64 pm

[Ans. (a)]

[Hint: For face-centred unit cell,

$$a\sqrt{2} = 4r$$

$$\frac{361 \times 1.414}{4} = r$$

$$r = 127.6 \text{ pm}]$$

31. The packing fraction of the element that crystallises in simple cubic arrangement is:

- (a)  $\frac{\pi}{4}$       (b)  $\frac{\pi}{6}$       (c)  $\frac{\pi}{3}$       (d)  $\frac{\pi}{2}$

[Ans. (b)]

[Hint: In simple unit cell  $a = 2r$

$$Z = 1$$

$$\therefore \text{Packing fraction} = \frac{\text{Occupied volume}}{\text{Total volume}}$$

$$= \frac{\frac{4}{3}\pi r^3}{a^3} = \frac{\frac{4}{3}\pi r^3}{(2r)^3} = \frac{\pi}{6}$$

32. How many unit cells are present in 39 g of potassium that crystallises in body-centred cubic structure?

- (a)  $N_A$       (b)  $\frac{N_A}{4}$       (c)  $0.5 N_A$       (d)  $0.75 N_A$

[Ans. (c)]

[Hint: Number of atoms =  $\frac{\text{Mass}}{\text{Atomic mass}} \times N_A$

$$= \frac{39}{39} \times N_A = N_A$$

In bcc unit cell,

$$Z = 2$$

$$\therefore \text{Number of unit cells} = \frac{N_A}{2} = 0.5 N_A$$

33. Sodium metal exists in bcc unit cell. The distance between nearest sodium atoms is 0.368 nm. The edge length of the unit cell is:

- (a) 0.368 nm      (b) 0.184 nm  
 (c) 0.575 nm      (d) 0.424 nm

[Ans. (d)]

[Hint: In bcc unit cell,  $a\sqrt{3} = 4r$

$$a = \frac{4r}{\sqrt{3}} = \frac{2}{\sqrt{3}} \times 2r$$

$$= \frac{2}{\sqrt{3}} \times 0.368 = 0.425 \text{ nm}]$$

34. If the distance between  $\text{Na}^+$  and  $\text{Cl}^-$  ions in  $\text{NaCl}$  crystal is 265 pm, then edge length of the unit cell will be?

- (a) 265 pm      (b) 530 pm      (c) 795 pm      (d) 132.5 pm

[Ans. (b)]

[Hint: In  $\text{NaCl}$ :

$$\text{Edge length} = 2 \times \text{distance between } \text{Na}^+ \text{ and } \text{Cl}^- \text{ ions}$$

$$= 2 \times 265 = 530 \text{ pm}]$$

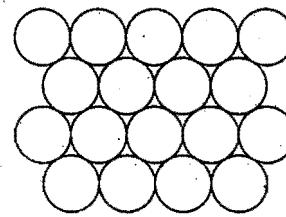
35. The interionic distance for caesium chloride crystal will be: [PMT (MP) 2007]

- (a)  $a$       (b)  $\frac{a}{2}$       (c)  $\frac{a\sqrt{3}}{2}$       (d)  $\frac{2a}{\sqrt{3}}$

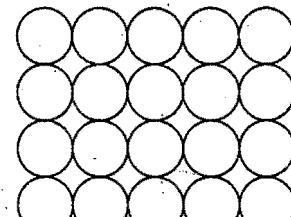
[Ans. (c)]

### 4.22 PACKING OF IDENTICAL SOLID SPHERES

The constituent particles in the formation of crystals are either atoms, ions or molecules. These particles may be of various shapes and thus, the mode of packing of these particles will change according to their shapes. The simplest way will be to consider these particles as spheres of equal size. The packing of spheres is done in such a way as to use the available space in the most economical manner.



Arrangement (i)



Arrangement (ii)

Fig. 4.35 Two common ways of packing spheres of equal size

There are two common ways in which spheres of equal size can be packed. This has been shown in Fig. 4.35. The arrangement (i) is more economical in comparison to arrangement (ii) as 60.4% volume is occupied in arrangement (i) and 52.4% volume in arrangement (ii). Arrangement (i) represents a close packing of spheres.

In arrangement (i), the spheres are packed in such a manner that their centres are at the corners of an equilateral triangle. Each sphere is surrounded by six other similar spheres as shown in Fig. 4.36. This arrangement can be extended in three dimensions by adjusting spheres on the top of hollows or voids of the two-dimensional layer which is called the first layer or 'A' layer. There are two types of hollows in the first layer which have been marked by dots (.) and cross (x). All the hollows are equivalent. The spheres of the second layer may be put either on hollows marked by dots or by crosses. Half of the hollows remain unoccupied in the second layer (Fig. 4.37). The second layer is marked as 'B' layer. The spheres have been placed on the hollows marked by dots.

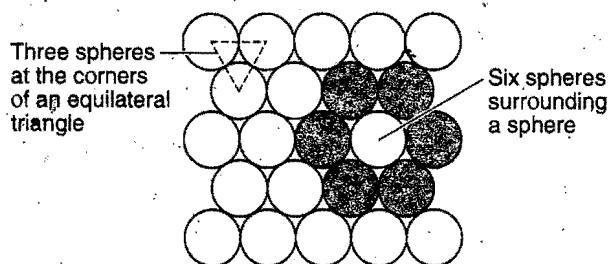


Fig. 4.36 Close packing of spheres

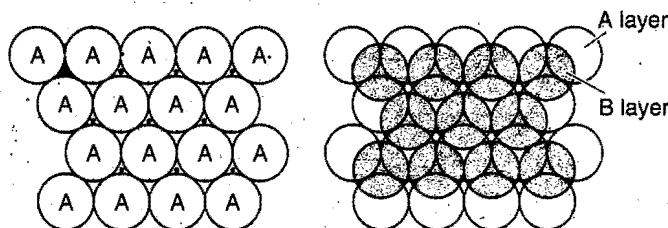


Fig. 4.37 Building of second layer (B, shown shaded) covering hollows marked by dots (•). The hollows marked by a cross (x) unoccupied

To build up the third layer of spheres, there are two alternative ways. In the first way the spheres are placed on the hollows of second layer. It is observed that each sphere of third layer lies exactly above the spheres of first layer. When this arrangement is continued indefinitely, the system obtained is found to possess hexagonal symmetry and is called hexagonal close packing of

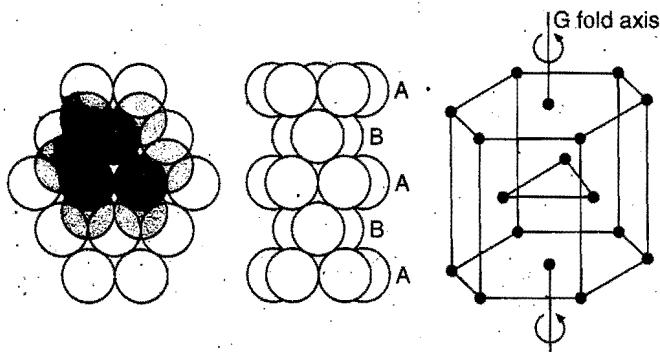


Fig. 4.38 ABABAB... or hexagonal close packing (hcp) of spheres

spheres and is abbreviated as hcp or *ABABAB...*. This is shown in Fig. 4.38. In the second way, spheres are placed on the unoccupied hollows of the first layer, marked by 'crosses'. It is observed that spheres of the third layer do not come over those of first layer. This arrangement of close packing is referred to as ABC. However, it is noted that spheres in the fourth layer will correspond with those in the first layer. When such an arrangement is continued indefinitely, the system is found to possess cubic symmetry and called cubic close packing of spheres and is abbreviated as ccp or *ABCABC...*. This is shown in Fig. 4.39. The system *ABCABC...* shows that there is a sphere at the centre of each face of the unit cube and thus, this system is also referred to as face-centred cubic or fcc.

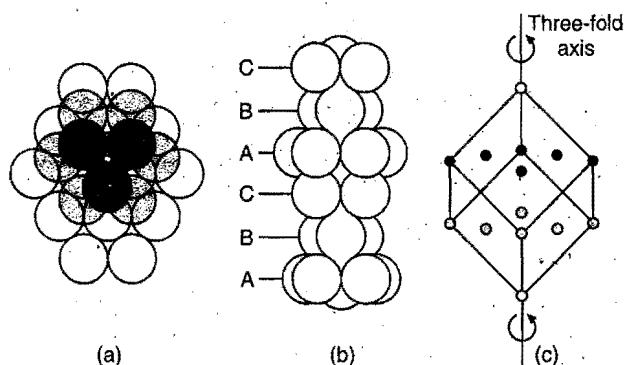


Fig. 4.39 ABCABCABC... or cubic close packing (ccp) of spheres

It is noted that in both the above systems hcp or ccp, each sphere is surrounded by twelve other spheres shown in Fig. 4.40. There is a third arrangement of packing of spheres which is known as **body-centred cubic** arrangement (bcc). This arrangement is obtained when the spheres in the first layer are slightly opened up, i.e., none of the spheres touches each other. In the second layer, the spheres are placed at the top of hollows in the first layer. In the third layer, spheres are placed exactly above the first layer. Each sphere in this system of packing is in contact with eight spheres, four in the lower layer and four in the upper layer. This arrangement has been shown in Fig. 4.41.

Most of the metals belonging to s-block and d-block elements possess any one of the following close packing arrangements:

- (i) Cubic closed packed, (ii) Hexagonal closed packed, and
- (iii) Body-centred cubic packed.

#### Examples:

Metals	Structure
Mg, Zn, Mo, V, Cd	hcp
Cu, Ag, Au, Ni, Pt	ccp or fcc
Li, Na, K, Rb, Cs, Ba	bcc

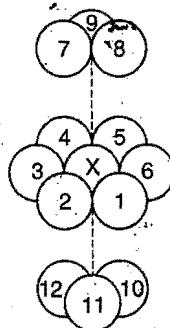
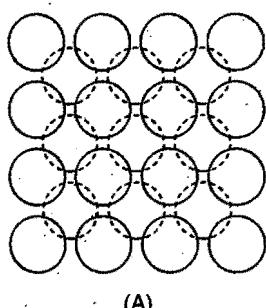
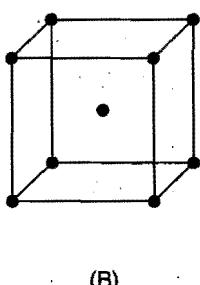


Fig. 4.40 Coordination number in hcp and ccp structure



(A)



(B)

**Fig. 4.41 (A) Body-centred cubic packing of spheres  
(B) Body-centred cubic arrangement**

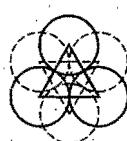
**Interstitial sites in close packed lattices:** In a close packing of spheres, there is always some empty space left. The empty space is called hole or void or interstitial site. Common interstitial sites in closely packed spheres are tetrahedral and octahedral.

**Tetrahedral site:** When one sphere is placed upon the three other spheres which are touching each other, tetrahedral structure results. The four spheres leave a small space in between which is called a tetrahedral site. The site is much smaller than that of the spheres. However, when the spheres are bigger in size, the tetrahedral site becomes larger. In hcp and ccp, each sphere is in contact with three spheres above and three spheres below. Thus, there are two tetrahedral sites associated with each sphere.

**Octahedral site:** This site is formed at the centre of six spheres, the centres of which lie at the apices of a regular octahedron. Each octahedral site is created by superimposing two equilateral triangles with apices in opposite direction, drawn by joining centres of three spheres in one plane and three spheres in other plane. There is an octahedral site for each sphere. Thus, octahedral sites are half of tetrahedral sites. Tetrahedral and octahedral voids are represented in Fig. 4.42 and 4.43.



**Fig. 4.42 Tetrahedral voids**



**Fig. 4.43 Octahedral voids**

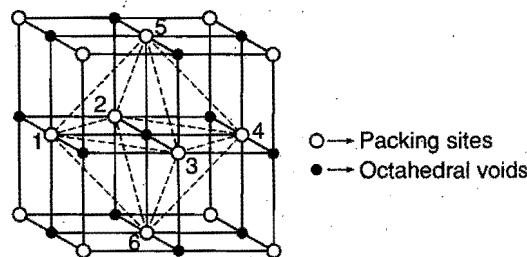
#### Location of Octahedral and Tetrahedral Voids in Cubic Close Packing

**Octahedral voids :** In the Fig. 4.44 a unit cell of ccp or fcc lattice is drawn. Corners and face-centres are the packing sites. In the face-centred cubic unit cell; octahedral voids are located at the body-centre and all the edge centres of cube.

$$\text{Number of constituent units at packing sites} = 8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$$

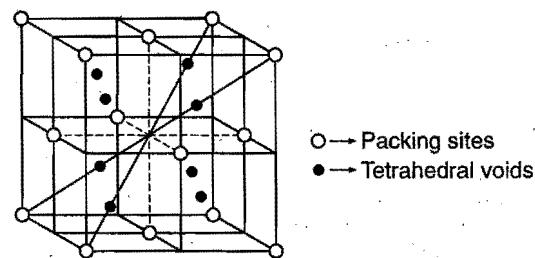
$$\text{Number of octahedral voids (one at body-centre and twelve at edge-centres)} = 1 + \frac{1}{4} \times 12 = 4$$

∴ Number of octahedral voids is equal to the number of constituent units at packing sites. Each octahedral void is surrounded by six constituent units.



**Fig. 4.44**

**Tetrahedral voids :** In cubic close packing, there are eight tetrahedral voids in each unit cell. Tetrahedral voids are located on body diagonals. Two tetrahedral voids are located on each body diagonal; these are represented in the Fig. 4.45.



**Fig. 4.45**

$$\text{Number of constituent units at packing sites (corners and face-centres)} = 8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$$

$$\text{Number of tetrahedral voids} = 8$$

Thus, number of tetrahedral voids is twice the number of constituent units present at packing sites.

In a multilayered closest-packed structure, there is a tetrahedral void above and below each atom, hence there are twice as many tetrahedral voids as those of closest-packed constituent units.

Tetrahedral and octahedral voids can be located as

- Second closest packed layer
- Tetrahedral voids
- Octahedral voids
- Tetrahedral voids
- First closest packed layer

#### ILLUSTRATIONS OF OBJECTIVE QUESTIONS

36. In a compound, atoms of element Y form ccp lattice and those of element X occupy 2/3rd tetrahedral voids. The formula of the compound will be : (AIEEE 2008)

- (a)  $X_3Y_4$     (b)  $X_4Y_3$     (c)  $X_2Y_3$     (d)  $X_2Y$

[Ans. (b)]

[Hint : Let number of atoms of Y used in packing = n]

Number of tetrahedral voids =  $2n$

$$\text{Number of atoms of } X = \frac{2}{3} \times 2n = \frac{4}{3}n$$

$$Y : X = n : \frac{4}{3}n = 3 : 4$$

Formula of compound =  $X_4Y_3$ ]

37. A solid compound contains  $X$ ,  $Y$  and  $Z$  atoms in a cubic lattice with  $X$  atoms occupying the corners,  $Y$  atoms in the body centred positions and  $Z$  atoms at the centre of the faces of the unit cell. What is the empirical formula of the compound?

- (a)  $XY_2Z_3$     (b)  $XYZ_3$     (c)  $X_2Y_2Z_3$     (d)  $X_8YZ_6$   
(e)  $XYZ$

[Ans. (b)]

[Hint : Number of atoms of  $X$  in a unit cell =  $\frac{1}{8} \times 8 = 1$

Number of atoms of  $Y$  in a unit cell = 1

Number of atoms of  $Z$  in a unit cell =  $\frac{1}{2} \times 6 = 3$

Empirical formula of the compound =  $XYZ_3$ ]

38. In a crystalline solid, atoms of  $X$  form fcc packing and the atoms of  $Y$  occupy all octahedral voids. If all the atoms along one body diagonal are removed then the simplest formula of the crystalline solid will be :

- (a)  $XY$     (b)  $X_4Y_3$     (c)  $X_5Y_4$     (d)  $X_4Y_5$

[Ans. (c)]

[Hint : Number of atoms of  $X$  in fcc packing (at corners and face centres of cubic unit cell) =  $8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$

Number of atoms of  $Y$  at octahedral voids = 4

Along one body diagonal there are two  $X$  atoms and one  $Y$  atom.

Number of effective atoms of  $X$  after removal

$$= 4 - 2 \times \frac{1}{8} = \frac{15}{4}$$

Number of effective atoms of  $Y$  after removal =  $4 - 1 = 3$

$$X : Y = \frac{15}{4} : 3$$

$$= 5 : 4$$

Simplest formula =  $X_5Y_4$ ]

## 4.23 TYPES OF CRYSTALS

Crystals are classified into four main types depending upon the nature of forces that hold the constituent particles together in the crystal lattice.

1. Ionic crystals: The forces operating in ionic crystals are electrostatic. The lattice points in such crystals are occupied by positively and negatively charged ions. Each ion is surrounded by the largest possible number of oppositely charged ions. This number of oppositely charged ions surrounding each ion is termed its **coordination number**. The coordination numbers of positive or negative ions may be same or different. For example, in sodium chloride, each  $\text{Na}^+$  ion is surrounded by six  $\text{Cl}^-$  ions and each  $\text{Cl}^-$  ion is surrounded by six  $\text{Na}^+$  ions. Thus, both the

ions have coordination number six. In  $\text{CsCl}$ , each  $\text{Cs}^+$  ion is surrounded by eight  $\text{Cl}^-$  ions and vice-versa. Thus, both the ions have coordination number eight. In the case of  $\text{CaF}_2$ , the coordination number of  $\text{Ca}^{2+}$  is eight while that of  $\text{F}^-$  ion, is four.

The coordination numbers commonly encountered in ionic crystals are 8 (body-centred cubic arrangement), 6 (octahedral arrangement) and 4 (tetrahedral arrangement).

It is impossible for both anions and cations to have closed packed structures but if one of the ions is much bigger than the other, it is common for the bigger ions alone to approach a closed packed structure and smaller ions to fit into holes in this structure.

In ionic crystals, the coordination numbers as well as the geometrical shapes of the crystals depend mainly on the relative sizes of the ions. The ratio of the radii of the positive and negative ions is called radius ratio.

$$\text{Radius ratio} = \frac{\text{Radius of positive ion (cation)}}{\text{Radius of negative ion (anion)}} = \frac{r_c^+}{r_a^-}$$

Common coordination numbers are 3, 4, 6 and 8.

The following table shows the radius ratio values, permitted coordination numbers and the shapes of ionic crystals:

Radius ratio ( $r_c^+ / r_a^-$ )	Permitted coordination number	Arrangement of anions round the cations	Example
0.155–0.225	3	Plane Triangular	$\text{B}_2\text{O}_3$
0.225–0.414	4	Tetrahedral	$\text{ZnS}$
0.414–0.732	6	Octahedral	$\text{NaCl}$
0.732–1.000	8	Cubic (body-centred)	$\text{CsCl}$

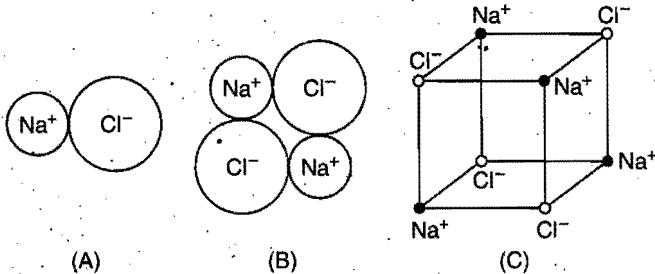
### Types of Structure of Ionic Solids

Crystal structure of ionic solids are described into following types:

Crystal structure (Type)	Example
1. Rock salt	$\text{NaCl}$ , $\text{LiCl}$ , $\text{KBr}$ , $\text{RbI}$ , $\text{AgCl}$ , $\text{AgBr}$ , $\text{FeO}$ , $\text{CaO}$
2. Cesium chloride	$\text{CsCl}$ , $\text{CaS}$ , $\text{CsCN}$
3. Fluorite	$\text{CaF}_2$ , $\text{UO}_2$ , $\text{BaCl}_2$ , $\text{HgF}_2$
4. Antifluorite	$\text{K}_2\text{O}$ , $\text{K}_2\text{S}$ , $\text{Li}_2\text{O}$ , $\text{Na}_2\text{O}$ , $\text{Na}_2\text{S}$
5. Nickel Arsenite	$\text{NiAs}$ , $\text{NiS}$ , $\text{FeS}$ , $\text{CoS}$
6. Rutile	$\text{TiO}_2$ , $\text{MnO}_2$ , $\text{SnO}_2$
7. Perovskite	$\text{CaTiO}_3$ , $\text{BaTiO}_3$ , $\text{SrTiO}_3$
8. Zinc blende (sphalerite)	$\text{ZnS}$ , $\text{CuCl}$ , $\text{CdS}$ , $\text{HgS}$
9. Wurtzite	$\text{ZnS}$ , $\text{ZnO}$ , $\text{BeO}$ , $\text{MnS}$ , $\text{AgI}$

Packing of ions in ionic crystal (Formation of  $\text{NaCl}$  crystal): The formation of  $\text{NaCl}$  crystal can be explained in the following manner. The two ions form one ion-pair of opposite charges by the electrostatic force of attraction. Each of the ions

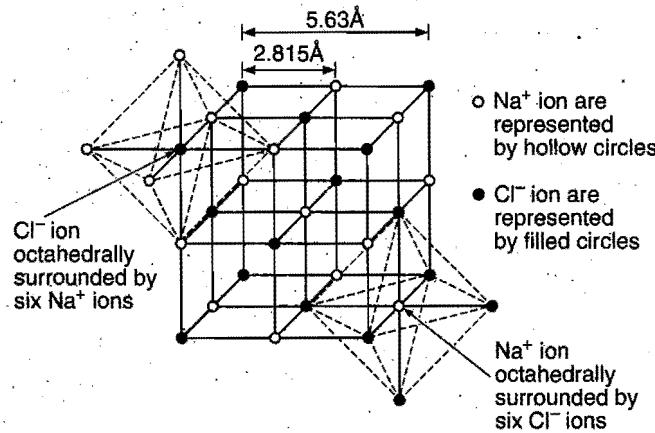
has a strong residual field around it and will naturally attract another ion-pair much in the same way as two magnets attract each other, i.e., a cluster is formed. Two clusters combine together to give a unit cell. Finally, large number of unit cells unite together to form three-dimensional cubic crystal.



**Fig. 4.46 Filling up of ion pairs in stages: (A) shows an ion-pair, (B) two ion-pairs and (C) four ion-pairs of sodium chloride**

An examination of NaCl crystal (Fig. 4.47) makes the following points clear:

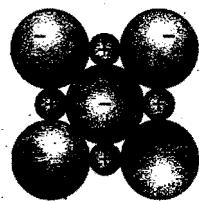
(i) Each  $\text{Na}^+$  ion is surrounded by six  $\text{Cl}^-$  ions at the corners of a regular octahedron and similarly each  $\text{Cl}^-$  ion is surrounded by six  $\text{Na}^+$  ions. It is, therefore, termed as 6:6 arrangement. The radius ratio  $[r_{\text{Na}}^+ / r_{\text{Cl}}^- = 0.95 / 1.81 = 0.524]$  suggests that coordination number of each ion is six.



**Fig. 4.47 Unit cell representation on NaCl structure**

(ii) In the octahedral structure,  $\text{Cl}^-$  ions may be regarded as having a cubic closed packed (ccp) arrangement in which all octahedral holes are filled by  $\text{Na}^+$  ions.

(iii) This type of structure is possessed by most of the alkali metal halides ( $\text{KCl}$ ,  $\text{NaI}$ ,  $\text{RbF}$ ,  $\text{RbI}$ ), alkaline earth metal oxides and  $\text{AgF}$ ,  $\text{AgCl}$ ,  $\text{AgBr}$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{Br}$ , etc.



**Fig. 4.48**

$$\text{Here, } 4r_- = \sqrt{2}a \text{ and } (2r_- + 2r_+) = a$$

Packing fraction ( $\phi$ ):

$$\phi = 4 \times \frac{4}{3} \pi \frac{(r_+^3 + r_-^3)}{a^3} = \frac{\pi}{3\sqrt{2}} \left[ \left( \frac{r_+}{r_-} \right)^3 + 1 \right].$$

The unit cell of sodium chloride has four sodium ions and four chloride ions.

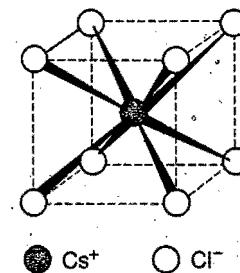
$$(a) \text{ Number of sodium ions} = 12 \text{ (at the edge-centres)} \times \frac{1}{4} + 1 \text{ (at body-centre)} = 4$$

$$(b) \text{ Number of chloride ions} = 8 \text{ (at the corners)} \times \frac{1}{8} + 6 \text{ (at face-centres)} \times \frac{1}{2} = 4$$

### Structure of Some Other Ionic Compounds

In CsCl crystal, the coordination number of each ion is 8 as the radius ratio  $\left( \frac{r_{\text{Cs}^+}}{r_{\text{Cl}^-}} \right)$  is 0.933. It is termed as 8:8 arrangement.

The arrangement of the ions in this crystal is body-centred cubic type, i.e., the unit cell has one ion at the centre and oppositely charged ions at the corners of the cube. This has been shown in Fig. 4.49. This type of structure is possessed by CsBr, CsI, TlCl, TlBr, etc.



**Fig. 4.49 Structure of CsCl**

Here,  $\text{Cs}^+$  ion is present at the body centre and chloride ions at eight corners. In their limiting case :

$$2r_- = a \text{ and } (2r_- + 2r_+) = \sqrt{3}a$$

$a$  = edge length of unit cell

Packing fraction ( $\phi$ ):

$$\phi = \frac{4}{3} \pi \frac{(r_+^3 + r_-^3)}{a^3} = \frac{4\pi}{3 \times 8} \left[ \left( \frac{r_+}{r_-} \right)^3 + 1 \right]$$

ZnS crystal has two types of structures:

- (i) Zinc blende structure and
- (ii) Wurtzite structure.

(i) **Zinc blende structure:** It has cubic close-packed (ccp) structure. The  $\text{S}^{2-}$  ions are present at the corners of the cube and at the centre of each face. Zinc ions occupy half of the tetrahedral sites. Each zinc ion is surrounded by four sulphide ions which are disposed towards the corners of a regular tetrahedron. Similarly,

each  $S^{2-}$  ion is surrounded by four  $Zn^{2+}$  ions. This structure is similar to diamond.

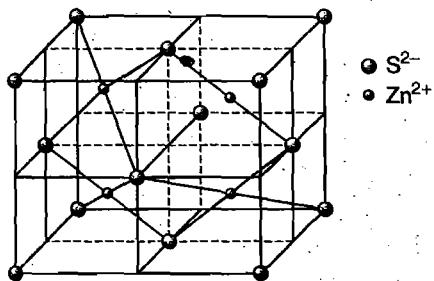


Fig. 4.50 Zinc blende

$$4r_+ = \sqrt{2}a$$

Packing fraction ( $\phi$ ) :

$$= 4 \times \frac{4}{3} \pi \frac{(r_+^3 + r_-^3)}{a^3} = \frac{\pi}{3\sqrt{2}} \left[ \left( \frac{r_+}{r_-} \right)^3 + 1 \right]$$

(ii) Wurtzite structure: It has hexagonal close-packed (hcp) structure.  $S^{2-}$  ions adopt hcp arrangement and  $Zn^{2+}$  ions occupy half of the tetrahedral sites.

The above structures are termed 4 : 4 arrangement possessed by  $ZnO$ ,  $AgI$ ,  $SiC$ , etc.

$CaF_2$  crystal: The  $Ca^{2+}$  ions are arranged in ccp arrangement, i.e.,  $Ca^{2+}$  ions are present at all corners and at the centre of each face of the cube. The fluoride ions occupy all the tetrahedral sites. This is 8 : 4 arrangement, i.e., each  $Ca^{2+}$  ion is surrounded by 8  $F^-$  ions and each  $F^-$  ion by four  $Ca^{2+}$  ions.

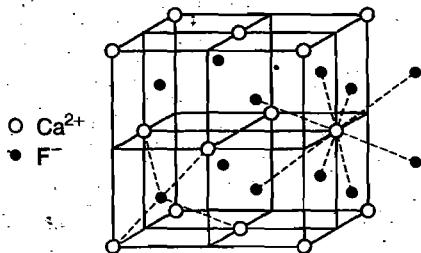


Fig. 4.51 Fluorite structure—Structure of calcium fluoride

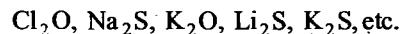
#### Structure of Sodium Oxide ( $Na_2O$ )—Antifluorite Structure

Sodium oxide has antifluorite structure. The structure is similar to the structure of calcium fluoride with the difference that the anions occupy the positions of cations and vice-versa.

(i) It has cubic close packing arrangement of  $O^{2-}$  ions, i.e., these ions are present at the corners and at the centres of all the six faces of the unit. Sodium ions on the other hand, are present at the sites of all the tetrahedral voids.

(ii) Each  $Na^+$  ion is surrounded by four  $O^{2-}$  ions and each  $O^{2-}$  ion is surrounded by eight  $Na^+$  ions. Thus,  $Na_2O$  has 4 : 8 coordination structure.

Other examples with antifluorite structures are :



#### Structures of Oxides of Iron

Iron is known to form three major oxides, which are  $FeO$ ,  $Fe_2O_3$ ,  $Fe_3O_4$ . These oxides are interconvertible due to oxidation and reduction. Non-metal excess non-stoichiometry is also known in these oxides. Crystal structures of these oxides are very interesting.

1. Structure of  $FeO$  : This oxide has a structure like rock salt ( $NaCl$ ). Oxide ions ( $O^{2-}$ ) form a face-centred cubic close packing and  $Fe^{2+}$  ions occupy all octahedral voids. It is a perfect rock salt type structure with formula  $FeO$ . This oxide is known to form non-metal excess non-stoichiometric compound with the composition  $Fe_{0.95}O$  (Wustite). In the non-stoichiometric compound some of the  $Fe^{2+}$  ions present in octahedral voids are replaced by  $Fe^{3+}$  ions. Three  $Fe^{2+}$  ions will be replaced by two  $Fe^{3+}$  ions to maintain electrical neutrality.

[Normal Spinel Structure.: Spinel is the common name of the mineral,  $MgAl_2O_4$ . The crystal structure of this mineral is also called spinel structure. In this type of structure, both tetrahedral and octahedral voids are simultaneously occupied. General formula of the compound having spinel structure is  $AB_2O_4$  where 'A' stands for a divalent cation and 'B' stands for a trivalent cation. It has a cubic close packed arrangement of oxide ions. Half of the octahedral voids are occupied by trivalent cations and one-eighth of the tetrahedral voids are occupied by divalent cations.

Ferrites are the spinel type compounds having the general formula  $AFe_2O_4$  where 'A' stands for divalent cation such as  $Zn^{2+}$ . Ferrites are used for making powerful, permanent and non-rusting magnets. Ferrites are used in telephones and memory units of computers.]

2. Structure of  $Fe_3O_4$  : Magnetite,  $Fe_3O_4$ , is considered as a mixed oxide. It contains mixture of  $FeO$  and  $Fe_2O_3$ . It has an **inverse spinel structure**. Oxide ions ( $O^{2-}$ ) form face-centred cubic arrangement. Dipositive ions ( $Fe^{2+}$ ) are present in octahedral voids and tripositive ions ( $Fe^{3+}$ ) are equally distributed among tetrahedral and octahedral voids.

$$\begin{array}{ll} \text{Number of } O^{2-} \text{ ions in the unit cell} & = 4 \\ \text{Thus, Number of tetrahedral voids} & = 8 \\ \text{and Number of octahedral voids} & = 4 \end{array}$$

$$\begin{array}{ll} \text{Number of } Fe^{2+} \text{ ions present in octahedral void} & = 1 \\ \text{Number of } Fe^{3+} \text{ ions present in tetrahedral void} & = 1 \\ \text{Number of } Fe^{3+} \text{ ions present in octahedral void} & = 1 \end{array}$$

Thus, half of the octahedral voids are occupied by  $Fe^{2+}$  and  $Fe^{3+}$  ions and one-eighth of the tetrahedral voids are occupied by  $Fe^{3+}$  ions.

3. Structure of  $\text{Fe}_2\text{O}_3$ : If all the  $\text{Fe}^{2+}$  ions are replaced by  $\text{Fe}^{3+}$  ions, then as every three  $\text{Fe}^{2+}$  ions can be replaced by two  $\text{Fe}^{3+}$  ions to maintain electrical neutrality, the ratio between Fe and O will now be 2 : 3, i.e., we get  $\text{Fe}_2\text{O}_3$ .

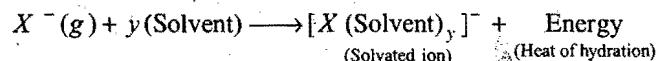
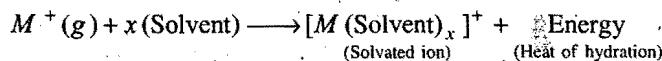
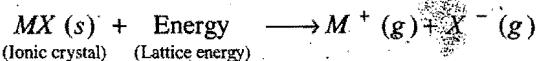
### Properties of Ionic Crystals

(i) Physical state: Ionic crystals are crystalline solids at room temperature. They are never liquids or gases under ordinary temperature and pressure as the ions do not have freedom of movement.

Since, high energy is required to separate cations and anions from one another from their allotted positions on account of very strong electrostatic forces of attraction, the **ionic crystals are quite hard, have low volatility and have high melting and boiling points.**

(ii) Electrical conductivity: Ionic crystals are insulators, i.e., do not conduct electricity in solid state. The reason is that ions are held firmly in fixed positions in the crystal lattice and cannot move when electric field is applied. **However, when melted they become good conductors of electricity**, i.e., ions are free to move in liquid medium.

(iii) Solubility: Ionic crystals are soluble in polar solvents or solvents having high values of dielectric constant. They are insoluble in non-polar solvents. When they dissolve in non-polar medium colloidal solutions are formed, e.g.,  $\text{NaCl}$  in kerosene oil. The dissolution of an ionic crystal in a polar solvent depends on the relative magnitudes of lattice and hydration energies.



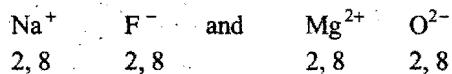
The ionic compound will be soluble if total hydration energy is higher than lattice energy.

Ionic crystals are good conductors in molten state or when dissolved in water.

(iv) Brittleness: Ionic solids are highly brittle in nature. When external force is applied, these are easily broken into pieces. Ionic solids are composed of parallel layers which contain cations and anions. When external force is applied, one layer slides a bit over the other and like ions come in front of each other. Due to repulsion between two layers the ionic solid breaks down.

Ionic crystals have high density due to close packing.

(v) Isomorphism: Ionic crystals possess same crystalline structure, i.e., show isomorphism if the ions (cations and anions) have same electronic configuration.  $\text{NaF}$  and  $\text{MgO}$  are isomorphous compounds.



2. Covalent crystals: In covalent crystals, the lattice points are occupied by neutral atoms either of same element or of

different elements. These atoms are held together by covalent bonds. Covalent crystals are of two types:

(i) The covalent bonds extend in three-dimensions forming a giant interlocking structure. Examples are diamond, silicon carbide ( $\text{SiC}$ ), aluminium nitride, etc.

In **diamond**, each carbon atom is  $sp^3$ -hybridized and thus, covalently bonded to four other carbon atoms present at the four corners of a regular tetrahedron. This leads to a rigid three-dimensional network. The entire crystal is regarded as one large carbon molecule and is called a **macromolecule**. The structure of diamond explains the properties such as high density, non-conducting nature, extreme hardness and high melting and boiling point of the diamond.

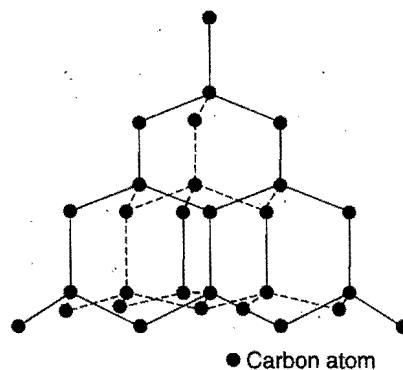


Fig. 4.52 Structure of diamond

(ii) The covalent bonds extend in two-dimensions forming a giant layer. These layers are then held together by van der Waals' forces. Examples are graphite, boron nitride (BN), cadmium iodide, etc.

In **graphite**, each carbon is  $sp^2$ -hybridized and is thus bonded to three carbon atoms in the same plane. The C—C distance is 1.42 Å which is intermediate between single bond distance (1.54 Å) and double bond distance (1.33 Å). The unit cell consists of a hexagon of six carbon atoms. The unit cells are interlocked giving a layer or sheet structure. The distance between two adjacent layers is 3.35 Å. The structure explains the properties of graphite such as being soft, good conductor of electricity, flaky and slippery.

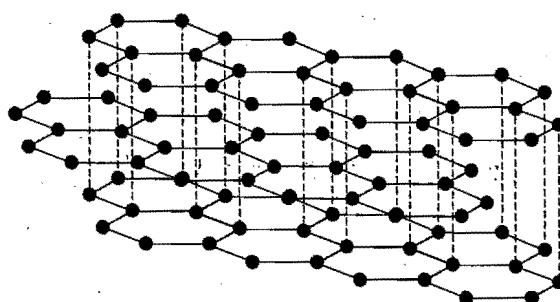


Fig. 4.53 Structure of graphite

In general, the packing of atoms in covalent crystals is loose in comparison to ionic and metallic crystals. Thus, covalent crystals have open structure.

**3. Metallic crystals:** The metallic crystals have positive metal ions as lattice points surrounded by a sea of mobile electrons. Each electron belongs to a number of positive ions and each positive ion belongs to a number of electrons. The force that binds a metal ion to a number of electrons within its sphere of influence is known as **metallic bond**. Metallic crystals mostly belong to cubic face-centred (fcc), cubic body-centred (bcc) and hexagonal close-packed (hcp) systems. Metallic crystals exhibit the following properties:

(i) **Good conductors:** On account of the presence of mobile electrons, metals are good conductors of electricity. The electrical conductivity decreases with increase of temperature. This is due to the fact that positive ions also begin to oscillate with the increase of temperature. The oscillation of positive ions hinders the movement of mobile electrons. Metals are also good conductors of heat.

(ii) **Lustre:** When freshly cut or scratched, most of the metals have a shining surface. When light falls on freshly cut surface, the electrons get excited. The excited electrons give off energy in the form of light when they return to their original position and hence the metal looks bright. The metallic properties are explained on the basis that the metallic bond is non-directional and non-rigid. The result is that  $M^{n+}$  ions can be easily moved from one lattice site to another. The nearest neighbours can be thus changed easily and new metal bonds can be formed readily. This explains why metals are malleable and ductile.

(iii) **Physical characteristics:** Most of the metals are quite hard and tough. They are malleable and ductile. They have high tensile strength. Except alkali metals, they have high melting and boiling points. They also possess elasticity.

**4. Molecular crystals:** In molecular crystals, the lattice points are occupied by molecules which do not carry any charge. The forces responsible for binding these molecules are dipole-dipole attractions and van der Waals' forces. Dipole-dipole forces are present in solids when polar molecules occupy the lattice points as in the case of water. van der Waals' forces are more general and occur in all kinds of molecular crystals. The binding energy in molecular crystals is, therefore, weak. Molecular crystals show the following general properties:

- (i) They are generally soft and easily compressible.
- (ii) They have low melting or boiling points.
- (iii) They are bad conductors of electricity as the electrons are localised in the bonds.
- (iv) They have low density.

The following table provides a comparative summary of the properties of various types of crystals:

Property	Ionic crystals	Covalent crystals	Metallic crystals	Molecular crystals
1. Constituent particles occupying lattice points	Positive and negative ions	Neutral atoms	Positive ion in sea of electrons	Molecules polar or non-polar
2. Binding force	Electrostatic attraction	Shared pairs of electrons	Electrostatic attractions between positive ions and electrons	Weak polar forces or van der Waals' forces
3. Hardness	Hard and brittle	Very hard	Hard or soft	Very soft
4. Melting and boiling points	High	Very high	High or low	Low
5. Electrical conductivity	Bad conductors; Good conductors in fused state or in solution	Bad conductors with few exceptions	Good conductors	Bad conductors
6. Examples	NaCl, KNO <sub>3</sub> , CaF <sub>2</sub>	Diamond, graphite, carbonium	Cu, Na, Fe metals	Ice, solid CO <sub>2</sub>

#### 4.24 IMPERFECTION IN SOLIDS

An ideal crystal is one which has the same unit cell containing the same lattice points across the whole crystal. Any departure from perfectly ordered arrangement of constituent particles in the crystals is called imperfection or defect.

Perfect of ideal crystals can exist only at absolute zero or zero Kelvin. At absolute zero the crystalline substances have zero entropy, i.e., have no randomness. Above absolute zero, entropy or randomness increases, i.e., some deviations from perfectly ordered arrangement takes places.

The imperfection may be **intrinsic** or **extrinsic**. Crystalline defects can profoundly alter the properties of a solid material. Imperfections or defects not only alter the properties but also give rise to new characteristics. Extrinsic defects due to presence of certain impurities give rise to interesting changes in the properties. For example, gem stones are crystals containing impurities that give them beautiful colours. The presence of Fe<sup>3+</sup> ions makes sapphire blue and Cr<sup>3+</sup> ions presence makes ruby red. (Gems are actually crystals of Al<sub>2</sub>O<sub>3</sub> which is colourless).

There are mainly two types of imperfections.

1. Electronic imperfections
2. Atomic imperfections.

## 1. Electronic Imperfections

This type of imperfection arises due to irregular arrangement of electrons in the crystal structure. At 0 K (absolute zero), the electrons in both ionic and covalent solids are present in fully occupied lowest energy orbitals or states and these electrons do not move under the influence of applied electric field. However, when temperature is raised above 0 K, some electrons may occupy higher energy states. For example, in crystals of pure silicon or germanium, some electrons are released from the covalent bonds above 0 K. These free or mobile electrons become responsible for electrical conductance. The bonds from which the electrons have been removed on heating become electron deficient and these are referred to as **holes**. Like free electrons, holes also conduct electric current. Holes in an electric field move in a direction opposite to that in which electrons move. Both electrons and holes present in the solids give rise to electronic imperfection. Electrons and holes are denoted by the symbols 'e' and 'h' and their concentrations are represented by 'n' and 'p'. In pure covalent solids like silicon and germanium, the number of free electrons and holes will be equal. Electrons and holes can be obtained preferentially according to the requirement by adding appropriate impurities.

Silicon and germanium are the elements of group 14th; thus, they have maximum covalency of four. A number of solids can be obtained by the combination of the elements of groups 13 and 15 or groups 12 and 16 to get average valency of four as in silicon and germanium. Examples are : InSb; AlP; GaAs. In these materials, In, Al and Ga belong to group 13 and Sb, P and As belong to group 15 of the extended form of the periodic table. Other examples are : ZnS, CdS, CdSe, HgTe. In these materials, Zn, Cd and Hg belong to group 12 and S, Se and Te belong to group 16 of the periodic table. These combinations are not purely covalent but possess an ionic character due to difference in the electronegativities of the two elements. These combinations show interesting electrical, magnetic and optical properties which have been utilised in the electronic industries for photovoltaic cells, light emitting diodes, thermocouples and semiconductors, etc.

## 2. Atomic Imperfections or Point Defects

When the deviations exist in the regular or periodic arrangement of the constituent particles (atoms or ions) in the crystal, these defects are termed atomic imperfections or point defects.

These defects are caused by the following points.

- (i) When some of the constituent particles are missing from their normal positions, these unoccupied position are termed **holes or vacancies**.
- (ii) When some of the constituent particles are missing from their positions and these particles have shifted either to interstitial vacant sites or to positions which are meant for other particles.

**Types of point defects :** Point defects are classified into the following three types:

- (A) Defects in stoichiometric crystals,
- (B) Defects in non-stoichiometric crystals,
- (C) Impurity defects

### (A) Defects in stoichiometric crystals

The crystals in which cations and anions are exactly in the same ratio as indicated by their molecular formulae are termed **stoichiometric crystals**. Points defects do not alter the stoichiometry of the solid; these defects are called as intrinsic or thermodynamic defect. Two types of point defects are observed in these crystals :

- (i) Schottky defect, (ii) Frenkel defect.

(i) Schottky defect : This defect was first observed by the German scientist Schottky in 1930. In this defect equal number of cations and anions (from AB type crystal) are missing from their normal lattice sites, i.e., equal number of cationic and anionic **vacancies or holes** will be developed. The crystal maintains electrical neutrality.

This defect is usually observed in strongly ionic compounds which have high coordination number and the sizes of two ions (cations and anions) are almost same.

**Examples :** NaCl, KCl, KBr, CsCl, AgBr etc.

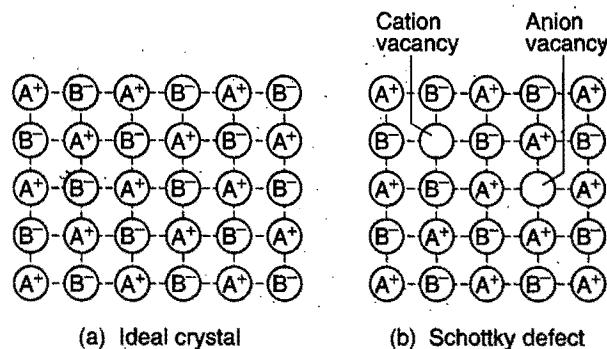


Fig. 4.54

In 1 cm<sup>3</sup> of NaCl there are  $10^{22}$  ions and  $10^6$  Schottky pairs, thus there is one Schottky defect per  $10^{16}$  ions.

#### Consequences of Schottky defect

- (a) Due to Schottky defect, the density of crystalline solid decreases.
- (b) Lattice energy and thereby stability of the crystalline solid decreases.
- (c) Entropy increases.

(ii) Frenkel defect : This defect was discovered and studied by a Russian scientist, Frenkel, in 1926. This defect is caused if some of the ions (usually the cations) of the lattice occupy interstitial sites leaving a corresponding number of normal lattice sites vacant. This defect creates **vacancy defect** at original site and **interstitial defect** at new site. Frenkel defect is also called **dislocation defect**.

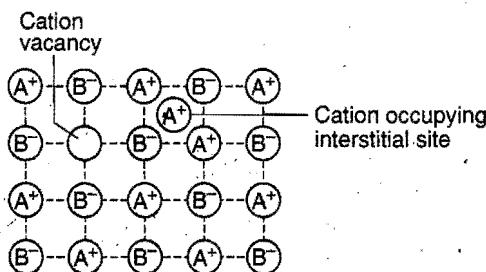


Fig. 4.55 Frenkel defect in the crystal

Main conditions for Frenkel defect are:

- Coordination number should be low.
- Size of anion should be bigger than cation.

**Examples :** This defect is not found in alkali metal halides because cations and anions have almost equal sizes and cations cannot be accommodated in interstitial sites. This defect is mainly found in transition metal halides like AgCl, AgBr, AgI, ZnS, etc. Silver ion ( $\text{Ag}^+$ ) being smaller in size can be accommodated in interstitial site. AgBr shows both Frenkel and Schottky defect.

#### Consequences of Frenkel defect

- (a) There is no change in the density of the solid.
- (b) There is increase in the dielectric constant as the like charge ions come closer.
- (c) The solids having Frenkel defect show conductivity and diffusion in solid state due to presence of vacant lattice sites.
- (d) Lattice energy and thereby stability of crystalline solids decreases.
- (e) This defect influences the chemical properties of ionic compound.
- (f) Entropy of the solid increases.

**Thermodynamic facts about point defects in stoichiometric solids :** Frenkel and Schottky defects are also called as intrinsic or thermodynamic defects.

Number of point defects increases with temperature. The number of defects formed per unit volume ( $\text{cm}^3$ ) 'n' is given by,

$$n = Ne^{-W/2RT}$$

where,  $N$  = number of sites per unit volume ( $\text{cm}^3$ ) which could be left vacant

$W$  = Work necessary to create a defect

$T$  = Absolute temperature

Electrical conductance of crystals increases due to point defects. When potential difference is applied to the solid then ions may move from the lattice sites to occupy the holes or vacancies. Such movement is responsible for electrical conductance.

#### Difference between Schottky and Frenkel defect

Schottky defect	Frenkel defect
1. Equal number of cationic and anionic vacancies are present in this defect.	Some ions are displaced from normal lattice sites to the interstitial sites.

- |  |   |
|--|---|
| 2. Density is lowered in this defect.  | Density is unaffected in it.  |
| 3. Dielectric constant remains same.   | Dielectric constant increases.  |
| 4. It is shown by those ionic compounds which have high coordination number, sizes of cations and anions are almost equal. | It is shown by those ionic compounds which have low coordination number and size of cations is smaller than size of anions. |

#### (B) Defects in non-stoichiometric solids

The compounds in which the number of positive and negative ions are not exactly in the ratio as indicated by their chemical formulae are called non-stoichiometric compounds. Non-stoichiometric solids are also known as Berthollide compounds.

##### Examples :

- (i) Ferrous oxide  $\text{FeO}$  exists in non-stoichiometric form as  $\text{Fe}_{0.95}\text{O}$  called wüstite.
- (ii) Vanadium oxide has non-stoichiometric formula  $\text{VO}_x$ , where  $x$  lies between 0.6 and 1.3.
- (iii)  $\text{ZnO}$  exists as a non-stoichiometric compound having excess zinc.
- (iv) Stoichiometric compounds like  $\text{NaCl}$ ,  $\text{KCl}$ , etc., can be non-stoichiometric under suitable conditions.

The defects which bring change in overall chemical composition are termed as **non-stoichiometric defects**. In such crystals, there is excess of either positive particles (cations) or negative particles (anions). However, the crystal as a whole is neutral in nature. If positive particles are in excess, the charge is balanced by the presence of extra electrons. In case the negative particles are in excess, the charge is balanced by acquiring higher oxidation state by metal atoms.

Non-stoichiometric defects are of two types:

1. Metal excess defect, 2. Non-metal excess defect

**1. Metal excess defect :** In this defect, metal ions or cations are in excess. This defect may develop on account of the following two ways :

**(a) Anion vacancies :** A negative ion may be missing from its lattice site leaving behind a vacancy or hole. This vacancy or hole is occupied by an extra electron to maintain electrical neutrality. This defect is somewhat similar to Schottky defect but differs in having only one hole and not a pair as in the latter case.

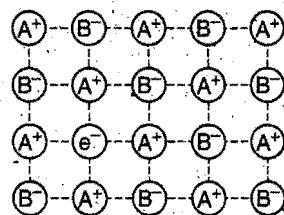


Fig. 4.56 Metal excess defect due to anion vacancy

Anion vacancies in alkali metal halides are produced by heating the metal halides in the atmosphere of alkali metal

vapours. Metal atoms get adsorbed on the surface of the metal halides. Halide ions move towards the surface and combine with metal ions formed by the adsorbed atoms on account of their ionisation. The electrons released in the process diffuse into the crystal and occupy anion vacancies. The electrons trapped in anion vacancies are referred to as F-centres. 'F' stands for **Farben**, a German word, meaning colour. Greater is the number F-centres, more is the intensity of colour. For example, non-stoichiometric sodium chloride with excess sodium is yellow, non-stoichiometric potassium chloride with excess of potassium is violet and non-stoichiometric lithium chloride with excess of lithium is pink.

**(b) Excess cations occupying interstitial positions :** Metal excess defect may also be developed by the presence of extra cation in the interstitial site. Electrical neutrality is achieved by an electron presence in another interstitial site. This defect is similar to Frenkel defect. For example, when ZnO is heated, it loses oxygen and turns yellow.

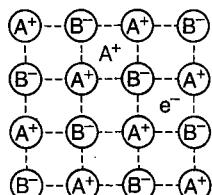
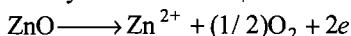


Fig. 4.57 Metal excess defect due to the presence of extra cation in the interstitial position

The  $\text{Zn}^{2+}$  ions thus formed occupy interstitial sites and the electrons occupy the neighbouring interstitial sites. The crystals having metal excess defects contain few free electrons and, thus, such solids act as semi-conductors.

**2. Non-metal excess or metal deficiency defect :** These contain lesser number of positive particles than negative particles. These defects arise due to cation vacancies or anions occupying interstitial sites. The extra negative charge is balanced by oxidation of some of the nearby metal ions. Thus, this defect occurs when metal shows variable valency, i.e., especially in the case of transition metals. Examples are : FeO, FeS, NiO, etc. Crystals with metal deficient defects are semiconductors of p-type.

### (C) Impurity defects in ionic crystalline solids

A defect in an ionic solid can be introduced by adding foreign ions. If the impurity ions have a different oxidation state than that

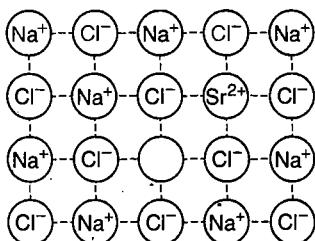


Fig. 4.58 Impurity defect

of the host ions, vacancies are created. For example, if molten NaCl containing a little  $\text{SrCl}_2$  or  $\text{CaCl}_2$  as impurity is allowed to cool, some lattice sites will be occupied either by  $\text{Ca}^{2+}$  ions or  $\text{Sr}^{2+}$  ions in place of  $\text{Na}^+$  ions. For every  $\text{Ca}^{2+}$  ion or  $\text{Sr}^{2+}$  ion, two  $\text{Na}^+$  ions are removed in the crystal lattice in order to maintain electrical neutrality. Thus, one of these lattice sites is occupied by  $\text{Ca}^{2+}$  or  $\text{Sr}^{2+}$  ion and the other site remains vacant.

Cationic vacancies developed due to introduction of impurity cause higher electrical conductivity of ionic solids. Addition of about 0.1%  $\text{SrCl}_2$  to NaCl increases the electrical conductivity by 10000 times. Solid solution of  $\text{CdCl}_2$  and  $\text{AgCl}$  is another example of this type of impurity defect.

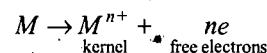
### Electric Properties of Solids

On the basis of electrical conductivity, solids are divided into three categories:

- (i) Metals (ii) Insulators (iii) Semiconductors

Metals have conductivity  $10^8 \text{ ohm}^{-1} \text{ cm}^{-1}$  and insulators have  $10^{-12} \text{ ohm}^{-1} \text{ cm}^{-1}$ .

**Metals:** Metals have free electrons and fixed kernels at their lattice sites:



Free electrons make the metal good conductor of electricity and heat. Conductivity of metals is nearly independent of impurity of metals. Resistance ratio may be taken to check the impurity level of metals, i.e.,  $\rho_{300\text{K}} / \rho_{4.2\text{K}}$ . Conductivity of metals depends on number of valence electrons, i.e., number of free electrons produced by the metal.

### Nature of Metallic Bond

A metal is regarded as group of positively charged metal ions packed as closely as possible in a regular geometrical fashion and immersed in a sea or pool of mobile electrons. The attraction force that binds the metal ions and mobile electrons is called metallic bonding.

**1. Conductivity:** When potential difference is applied electrons (mobile) conduct electric current. It has been observed that the conductivity of most of the metals decreases with increase in temperature. At high temperature, positive metal ions start vibration and create resistance to the flow of electrons; thus resistance of metal increases.

Good thermal conductivity of metals can also be explained on the basis of mobile electrons.

**2. Opaqueness and lustre:** Mobile electrons absorb quantum energy of visible light and become excited; when excited electrons return to normal state, visible light is evolved. Since, the light is fully absorbed by metal hence it is opaque.

**3. Elasticity:** On applying mechanical stress, temporary deformation of the metal crystal takes place and the kernels with their electron cloud return to their original position as soon as mechanical stress is removed.

**4. Microproperties of metals:** Some other properties of metals are summarised ahead:

- (a) Metals possess high tensile stress.
- (b) Metals are usually hard and solid.
- (c) Some metals like alkali and alkaline earth metals show photoelectric effect, i.e., ejection of electron from metal surface when exposed to light of appropriate energy.
- (d) Metals have low ionization energy.
- (e) Strength of metallic bond depends on the following factors:

Strength increases with:

- (i) increase in number of valence electrons,
- (ii) increase in charge on the nucleus,
- (iii) decrease in size of positive metal ion.

**Valence band:** Group of electrons containing valence electrons.

**Conduction band:** The free electrons for conduction constitute conduction band.

Band structure of metals may be given as shown in Fig. 4.59.

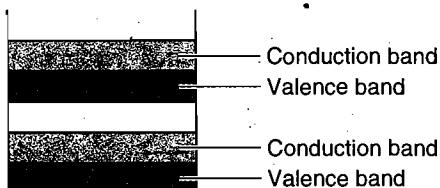


Fig. 4.59

There is no energy gap between valence and conduction band, i.e., width of forbidden zone is zero. Thus, as soon as potential difference is applied electrons jump to conduction band from valence band and conduct electric current. All valence electrons are free to conduct electric current. **When temperature is raised conductance of metals decreases because at high temperature kernels vibrate and create obstruction in the flow of electron.**

**Semiconductors:** Conductivity of semiconductors is intermediate between metals and insulators. These are of two types:

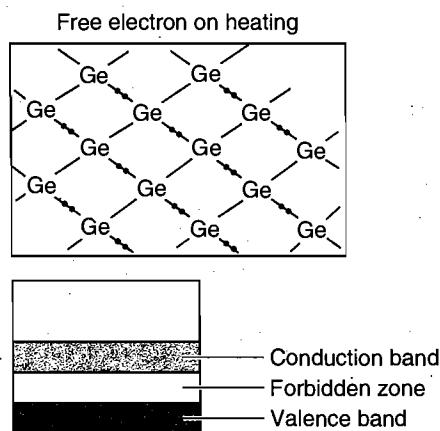


Fig. 4.60

**(i) Intrinsic semiconductors:** These are insulators at room temperature and become semiconductors when temperature is raised.

On heating, some covalent bonds are broken to give free electrons. These free electrons make it semiconductor.

Width of forbidden zone in semiconductors is very low; thus on heating, electrons are easily tossed to conduction band from valence band and conduct electric current.

**(ii) Extrinsic semiconductors or Impurity semiconductors:** These are formed by doping impurity of lower or higher group.

### n-type Semiconductor

Dopping of higher group impurity forms n-type semiconductor, e.g., when 'As' is dopped to 'Ge', an extra valence electron of arsenic makes the mixture n-type semiconductor. Current carriers are negatively charged, hence called n-type.

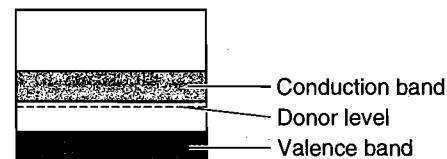
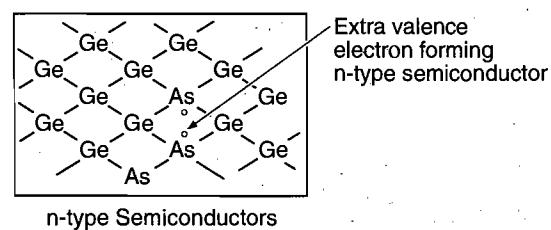


Fig. 4.61 n-type Semiconductor

Impurity doping creates donor level just below the conduction band.

On applying potential difference, electrons jump from donor level to the conduction band and conduct electric current.

### p-type Semiconductor

Impurity of lower group creates acceptor level just above the valence band. When electrons jump from valence band to acceptor level, a p-hole (positively charged hole) is created in valence band. On applying potential difference, these p-holes conduct electric current.

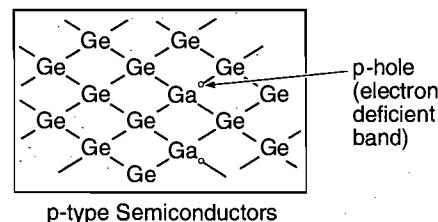


Fig. 4.62 p-type Semiconductor

**Insulators:** Such substances do not conduct electric current; their conductivity is very low. Width of forbidden zone between valence and conduction band is very big; hence electrons are not tossed from valence band to conduction band. On heating they decompose but do not give free conducting electrons.



Fig. 4.63

**Examples: Classification of transition metal oxides**

Metallic	Semiconductors	Insulators
VO	FeO, V <sub>2</sub> O <sub>5</sub>	MnO
TiO	Fe <sub>2</sub> O <sub>3</sub> , Mn <sub>2</sub> O <sub>3</sub> Co <sub>3</sub> O <sub>4</sub> , Mn <sub>3</sub> O <sub>4</sub>	
CrO <sub>2</sub>	CuO Cu <sub>2</sub> O	

TiO and NbO become superconductors at low temperature, about 2 K.

## 4.25 MAGNETIC PROPERTIES

### (I) Paramagnetic Solids

The presence of one or more unpaired electrons in an atom, molecule or ion gives rise to paramagnetism. Such materials are weakly attracted in the field. When they are placed in a magnetic field they become parallel to the field. Domain significance of unpaired electrons are given below:

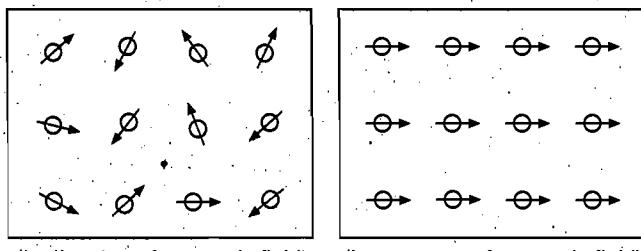


Fig. 4.64

Resultant magnetic field for  $n$ -unpaired electrons may be calculated as:

$$\mu_M = \sqrt{n(n+2)}$$

The magnetic field produced by unpaired electrons is due to—  
(a) their spin and (b) their orbital motion.

Magnetic moment is measured in Bohr Magneton (BM)

$$BM = \frac{e\hbar}{4\pi mc^2}$$

$\mu_S = 1.73$  BM (one unpaired electron)

$\mu_S = 2.83$  BM (two unpaired electrons)

$\mu_S = 3.87$  BM (three unpaired electrons)

$\mu_S = 4.90$  BM (four unpaired electrons)

5.92, 6.93, 7.94 values for five, six and seven unpaired electrons respectively.

### (ii) Diamagnetic Solids

The solids, which are weakly repelled by external magnetic field, are called diamagnetic solids and the property thus exhibited is called diamagnetism.

In diamagnetic solids, all electrons have paired spins, i.e., only fully filled orbitals are present. Examples are : NaCl, TiO<sub>2</sub>, ZrO<sub>2</sub>, KCl etc. Some diamagnetic solids like TiO<sub>2</sub> show para magnetism due to presence of slight non-stoichiometry.

### (iii) Ferromagnetic Solids

The solids which are strongly attracted by external magnetic field and do not lose their magnetism when the external field is removed, are called ferromagnetic solids. The property thus, exhibited is termed ferromagnetism.

Ferromagnetic substances can be permanently magnetised. Only three elements, iron (Fe), cobalt (Co) and nickel (Ni) show ferromagnetism at room temperature. Some other examples are : EuO, CrO<sub>2</sub>, etc. CrO<sub>2</sub> is the oxide used to make magnetic tapes for use in cassette recorders.

Ferromagnetism arises due to spontaneous alignment of magnetic moments due to unpaired electrons in the same direction as shown below (Fig. 4.65).

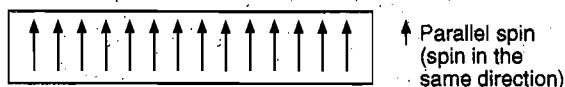


Fig. 4.65 Ferromagnetism

### Mechanism of magnetisation of ferromagnetic substances:

Unpaired electron in one atom interacts strongly with unpaired electron of neighbourhood atom, thus they align themselves spontaneously in a common direction in a small volume of solid called domains. Magnetic moments of all atoms in a domain are parallel to each other hence the domain possesses a net magnetic dipole moment. In absence of external magnetic field, the direction of magnetic moments in different domains are randomly oriented in different direction. When external magnetic field is applied then the domains in which the magnetic moments are parallel to external field, expand at the expense of remaining domains and ultimately all the magnetic moments align themselves in the direction of external magnetic field.

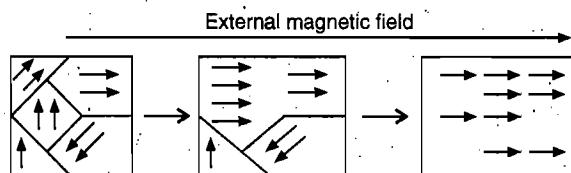


Fig. 4.66 Magnetisation of ferromagnetic substance

### (iv) Antiferromagnetic Solids

The solids which are expected to show paramagnetism or ferromagnetism on the basis of unpaired electrons but actually

have zero net magnetic moment are called antiferromagnetic solids.

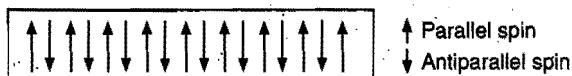


Fig. 4.67 Antiferromagnetism

Magnetic moments are aligned in a compensatory way so as to give zero net magnetic moment. Antiferromagnetism is due to the presence of equal number of magnetic moments in opposite directions as shown above (Fig. 4.67). The important examples are : MnO, MnO<sub>2</sub>, Mn<sub>2</sub>O<sub>3</sub>, NiO, CoO, etc.

#### (v) Ferrimagnetic Solids

The solids which are expected to show large magnetism due to the presence of unpaired electrons but in fact have small net magnetic moment are called ferrimagnetic solids.

Ferrimagnetism arises due to alignment of magnetic moments in parallel and antiparallel directions in unequal numbers resulting in some net magnetic moment. This alignment has been shown ahead (Fig. 4.68).

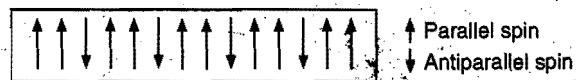


Fig. 4.68 Ferrimagnetism

Examples are : Fe<sub>3</sub>O<sub>4</sub> and ferrites of the formula  $M^{2+}Fe_2O_4$  where M = Zn, Cu, Mg, etc.

#### Influence of temperature on magnetic character of solids :

All magnetically ordered solids (ferromagnetic, antiferromagnetic and ferrimagnetic) change into paramagnetic state on increasing temperature. This is due to randomisation of their spins. The following examples explain this point :

(i) Ferrimagnetic solid, Fe<sub>3</sub>O<sub>4</sub>, becomes paramagnetic when heated to 850 K.

(ii) Antiferromagnetic solid, V<sub>2</sub>O<sub>3</sub>, becomes paramagnetic when heated to 750 K.

It should be noted that each ferromagnetic solid has a characteristic temperature above which it becomes paramagnetic. The characteristic temperature is called **Curie point** for Curie temperature.

Table 4.1 Magnetic Properties of Solid at a Glance

Properties	Information	Magnetic alignment	Example	Application
1. Diamagnetic	Repelled weakly in magnetic field. Such solids have only paired electrons.	↓↓↓↓↓↓	Benzene, NaCl, TiO <sub>2</sub> , V <sub>2</sub> O <sub>5</sub> , etc.	Insulators
2. Paramagnetic	Have unpaired electrons; weakly attracted in magnetic field. They cannot be permanently magnetised.	↖↖→↑↖↖	O <sub>2</sub> , VO, CuO, TiO	Electronic devices
3. Ferromagnetic	Also, have unpaired electrons. Strongly attracted in magnetic field. Such solids can be permanently magnetised. On heating to a temperature called Curie Point, these solids change to paramagnetic solid.	↑↑↑↑↑↑↑↑	Fe, Ni, Co, CrO <sub>2</sub>	CrO <sub>2</sub> is used in audio, video tapes.
4. Antiferromagnetic	In these solids, unpaired electrons align themselves in such a way that resultant magnetic moment is zero.	↑↓↑↓↑↓↑↓	Cr <sub>2</sub> O <sub>3</sub> , CoO, Co <sub>3</sub> O <sub>4</sub> , Fe <sub>2</sub> O <sub>3</sub> , MnO, MnO <sub>2</sub>	Used in the instruments of magnetic susceptibility measurement
5. Ferrimagnetic	Unpaired electrons align themselves in such a way that there is a net magnetic moment.	↑↓↓↑↓↓↑↓↓ OR ↑↑↓↓↑↑↓↓↑↑↓↓↑↑ and so on	Fe <sub>3</sub> O <sub>4</sub> , ferrites	

Table 4.2 Dielectric Properties of Solid at a Glance

Properties	Information	Dipolar property	Example	Application
1. Piezoelectricity	When a crystal of dielectrics is subjected to mechanical stress, then small magnitude current is produced. It is called direct Piezoelectric effect.	Development of charge in some part of crystal.	Quartz and Rochelle salt	Used in mechanical electric transducer, e.g., in record player, transmission of direct signals, sounding of sea depths.
2. Anti piezoelectricity	In some solids, electric field develops mechanical effect.	Crystal suffers elastic deformation in an electric field	—	
3. Ferroelectricity	Piezoelectric crystals having permanent dipoles are said to possess ferroelectricity.	↑↑↑↑↑↑	Ba TiO <sub>3</sub> , KH <sub>2</sub> PO <sub>4</sub> Rochelle salt	Electromagnetic appliances.
4. Anti ferroelectricity	Piezoelectric crystals with zero dipole are said to possess anti ferroelectricity.	↑↓↑↓↑↓	PbZrO <sub>3</sub> Lead zirconate	
5. Pyroelectricity	Some polar crystals produce electric impulse on heating.	—	Crystals of tartaric acid	Used in fire alarms, and thermostat

### Superconductors

Copper and most other metals are good conductors of electricity. But even the best conductors present some resistance to the flow of electricity and a part of electrical energy is converted into heat energy. Thus, generators, turbines, motors of all kinds, transmission lines and other electrical equipment always operate at less than 100% efficiency.

A superconductor is a material that loses all electrical resistance below a characteristic temperature called the superconducting transition temperature, i.e., a superconductor presents no resistance to the flow of electricity.

Electrons move freely through a superconductor without any resistance or friction.

This phenomenon was discovered, in 1911, by the Dutch scientist **Heike Kamerlingh Onnes**, who found that mercury abruptly loses its electrical resistance when it is cooled with liquid helium to 4.2 K. Below its critical temperature ( $T_c$ ), a superconductor becomes a perfect conductor and an electric current, once started, flows indefinitely without loss of energy. Most metals become superconductors at very low temperatures (generally around 2–5 K), but this temperature is far too cold for any commercial applications.

Since, 1911, scientists have been searching for materials that superconduct or at higher temperatures and more than 6000 superconductors are now known. Niobium alloys are particularly good superconductors and in 1973, a niobium alloy, Nb<sub>3</sub>Ge, was found to show superconductivity at 23.2K. The situation changed dramatically in 1986 when **Müller** and **Bednorz** reported a  $T_c$  of 35K for the non-stoichiometric barium lanthanum copper oxide, Ba<sub>x</sub>La<sub>2-x</sub>CuO<sub>4</sub>, where  $x$  has a value of about 0.1. Soon

thereafter even higher values of  $T_c$  for other copper containing oxides : 90 K for YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>, 125K for Tl<sub>2</sub>Ca<sub>2</sub>Ba<sub>2</sub>Cu<sub>3</sub>O<sub>10</sub> and 133 K for HgCa<sub>2</sub>Ba<sub>2</sub>Cu<sub>3</sub>O<sub>8+x</sub>. [YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> is also called 1-2-3 compound, i.e., 1 yttrium, 2 bariums and 3 coppers].

Room temperature ' $T_c$ ' superconductors are yet to be discovered. The great advantage of these materials that offer no electrical resistance is the elimination of heating effects as electricity passes through. The energy saving and efficiencies that would be realised are substantial. Superconducting coils of wire could store electricity (in principle) forever, since no energy is lost. Thus, the energy can be tapped as needed. One of the most dramatic properties of a superconductor is its ability to levitate a magnet. When a superconductor is cooled below its  $T_c$  and a magnet is lowered towards it, the superconductor and magnet repel each other and the magnet hovers above the superconductor as though suspended in midair. The potential application of this effect will be in the high speed magnetically levitated trains. Some applications of superconductors already exist. For example, powerful superconducting magnets are essential components in the magnetic resonance imaging (MRI) instruments used in medical diagnosis. Superconductors are also used to make the magnets that bend the path of the charged particles in high energy particle accelerators. All the present applications, however, use conventional superconductors ( $T_c \leq 20$  K). Of course, the search goes on for materials with higher values of  $T_c$ . For applications such as long distance electric power transmission, the goal is a material that superconducts at room temperature.

## MISCELLANEOUS NUMERICAL EXAMPLES

**Example 1.** There is a collection of crystalline substances in a hexagonal closed packing. If the density of matter is  $2.6 \text{ g/cm}^3$ , what would be the average density of matter in collection? What fraction of space is actually unoccupied?

**Solution:** In hexagonal closed packing, the packing efficiency is 74.05%.

$$\text{Density of matter} = \text{Packing fraction} \times \text{Total density}$$

$$= \frac{74.05}{100} \times 2.6 = 1.93 \text{ g cm}^{-3}$$

$$\% \text{ empty space} = 100 - 74.05 = 25.95\%$$

**Example 2.** The unit cell length of NaCl is observed to be  $0.5627 \text{ nm}$  by X-ray diffraction studies; the measured density of NaCl is  $2.164 \text{ g cm}^{-3}$ . Correlate the difference of observed and calculated density and calculate % of missing  $\text{Na}^+$  and  $\text{Cl}^-$  ions.

**Solution:** We know that,

$$Z = \frac{a^3 \times d \times N}{M}$$

where,  $Z$  = number of constituent units per unit cell  
= 4 in fcc

$$a = \text{edge length} = 0.5627 \times 10^{-7} \text{ cm}$$

$d$  = density

$N$  = Avogadro's number

$M$  = molar mass

$$\frac{(0.5627 \times 10^{-7})^3 \times d \times 6.023 \times 10^{23}}{58.5} = 4$$

$$d = 2.1805 \text{ g/cm}^3$$

Observed density =  $2.164 \text{ g/cm}^3$  which is less than calculated density because some places are missing.

Actual constituent units per unit cell can be calculated as:

$$Z = \frac{(0.5627 \times 10^{-7})^3 \times 2.164 \times 6.023 \times 10^{23}}{58.5} = 3.969$$

$$\text{Missing units} = 4 - 3.969 = 0.031$$

$$\% \text{ missing} = \frac{0.031}{4} \times 100 = 0.775\%$$

**Example 3.** In a cubic lattice, the closed packed structure of mixed oxides of the lattice is made up of oxide ions; one eighth of the tetrahedral voids are occupied by divalent ions ( $A^{2+}$ ) while one half of the octahedral voids are occupied by trivalent ions ( $B^{3+}$ ). What is the formula of the oxides?

**Solution:** Let there be 80  $\text{O}^{2-}$  in the crystal.

$$\text{Octahedral voids} = 80$$

$$\text{Tetrahedral voids} = 160$$

$$A^{2+} \text{ ions} = \frac{1}{8} \times 160 = 20$$

$$B^{3+} \text{ ions} = \frac{1}{2} \times 80 = 40$$

$$A^{2+} : B^{3+} : \text{O}^{2-} = 20 : 40 : 80$$

$$= 1 : 2 : 4$$

∴ Formula is  $AB_2\text{O}_4$ .

**Example 4.** At  $1425^\circ\text{C}$ , Fe crystallises in a body-centred cubic lattice whose edge length is  $2.93 \text{ \AA}$ . Assuming the atoms to be packed spheres, calculate:

(a) the radius of the spheres,

(b) the distance between centres of neighbouring spheres,

(c) the number of atoms of Fe per unit lattice and

(d) the total volume occupied by an atom of Fe.

**Solution:** (a)  $a\sqrt{3} = 4r$  where,  $a$  = edge length

$$r = \frac{a\sqrt{3}}{4} = \frac{2.93 \times \sqrt{3}}{4} = 1.268 \text{ \AA}$$

(b) Distance between the centres of neighbouring spheres

$$= 2r = 2 \times 1.268 = 2.537 \text{ \AA}$$

(c) No. of atoms per unit cell =  $\frac{8}{8} + 1 = 2$ .

(d) Volume occupied by an atom of iron =  $\frac{4}{3}\pi r^3$ .

**Example 5.** In face-centred cubic (fcc) crystal lattice, edge length of the unit cell is  $400 \text{ pm}$ . Find the diameter of the greatest sphere which can be fitted into the interstitial void without distortion of lattice. (IIT 2005)

**Solution:** In fcc unit cell, we can use

$$a\sqrt{2} = 4r$$

$$r = \frac{a\sqrt{2}}{4} = \frac{400 \times \sqrt{2}}{4} = 141.4 \text{ pm}$$

For octahedral void,

$$2(r + R) = a$$

$$2R = a - 2r$$

$$2R = a - 2r = 400 - 2 \times 141.4 = 117.16 \text{ pm}$$

Diameter of greatest sphere =  $117.16 \text{ pm}$ .

**Example 6.** The distance between planes of ions parallel to the face of the unit cell of sodium chloride is  $282 \text{ pm}$ . The smallest angle of reflection observed in the X-ray diffraction pattern is  $5.97^\circ$ . Calculate the wavelength of the incident radiation.

**Solution:** Using Bragg's equation,

$$n\lambda = 2d \sin \theta$$

$$1 \times \lambda = 2 \times 282 \times 10^{-12} \sin 5.97^\circ$$

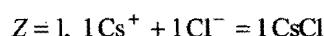
$$\lambda = 5.86 \times 10^{-11} \text{ m} = 58.6 \text{ pm}$$

**Example 7.** CsCl has cubic structure of ions in which  $\text{Cs}^+$  ion is present in the body-centre of the cube. If density is  $3.99 \text{ g cm}^{-3}$ ,

- (a) Calculate the length of the edge of a unit cell.  
 (b) What is the distance between  $\text{Cs}^+$  and  $\text{Cl}^-$  ions?  
 (c) What is the radius of  $\text{Cs}^+$  ion if the radius of  $\text{Cl}^-$  ion is 180 pm?

**Solution:** We know that,

$$(a) Z = \frac{a^3 \times \rho \times N_A}{M}$$



$$M = 168.5$$

$$1 = \frac{a^3 \times 3.99 \times 6.023 \times 10^{23}}{168.5}$$

$$a = 4.123 \times 10^{-8} \text{ cm} = 412 \text{ pm}$$

- (b) Distance between  $\text{Cs}^+$  and  $\text{Cl}^-$  ions

$$= \frac{a\sqrt{3}}{2} = \frac{412 \times \sqrt{3}}{2} = 356.8 \text{ pm}$$

$$(c) r_{\text{Cs}^+} + r_{\text{Cl}^-} = 356.8$$

$$r_{\text{Cs}^+} + 180 = 356.8$$

$$r_{\text{Cs}^+} = 176.8 \text{ pm}$$

**Example 8.** If  $\text{NaCl}$  is doped with  $10^{-3}$  mol per cent of  $\text{SrCl}_2$ , what is the concentration of cation vacancy?

**Solution:**

$\text{Na}^+$	$\text{Cl}^-$	$\text{Na}^+$	$\text{Cl}^-$
$\text{Cl}^-$		$\text{Cl}^-$	$\text{Na}^+$
$\text{Sr}^{2+}$	$\text{Cl}^-$	$\text{Na}^+$	$\text{Cl}^-$
$\text{Cl}^-$	$\text{Na}^+$	$\text{Cl}^-$	$\text{Na}^+$

Number of cationic vacancies per mol

$$= \frac{10^{-3} \times 6.023 \times 10^{23}}{100} = 6.023 \times 10^{18} \text{ vacancies per mol}$$

**Example 9.** A metal crystallises into two cubic phases, face-centred cubic (fcc) and body-centred cubic (bcc) whose unit lengths are 3.5 and 3.0 Å respectively. Calculate the ratio of densities of fcc and bcc.

(IIT 1999)

**Solution:** Density of fcc =  $\frac{Z_1 \times \text{At. mass}}{\text{Av. no.} \times V_1}$

and density in bcc =  $\frac{Z_2 \times \text{At. mass}}{\text{Av. no.} \times V_2}$

$$\frac{d_{\text{fcc}}}{d_{\text{bcc}}} = \frac{Z_1}{Z_2} \times \frac{V_2}{V_1}$$

$$\text{For fcc } Z_1 = 4; V_1 = a^3 = (3.5 \times 10^{-8})^3$$

$$\text{For bcc } Z_2 = 2; V_2 = a^3 = (3.0 \times 10^{-8})^3$$

$$\frac{d_{\text{fcc}}}{d_{\text{bcc}}} = \frac{4 \times (3.0 \times 10^{-8})^3}{2 \times (3.5 \times 10^{-8})^3} = 1.259$$

**Example 10.** A solid AB has the  $\text{NaCl}$  structure. If radius of the cation  $A^+$  is 120 pm, calculate the maximum value of the radius of the anion B.

**Solution:** Since,  $\text{NaCl}$  has octahedral structure,

$$\text{The limiting ratio } \frac{r_A^+}{r_B^-} = 0.414$$

$$\text{or } \frac{r_B^-}{r_A^+} = \frac{120}{0.414} = \frac{120}{0.414} = 290 \text{ pm}$$

**Example 11.** You are given marbles of diameter 10 mm. They are to be placed such that their centres are lying in a square bond by four lines each of length 40 mm. What will be the arrangement of marbles in a plane, so that, maximum number of marbles can be placed inside the area. Sketch the diagram and derive expression for the number of marbles per unit area.

(IIT 2003)

**Solution:** In order to accomodate maximum number of spheres, there should be hcp (hexagonal closed packing).

Area of square having spherical marbles = 16 cm<sup>2</sup>

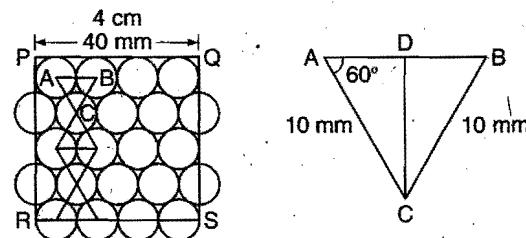
Maximum number of spheres = 14 (full) + 8 (half)

Number of spheres = 18

$$\text{Per unit area (per cm}^2) = \frac{18}{16} = 1.125$$

Length PQ of square = 4 cm

Length PR =  $5 + 4 \times \sqrt{3} = 40 \text{ mm} = 4 \text{ cm}$



$$CD = 10 \sin 60^\circ = \frac{10\sqrt{3}}{2} = 5\sqrt{3}$$

**Example 12.** Calculate the density of diamond from the fact that it has face-centred cubic structure with two atoms per lattice point and a unit cell of edge length 3.569 Å.

**Solution:**  $Z = 8, M = 12$

$$Z = \frac{l^3 \times \rho \times N_A}{M}$$

$$\text{Density } \rho = \frac{ZM}{l^3 N} = \frac{8 \times 12}{(3.569 \times 10^{-8})^3 \times 6.023 \times 10^{23}}$$

$$= 3.506 \text{ g cm}^{-3}$$

**Example 13.** An element crystallises into a structure which may be described by a cubic unit cell having one atom at each corner of the cube and two atoms on one of its diagonals. If the volume of this unit cell is  $24 \times 10^{-24} \text{ cm}^3$  and density of element is  $7.2 \text{ g/cm}^3$ . Calculate the number of atoms present in  $200 \text{ g}$  of the element.

**Solution:** Number of atoms in a unit cell ( $Z$ ) =  $1 + 2 = 3$

$$Z = \frac{l^3 \times \rho \times N_A}{M}$$

$$M = \frac{l^3 \times \rho \times N_A}{Z}$$

$$= \frac{24 \times 10^{-24} \times 7.2 \times 6.023 \times 10^{23}}{3} = 34.69$$

$$\text{Number of atoms} = \frac{\text{Mass}}{\text{Molar mass}} \times 6.023 \times 10^{23}$$

$$= \frac{200}{34.69} \times 6.023 \times 10^{23} = 3.47 \times 10^{24}$$

**Example 14.** Analysis shows that nickel oxide has formula  $\text{Ni}_{0.98}\text{O}_1$ . What fraction of nickel exist as  $\text{Ni}^{2+}$  and  $\text{Ni}^{3+}$  ions?

**Solution:** Let number of  $\text{Ni}^{3+}$  ions =  $x$

$$\text{Number of } \text{Ni}^{2+} \text{ ions} = (0.98 - x)$$

Since, molecule is neutral, its total charge is zero.

$$( +3 \times x ) + ( 0.98 - x ) \times 2 - 2 = 0$$

$$x = 0.04, \text{ i.e., } \text{Ni}^{3+} = 0.04; \text{Ni}^{2+} = 0.94$$

**Example 15.** Calcium crystallises in face-centred cubic unit cell with  $a = 0.556 \text{ nm}$ . Calculate density if

(i) it contained 0.1% Frenkel defect.

(ii) it contained 0.1% Schottky defect.

**Solution:** (i) Frenkel defect does not alter the density of solid.

$$d = \frac{MZ}{l^3 N_A} = \frac{40 \times 4}{(0.556 \times 10^{-7})^3 \times 6.023 \times 10^{23}}$$

$$= 1.5455 \text{ g/cm}^3$$

(ii) Schottky defect lowers the density of solid

$$Z = 4 - \frac{4 \times 0.1}{100} = 3.996$$

$$d = \frac{40 \times 3.996}{(0.556 \times 10^{-7})^3 \times 6.023 \times 10^{23}}$$

$$= 1.5440 \text{ g/cm}^3$$

**Example 16.** Density of lithium atom is  $0.53 \text{ g/cm}^3$ . The edge length of Li is  $3.5 \text{ \AA}$ . Find out the number of lithium atoms in a unit cell. Atomic mass of lithium is  $6.94$ .

[CBSE-PMT (Mains) 2005]

**Solution:**  $Z = \frac{a^3 \times \rho \times N_A}{M}$

$$= \frac{(3.5 \times 10^{-8})^3 \times 0.53 \times 6.023 \times 10^{23}}{6.94}$$

$$= 2$$

**Example 17.** Cu metal crystallises in face centred cubic lattice with cell edge,  $a = 361.6 \text{ pm}$ . What is the density of Cu crystal? (Atomic mass of copper =  $63.5 \text{ amu}$ ,  $N_A = 6.023 \times 10^{23}$ )

[CBSE-PMT (Mains) 2008]

**Solution:** We know

$$Z = \frac{a^3 \times d \times N_A}{M}$$

$$\therefore d = \frac{ZM}{a^3 N_A} \quad \dots(i)$$

$$Z = 4 \text{ for fcc unit cell}; M = 63.5 \text{ g mol}^{-1}$$

$$a = 361.6 \times 10^{-10} \text{ cm}; N_A = 6.023 \times 10^{23}$$

Putting these values in (i), we get

$$d = \frac{4 \times 63.5}{(361.6 \times 10^{-10})^3 \times 6.023 \times 10^{23}} = 8.94 \text{ g cm}^{-3}$$

**Example 18.** An LPG cylinder weighs  $14.8 \text{ kg}$  when empty. When full, it weighs  $29 \text{ kg}$  and shows a pressure of  $2.5 \text{ atm}$ . In the course of use at  $27^\circ\text{C}$ , the weight of the full cylinder reduced to  $23.2 \text{ kg}$ . Find out the volume of  $n$ -butane in cubic metres used up at  $27^\circ\text{C}$  and  $1 \text{ atm}$ .

[Molecular mass of  $n$  butane =  $58$ ] [CBSE-PMT (Mains) 2008]

**Solution:** Mass of  $n$ -butane used =  $29 - 23.2 = 5.8 \text{ kg}$

$$\text{Number of moles of butane used} = \frac{5800}{58} = 100$$

$$V = \frac{nRT}{P} = \frac{100 \times 0.0821 \times 300}{1}$$

$$= 2463 \text{ litre}$$

$$= 2.463 \text{ m}^3$$

**Example 19.**  $r_{\text{Na}^+}$  and  $r_{\text{Cl}^-}$  represents radius of  $\text{Na}^+$  and  $\text{Cl}^-$  ions respectively. If 'n' is the number of  $\text{NaCl}$  units per unit cell then give the equation you will use to obtain molar volume. [CBSE-PMT (Mains) 2009]

**Solution:** Edge length of unit cell ' $a$ ' =  $2(r_{\text{Na}^+} + r_{\text{Cl}^-})$

$$\text{Volume of unit cell} = a^3 = 8(r_{\text{Na}^+} + r_{\text{Cl}^-})^3$$

Volume occupied by one mole of  $\text{NaCl}$

$$= \frac{8(r_{\text{Na}^+} + r_{\text{Cl}^-})^3}{n} \times N_A$$

$$\text{where } N_A = 6.023 \times 10^{23}$$

**Example 20.** Two gases A and B of mass  $70.6 \text{ g}$  and  $167.5 \text{ g}$  ( $M_w$  of A =  $32$  and  $M_w$  of B =  $20$ ) are mixed. Then total pressure of mixture is  $25 \text{ bar}$ . Calculate partial pressure of A and B.

[CBSE-PMT (Mains) 2009]

**Solution:** Number of moles A,  $n_A = \frac{70.6}{32} = 2.2$

$$\text{Number of moles of } B, n_B = \frac{167.5}{20} = 8.375$$

$$= \frac{2.2}{2.2 + 8.375} \times 25 = 5.20 \text{ bar}$$

$$\text{Partial pressure of gas } A, p_A = \frac{n_A}{n_A + n_B} \times p$$

$$p_B = 25 - 5.20 = 19.8 \text{ bar}$$

## SUMMARY AND IMPORTANT POINTS TO REMEMBER

**1. Matter:** Matter is anything which has mass and occupies space. Matter exists in three states, viz., solid, liquid and gas. Any substance can exist in either of the three states depending on temperature and pressure. Liquid and solid states are condensed states as they have much higher densities. Both liquids and gases are termed as fluids as they have flowing ability.

**2. Gaseous state:** It is the simplest state and shows greatest uniformity in behaviour. The gases show almost the same behaviour irrespective of chemical nature, colour or odour. The molecules in a gas possess random motion in all directions. A gas has neither a definite shape nor a definite volume. Gases are characterised by low density, high degree of compressibility and expandability. Gases exert uniform pressure on the walls of the container. They diffuse rapidly and intermix to form homogeneous mixtures. All gases obey certain laws called gas laws.

**3. Gas laws:** Gas laws are based on experiments.

(i) **Boyle's law:** It states that the volume of the given amount of a gas is inversely proportional to its pressure at a constant temperature.

$$V \propto \frac{1}{P} \text{ or } PV = \text{constant} \text{ or } P_1 V_1 = P_2 V_2 = P_3 V_3 = \dots$$

$$\text{or } \frac{P_1}{d_1} = \frac{P_2}{d_2} \quad (\text{at constant temperature})$$

where,  $d_1$  and  $d_2$  are the densities of a gas at pressures  $P_1$  and  $P_2$ . The curves between  $P$  and  $V$  at constant temperature are hyperbolas and called isotherms.

(ii) **Charles' law:** At constant pressure, the volume of a given amount of a gas is directly proportional to its absolute temperature.

$$V \propto T \text{ or } \frac{V}{T} = \text{constant} \text{ or } \frac{V_1}{T_1} = \frac{V_2}{T_2} = \frac{V_3}{T_3} = \dots$$

Absolute temperature scale or Kelvin scale starts with  $-273^\circ\text{C}$  as zero.

$$\text{Absolute temperature (in K)} = 273 + t^\circ\text{C}$$

The absolute zero is that temperature where no gas can exist. The plots of volume against temperature (at constant pressure) are termed as isobars.

(iii) **Pressure law or Gay-Lussac law:** At constant volume, the pressure of a given amount of a gas varies directly as its absolute temperature.

$$P \propto T \text{ or } \frac{P}{T} = \text{constant} \text{ or } \frac{P_1}{T_1} = \frac{P_2}{T_2} = \frac{P_3}{T_3} = \dots$$

(iv) **Gas equation:**  $\frac{PV}{T} = \text{constant}$

For one mole of an ideal gas,  $PV = RT$

For  $n$  moles of an ideal gas,  $PV = nRT$

For  $w$  g of the gas (mol. mass  $M$ ),

$$PV = \frac{w}{M} RT$$

$$\text{or } P = \frac{w}{V} \frac{RT}{M} = d \times \frac{RT}{M} \quad (d = \text{density})$$

$R$  is a universal gas constant. It is expressed in the units of work per degree kelvin per mol. Value of  $R$  in different units is

$$R = 0.0821 \text{ litre-atm K}^{-1} \text{ mol}^{-1}$$

$$= 82.1 \text{ mL-atm K}^{-1} \text{ mol}^{-1}$$

$$= 8.314 \times 10^7 \text{ erg K}^{-1} \text{ mol}^{-1}$$

$$= 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$= 1.987 \approx 2 \text{ cal K}^{-1} \text{ mol}^{-1}$$

(v) **Avogadro's law:** Equal volumes of all gases contain equal number of molecules under similar conditions of temperature and pressure. Volume occupied by one mole of any gas at NTP ( $0^\circ\text{C}$  and 1 atm) is termed **molar volume**. It is 22.4 litre or 22400 mL.

[Note : At  $25^\circ\text{C}$  and 1 bar, one mole of a gas has a volume of 25 litre.]

(vi) **Dalton's law of partial pressures:** The total pressure exerted by a mixture of gases which do not react chemically is equal to the sum of their individual pressures (partial pressures) under similar conditions of temperature.

$$P = P_1 + P_2 + P_3 + \dots$$

Partial pressure of a gas = Molar fraction

$\times$  Total pressure of the gas

(vii) **Graham's law of diffusion:** The property of gases to mix with each other to form homogeneous mixture irrespective of gravity is called diffusion. Effusion is a special case of diffusion in which gas passes through a small aperture.

Under similar conditions of temperature and pressure, the relative rates of diffusion of gases are inversely proportional to the square root of their densities or vapour densities or molecular masses. This is Graham's law of diffusion.

$$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{V D_2}{V D_1}} = \sqrt{\frac{M_2}{M_1}}$$

$$\frac{r_1}{r_2} = \frac{P_1}{P_2} \sqrt{\frac{M_2}{M_1}}$$

**4. Kinetic theory of gases:** The theory with the help of which behaviour of gases can be interpreted mathematically is termed kinetic theory of gases. The main postulates of the theory are:

(a) All gases consist of very large number of small spherical elastic particles called molecules. These are in constant rapid motion in all directions.

(b) There is a lot of empty space between the molecules. The actual volume of gas molecules is negligible in comparison to total volume of the gas.

(c) The pressure exerted by the gas molecules is due to its collision by molecules against the walls of containing vessel. The collisions between gas molecules are perfectly elastic, i.e., there is no loss of energy during collisions.

(d) There is no effective force of attraction or repulsion between gas molecules. There is no effect of gravity on the motion of gas molecules.

(e) The average kinetic energy of gas molecules is directly proportional to the absolute temperature of the gas.

On the basis of above postulates, the following equation, known as kinetic gas equation, has been derived.

$$PV = \frac{1}{3} mnc^2$$

where,  $P$  = pressure;  $V$  = volume;  $m$  = mass of gas molecules;  $n$  = number of gas molecules and  $c$  = root mean square speed of the gas molecules.

$$\text{Also } PV = RT = \frac{1}{3} mnc^2 = \frac{2}{3} \cdot \frac{1}{2} mnc^2 = \frac{2}{3} KE$$

$$\text{or } KE = \frac{3}{2} RT = \frac{3}{2} PV$$

$$\begin{aligned} \text{KE of single molecule} &= \frac{3}{2} \frac{RT}{N} \\ &= \frac{3}{2} kT \end{aligned}$$

where,  $k$  = Boltzmann constant.

**5. Molecular speeds:** There are three kinds of speed.

(a) Root mean square speed: It is the square root of the mean of the squares of the speeds of all the molecules present in a gas.

$$\begin{aligned} \text{rms } c &= \sqrt{\frac{c_1^2 + c_2^2 + c_3^2 + \dots + c_n^2}{n}} \\ &= \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3P}{d}} \end{aligned}$$

(b) Average speed: It is the arithmetic mean of speeds of the molecules present in the gas.

$$\begin{aligned} \text{Average speed} &= \frac{c_1 + c_2 + c_3 + \dots + c_n}{n} = \sqrt{\frac{8RT}{\pi M}} \\ &= 0.9213 \times \text{rms} \end{aligned}$$

(c) Most probable speed: It is the speed possessed by majority of the gas molecules. It is equal to

$$\sqrt{\frac{2RT}{M}} \text{ or } (0.8164 \times \text{rms})$$

Most probable speed : Average speed : rms speed

:: 1 : 1.128 : 1.224

**6. van der Waals' equation:** It is an improved form of ideal gas equation. It has been derived after applying two corrections due to two wrong assumptions in kinetic theory of gases. Two corrections are:

(i) volume correction,  $V_i = (V - b)$  and

$$(ii) \text{pressure correction}, P_i = P_{\text{obs}} + \frac{a}{V^2}$$

The equation is  $\left( P + \frac{a}{V^2} \right) (V - b) = RT$  for one mole

and  $\left( P + \frac{n^2 a}{V^2} \right) (V - nb) = nRT$  for 'n' moles,

$a$  and  $b$  are constants. Units of  $a$  are atm lit<sup>2</sup> mol<sup>-2</sup> or Pa m<sup>6</sup> mol<sup>-2</sup> and units of  $b$  are litre or dm<sup>3</sup> or m<sup>3</sup>. This equation is applicable to real gases.

**Real gases:** These do not obey various gas laws strictly under all conditions of temperature and pressure. Deviations are large under high pressure and low temperature.

**Ideal gases:** These obey laws strictly under all conditions. Actually no gas is ideal.

(a) At very low pressure or at very high temperature,  $V$  is large, so  $\frac{a}{V^2}$  and  $b$  can be neglected. The equation becomes  $PV = RT$ , i.e., the gas behaves like ideal gas.

(b) At moderate pressure,  $V$  is not so large and  $\frac{a}{V^2}$  cannot be neglected. However,  $b$  can be neglected, so that we have

$$\left( P + \frac{a}{V^2} \right) V = RT$$

$$PV = RT - \frac{a}{V}$$

(c) At high pressure,  $V$  is so small that  $b$  cannot be neglected but  $a/V^2$  can be neglected. Hence, the equation becomes

$$P(V - b) = RT$$

$$PV = RT + Pb$$

(d) In case of H<sub>2</sub> and He, the intermolecular forces of attraction are negligible, i.e.,  $a$  is very small, so that  $\frac{a}{V^2}$  can be neglected. The equation becomes

$$P(V - b) = RT$$

$$PV = RT + Pb$$

**7. Compressibility factor:** The extent of deviation of a real gas from ideal behaviour is expressed in terms of compressibility factor,  $Z$ .

$$Z = \frac{PV}{nRT}; Z \text{ is unitless quantity.}$$

(i) For ideal gas  $Z = 1$ .

(ii) For real gas  $Z \neq 1$ .

When  $Z < 1$ , there is negative deviation from ideal behaviour and the gas is more compressible than ideal gas.

When  $Z > 1$ , there is positive deviation from ideal behaviour and the gas is less compressible than ideal gas.

**8. Critical phenomenon:** (i) **Critical temperature** is that temperature above which the gas cannot be liquefied with the help of pressure (ii) **Critical pressure** is the minimum pressure required to liquefy the gas at critical temperature (iii) **Critical volume** is the volume occupied by one mole of the gas at its critical temperature and critical pressure.

$$V_c = 3b; P_c = \frac{a}{27b^2}; T_c = \frac{8a}{27bR}$$

**Boyle's temperature:** It is the temperature above which the gas behaves like an ideal gas. In terms of van der Waals' constants,

$$\text{Boyle's temperature } (T_B) = \frac{a}{Rb}$$

$$T_B > T_c$$

**Inversion temperature:** It is the temperature to which the gas should be cooled so that expansion is accompanied by further cooling.

**9. Molar heat capacity:** It is the quantity of heat required to raise the temperature of one mole of a substance through  $1^\circ\text{C}$ .

Molar heat capacity = Specific heat capacity  $\times$  Molar mass

(i) **Molar heat capacity at constant pressure ( $C_P$ ):** It is the quantity of heat required to raise the temperature of 1 mole of gas through  $1^\circ\text{C}$  under constant pressure. It is equal to  $\frac{5}{2}R$ .

(ii) **Molar heat capacity at constant volume ( $C_V$ ):** It is the quantity of heat required to raise the temperature of 1 mole of gas through  $1^\circ\text{C}$  under constant volume. It is equal to  $\frac{3}{2}R$ .

$$C_P - C_V = R$$

$$\text{For monoatomic gases, } \frac{C_P}{C_V} = \gamma = 1.66$$

$$\text{For diatomic gases, } \frac{C_P}{C_V} = \frac{\frac{7}{2}R}{\frac{5}{2}R} = 1.40$$

$$\text{and for triatomic gases, } \frac{C_P}{C_V} = \frac{8R}{6R} = \frac{4}{3} = 1.33$$

$$(C_P)_{\text{mixture}} = \frac{n_1 \times (C_P)_1 + n_2 (C_P)_2}{n_1 + n_2}$$

$$10. (i) \text{Volume coefficient, } \alpha_V = \frac{V_t - V_0}{V_0 \times t}$$

$$\alpha_V = \frac{1}{273} \quad (\text{for all gases})$$

At constant pressure, increase in volume of a gas per degree rise of temperature per cc of gas at  $0^\circ\text{C}$  is called coefficient of volume expansion. Similarly, the pressure coefficient  $\alpha_P$  is defined as,

$$\alpha_P = \frac{P_t - P_0}{P_0 \times t} = \frac{1}{273} \quad (\text{for all gases})$$

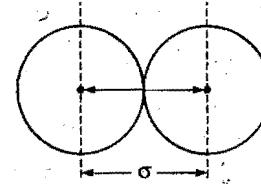
(ii)  $\text{CO, N}_2, \text{C}_2\text{H}_4$  and  $\text{B}_2\text{H}_6$  have same molar mass (28) and show same rate of diffusion under identical conditions.

(iii) **Atmolysis** is the process to separate two gases on the basis of difference in their densities and rate of diffusion.

(iv) Average molecular mass of air is 29. If a gas has molecular mass less than air, it is lighter than air and if it has molecular mass greater than air, it is heavier than air, e.g.,  $\text{Cl}_2$  (71),  $\text{CO}_2$  (44) and  $\text{SO}_2$  (64) are heavier than air, while  $\text{H}_2$  (2),  $\text{He}$  (4),  $\text{NH}_3$  (17) and  $\text{H}_2\text{O}$  (18) are lighter than air.

### 11. Transport phenomena of gases:

(i) **Collision diameter ( $\sigma$ ):** Distance of closest approach when two molecules are under collision.



(ii) **Collision number:** It is the number of collisions of a molecule with other molecules in one second.

$$N_c = \frac{\sqrt{2\pi} v_{av} \sigma^2 N}{V}$$

where,  $v_{av}$  = Average velocity of molecules

$N$  = Number of molecules

$V$  = Volume of molecules

(iii) **Collision frequency ( $Z$ ):** It is the number of molecular collisions taking place per second per unit volume of the gas.

$$Z = \frac{1}{\sqrt{2}} \pi v_{av} \sigma^2 \left( \frac{N}{V} \right)^2$$

(iv) **Mean free path ( $\lambda$ ):** It is the average distance travelled between two successive collisions.

$$\lambda = \frac{1}{\sqrt{2\pi}\sigma^2 \left( \frac{N}{V} \right)}$$

$\lambda \propto T$  (at constant pressure)

$\lambda \propto \frac{1}{P}$  (at constant temperature)

$\lambda \propto \frac{1}{\sigma}$  (at constant temperature and pressure)

**12. Liquid state:** Liquid state is condensed gas or molten solid. Liquids have definite volume but no definite shape.

Liquids diffuse slowly and are almost incompressible. Some important properties of liquids are:

(i) **Evaporation:** It is the spontaneous change in which a liquid changes into vapours at the surface of liquid. It increases with increase of surface area, increase in temperature and decrease in intermolecular forces. It causes cooling.

(ii) **Vapour pressure:** It is the pressure exerted by the vapours of a liquid in equilibrium with the liquid at a given temperature. It increases with increase of temperature. Liquids with low intermolecular forces have high vapour pressure.

(iii) **Boiling point:** It is the temperature at which the vapour pressure of a liquid becomes equal to atmospheric pressure. Temperature of the liquid remains constant after it starts boiling as the energy supplied increases the potential energy but its kinetic energy remains constant. Boiling point changes with the pressure of surroundings.

$$\log \left( \frac{P_2}{P_1} \right) = \frac{\Delta H_f}{2.303R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

where,  $\Delta H_f$  = latent heat of vaporisation;  $P_2$  and  $P_1$  are vapour pressures at  $T_2$  and  $T_1$ .

(iv) **Surface tension:** It is the force in dyne acting on the surface at right angles to any line of unit length. It decreases generally with increase in temperature. It is expressed in  $J m^{-2}$  or  $N m^{-1}$  or  $dyne\ cm^{-1}$ .

(a) Surface tension is molecular phenomenon of liquid involving the force of cohesion among the liquid molecules.

(b) Maximum potential energy of liquid molecules is on the surface.

(c) Surface tension is numerically equal to the surface energy. The work required to increase or extend the surface area by 1 sq. cm is called surface energy.

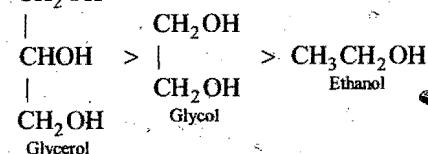
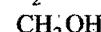
(d) Surface tension is a scalar quantity.

(e) Sparingly soluble solutes like soap and detergent decrease the surface tension of the liquid. However, fairly soluble solutes like sugar and salt increase the surface tension of the liquid.

(f) Liquid drops are spherical because liquid surface has a tendency to acquire minimum surface area.

(g) Greater is the intermolecular force, more is the surface tension.

e.g., Soap in water < Water < Mercury



Glycerol

(v) **Viscosity:** It is the resistance in a liquid to flow. The force in newton per square metre required to maintain a difference of velocity of one metre per second between two parallel layers of a liquid at a distance of one metre from each other is called coefficient of viscosity. It is expressed in  $g\ m^{-1}\ s^{-1}$ .

Or

The force per unit area required to maintain unit difference of velocity between two consecutive parallel layers of the liquid which are one centimetre apart. It is expressed in  $dyne\ cm^{-2}\ s^{-1}$  or poise.

The reciprocal of coefficient of viscosity is called fluidity. Liquids with low viscosity are termed mobile while others with high viscosity are called viscous. Viscosity is high in liquids with high intermolecular forces, high molecular masses and having branching in the chain of the molecule. Viscosity decreases with increase in temperature.

(vi) **Reynold's number:** The nature of flow of a liquid through a tube depends on the value of Reynold's number  $N_R$ .

$$N_R = \frac{2r\bar{v}\rho}{\eta}$$

where,  $r$  = Radius of the tube

$\bar{v}$  = Average velocity of the fluid

$\rho$  = Density of liquid

$\eta$  = Coefficient of viscosity

**Case I:** When  $N_R > 4000$ , the flow is called turbulent flow.

**Case II:** When  $N_R < 2100$ , the flow is called laminar flow.

**13. The solid state:** The particles are closely packed and are held together by strong intermolecular forces. The particles cannot move at random. They have only vibrational motion. Solids have definite shape and definite volume. They possess high density and low compressibility. Solids are divided into two classes: (i) amorphous solids and (ii) crystalline solids. In amorphous solids, the arrangement of building constituents is not regular but haphazard. Their melting points are not sharp. These are isotropic in nature.

In crystalline solids, building constituents arrange themselves in regular manner throughout the entire three-dimensional network. Crystalline solids consist of large number of units called crystals. A crystal is defined as a solid figure which has definite geometrical shape with flat faces and sharp edges. It has a sharp melting point and anisotropic in nature.

**14. Types of symmetry in crystals:** The total number of planes, axes and centres of symmetry possessed by a crystal are termed as elements of symmetry.

(i) **Centre of symmetry:** It is an imaginary point within the crystal such that any line drawn through it intersects the surface of the crystal at equal distances in both directions. A crystal always possess only one centre of symmetry.

(ii) **Plane of symmetry:** It is an imaginary plane which passes through the centre of a crystal and divides it into two equal portions such that one part is exactly the mirror image of the other.

(iii) **Axis of symmetry:** It is an imaginary straight line about which, if the crystal is rotated, it will present the same appearance more than once during the complete revolution.

A cubic crystal possesses a total of 23 elements of symmetry.

**15. Space lattice and unit cell:** The geometrical form consisting of a regular array of points in space is called a space

lattice or an array of points showing how molecules, atoms or ions are arranged in different sites, in three-dimensional space is called space lattice.

The smallest repeating unit in a space lattice which when repeated over and over again results in a crystal of the given substance is termed unit cell. A unit cell possesses all the structural properties of the given crystal. The edges of the unit cell are designated as  $a$ ,  $b$  and  $c$ , and the angles between three imaginary axes as  $\alpha$ ,  $\beta$  and  $\gamma$  respectively.

**16. Crystal systems:** Seven types of basic or primitive unit cells have been recognised among crystals. These are:

1. Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	NaCl, KCl, ZnS
2. Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	KNO <sub>3</sub> , BaSO <sub>4</sub>
3. Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	NH <sub>4</sub> Br, SnO <sub>2</sub>
4. Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ$ $\beta \neq 90^\circ$	Monoecilic sulphur, CaSO <sub>4</sub> · 2H <sub>2</sub> O
5. Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	CuSO <sub>4</sub> · SH <sub>2</sub> O H <sub>3</sub> BO <sub>3</sub>
6. Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$	ZnO, AgI, SiC
7. Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$	NaNO <sub>3</sub> , CaCO <sub>3</sub>

All crystals do not have simple lattices. There can be 14 different ways in which similar points can be arranged in a three dimensional space. The crystals belonging to a cubic system have three kinds of lattices:

(i) **Simple cubic lattice:** There are points only at the corners of each unit.

(ii) **Face-centred cubic lattice:** There are points at the corners as well as at the centre of each of the six faces of the cube.

(iii) **Body-centred cubic lattice:** There are points at the corners as well as in the centre of each cube.

Type of lattice point	Contribution to one unit cell
Corner	$\frac{1}{8}$
Edge	$\frac{1}{4}$
Face-centre	$\frac{1}{2}$
Body-centre	1

- Halides of alkali metals except those of Cs, ammonium halides, oxides and sulphides of alkaline earth metals except BeS and halides of silver except AgI have rock salt (NaCl type) structure.
- CsCl, CsBr, CsI, TiCl<sub>3</sub>, TiBr<sub>3</sub>, TiI<sub>3</sub> have CsCl type structure.
- CuCl, CuBr, CuI, AgI, BeS have zinc blende structure (ZnS type).
- SrCl<sub>2</sub>, SrF<sub>2</sub>, BaCl<sub>2</sub>, BaF<sub>2</sub>, CdF<sub>2</sub>, HgF<sub>2</sub> have fluorite (CaF<sub>2</sub>) structure.
- Na<sub>2</sub>O, K<sub>2</sub>O, Na<sub>2</sub>S, K<sub>2</sub>S have antifluorite (Li<sub>2</sub>O type) structure.

**17. Bragg's law:** When X-rays are incident on a crystal face, they penetrate into the crystal and strike the atoms in different planes. From each of these planes, X-rays are deflected.

Bragg presented a relationship between the wavelength of the X-rays and the distance between the planes,

$$n\lambda = 2d \sin \theta$$

Where,  $n$  is an integer such as, 1, 2, 3, ...,  $\lambda$  is the wavelength,  $d$  is the distance between repeating planes of particles and  $\theta$  the angle of deflection or glancing angle.

### 18. Characteristics of cubic systems:

(i) **Number of atoms per unit cell:** (a) Simple cubic structure—one atom per unit cell, (b) Face-centred cubic structure—4 atoms per unit cell and (c) Body-centred cubic structure—2 atoms per unit cell.

$$(ii) \text{Density of lattice matter} = \frac{n \times M}{N_0 \times a^3}$$

where,  $n$  is the number of atoms in unit cell,  $M$  is the atomic mass or molecular mass,  $N_0$  is Avogadro's number and  $a$  = edge length of the cubic unit cell.

### (iii) Atomic radius:

$$(a) \text{Simple cubic cell}—\text{Radius of atom} = \frac{a}{2}$$

$$(b) \text{Face-centred cubic cell}—\text{Radius of atom} = \frac{a}{2\sqrt{2}}$$

$$(c) \text{Body-centred cubic cell}—\text{Radius of atom} = \frac{\sqrt{3}}{4} a$$

**19. Close packing of constituents:** It refers to the arrangement in which constituents occupy maximum available space. The two common types of close packing are:

(a) *AB AB ...* arrangement. This gives hexagonal close packing.

(b) *ABC ABC ...* arrangement. This gives cubical close packing.

In the packing of constituents, some interstitial sites are left. These sites are termed voids. The interstitial site between four spheres is tetrahedral and between six spheres is octahedral.

The space occupied by hard spheres in hcp; ccp (fcc) is 74%; in bcc it is 68%; in simple cubic it is 52% and in diamond it is 34%; thus, only fcc and hcp are close packed structures.

(i) hcp is present in Be, Mg, Ca, Cr, Mo, V and Zn.

(ii) ccp is present in Fe, Cu, Ag, Au, Pt, Al and Ni.

(iii) bcc is present in alkali metals.

(iv) All noble gases have ccp structure except helium which has hcp structure.

If ' $n$ ' spheres are present in packing, then the numbers of tetrahedral and octahedral voids are  $2n$  and  $n$  respectively.

**20. The coordination number:** The nearest neighbours with which a given sphere is in contact is called coordination number. It depends upon structure.

(a) Simple cubic structure: coordination number = 6

(b) Face-centred cubic structure: coordination number = 12

(c) Body-centred cubic structure: coordination number = 8

For ionic solids, the ratio of the radius of cation to that of anion is called radius<sup>2</sup> ratio. The radius ratio for a given coordination number is fixed.

For radius ratio (0.155– 0.225) coordination number = 3

For radius ratio (0.225– 0.414) coordination number = 4

For radius ratio (0.414– 0.732) coordination number = 6

For radius ratio (0.732–1.0) coordination number = 8

**21. Types of crystals:** Depending upon the nature of forces that hold the constituent particles together in the crystal lattice, crystals are classified into four types:

(i) **Ionic crystals:** The forces are electrostatic. The lattice points are occupied by positively and negatively charged ions. These crystals are quite hard, have low volatility and have high melting and boiling points. These are insulators but become good conductors in molten state. These are soluble in polar solvents and highly brittle in nature. NaCl, KCl, BaCl<sub>2</sub>, etc., belong to this class.

(ii) **Covalent crystals:** The constituent particles are the atoms of same or different elements which are held by strong covalent bonds. These solids are very hard and have very high melting points. Diamond and carborundum belong to this class.

(iii) **Metallic crystals:** The metallic crystals have positive metal ions as lattice points surrounded by a sea of mobile electrons. Each electron belongs to a number of positive ions and each positive ion belongs to a number of electrons. The force that binds a metal ion to a number of electrons is known as metallic bond. Metallic crystals mostly belong to fcc, bcc and hcp systems. These are good conductors, possess lustre and are hard, tough, malleable and ductile in nature.

(iv) **Molecular crystals:** The constituent units of molecular crystals are molecules. The forces holding the molecules are weak van der Waals' forces. Molecular solids are soft and vaporise easily. These are bad conductors of electricity and possess low density. Examples are ice, solid CO<sub>2</sub>, etc.

**22. Defects in crystals:** An ideal crystal is the one which has the same unit cell containing the same lattice points

throughout the whole of the crystal. At absolute zero, the crystals are ideal but with rise in temperature, there is a chance of distortion. The defect may be at a point along a line or over a surface.

(i) **Schottky defect:** This defect is caused if some of the lattice points are unoccupied. The points which are unoccupied are called vacancies or holes. The number of missing positive and negative ions is the same and, thus, the crystal is neutral. Such defect is common in ionic compounds with high coordination number where the cations and anions are of similar size, e.g., NaCl, KCl, KBr, etc.

(ii) **Frenkel defect:** This defect is caused when some of the ions of the lattice occupy interstitial sites leaving lattice sites vacant. This defect appears generally in ionic crystals in which anion is much larger in size than the cation, e.g., AgBr, ZnS.

In Schottky defect, density decreases while in Frenkel defect it remains the same. In both the defects, electrical conductivity is observed to some extent. The overall chemical composition of the substance does not change. However, there are other defects in which there is change in overall chemical combination. Such defects are termed **non-stoichiometric defects**. In such crystals, there is excess of either positive particles or negative particles. However, the crystal is neutral in nature.

**Positive particle excess defects:** (i) A negative ion may be missing from the lattice site which is occupied by an extra electron. (ii) An extra positive particle is present in the interstitial position. To maintain neutrality, an extra electron also occupies a place in the interstitial space. Such crystals are usually coloured and semiconductors.

**Positive particle deficiency defect:** One of the positive particles may be missing from its lattice site. The extra negative charge may be balanced if a nearby positive particle acquires extra positive charge. Such crystals are also semiconductors. Examples are FeO, FeS, NiO, etc.

Certain defects in crystals arise due to presence of chemical impurities. These are known as **impurity defects**.

# Questions

**1. Matrix Match Type Questions:**

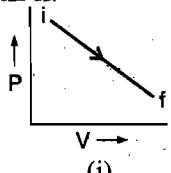
[A] Match the crystalline solids in Column-I with the coordination number of their ions in Column-II:

**Column-I**

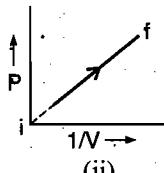
- (a) CsCl      (p) Coordination number of cation = 8
- (b) CaF<sub>2</sub>    (q) Coordination number of anion = 4
- (c) ZnS       (r) Coordination number of cation = 4
- (d) Na<sub>2</sub>O    (s) Coordination number of anion = 8

**Column-II**

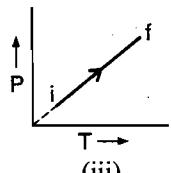
[B] The diagrams below depict the different processes for a given amount of an ideal gas. Match the Column-I and Column-II:



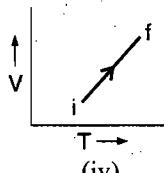
(i)



(ii)

i → initial state,  
f → final state

(iii)



(iv)

- | Column-I   | Column-II  |
|--|--|
| (a) Fig. (i) : System proceeding from initial state to final state   | (p) Temperature will remain constant   |
| (b) Fig. (ii) : System from initial state to final state             | (q) Pressure will decrease   |
| (c) Fig. (iii) : System proceeding from initial state to final state | (r) Volume will be constant  |
| (d) Fig. (iv) : System proceeding from initial state to final state  | (s) Temperature may increase or decrease or may first increase and then decrease |

[C] Match Column-I with Column-II for ideal gases:

**Column-I**

- (a) If temperature of given gas is increased
- (b) If the pressure of a given gas is increased at constant temperature
- (c) If the density of a given gas is lowered at constant temperature
- (d) If the volume of a given gas is increased at constant temperature

**Column-II**

- (p) Average speed of gas will increase
- (q) Root mean square speed of gas molecules will increase
- (r) Most probable speed of gas molecules will increase
- (s) Speed of gas molecules will not change

[D] Match the Column-I with Column-II:

**Column-I**

- (a) Boyle's temperature

(p)  $a/Rb$ 

- (b)  $\frac{1}{2}$  (Inversion temperature)

(q)  $8a/27Rb$ 

- (c) Critical temperature

(r) The gas cannot be liquefied above this temperature, on applying pressure

- (d) Critical pressure

(s)  $a/27b^2$ 

[E] Match the Column-I with Column-II:

**Column-I**

- (a) Real gas at high pressure

(p)  $PV = RT + Pb$ 

- (b) Force of attraction among gas molecules is negligible

(q)  $PV = nRT$ 

- (c) At high temperature and low pressure

(r)  $Z = 1$ 

- (d) Real gas at N.T.P.

(s)  $\left( P + \frac{an^2}{V^2} \right) (V - nb) = nRT$ 
**Column-II**

[F] Match the Column-I with Column-II:

**Column-I**

- (a) Internal energy of gas

(p)  $\frac{3}{2}RT$ 

- (b) Translational kinetic energy of gas molecules

(q)  $\frac{5}{2}RT$ 

- (c) The temperature at which there is no molecular motion

(r)  $-273^\circ C$ 

- (d) The lowest possible temperature at which gas molecules have no heat

(s) 3.716 kJ at 298 K

**Column-II**

[G] Match the Column-I with Column-II:

**Column-I**

- (a) NaCl

(p) Schottky defect

- (b) ZnS

(q) Frenkel defect

- (c) AgBr

(r) Develops yellow colour on heating due to F-centre

- (d) KCl

(s) Develops blue/violet colour on heating due to F-centre

**Column-II**

[H] Match the crystalline solids in Column-I with packing arrangement in Column-II:

Column-I	Column-II
(a) $\text{CaF}_2$	(p) Cations are in ccp arrangement
(b) $\text{NaCl}$	(q) Anions are in tetrahedral voids
(c) $\text{ZnS}$	(r) Anions are in ccp arrangement
(d) $\text{Na}_2\text{O}$	(s) Cations are in octahedral voids

[I] Match the crystal system in Column-I with unit cell dimensions in Column-II:

Column-I	Column-II
(a) Cubic	(p) $a = b = c$
(b) Rhombohedral	(q) $\alpha = \beta = \gamma = 90^\circ$
(c) Orthorhombic	(r) $a \neq b \neq c$
(d) Triclinic	(s) $\alpha \neq \beta \neq \gamma \neq 90^\circ$

[J] Match the crystal system in Column-I with Bravais lattice in Column-II:

Column-I (Crystal System)	Column-II (Bravais lattice)
(a) Cubic	(p) Primitive only
(b) Hexagonal	(q) Primitive, body centred
(c) Tetragonal	(r) Primitive, face centred, body centred
(d) Orthorhombic	(s) Primitive, face centred, body centred and end centred

[K] Match the Column-I with Column-II:

Column-I	Column-II
(a) Root mean square velocity	(p) $\sqrt{\frac{3P}{d}}$
(b) Average velocity	(q) $\sqrt{\frac{3RT}{m}}$
(c) Most probable velocity	(r) $\sqrt{\frac{8P}{\pi d}}$
(d) Velocity possessed by maximum fraction of molecules	(s) $\sqrt{\frac{2RT}{m}}$

## Answers

- [A] (a — p, s); (b — p, q); (c — q, r); (d — r, s)  
[B] (a — s); (b — p); (c — r); (d — q)  
[C] (a — p, q, r); (b — s); (c — p, q, r); (d — s)  
[D] (a — p); (b — p); (c — q, r); (d — s)  
[E] (a — p); (b — p); (c — q, r); (d — s)  
[F] (a — p, q, s); (b — p, s); (c — r); (d — r)

- [G] (a — p, r); (b — q); (c — p, q); (d — p, s)  
[H] (a — p, q); (b — r, s); (c — q); (d — q)  
[I] (a — p, q); (b — p); (c — q, r); (d — r, s)  
[J] (a — r); (b — p); (c — q); (d — s)  
[K] (a — p, q); (b — r); (c — s); (d — s)

## PRACTICE PROBLEMS

- A gas occupies a volume of  $250 \text{ cm}^3$  at 745 torr and  $25^\circ\text{C}$ . What additional pressure is required to reduce the gas volume to  $200 \text{ cm}^3$  at the same temperature?  
[Ans. 186.25 torr]
- A vessel of  $120 \text{ cm}^3$  contains a certain mass of a gas at  $20^\circ\text{C}$  and 750 torr pressure. The gas was transferred to a vessel of volume  $180 \text{ cm}^3$ . Calculate the pressure of the gas at the same temperature.  
[Ans. 500 torr]
- A gaseous system has a volume of  $580 \text{ cm}^3$  at a certain pressure. If its pressure is increased by 0.96 atm, its volume becomes  $100 \text{ cm}^3$ . Determine the pressure of the system.  
[Ans. 0.2 atm]  
[Hint:  $P \times 580 = (P + 0.96)100$ ]
- A gas filled freely collapsible balloon is pushed from the surface level of a lake to a depth of 50 m. Approximately what per cent of its original volume will the balloon finally have, assuming that the gas behaves ideally and temperature is same at the surface and at 50 m depth?

[Ans. 17.13]

[Hint:  $P_1 = \text{Pressure at the surface} = 1 \text{ atm}$   
 $= 76.0 \times 13.6 \times 981 \text{ dyne/cm}^2$

$$\begin{aligned} P_2 &= \text{Pressure at a depth of } 50 \text{ m} \\ &= 76.0 \times 13.6 \times 981 + (50 \times 100) \times 1 \times 981 \text{ dyne/cm}^2 \\ &= 981[76.0 \times 13.6 + 5000] \\ &= 981 \times (6033.6) \text{ dyne/cm}^2 \end{aligned}$$

Now apply Boyle's law,  $P_1V_1 = P_2V_2$

$$\text{or } \frac{V_2}{V_1} = \frac{P_1}{P_2} = \frac{76.0 \times 13.6 \times 981}{981 \times 6033.6} = 0.1713$$

$$\% = 0.1713 \times 100 = 17.13$$

- A sample of gas at room temperature is placed in an evacuated bulb of volume  $0.51 \text{ dm}^3$  and is found to exert a pressure of 0.24 atm. The bulb is connected to another evacuated bulb whose volume is  $0.63 \text{ dm}^3$ . What is the new pressure of the gas at room temperature?  
[Ans. 0.1074 atm]

6. It is desired to increase the volume of  $800 \text{ cm}^3$  of a gas by 20% keeping the pressure constant. To what temperature should the gas be heated, if the initial temperature is  $22^\circ\text{C}$ ?

[Ans.  $81^\circ\text{C}$ ]

7. A chamber of constant volume contains hydrogen gas. When the chamber is immersed in a bath of melting ice ( $0^\circ\text{C}$ ) the pressure of the gas is 800 torr. What pressure will be indicated when the chamber is brought to  $100^\circ\text{C}$ ?

[Ans. 1093 torr]

8. Calculate the volume occupied by  $4.045 \times 10^{23}$  molecules of oxygen at  $27^\circ\text{C}$  and having a pressure of 700 torr.

[Ans.  $17.97 \text{ dm}^3$ ]

$$[\text{Hint: No. of moles } n = \frac{4.045 \times 10^{23}}{6.023 \times 10^{23}} = 0.672; P = \frac{700}{760} \text{ atm}]$$

Now use the gas equation,  $PV = nRT$  ]

9. Calculate the moles of hydrogen present in a  $500 \text{ cm}^3$  sample of hydrogen gas at a pressure of 760 mm of Hg and  $27^\circ\text{C}$ .

[Ans.  $2.03 \times 10^{-2}$  mol]

$$[\text{Hint: } 500 \text{ cm}^3 = 0.5 \text{ L}, 760 \text{ mm of Hg} = 1 \text{ atm. Now apply the gas equation, } n = \frac{PV}{RT}]$$

10. Calculate the volume occupied by 4 mole of an ideal gas at  $2.5 \times 10^5 \text{ Nm}^{-2}$  pressure and 300 K temperature.

[Ans.  $39.9 \text{ dm}^3$ ]

$$[\text{Hint: } V = \frac{nRT}{P}, \text{ Given, } n = 4; R = 8.314 \text{ Nm K}^{-1} \text{ mol}^{-1}; T = 300; P = 2.5 \times 10^5 \text{ Nm}^{-2}]$$

11. What is the volume occupied by 11 g of carbon dioxide at  $27^\circ\text{C}$  and 780 mm of Hg pressure?

[Ans. 6 litre]

$$[\text{Hint: } 780 \text{ mm of Hg} = \frac{780}{760} \text{ atm}; w = 11 \text{ g}; M = 44 \text{ g mol}^{-1}]$$

$$\text{Now apply } V = \frac{w}{M} \cdot \frac{RT}{P}$$

12. A certain quantity of a gas occupies 200 mL when collected over water at  $15^\circ\text{C}$  and 745 mm pressure. It occupies 182.6 mL in dry state at NTP. Find the vapour pressure of water at  $15^\circ\text{C}$ .

[Ans. 13 mm]

13. The density of a gas is found to be  $2.07 \text{ g L}^{-1}$  at  $30^\circ\text{C}$  and 2 atmospheric pressure. What is its density at NTP?

[Ans.  $1.149 \text{ g L}^{-1}$ ]

$$[\text{Hint: Apply } P_1 = \frac{D_1}{M} RT_1, P_2 = \frac{D_2}{M} RT_2]$$

$$\text{So, } \frac{P_1}{D_1 T_1} = \frac{P_2}{D_2 T_2}$$

14. At the top of a mountain, the thermometer reads  $0^\circ\text{C}$  and the barometer reads 700 mm Hg. At the bottom of the mountain the thermometer reads  $30^\circ\text{C}$  and the pressure 760 mm Hg. Compare the density of the air at the top with that at the bottom.

[Ans. 1.02 : 1]

[Hint: Density is inversely proportional to volume.

$$\frac{d_{\text{top}}}{d_{\text{bottom}}} = \frac{V_b}{V_t} = \frac{T_b P_t}{T_t P_b} = \frac{303 \times 700}{273 \times 760} = \frac{1.02}{1}$$

15. Calculate the volume occupied by 5 g of acetylene gas at  $50^\circ\text{C}$  and 740 mm of pressure. (IIT 1991)

[Ans. 5.23 litre]

16. Calculate the volume occupied by 7 g of nitrogen gas at  $27^\circ\text{C}$  and 750 mm Hg pressure. (MLNR 1992)

[Ans. 6.24 litre]

17. A spherical balloon of 21 cm diameter is to be filled up with hydrogen at NTP from a cylinder containing the gas at 20 atm and  $27^\circ\text{C}$ . The cylinder can hold 2.82 litre of water at NTP. Calculate the number of balloons that can be filled up. (MLNR 1991)

[Ans. 10]

[Hint: Volume of one balloon

$$= \frac{4}{3} \pi r^3 = \frac{4}{3} \times \frac{22}{7} \times \left( \frac{21}{2} \right)^3 = 4851 \text{ cm}^3 \\ = 4.851 \text{ litre}$$

Let  $n$  balloons be filled; thus, total volume of hydrogen used in filling balloons

$$= 4.851 \times n \text{ litre}$$

Total volume of hydrogen in the cylinder at NTP,

$$V = \frac{20 \times 2.82 \times 273}{300 \times 1} = 51.324 \text{ litre}$$

Actual volume of  $\text{H}_2$  to be transferred to balloons

$$= 51.324 - 2.82 \text{ (2.82 litre retained in the cylinder)} \\ = 48.504 \text{ litre}$$

$$\text{No. of balloons filled } n = \frac{48.504}{4.851} \approx 10$$

18. An open vessel at  $27^\circ\text{C}$  is heated until three-fifth of the air in it has been expelled. Assuming that the volume of the vessel remains constant, find the temperature to which the vessel has been heated? (MLNR 1990).

[Ans.  $477^\circ\text{C}$ ]

[Hint: Both volume and pressure are constant as the vessel is open,

$$\text{i.e., } n_1 RT_1 = n_2 RT_2$$

$$\text{or } \frac{n_1}{n_2} = \frac{T_2}{T_1}$$

$$\text{If } n_1 = 1, n_2 = 1 - \frac{3}{5} = \frac{2}{5}$$

$$\text{So, } \frac{5}{2} = \frac{T_2}{300} \text{ or } T_2 = 750 \text{ K} = 477^\circ\text{C}$$

19. A gaseous mixture of He and  $\text{O}_2$  is found to have a density of  $0.518 \text{ g L}^{-1}$  at  $25^\circ\text{C}$  and 720 torr. What is the per cent by mass of helium in this mixture?

[Ans. 19.88]

[Hint: First determine the average molecular mass and then number of moles of helium and oxygen.

$$\text{Moles of helium} = 0.665; \text{ Moles of oxygen} = 0.335$$

$$\text{Mass per cent of helium} = \frac{4 \times 0.665}{4 \times 0.665 + 32 \times 0.335} \times 100 \\ = 19.88$$

20. A sample of natural gas is 85.2% methane and 14.8% ethane by mass. What is the density of this mixture at  $18^\circ\text{C}$  and 748 mm Hg?

[Ans.  $0.74 \text{ g L}^{-1}$ ]

[Hint: Molecular mass of mixture,

$$M = \frac{85.2}{100} \times 16 + \frac{14.8}{100} \times 30 = 13.632 + 4.44 = 18.07$$

$$PM = dRT \\ d = \frac{PM}{RT} = \frac{748}{760} \times \frac{18.07}{0.0821 \times 291} = 0.74 \text{ g L}^{-1}$$

21. 125 mL of a gas A of pressure 500 mm is mixed with 200 mL of another gas B at a pressure of 300 mm in a vessel of 150 mL capacity. What will be the total pressure of the resulting mixture if the temperature is kept constant?

[Ans. 816.67 mm]

22. Two vessels whose volumes are in the ratio 2 : 1 contain nitrogen and oxygen at 800 mm and 680 mm pressures respectively, when they are connected together what will be the pressure of the resulting mixture?

[Ans. 760 mm]

23. A 10 litre flask at 298 K contains a gaseous mixture of CO and CO<sub>2</sub> at a total pressure of 2 atm. If 0.20 mole of CO is present, find its partial pressure and also that of CO<sub>2</sub>.

[Ans. Partial pressure of CO = 0.49 atm; partial pressure of CO<sub>2</sub> = 1.51 atm]

24. Calculate the total pressure in a mixture of 4 g of oxygen and 3 g of hydrogen confined in a total volume of one litre at 0°C.

(MLNR 1991)

[Ans. 25.18 atm]

[Hint: Determine total number of moles and then apply

$$PV = n_{\text{total}} RT$$

25. A gas cylinder contains 55% nitrogen, 20% oxygen and 25% carbon dioxide by mass, at 760 mm pressure. Calculate the partial pressure of each gas.

[Ans. 472.8 mm, 150.44 mm, 136.74 mm]

26. The density of a mixture of N<sub>2</sub> and O<sub>2</sub> at NTP is 1.3 g L<sup>-1</sup>. Calculate partial pressure of O<sub>2</sub>.

[Ans. 0.28 atm]

[Hint: Let n<sub>1</sub> and n<sub>2</sub> moles of N<sub>2</sub> and O<sub>2</sub> be present in the mixture respectively.

$$\text{Average molecular mass of the mixture} = \frac{28n_1 + 32n_2}{n_1 + n_2} \quad \dots (i)$$

Average molecular mass from general gas equation,

$$M = \frac{D}{P} \times RT = \frac{1.3}{1} \times 0.0821 \times 273 = 29.137 \quad \dots (ii)$$

$$\text{So, } \frac{28n_1 + 32n_2}{n_1 + n_2} = 29.137 \text{ or } \frac{4n_2}{n_1 + n_2} = 1.137$$

$$\text{or } \frac{n_2}{n_1 + n_2} = 0.28 = \text{mole fraction of oxygen}$$

Partial pressure of O<sub>2</sub> = 0.28 × 1 = 0.28 atm]

27. At a definite pressure and temperature, 100 mL of hydrogen diffused in 20 minute. How long will 40 mL of oxygen take to diffuse under similar conditions?

[Ans. 32 minute]

28. At a given temperature and pressure, 20 mL of air diffused through a porous membrane in 15 second. Calculate the volume of carbon dioxide which will diffuse in 10 second if the vapour density of air is 14.48.

[Ans. 10.8 mL]

29. At room temperature, ammonia gas at one atmospheric pressure and hydrogen chloride at P atmospheric pressure are allowed to effuse through identical pinholes from opposite ends of a glass tube of one metre length and uniform cross reaction. NH<sub>4</sub>Cl is first formed at a distance of 60 cm from the end through which HCl gas is sent in. What is the value of P?

[Ans. 2.198 atm]

$$[\text{Hint: } \frac{r_{\text{HCl}}}{r_{\text{NH}_3}} = \sqrt{\frac{M_{\text{NH}_3}}{M_{\text{HCl}}} \times \frac{P_{\text{HCl}}}{P_{\text{NH}_3}}}]$$

30. The rate of effusion of an unknown gas (X) through a pinhole is found to be 0.279 times the rate of effusion of hydrogen gas through the same pinhole, if both are at STP. What is the molecular mass of the unknown gas? [CEE (Bihar) 1991]

[Ans. 25.69]

31. In a 2 m long narrow tube, HCl is allowed to diffuse in the tube from one end and NH<sub>3</sub> from the other end. If diffusion is started at the same time, predict at what point the white fumes of NH<sub>4</sub>Cl will form?

[Ans. NH<sub>4</sub>Cl will form at 1.1886 m from the NH<sub>3</sub> end of the tube]

32. The composition of air is approximately 80% N<sub>2</sub> and 20% O<sub>2</sub> by mass. Calculate density of air at 293 K and 76 cm Hg pressure.

[Ans. 1.19 g L<sup>-1</sup>]

[Hint: Determine first average molecular mass of air and then apply  $D = \frac{P \times M_{\text{av}}}{RT}$ ]

33. Calculate the internal energy of one gram mole of nitrogen at 150°C assuming it to be an ideal gas.

[Ans.  $5.275 \times 10^{10}$  erg]

34. Calculate the kinetic energy of 5 mole of a gas at 27°C in erg and calorie.

[Ans.  $1.8706 \times 10^{11}$  erg, 4477 cal]

35. A glass tumbler containing 243 mL of air at 100 kPa and 20°C is turned upside down and immersed in a water bath to a depth of 20.5 metre. The air in the glass is compressed by the weight of water above it. Calculate the volume of air in the glass assuming the temperature and the barometric pressure have not changed.

[Ans. 80.7 mL]

[Hint: Hydrostatic pressure =  $h \times d \times g$   
 $= 20.5 \times 1 \times 9.81$   
 $\approx 201.105 \text{ kPa}$

Inside the water bath atmospheric pressure and hydrostatic pressure acts:

$$P_{\text{total}} = 100 + 201.105 = 301.105 \text{ kPa}$$

$$P_1 V_1 = P_2 V_2$$

$$100 \times 243 = 301.105 \times V_2$$

$$V_2 = 80.70 \text{ mL}$$

36. Calculate the rms speed of the molecules of ethane gas of volume 1.5 litre at 750 mm of Hg pressure.

[Ans.  $1.225 \times 10^4$  cm/sec]

37. The density of a gas at 1.5 atm is 1.52 g L<sup>-1</sup>. Calculate the rms speed of the molecules of the gas.

[Ans.  $5.476 \times 10^4$  cm/sec]

38. At what temperature will the rms speed of hydrogen be the same as that of oxygen at 25°C?

[Ans. 18.62 K or -254.38°C]

39. Calculate the average rms and most probable speed of SO<sub>2</sub> molecules at 27°C.

[Ans.  $3.15 \times 10^4$  cm/sec,  $3.419 \times 10^4$  cm/sec,  $2.792 \times 10^4$  cm/sec]

40. The average speed at temperature  $T_1$  and most probable speed at  $T_2$  of CO<sub>2</sub> gas is  $9 \times 10^4$  cm/sec. Calculate the values of  $T_1$  and  $T_2$ .

[Ans. 1682.5 K, 2143.4 K]

41. How many times would the average molecular speed of nitrogen increase as its temperature is raised from -73°C and 127°C?

[Ans. 1.414 times]

42. A 4 : 1 molar mixture of He and CH<sub>4</sub> is contained in a vessel at 20 bar pressure. Due to hole in the vessel the gas mixture leaks out. What is the composition of the mixture effusing out initially? (IIT 1994)

[Ans. 8 : 1]

[Hint: Partial pressure ratio of He and CH<sub>4</sub> is 16 : 4.]

$$\text{For diffusion } \frac{r_{\text{He}}}{r_{\text{CH}_4}} = \sqrt{\frac{M_{\text{CH}_4}}{M_{\text{He}}}} \times \frac{P_{\text{He}}}{P_{\text{CH}_4}}$$

$$\frac{n_{\text{He}}}{n_{\text{CH}_4}} = \sqrt{\frac{16}{4}} \times \frac{16}{4} = 8$$

i.e., mole ratio of diffusion for He and CH<sub>4</sub> is 8 : 1.]

43. Pure O<sub>2</sub> diffuses through an aperture in 224 second, whereas mixture of O<sub>2</sub> and another gas containing 80% O<sub>2</sub> diffuses from the same in 234 second. What is the molecular mass of gas?

[Ans. 46.6]

44. 56 g of nitrogen are confined to a 6 litre flask at 37°C. Calculate its pressure using van der Waals' equation for nitrogen.  $a = 4.17 \text{ atm litre}^2 \text{ mol}^{-2}$  and  $b = 0.037 \text{ litre mol}^{-1}$ .

[Ans. 8.1175 atm]

45. One mole of carbon dioxide was found to occupy a volume of 1.32 litre at 48°C under a pressure of 16.4 atm. Calculate the pressure that would have been expected from:

(i) the ideal gas equation,

(ii) van der Waals' equation.

$$(a = 3.59 \text{ atm litre}^2 \text{ mol}^{-2}, b = 4.27 \times 10^{-3} \text{ litre mol}^{-1}$$

$$\text{and } R = 0.0821 \text{ litre-atm K}^{-1} \text{ mol}^{-1})$$

[Ans. (i) 19.96 atm (ii) 18.64 atm]

46. Calculate the compressibility factor for SO<sub>2</sub>, if 1 mole of it occupies 0.35 litre at 300 K and 50 atm pressure. Comment on the result.

$$[\text{Hint: } Z = \frac{PV}{nRT} = \frac{50 \times 0.35}{1 \times 0.0821 \times 300} = 0.711]$$

Since,  $Z < 1$ ; the gas SO<sub>2</sub> will be more compressible than ideal gas.]

47. The average velocity of gas molecules is 400 m/sec. Calculate its rms velocity at the same temperature. (IIT 2003)

[Ans. 434 m/sec]

48. A chamber contains monoatomic 'He' at STP, determine its number density.

[Ans.  $2.68 \times 10^{25} \text{ m}^{-3}$ ]

$$[\text{Hint: Number density} = \frac{P}{kT}]$$

(where,  $k$  = Boltzmann constant)

$$PV = nRT$$

$$= (n \times N) \frac{R}{N} T$$

$$= (n \times N) kT$$

$$\frac{P}{kT} = \frac{n \times N}{V} = \text{number density}$$

$$\therefore \text{Number density} = \frac{1.01 \times 10^5}{1.38 \times 10^{-23} \times 273} = 2.68 \times 10^{25} \text{ m}^{-3}$$

49. Two perfect gases at absolute temperature  $T_1$  and  $T_2$  are mixed. There is no loss of energy. Find the temperature of the mixture if masses of molecules are  $m_1$  and  $m_2$  and the number of moles of the gases are  $n_1$  and  $n_2$  respectively.

$$[\text{Ans. } T = \frac{n_1 T_1 + n_2 T_2}{n_1 + n_2}]$$

[Hint: Let final temperature is  $T$

$$\frac{3}{2} n_1 RT_1 + \frac{3}{2} n_2 RT_2 = \frac{3}{2} (n_1 + n_2) RT$$

$$T = \frac{n_1 T_1 + n_2 T_2}{n_1 + n_2}$$

50. van der Waals' constant 'b' for oxygen is  $32 \text{ cm}^3/\text{mol}$ . Assume  $b$  is four times the actual volume of a mole of "billiard-ball" O<sub>2</sub> molecules and compute the diameter of an O<sub>2</sub> molecule.

51. The speed of ten particles in metre/sec are 0, 1, 2, 3, 3, 3, 4, 4, 5 and 6. Find (a) average speed (b) the root mean square speed (c) most probable speed.

[Ans.  $c_{av} = 3.1 \text{ m sec}^{-1}$ ,  $c_{rms} = 12.5 \text{ m sec}^{-1}$ ,  $c_{mp} = 3 \text{ m sec}^{-1}$ ]

52. Using van der Waals' equation, calculate the constant 'a' when two moles of a gas confined in a four litre flask exerts a pressure of 11 atm at a temperature of 300 K. The value of 'b' is  $0.05 \text{ litre mol}^{-1}$ . (IIT 1998)

[Ans.  $6.46 \text{ atm litre}^2 \text{ mol}^{-2}$ ]

53. (a) Calculate the pressure exerted by 5 moles of CO<sub>2</sub> in one litre vessel at 47°C using van der Waals' equation. Also, report the pressure of the gas if it behaves ideally in nature. Given that  $a = 3.592 \text{ atm litre}^2 \text{ mol}^{-2}$ ,  $b = 0.0427 \text{ litre mol}^{-1}$  (IIT 2002)

(b) If volume occupied by CO<sub>2</sub> molecule is negligible, then calculate the pressure exerted by one mol of CO<sub>2</sub> gas at 273 K. (IIT 2000)

[Ans. (a) 77.218 atm, 131.36 atm and (b) 0.9922 atm]

54. A compound alloy of gold and copper crystallises in a cubic lattice in which gold atoms occupy corners of cubic unit cell and copper atoms occupy the centre of faces of cube. What is formula of alloy compound?

[Ans. AuCu<sub>3</sub>]

55. A compound formed by elements *A* and *B* crystallises in the cubic structure where *A* atoms are at the corners of the cube

- and  $B$  atoms at the centre of the cube. What is the formula of the compound?  
 [Ans.  $AB$ ]
56. A fcc element (atomic mass = 60) has a cell edge of 400 pm. What is its density?  
 [Ans.  $6.23 \text{ g cm}^{-3}$ ]  
 [Hint: Apply density =  $\frac{Z \times M}{N_0 \times V}$ ,  $Z = 4$  and  $V = (4 \times 10^{-8})^3 \text{ cm}^3$  ( $1 \text{ pm} = 10^{-12} \text{ m} = 10^{-10} \text{ cm}$ )]
57. The face-centred unit cell of nickel has an edge length of 352.39 pm. The density of nickel is  $8.9 \text{ g cm}^{-3}$ . Calculate the value of Avogadro's number. The atomic mass of nickel is 58.7 and 1 pm is equal to  $10^{-10} \text{ cm}$ .  
 [Ans.  $6.029 \times 10^{23}$ ]
58. The unit cell of aluminium is a cube with an edge length of 405 pm. The density of aluminium is  $2.70 \text{ g cm}^{-3}$ . What type of unit cell of aluminium is?  
 [Ans. The unit cell is face-centred]  
 [Hint: Apply the formula, density =  $\frac{Z \times M}{N_0 \times V}$  and find the value of  $Z$ .]
59. A substance forms face-centred cubic crystals. Its density is  $1.984 \text{ g cm}^{-3}$  and the edge length of the unit cell is 630 pm. Calculate the molar mass of the substance.  
 [Ans.  $74.70 \text{ g mol}^{-1}$ ]
60. Molybdenum forms body-centred cubic crystals whose density is  $10.3 \text{ g cm}^{-3}$ . Calculate the edge length of the unit cell. The molar mass of Mo is  $95.94 \text{ g mol}^{-1}$ .  
 [Ans.  $313.9 \text{ pm}$ ]
61. An element crystallises in a structure having a fcc unit cell of an edge 200 pm. Calculate its density if 200 g of this element contains  $24 \times 10^{23}$  atoms.  
 [Ans.  $4.166 \text{ g cm}^{-3}$   
 [Hint: Molar mass =  $\frac{200}{24 \times 10^{23}} \times 6.023 \times 10^{23} = 50.19 \text{ g mol}^{-1}$   
 For fcc,  $Z = 4$ ,  $V = a^3 = (200 \times 10^{-10})^3$   
 Apply density =  $\frac{ZM}{N_0 \times V}$ ]
62. The element chromium exists in bcc lattice with unit cell edge  $2.88 \times 10^{-10} \text{ m}$ . The density of chromium is  $7.2 \times 10^3 \text{ kg m}^{-3}$ . How many atoms does  $52 \times 10^{-3} \text{ kg}$  of chromium contain?  
 [Ans.  $6.04 \times 10^{23}$ ]
63. A cubic solid is made up of two elements  $P$  and  $Q$ . Atoms  $Q$  are present at the corners of the cube and atoms  $P$  at the body-centre. What is the formula of the compound? What are the coordination numbers of  $P$  and  $Q$ ?  
 [Ans.  $PQ$ , 8, 8]
64. A metallic element crystallises into a lattice containing a sequence of layers of  $AB\ AB\ AB\dots$  Any packing of spheres leaves out voids in the lattice. What percentage by volume of this lattice is empty space? (IIT 1996)  
 [Ans. 26%]
65. A lead(II) sulphide crystal has an NaCl structure. What is its density? The edge length of the unit cell is 500 pm.  $N_0 = 6.023 \times 10^{23}$ ; atomic mass: Pb = 207.2, S = 32.  
 [Ans.  $12.708 \text{ g cm}^{-3}$ ]
66. The unit cell of metallic gold is face-centred cubic.  
 (a) How many atoms occupy the gold unit cell?  
 (b) What is the mass of a gold unit cell?  
 [Ans. (a) 4 atoms (b)  $1.308 \times 10^{21} \text{ g}$ ]
67. Polonium crystallises in a simple cubic unit cell. It has atomic mass 209 and density  $91.5 \text{ kg m}^{-3}$ . What is the edge length of its unit cell?  
 [Ans.  $15.59 \times 10^{-8} \text{ cm}$ ]
68. The unit cell of nickel is a face-centred cube. The length of its side is 0.352 nm. Calculate the atomic radius of nickel.  
 [Ans.  $0.124 \text{ nm}$ ]
69. Determine the simplest formula of an ionic compound in which cations are present at the corners and the anions occur at the centre of each face.  
 [Ans.  $AB_3$ ;  $A$  and  $B$  are cation and anion respectively.]
70. Sodium metal crystallises in a body-centred cubic lattice with cell edge,  $a = 4.29 \text{ \AA}$ . What is the radius of sodium atom?  
 (IIT 1994)  
 [Ans.  $1.8576 \text{ \AA}$   
 [Hint:  $4r = \sqrt{3}a$ ]
71. If three elements  $P$ ,  $Q$  and  $R$  crystallise in a cubic type lattice with  $P$  atoms at the corners,  $Q$  atoms at the cube centre and  $R$  atoms at the edges, then write the formula of the compound.  
 [Ans.  $PQR_3$ ]
72. The first order reflection of the beam of X-ray from a given crystal occurs at  $5^\circ 15'$ . At what angle will be the third order reflection?  
 [Ans.  $15^\circ 56'$ ]
73. The figures given below show the location of atoms in three crystallographic planes in a fcc lattice. Draw the unit cell for the corresponding structure and identify these planes in your diagram. (IIT 2000)
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# OBJECTIVE QUESTIONS

**Set-1: Questions with single correct answer**

- At constant temperature, the product of pressure and volume of a given amount of a gas is constant. This is:  
 (a) Gay-Lussac law      (b) Charles' law  
 (c) Boyle's law      (d) Pressure law
- A curve drawn at constant temperature is called an isotherm. This shows the relationship between:  
 (a)  $P$  and  $\frac{1}{V}$       (b)  $PV$  and  $V$   
 (c)  $V$  and  $\frac{1}{P}$       (d)  $P$  and  $V$
- Charles' law is represented mathematically as:  
 (a)  $V_t = KV_0 t$       (b)  $V_t = \frac{KV_0}{t}$   
 (c)  $V_t = V_0 \left(1 + \frac{273}{t}\right)$       (d)  $V_t = V_0 \left(1 + \frac{t}{273}\right)$
- Correct gas equation is: [UGET (Manipal Medical) 2006]  
 (a)  $\frac{PV_1}{P_2V_2} = \frac{T_1}{T_2}$       (b)  $\frac{V_1T_2}{P_1} = \frac{V_2T_1}{P_2}$   
 (c)  $\frac{P_1T_1}{V_1} = \frac{P_2T_2}{V_2}$       (d)  $\frac{V_1V_2}{T_1T_2} = P_1P_2$
- In general gas equation,  $PV = nRT$ ,  $V$  is the volume of:  
 (a)  $n$  moles of a gas      (b) any amount of a gas  
 (c) one mole of a gas      (d) one gram of a gas
- In the equation of state of an ideal gas  $PV = nRT$ , the value of universal gas constant would depend only on: (CPMT 1991)  
 (a) the nature of the gas      (b) the units of measurement  
 (c) the pressure of the gas      (d) the temperature of the gas
- The value of gas constant per degree per mol is approximately:  
 (a) 1 cal      (b) 2 cal      (c) 3 cal      (d) 4 cal
- Which one of the following is not the value of  $R$ ?  
 (a) 1.99 cal  $K^{-1} mol^{-1}$       (b) 0.0821 litre-atm  $K^{-1} mol^{-1}$   
 (c) 9.8 kcal  $K^{-1} mol^{-1}$       (d) 8.3 J  $K^{-1} mol^{-1}$
- One litre of a gas collected at NTP will occupy at 2 atmospheric pressure and 27°C:  
 (a)  $\frac{300}{2 \times 273}$  litre      (b)  $\frac{2 \times 300}{273}$  litre  
 (c)  $\frac{273}{2 \times 300}$  litre      (d)  $\frac{2 \times 273}{300}$  litre
- 10 g of a gas at atmospheric pressure is cooled from 273°C to 0°C keeping the volume constant; its pressure would become:  
 (a)  $\frac{1}{2}$  atm      (b)  $\frac{1}{273}$  atm      (c) 2 atm      (d) 273 atm
- 56 g of nitrogen and 96 g of oxygen are mixed isothermally and a total pressure of 10 atm. The partial pressures of oxygen and nitrogen (in atm) are respectively: [PET (Kerala) 2010]  
 (a) 4, 6      (b) 5, 5      (c) 2, 8      (d) 8, 2  
 (e) 6, 4

[Hint:  $n_{N_2} = \frac{56}{28} = 2$ ;  $n_{O_2} = \frac{96}{32} = 3$

$$P_{N_2} = x_{N_2} \times P_{\text{total}}$$

$$= \frac{2}{2+3} \times 10 = 4 \text{ atm},$$

$$P_{O_2} = 10 - 4 = 6 \text{ atm}]$$

- 273 mL of a gas at STP was taken to 27°C and 600 mm pressure. The final volume of the gas would be: (CPMT 1992)  
 (a) 273 mL      (b) 300 mL  
 (c) 380 mL      (d) 586 mL
- The density of the gas is equal to: (CBSE 1991)  
 (a)  $nP$       (b)  $MP/RT$       (c)  $P/RT$       (d)  $M/V$   
 [ $P$  = Pressure;  $V$  = Volume;  $T$  = Temperature;  $R$  = Gas constant;  $n$  = number of mole;  $M$  = molecular mass]
- The density of a gas is 1.964 g dm<sup>-3</sup> at 273 K and 76 cm Hg. The gas is: (KCET 2006)  
 (a) CH<sub>4</sub>      (b) C<sub>2</sub>H<sub>6</sub>      (c) CO<sub>2</sub>      (d) Xe
- Compressed oxygen is sold at a pressure of 100 atmosphere in a cylinder of 49 litre. The number of moles of oxygen in the cylinder is:  
 (a) 400      (b) 100      (c) 300      (d) 200  
 [Hint: One mole occupies a volume approximately 24.5 litre under ordinary atmospheric conditions.]
- If the pressure and absolute temperature of 2 litre of carbon dioxide are doubled, the volume of carbon dioxide would become: (CBSE 1991)  
 (a) 7 litre      (b) 5 litre      (c) 4 litre      (d) 2 litre
- One gram mole of a gas at NTP occupies 22.4 litre as volume. This fact was derived from:  
 (a) Dalton's theory      (b) Avogadro's hypothesis  
 (c) Berzelius hypothesis      (d) law of gaseous volumes
- 4.4 g of CO<sub>2</sub> contains how many litre of CO<sub>2</sub> at STP? (AFMC 2004)  
 (a) 2.4 litre      (b) 2.24 litre      (c) 44 litre      (d) 22.4 litre
- Five gram each of the following gases at 87°C and 750 mm pressure are taken. Which of them will have the least volume? (MLNR 1991)  
 (a) HF      (b) HCl      (c) HBr      (d) HI
- If molecular mass of O<sub>2</sub> and SO<sub>2</sub> are 32 and 64 respectively. If one litre of O<sub>2</sub> at 15°C and 750 mm pressure contains  $N$  molecules, the number of molecules in two litre of SO<sub>2</sub> under the same conditions of temperature and pressure will be:  
 (a) 2 $N$       (b)  $N$       (c)  $N/2$       (d) 4 $N$   
 (MLNR 1991)
- Rate of diffusion of a gas is:  
 (a) directly proportional to its density  
 (b) directly proportional to its molecular mass  
 (c) directly proportional to the square of its molecular mass  
 (d) inversely proportional to the square root of its molecular mass
- The rate of diffusion of hydrogen is about: (CPMT 1991)  
 (a) one-half that of helium      (b) 1.4 times that of helium  
 (c) twice that of helium      (d) four times that of helium

23. The rate of diffusion of methane at a given temperature is twice that of gas  $X$ . The molecular mass of gas  $X$  is:  
 (IIT 1990; MLNR 1995)  
 (a) 64.0    (b) 32.0    (c) 4.0    (d) 8.0
24. Some moles of  $O_2$  diffuse through a small opening in 18 second. Same number of moles of an unknown gas diffuse through the same opening in 45 second. Molecular mass of the unknown gas is:  
 (a)  $32 \times \frac{(45)^2}{(18)^2}$     (b)  $32 \times \frac{(18)^2}{(45)^2}$   
 (c)  $(32)^2 \times \frac{45}{18}$     (d)  $(32)^2 \times \frac{18}{45}$
25. A bottle of dry ammonia and a bottle of dry hydrogen chloride connected through a long tube are opened simultaneously at both the ends. The white ring first formed will be:  
 (a) at the centre of the tube  
 (b) near the ammonia bottle  
 (c) near the  $HCl$  bottle  
 (d) throughout the length of the tube
26. 0.5 mole of each  $H_2$ ,  $SO_2$  and  $CH_4$  are kept in a container. A hole was made in the container. After 3 hours, the order of partial pressures in the container will be :  
 [CET (Karnataka) 2009]  
 (a)  $p_{SO_2} > p_{CH_4} > p_{H_2}$     (b)  $p_{H_2} > p_{SO_2} > p_{CH_4}$   
 (c)  $p_{H_2} > p_{CH_4} > p_{SO_2}$     (d)  $p_{SO_2} > p_{H_2} > p_{CH_4}$
27. The mass of  $6.02 \times 10^{23}$  molecules of CO is:  
 (a) 28 g    (b) 14 g    (c) 7.0 g    (d) 56 g
28. 10 g of hydrofluoric acid occupy 5.6 litre of volume at NTP. The empirical formula of the gas is HF. The molecular formula of the gas will be (At. mass of fluorine = 19):  
 (a)  $H_4F_4$     (b) HF  
 (c)  $H_3F_3$     (d)  $H_2F_2$
29. A fire extinguisher contains 4.4 kg of  $CO_2$ . The volume of  $CO_2$  delivered by this fire extinguisher at room temperature is:  
 (a) 24.5 litre    (b)  $100 \times 24.5$  litre  
 (c)  $10 \times 24.5$  litre    (d)  $1000 \times 24.5$  litre
30. The number of moles of  $H_2$  in 0.224 litre of hydrogen gas at STP is:  
 [MLNR 1994]  
 (a) 1    (b) 0.1    (c) 0.01    (d) 0.001
31. A gas has a vapour density 11.2. The volume occupied by 1 g of the gas at NTP is:  
 (a) 1 L    (b) 11.2 L    (c) 22.4 L    (d) 4 L
32. "The total pressure exerted by a number of non-reacting gases is equal to the sum of partial pressures of the gases under the same conditions" is known as:  
 (a) Boyle's law    (b) Dalton's law  
 (c) Avogadro's law    (d) Charles' law
33. Equal masses of methane and oxygen are mixed in an empty container at  $25^\circ C$ . The fraction of the total pressure exerted by oxygen is:  
 (a)  $\frac{1}{3}$     (b)  $\frac{1}{2}$     (c)  $\frac{2}{3}$     (d)  $\frac{1}{3} \times \frac{273}{298}$
34. Equal masses of methane and hydrogen are mixed in an empty container at  $25^\circ C$ . The fraction of the total pressure exerted by hydrogen is:
- (a)  $\frac{1}{2}$     (b)  $\frac{8}{9}$   
 (c)  $\frac{1}{9}$     (d)  $\frac{16}{17}$
35. A gaseous mixture of 2 moles of  $A$ , 3 moles of  $B$ , 5 moles of  $C$  and 10 moles of  $D$  is contained in a vessel. Assuming that gases are ideal and the partial pressure of  $C$  is 1.5 atm, the total pressure is:  
 (a) 3 atm    (b) 6 atm    (c) 9 atm    (d) 15 atm  
 [Hint: 5 moles of  $C$  produce pressure 1.5 atm; therefore partial pressures of  $D = 3$  atm,  $B = \frac{1.5}{5} \times 3 = 0.9$  atm and  $A = \frac{1.5}{5} \times 2 = 0.6$  atm]
36. 50 mL of a gas  $A$  diffuse through a membrane in the same time as for the diffusion of 40 mL of gas  $B$  under identical conditions of pressure and temperature. If the molecular mass of  $A$  is 64; that of  $B$  would be:  
 (CBSE 1992)  
 (a) 100    (b) 250    (c) 200    (d) 80
37. 3.2 g of oxygen (At. mass = 16) and 0.2 g of hydrogen (At. mass = 1) are placed in a 1.12 litre flask at  $0^\circ C$ . The total pressure of the gas mixture will be:  
 (CBSE 1992)  
 (a) 1 atm    (b) 2 atm    (c) 3 atm    (d) 4 atm
38. Select the correct statement:  
 In the gas equation,  $PV = nRT$   
 (a)  $n$  is the number of molecules of a gas  
 (b)  $n$  moles of the gas have volume  $V$   
 (c)  $V$  denotes volume of one mole  
 (d)  $P$  is the pressure of the gas when only one mole of gas is present
39. The density of a gas at  $27^\circ C$  and 1 atm is  $d$ . Pressure remaining constant, at which of the following temperatures will its density become  $0.75d$ ?  
 (CBSE 1992)  
 (a)  $20^\circ C$     (b)  $30^\circ C$     (c) 400 K    (d) 300 K
40. If 4 g of oxygen diffuse through a very narrow hole, how much hydrogen would have diffused under identical conditions?  
 (a) 16 g    (b) 1 g    (c)  $\frac{1}{4}$  g    (d) 64 g  
 [Hint:  $\frac{w/2}{4/32} = \sqrt{\frac{M_{O_2}}{M_{H_2}}}$  ]
41. A closed vessel contains equal number of hydrogen and nitrogen molecules. The total pressure is 740 mm of Hg. If  $N_2$  molecules are removed, the pressure would become/remain:  
 (a) double of 740 mm of Hg  
 (b) one-ninth of 740 mm of Hg  
 (c) unchanged  
 (d) one-half of 740 mm of Hg
42. The pressure  $P$  exerted by a mixture of three gases having partial pressures  $P_1$ ,  $P_2$  and  $P_3$  is given by:  
 (a)  $P = P_1 + P_2 - P_3$     (b)  $P = \sqrt{P_1 + P_2 + P_3}$   
 (c)  $P = P_1 - P_2 + P_3$     (d)  $P = P_1 + P_2 + P_3$
43. Two sealed containers of same capacity at the same temperature are filled with 44 g of hydrogen gas in one and 44 g of  $CO_2$  in the other. If the pressure of  $CO_2$  is 1 atm, what is the pressure in the hydrogen container?  
 (a) 1 atm    (b) Zero atm    (c) 22 atm    (d) 44 atm

44. Absolute zero is the temperature where all gases are expected to have:  
 (a) different volumes      (b) same volume  
 (c) zero volume      (d) none of these
45. If a gas is heated at constant pressure, its density:  
 (a) will decrease      (b) will increase  
 (c) may increase or decrease      (d) will remain unchanged
46. Density of neon will be highest at:  
 (a) STP      (b) 0°C, 2 atm  
 (c) 273°C, 1 atm      (d) 273°C, 2 atm
47. Equal masses of ethane and hydrogen are mixed in an empty container at 25°C. The fraction of the total pressure exerted by hydrogen is: (IIT 1993)  
 (a) 1 : 2      (b) 1 : 1      (c) 1 : 16      (d) 15 : 16
48. According to kinetic theory of gases:  
 (a) there are intermolecular attractions  
 (b) molecules have considerable volume  
 (c) there is no intermolecular attraction  
 (d) speed of molecules decreases for each collision
49. Postulate of kinetic theory is:  
 (a) atom is indivisible  
 (b) gases combine in simple ratio  
 (c) there is no influence of gravity on the molecules of the gas  
 (d) none of the above
50. Which of the following statements is not consistent with the postulates of kinetic theory of gases?  
 (a) Gases consist of large number of tiny particles  
 (b) Particles are in constant motion  
 (c) All the particles have same speed  
 (d) Pressure is due to hits recorded by particles against the walls of containing vessel
51. A helium atom is two times heavier than a hydrogen molecule. At 298 K, the average kinetic energy of a helium atom is:  
 (a) two times that of a hydrogen molecule  
 (b) four times that of a hydrogen molecule  
 (c) half that of a hydrogen molecule  
 (d) same as that of a hydrogen molecule
52. The kinetic theory of gases predicts that total kinetic energy of a gas depends on:  
 (a) pressure of the gas  
 (b) temperature of the gas  
 (c) volume of the gas  
 (d) pressure, temperature and volume of the gas
53. If a gas is allowed to expand at constant temperature then:  
 (a) number of molecules of the gas decreases  
 (b) the kinetic energy of the gas molecules decreases  
 (c) the kinetic energy of the gas molecules increases  
 (d) the kinetic energy of the gas molecules remains the same
54. Gases deviate from ideal behaviour because molecules:  
 (a) are colourless      (b) are spherical  
 (c) attract each other      (d) have high speeds
55. Deviations from ideal behaviour will be more if the gas is subjected to:  
 (a) low temperature and high pressure  
 (b) high temperature and low pressure
- (c) low temperature  
 (d) high temperature
56. In a closed vessel, a gas is heated from 300 K to 600 K; the kinetic energy becomes/remains:  
 (a) double      (b) half      (c) same      (d) four times
57. A mixture contains 56 g of nitrogen, 44 g of CO<sub>2</sub> and 16 g of methane. The total pressure of the mixture is 720 mm Hg. The partial pressure of methane is: (EAMCET 1991)  
 (a) 180 mm      (b) 360 mm      (c) 540 mm      (d) 720 mm
58. The root mean square speed of an ideal gas at 27°C is 0.3 m/sec. Its rms velocity at 927°C is: (EAMCET 1991)  
 (a) 3.0 m/sec      (b) 2.4 m/sec      (c) 0.9 m/sec      (d) 0.6 m/sec
59. The rms speed at NTP of the species can be calculated from the expression: (EAMCET 1990)  
 (a)  $\sqrt{\frac{3P}{d}}$       (b)  $\sqrt{\frac{3PV}{M}}$       (c)  $\sqrt{\frac{3RT}{M}}$       (d) all of these
60. At constant volume, for a fixed number of mole of a gas, the pressure of the gas increases with rise of temperature due to:  
 (a) increase in average molecular speed  
 (b) increased rate of collisions amongst molecules  
 (c) increase in molecular attraction  
 (d) decrease in mean free path
61. Non-ideal gases approach ideal behaviour: (IIT 1999; KCET 2004)  
 (a) high temperature and high pressure  
 (b) high temperature and low pressure  
 (c) low temperature and high pressure  
 (d) low temperature and low pressure
62. The ratio of root mean square speed and average speed of a gas molecule, at a particular temperature, is:  
 (a) 1 : 1.086      (b) 1.086 : 1  
 (c) 2 : 1.086      (d) 1.086 : 2
63. Most probable speed, average speed and rms speed are related as:  
 (a) 1 : 1.224 : 1.128      (b) 1.128 : 1 : 1.224  
 (c) 1 : 1.128 : 1.224      (d) 1.224 : 1.128 : 1
64. In a closed flask of 5 litre, 1.0 g of H<sub>2</sub> is heated from 300–600 K. Which statement is not correct? (CBSE 1991)  
 (a) The rate of collision increases  
 (b) The energy of gaseous molecules increases  
 (c) The number of mole of the gas increases  
 (d) Pressure of the gas increases
65. The root mean square speed is expressed as:  
 (a)  $\left[ \frac{3}{2} RT \right]^{1/2}$       (b)  $\left[ \frac{2RT}{M} \right]^{1/2}$   
 (c)  $\left[ \frac{3RT}{M} \right]^{1/2}$       (d)  $\left[ \frac{3RT}{M} \right]^{1/2}$
66. The rms speed of hydrogen molecules at room temperature is 2400 ms<sup>-1</sup>. At room temperature the rms speed of oxygen molecules would be:  
 (a) 400 ms<sup>-1</sup>      (b) 300 ms<sup>-1</sup>  
 (c) 600 ms<sup>-1</sup>      (d) 1600 ms<sup>-1</sup>

[Hint:  $\frac{C_{O_2}}{C_{H_2}} = \sqrt{\frac{M_{H_2}}{M_{O_2}}}$ ]

67. The molecules of which of the following gas have highest speed?  
 (a) Hydrogen at  $-50^{\circ}\text{C}$       (b) Methane at  $298\text{ K}$   
 (c) Nitrogen at  $1000^{\circ}\text{C}$       (d) Oxygen at  $0^{\circ}\text{C}$
68. Which one of the following is an ideal gas?  
 (a) Hydrogen      (b) Nitrogen  
 (c) Carbon dioxide      (d) None of these
69. van der Waals' equation explains the behaviour of:  
 (a) ideal gases      (b) real gases  
 (c) mixture of gases      (d) diatomic gases
70. The critical temperature of a gas is that temperature:  
 (a) above which it can no longer remain in the gaseous state  
 (b) above which it cannot be liquefied by pressure  
 (c) at which it solidifies  
 (d) at which the volume of the gas becomes zero
71. The van der Waals' equation for a real gas is:  
 (a)  $\left(P + \frac{a}{V^2}\right)(V - b) = nRT$   
 (b)  $\left(P + \frac{an^2}{V^2}\right)(V - b) = nRT$   
 (c)  $\left(P + \frac{a}{V^2}\right)(V + b) = nRT$   
 (d)  $P = \frac{nRT}{(V - nb)} - \frac{n^2a}{V^2}$
72. In van der Waals' equation of state for a non-ideal gas the term that accounts for intermolecular force is:  
 (a)  $\left(P + \frac{a}{V^2}\right)$       (b)  $(V - b)$       (c)  $RT$       (d)  $\frac{1}{RT}$
73. The units of ' $a$ ' in van der Waals' equation are:  

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$
  
 (a) atom litre $^2$  mol $^{-2}$       (b) atom litre mol $^{-2}$   
 (c) atom litre mol $^{-1}$       (d) atom litre $^2$  mol $^{-1}$
74. If  $1000\text{ mL}$  of gas  $A$  at  $600\text{ torr}$  and  $500\text{ mL}$  of gas  $B$  at  $800\text{ torr}$  are placed in a  $2\text{ litre}$  flask, the final pressure will be:  
 (a)  $2000\text{ torr}$       (b)  $1000\text{ torr}$   
 (c)  $500\text{ torr}$       (d)  $400\text{ torr}$
75. Two samples of gases  $A$  and  $B$  are at the same temperature. The molecules of  $A$  are travelling four times faster than the molecules of  $B$ . The ratio of  $m_A/m_B$  of their masses will be:  
 (a) 16      (b) 4      (c)  $1/4$       (d)  $1/16$   
 [Hint.  $\frac{m_A}{m_B} = \frac{C_2^2}{C_1^2}$ ]
76. The root mean square speed of a certain gas at  $27^{\circ}\text{C}$  is  $3 \times 10^4\text{ cm s}^{-1}$ . The temperature at which the velocity will be  $6 \times 10^4\text{ cm s}^{-1}$  is:  
 (a)  $54^{\circ}\text{C}$       (b)  $108^{\circ}\text{C}$       (c)  $1200\text{ K}$       (d)  $600\text{ K}$
77. The temperature at which real gases obey the ideal gas laws over a wide range of pressure is called: [NPMT 2009]  
 (a) critical temperature      (b) Boyle temperature  
 (c) inversion temperature      (d) reduced temperature
78. The value of van der Waals' constant ' $a$ ' for gases  $\text{O}_2$ ,  $\text{N}_2$ ,  $\text{NH}_3$  and  $\text{CH}_4$  are  $1.360$ ,  $1.390$ ,  $4.170$  and  $2.253\text{ litre}^2\text{-atm mol}^{-2}$  respectively. The gas which can be most easily liquefied is:  
 (a)  $\text{O}_2$       (b)  $\text{N}_2$       (c)  $\text{NH}_3$       (d)  $\text{CH}_4$
79. According to kinetic theory of gases for a diatomic molecule: (IIT 1991)  
 (a) the pressure exerted by the gas is proportional to the mean square speed of the molecules  
 (b) the pressure exerted by the gas is proportional to the root mean square speed of the molecules  
 (c) the root mean square speed is inversely proportional to the temperature  
 (d) the mean translational KE of the molecule is directly proportional to the absolute temperature
80. A real gas obeying van der Waals' equation will resemble an ideal gas if the:  
 (a) constants  $a$  and  $b$  are small  
 (b)  $a$  is large and  $b$  is small  
 (c)  $a$  is small and  $b$  is large  
 (d) constants  $a$  and  $b$  are large
81. When the universal gas constant ( $R$ ) is divided by Avogadro's number ( $N$ ), their ratio is called:  
 (a) Planck's constant      (b) Rydberg's constant  
 (c) Boltzmann's constant      (d) van der Waals' constant
82. The compressibility factor of a gas is defined as  $Z = \frac{PV}{RT}$ . The compressibility factor of an ideal gas is: [PMT (MP) 2004]  
 (a) 0      (b) 1      (c)  $-1$       (d) infinity
83. An ideal gas is one which obeys:  
 (a) gas laws      (b) Boyle's law  
 (c) Charles' law      (d) Avogadro's law
84. A mixture of three gases  $X$  (density  $1.0$ ),  $Y$  (density  $0.2$ ) and  $Z$  (density  $0.4$ ) is enclosed in a vessel at constant temperature. When the equilibrium is established, the gas/gases:  
 (a)  $X$  will be at the top of the vessel  
 (b)  $Y$  will be at the top of the vessel  
 (c)  $Z$  will be at the top of the vessel  
 (d) will mix homogeneously throughout the vessel
85.  $16\text{ g}$  of oxygen and  $3\text{ g}$  of hydrogen are mixed and kept at  $760\text{ mm}$  pressure at  $0^{\circ}\text{C}$ . The total volume occupied by the mixture will be nearly: [CMC (Vellore) 1991]  
 (a)  $22.4\text{ litre}$       (b)  $33.6\text{ litre}$       (c)  $44800\text{ mL}$       (d)  $4480\text{ mL}$
86. Which of the following expressions does not represent Boyle's law?  
 (a)  $PV = \text{constant}$       (b)  $V \propto \frac{1}{P}$   
 (c)  $V_1T_2 = V_2T_1$       (d)  $P_1V_1 = P_2V_2$
87. When an ideal gas undergoes unrestricted expansion, no cooling occurs because the molecules:  
 (a) exert no attractive forces on each other  
 (b) do work equal to loss of kinetic energy  
 (c) collide without loss of energy  
 (d) are above the inversion temperature
88. Which of the following mixture of gases at room temperature does not follow Dalton's law of partial pressures?

- (a)  $\text{NO}_2$  and  $\text{O}_2$       (b)  $\text{NH}_3$  and  $\text{HCl}$   
 (c)  $\text{CO}$  and  $\text{CO}_2$       (d)  $\text{SO}_2$  and  $\text{O}_2$
89. The speed possessed by most of the gaseous molecules is:  
 (a) most probable speed      (b) average speed  
 (c) root mean square speed      (d) none of these
90. In which of the following pairs the gaseous species diffuse through a porous plug along with the same rate of diffusion?  
 (EAMCET 1990)  
 (a)  $\text{NO}$ ,  $\text{CO}$       (b)  $\text{NO}$ ,  $\text{CO}_2$   
 (c)  $\text{NH}_3$ ,  $\text{PH}_3$       (d)  $\text{NO}$ ,  $\text{C}_2\text{H}_6$
91. Which of the following statements is correct?  
 (a)  $3PV = mnC^2$  is the expression for real gases  
 (b) At normal temperature and pressure most gases behave nearly as ideal gases  
 (c) The molecules of real gases have both volume and mutual attraction  
 (d) Pressure depends on number of molecules and volume
92. For one gram molecule of an ideal gas:  
 (a)  $\frac{PV}{T} = \frac{3}{2} \text{ cal}$       (b)  $\frac{PV}{T} = 2 \text{ cal}$   
 (c)  $\frac{PV}{T} = 8.31 \text{ cal}$       (d)  $\frac{PV}{T} = 0.0821 \text{ cal}$
93. When helium is allowed to expand into vacuum, heating effect is observed. This is due to the fact that:  
 (a) helium is an inert gas  
 (b) helium is a noble gas  
 (c) helium is an ideal gas  
 (d) the inversion temperature of helium is very low
94. At STP, the order of mean square velocity of molecules of  $\text{H}_2$ ,  $\text{N}_2$ ,  $\text{O}_2$  and  $\text{HBr}$  is: (CBSE 1991)  
 (a)  $\text{H}_2 > \text{N}_2 > \text{O}_2 > \text{HBr}$       (b)  $\text{HBr} > \text{O}_2 > \text{N}_2 > \text{H}_2$   
 (c)  $\text{HBr} > \text{H}_2 > \text{O}_2 > \text{N}_2$       (d)  $\text{N}_2 > \text{O}_2 > \text{H}_2 > \text{HBr}$
95. At constant temperature in a given mass of an ideal gas: (CBSE 1991)  
 (a) the ratio of pressure and volume always remains constant  
 (b) volume always remains constant  
 (c) pressure always remains constant  
 (d) the product of pressure and volume always remains constant
96. The non-compressible volume of a gas is . . . times the actual volume of gas molecules:  
 (a) 2      (b) 4      (c) 3      (d) 2.5
97. One mole of an ideal monoatomic gas is mixed with 1 mole of an ideal diatomic gas. The molar specific heat of the mixture at constant volume is:  
 (a) 3 cal      (b) 4 cal      (c) 5 cal      (d) 8 cal
98. In an experiment during the analysis of a carbon compound, 145 mL of  $\text{H}_2$  was collected at 760 mm Hg pressure and 27°C. The mass of  $\text{H}_2$  is nearly:  
 (a) 10 mg      (b) 6 g      (c) 12 mg      (d) 12 g  
 [Hint: Apply  $PV = \frac{w}{M} RT$ ;  $1 \times 0.145 = \frac{w}{2} \times 0.0821 \times 300$ ]
99. The kinetic energy of  $N$  molecules of  $\text{O}_2$  is  $x$  joule at  $-123^\circ\text{C}$ . Another sample of  $\text{O}_2$  at  $27^\circ\text{C}$  has a kinetic energy of  $2x$  joule. The latter sample contains:  
 (a)  $N$  molecules of  $\text{O}_2$       (b)  $2N$  molecules of  $\text{O}_2$   
 (c)  $\frac{N}{2}$  molecules of  $\text{O}_2$       (d)  $\frac{N}{4}$  molecules of  $\text{O}_2$
100. A balloon filled with  $\text{N}_2\text{O}$  is pricked with a sharper point and plunged into a tank of  $\text{CO}_2$  under the same pressure and temperature. The balloon will:  
 (a) be enlarged      (b) shrink  
 (c) collapse completely      (d) remain unchanged in size
101. The three states of matter are solid, liquid and gas. Which of the following statements is true about them?  
 (a) Gases and liquids have viscosity as a common property  
 (b) The molecules in all the three states possess random translational motion  
 (c) Gases cannot be converted into solids without passing through the liquid phase  
 (d) Solids and liquids have pressure as a common property
102. Strong intermolecular forces exist in:  
 (a) gases      (b) liquids  
 (c) amorphous solids      (d) crystalline solids
103. Association of molecules in water is due to:  
 (a) covalent bonding      (b) hydrogen bonding  
 (c) ionic bonding      (d) van der Waals' forces
104. Which of the following statements is wrong?  
 (a) Evaporation is a spontaneous process  
 (b) Evaporation is a surface phenomenon  
 (c) Vapour pressure decreases with increase of temperature  
 (d) The vapour pressure of a solution is always less than the vapour pressure of a pure solvent
105. Normal boiling point of a liquid is that temperature at which vapour pressure of the liquid is equal to:  
 (a) zero      (b) 380 mm of Hg  
 (c) 760 mm of Hg      (d) 100 mm of Hg
106. Water boils at lower temperature on high altitudes because:  
 (a) atmospheric pressure is low there  
 (b) atmospheric pressure is high there  
 (c) water is weakly hydrogen bonded there  
 (d) water in pure form is found there
107. When a student was given a viscometer, the liquid was sucked with difficulty; the liquid may be:  
 (a) benzene      (b) toluene      (c) water      (d) glycerine
108. Mark the statement which is correct:  
 (a) surface tension of a liquid increases with temperature  
 (b) addition of chemicals reduces the surface tension of a liquid  
 (c) stalagmometer is used for measuring viscosity of the liquid  
 (d) viscosity of the liquid does not depend on intermolecular forces
109. With the increasing molecular mass of a liquid, the viscosity: (Jiwaji 1990)  
 (a) decreases      (b) increases  
 (c) no effect      (d) all are wrong
110. The viscosity of which liquid is the maximum?  
 (a) water      (b) glycol  
 (c) acetone      (d) ethanol

111. The rise of a liquid in a capillary tube is due to:  
 (a) viscosity                      (b) osmosis  
 (c) diffusion                      (d) surface tension
112. With increase in temperature, the fluidity of liquids:  
 (a) increases                      (b) decreases  
 (c) remains constant              (d) may increase or decrease
113. If  $\eta_1$  and  $\eta_2$  are the coefficients of viscosity of two liquids,  $d_1$  and  $d_2$  their densities and  $t_1$  and  $t_2$  the flow times in Ostwald viscometer, then:  
 (a)  $\frac{\eta_1}{\eta_2} = \frac{d_1 t_2}{d_2 t_1}$                       (b)  $\frac{\eta_1}{\eta_2} = \frac{d_2 t_2}{d_1 t_1}$   
 (c)  $\frac{\eta_1}{\eta_2} = \frac{d_1 t_1}{d_2 t_2}$                       (d)  $\frac{\eta_1}{\eta_2} = \frac{d_2 t_1}{d_1 t_2}$
114. Which of the following expressions regarding the unit of coefficient of viscosity is not true?  
 (a) dyne cm<sup>-2</sup> sec              (b) dyne cm<sup>2</sup> sec<sup>-1</sup>  
 (c) Nm<sup>-2</sup> sec                    (d) 1 poise =  $10^{-1}$  Nm<sup>-2</sup> sec
115. The boiling points of water, ethyl alcohol and diethyl ether are 100°C, 78.5°C and 34.6°C respectively. The intermolecular forces will be in the order of:  
 (a) water > ethyl alcohol > diethyl ether  
 (b) ethyl alcohol > water > diethyl ether  
 (c) diethyl ether > ethyl alcohol > water  
 (d) diethyl ether > water > ethyl alcohol
116. The unit cell in a body centered cubic lattice is given in the figure. Each sphere has a radius,  $r$  and the cube has a side,  $a$ . What fraction of the total cube volume is empty. (TIFR 2010)
- 
- (a)  $1 - \frac{8}{3}\pi \frac{r^3}{a^3}$                       (b)  $\frac{4}{3}\pi \frac{r^3}{a^3}$   
 (c)  $\frac{r}{a}$                               (d)  $2 - \frac{4}{3}\pi \frac{r^3}{a^3}$
117. Which one is not the property of crystalline solid?  
 (a) Isotropic  
 (b) Sharp melting point  
 (c) A definite and regular geometry  
 (d) High intermolecular forces
118. The number of crystal systems known is:  
 (a) 7                              (b) 8                              (c) 6                              (d) 4
119. Tetragonal crystal system has the following unit cell dimensions: [PMT (MP) 1993]  
 (a)  $a = b = c$  and  $\alpha = \beta = \gamma = 90^\circ$   
 (b)  $a = b \neq c$  and  $\alpha = \beta = \gamma = 90^\circ$   
 (c)  $a \neq b \neq c$  and  $\alpha = \beta = \gamma = 90^\circ$   
 (d)  $a = b \neq c$  and  $\alpha = \beta = 90^\circ, \gamma = 120^\circ$
120. A match box exhibits: [PET (MP) 1993]  
 (a) cubic geometry              (b) monoclinic geometry  
 (c) orthorhombic geometry    (d) tetragonal geometry
121. In the crystal of CsCl, the nearest neighbours of each Cs ion are: [PET (MP) 1993]  
 (a) six chloride ions            (b) eight Cs ions  
 (c) six Cs ions                   (d) eight chloride ions
122. How many chloride ions are there around sodium ion in sodium chloride crystal?  
 (a) 3                              (b) 8                              (c) 4                              (d) 6
123. The number of atoms contained in one face-centred cubic unit cell of monoatomic substance is: [PMT (Vellore) 2006; PET (MP) 2007]  
 (a) 1                              (b) 2                              (c) 4                              (d) 3
124. The number of close neighbours in a body-centred cubic lattice of identical spheres is:  
 (a) 4                              (b) 12                            (c) 6                              (d) 8
125. The coordination number of each sphere in (hcc) arrangement is:  
 (a) 8                              (b) 12                            (c) 6                              (d) 4
126. Bragg's law is given by the equation: [BHU 1990]  
 (a)  $n\lambda = 2\theta \sin \theta$                       (b)  $n\lambda = 2d \sin \theta$   
 (c)  $2n\lambda = d \sin \theta$                             (d)  $n \frac{\theta}{2} = \frac{d}{2} \sin \theta$
127. In Bragg's equation for diffraction of X-rays, 'n' represents:  
 (a) the number of mole           (b) quantum number  
 (c) the order of reflection    (d) Avogadro's number
128. The coordination number for an atom in a primitive cubic unit cell is:  
 (a) 6                              (b) 8                              (c) 10                              (d) 12
129. The number of atoms per unit cell in a simple cubic, face-centred cubic and body-centred cubic are . . . . . respectively:  
 (a) 1, 4, 2                      (b) 4, 1, 2  
 (c) 2, 4, 1                      (d) 4, 8, 2
130. In a solid lattice, the cation has left a lattice site and is located at interstitial position, the lattice defect is: (VITEEE 2007)  
 (a) interstitial defect         (b) vacancy defect  
 (c) Frenkel defect             (d) Schottky defect
131. Schottky defects occur mainly in ionic compounds where: (VITEEE 2008)  
 (a) positive and negative ions are of different size  
 (b) positive and negative ions are of same size  
 (c) positive ions are small and negative ions are big  
 (d) positive ions are big and negative ions are small
132. What type of crystal defect is indicated in the diagram below?  

$$\begin{array}{ccccccc} \text{Na}^+ & \text{Cl}^- & \text{Na}^+ & \text{Cl}^- & \text{Na}^+ & \text{Cl}^- \\ \text{Cl}^- & & \text{Cl}^- & \text{Na}^+ & & \text{Na}^+ \\ \text{Na}^+ & \text{Cl}^- & & \text{Cl}^- & \text{Na}^+ & \text{Cl}^- \\ \text{Cl}^- & \text{Na}^+ & \text{Cl}^- & \text{Na}^+ & \text{Na}^+ & \end{array}$$
 (AIEEE 2004)  
 (a) Frenkel defect             (b) Schottky defect  
 (c) Interstitial defect       (d) Frenkel and Schottky defects
133. In a closed packed array of  $N$  spheres, the number of tetrahedral holes is:  
 (a)  $N/2$                            (b)  $N$   
 (c)  $4N$                             (d)  $2N$

134. In a closed packed array of  $N$  spheres, the octahedral holes are:  
 (a)  $N/2$       (b)  $2N$       (c)  $4N$       (d)  $N$
135.  $AB$  crystallizes in a body centred cubic lattice with edge length ' $a$ ' equal to 387 pm. The distance between two oppositely charged ions in the lattice is: [CBSE (PMT) 2010]  
 (a) 335 pm      (b) 250 pm  
 (c) 200 pm      (d) 300 pm

[Hint : Distance between two oppositely charged ions

$$(r^+ + r^-) = \frac{a\sqrt{3}}{2} = \frac{387 \times \sqrt{3}}{2} \\ = 335.14 \text{ pm}$$

136. Germanium or silicon becomes semiconductor due to:  
 (a) Schottky defect      (b) chemical impurity  
 (c) Frenkel defect      (d) none of these
137. A particular solid is very hard and has a high melting point. In solid state it is a non conductor and its melt is a conductor of electricity. Classify the solid: [CMC Vellore (Med.) 2008]  
 (a) metallic      (b) molecular  
 (c) network      (d) ionic  
 (e) amorphous
138. Which one has the highest melting point?  
 (a) Ionic crystal      (b) Molecular crystal  
 (c) Covalent crystal      (d) Metallic crystal

139. For an ionic crystal of general formula  $AX$  and coordination number 6, the value of radius ratio will be: [PMT (MP) 1993]  
 (a) greater than 0.73      (b) in between 0.73 and 0.41  
 (c) in between 0.41 and 0.22      (d) less than 0.22

140. The  $\text{Ca}^{2+}$  and  $\text{F}^-$  are located in  $\text{CaF}_2$  crystal respectively at face-centred cubic lattice points and in: [AIIMS 2006]  
 (a) tetrahedral voids      (b) half of tetrahedral voids  
 (c) octahedral voids      (d) half of octahedral voids

141. In calcium fluoride structure, the coordination numbers of calcium and fluoride ions are:  
 (a) 8 and 4      (b) 6 and 8  
 (c) 4 and 4      (d) 4 and 8

142. The unit cell of a binary compound of  $A$  and  $B$  metals has a CCP structure with  $A$  atoms occupying the corners and  $B$  atoms occupying the centres of each faces of the cubic unit cell. If during the crystallisation of this alloy, in the unit cell two  $A$  atoms are missed, the overall composition per unit cell is:  
 [CET (J&K) 2009]

$$(a) AB_6 \quad (b) AB_4 \quad (c) AB_8 \quad (d) A_6B_{24}$$

[Hint : Number of atoms of  $A = 6 \times \frac{1}{8} = \frac{3}{4}$

$$\text{Number of atoms of } B = 6 \times \frac{1}{2} = 3$$

$$A : B = \frac{3}{4} : 3 = 1 : 4$$

∴ Composition of alloy =  $AB_4$ ]

143. In a solid lattice, the cation has left a lattice site and is located at an interstitial position. The lattice defect is :  
 [BHU (screening) 2008]  
 (a) interstitial defect      (b) vacancy defect  
 (c) Frenkel defect      (d) Schottky defect
144. Which of the following statements is incorrect about amorphous solids? [KCET 2004]

- (a) They are anisotropic  
 (b) They are rigid and incompressible  
 (c) They melt over a wide range of temperature  
 (d) There is no orderly arrangement of particles
145. Which defect causes decrease in the density of a crystal?  
 (a) Frenkel      (b) Schottky  
 (c) Interstitial      (d)  $F$ -centre
146. For tetrahedral coordination number, the radius ratio  $r_c^+ / r_a^-$  is:  
 (KCET 2008)  
 (a) 0.732 – 1.0      (b) 0.225 – 0.414  
 (c) 0.414 – 0.732      (d) 0.155 – 0.225
147. What is the total number of ions present in one unit cell of sodium chloride lattice? (EAMCET 2006)  
 (a) 2      (b) 6      (c) 12      (d) 8
148. The formula for determination of density of cubic unit cell is:  
 (a)  $\frac{a^3 N_0}{Z \times M} \text{ g cm}^{-3}$       (b)  $\frac{Z \times N_0}{M \times a^3} \text{ g cm}^{-3}$   
 (c)  $\frac{a^3 \times M}{Z \times N_0} \text{ g cm}^{-3}$       (d)  $\frac{Z \times M}{N_0 \times a^3} \text{ g cm}^{-3}$
149. The closest-packing sequence  $ABAB \dots$  represents:  
 (a) primitive cubic packing  
 (b) body-centred cubic packing  
 (c) face-centred cubic packing  
 (d) hexagonal packing
150. The closest-packing sequence  $ABCABC \dots$  represents:  
 (a) primitive cubic packing  
 (b) body-centred cubic packing  
 (c) face-centred cubic packing  
 (d) hexagonal packing
151. The edge length of face centred cubic cell of an ionic substance is 508 pm. If the radius of cation is 110 pm, the radius of anion is:  
 (AIEEE 2010)  
 (a) 618 pm      (b) 144 pm  
 (c) 288 pm      (d) 398 pm
- [Hint : Edge length =  $2(r^+ + r^-)$   
 $508 = 2(110 + r^-)$   
 $r^- = 144 \text{ pm}$ ]
152. Close packing is maximum in the crystal lattice of:  
 (a) face-centred cubic      (b) body-centred cubic  
 (c) simple-centred cubic      (d) none of these
153. The ratio between the root mean square speed of  $\text{H}_2$  at 50 K and that of  $\text{O}_2$  at 800 K is: (IIT 1996)  
 (a) 4      (b) 2      (c) 1      (d) 1/4
154.  $X$  mL of  $\text{H}_2$  gas effused through a hole in a container in 5 second. The time taken for the effusion of the same volume of the gas specified below under identical conditions is:  
 (IIT 1996)  
 (a) 10 second : He      (b) 20 second :  $\text{O}_2$   
 (c) 25 second : CO      (d) 55 second :  $\text{CO}_2$
155. The energy of a gas per litre is 300 joule. Its pressure will be:  
 (a)  $3 \times 10^5 \text{ N/m}^2$       (b)  $6 \times 10^5 \text{ N/m}^2$   
 (c)  $10^5 \text{ N/m}^2$       (d)  $2 \times 10^5 \text{ N/m}^2$
156. If the universal gas constant is  $8.3 \text{ joule mol}^{-1} \text{ K}^{-1}$  and the Avogadro's number is  $6 \times 10^{23}$ . The mean kinetic energy of the oxygen molecules at  $327^\circ\text{C}$  will be:

- (a)  $415 \times 10^{-23}$  joule      (b)  $2490 \times 10^{-22}$  joule  
 (c)  $1245 \times 10^{-23}$  joule      (d)  $830 \times 10^{-22}$  joule
157. If increase in temperature and volume of an ideal gas is two times, then initial pressure of  $P$  changes to:  
 [JEE (Orissa) 2006]  
 (a)  $4P$       (b)  $2P$       (c)  $P$       (d)  $3P$
158. The average kinetic energy of one molecule of an ideal gas at  $27^\circ\text{C}$  and 1 atm pressure is:  
 (EAMCET 2009)  
 (a)  $900 \text{ cal K}^{-1} \text{ mol}^{-1}$   
 (b)  $6.21 \times 10^{-21} \text{ J K}^{-1} \text{ molecule}^{-1}$   
 (c)  $336.7 \text{ J K}^{-1} \text{ molecule}^{-1}$   
 (d)  $3741.3 \text{ J K}^{-1} \text{ mol}^{-1}$
- [Hint : KE =  $\frac{3}{2} \frac{R}{N} T$   
 $= \frac{3}{2} \times \frac{8.314}{6.023 \times 10^{23}} \times 300$   
 $= 6.21 \times 10^{-21} \text{ J K}^{-1} \text{ molecule}^{-1}$ ]
159. The respective speeds of five molecules are 2, 1.5, 1.6, 1.6 and 1.2 km/sec. The most probable speed in km/sec will be:  
 (a) 2      (b) 1.58      (c) 1.6      (d) 1.31
160. If one mole of a monoatomic gas ( $\gamma = \frac{5}{3}$ ) is mixed with one mole of diatomic gas ( $\gamma = \frac{7}{5}$ ), the value of  $\gamma$  for the mixture is:  
 (a) 1.40      (b) 1.50      (c) 1.53      (d) 3.07
161. The root mean square speed of hydrogen molecule of an ideal hydrogen gas kept in a gas chamber at  $0^\circ\text{C}$  is 3180 metre/second. The pressure on the hydrogen gas is: (density of hydrogen gas is  $8.99 \times 10^{-2} \text{ kg/m}^3$ , 1 atmosphere =  $1.01 \times 10^5 \text{ N/m}^2$ )  
 (a) 1.0 atmosphere      (b) 1.5 atmosphere  
 (c) 2.0 atmosphere      (d) 3.0 atmosphere
162.  $\text{CH}_4$  diffuses two times faster than a gas  $X$ . The number of molecules present in 32 g of gas  $X$  is: ( $N$  is Avogadro number)  
 [EAMCET (Engg.) 2010]  
 (a)  $N$       (b)  $\frac{N}{2}$       (c)  $\frac{N}{4}$       (d)  $\frac{N}{16}$
- [Hint:  $\frac{r_{\text{CH}_4}}{r_{\text{gas}}} = \sqrt{\frac{m_{\text{gas}}}{m_{\text{CH}_4}}}$   
 $2 = \sqrt{\frac{m_{\text{gas}}}{16}}$   
 $m_{\text{gas}} = 64$   
 Number of molecules =  $\frac{w}{\text{molar mass}} \times N$   
 $= \frac{32}{64} \times N = \frac{N}{2}$ ]
163. At what temperature would the rms speed of a gas molecule have twice its value at  $100^\circ\text{C}$ ?  
 (a) 4192 K      (b) 1492 K  
 (c) 9142 K      (d) 2491 K
164. Find the rms speed of an argon molecule at  $27^\circ\text{C}$  (Molecular weight of argon = 40 gm/mol):  
 (a) 234.2 m/s      (b) 342.2 m/s  
 (c) 432.2 m/s      (d) 243.2 m/s
165. At a temperature  $T$  K, the pressure of 4 g argon in a bulb is  $P$ . The bulb is put in a bath having a temperature higher by 50 K than the first one. 0.8 g of argon gas had to be removed to maintain original pressure. The temperature  $T$  is equal to:  
 (IIT 1999)
- (a) 510 K      (b) 200 K  
 (c) 100 K      (d) 73 K
166. At  $25^\circ\text{C}$  and 730 mm pressure, 380 mL of dry oxygen was collected. If the temperature is constant, what volume will the oxygen occupy at 760 mm pressure?  
 (CBSE 1999)  
 (a) 265 mL      (b) 365 mL      (c) 569 mL      (d) 621 mL
167. Which of the following solids shows electrical conduction?  
 (CBSE 1999)  
 (a) Graphite      (b) Potassium chloride  
 (c) Diamond      (d) Sodium chloride
168. Schottky defect in solids is due to:  
 [PMT (Vellore) 2006; VITEEE 2006]  
 (a) a pair of cation and anion vacancies  
 (b) occupation of interstitial site by a pair of cation and anion  
 (c) occupation of interstitial site by a cation  
 (d) occupation of interstitial site by an anion
169. Copper crystallises in face-centred cubic lattice with a unit cell length of 361 pm. What is the radius of copper atom in pm?  
 [CBSE (PMT) 2009; AIEEE 2009]  
 (a) 108      (b) 128      (c) 157      (d) 181
- [Hint:  $a\sqrt{2} = 4r$   
 $361\sqrt{2} = 4r$   
 $r = 128 \text{ pm}$ ]
170. The second order Bragg diffraction of X-rays with  $\lambda = 1 \text{ \AA}$  from a set of parallel planes in a metal occurs at an angle of  $60^\circ$ . The distance between the scattering planes in the crystal is:  
 (a) 0.575 \AA      (b) 1.00 \AA  
 (c) 2.00 \AA      (d) 1.15 \AA
171. According to Graham's law at a given temperature, the ratio of the rates of diffusion  $r_A / r_B$  of gases  $A$  and  $B$  is given by:  
 (IIT 1998)
- (a)  $\frac{P_A}{P_B} \cdot \left(\frac{M_A}{M_B}\right)^{1/2}$       (b)  $\frac{M_A}{M_B} \cdot \left(\frac{P_A}{P_B}\right)^{1/2}$   
 (c)  $\frac{P_A}{P_B} \cdot \left(\frac{M_B}{M_A}\right)^{1/2}$       (d)  $\frac{M_A}{M_B} \cdot \left(\frac{P_B}{P_A}\right)^{1/2}$
172. The root mean square velocity of an ideal gas at constant pressure varies with density as:  
 [IIT (Screening) 2000]  
 (a)  $d^2$       (b)  $d$       (c)  $\sqrt{d}$       (d)  $1/\sqrt{d}$
173. Match the following:  
 List-I                  List-II  
 (A) Inversion temperature      (i)  $a/R_b$   
 (B) Boyle's temperature      (ii)  $8a/27R_b$   
 (C) Critical temperature      (iii)  $2a/R_b$   
 (a) A—(i), B—(ii), C—(iii)      (b) A—(iii), B—(ii), C—(i)  
 (c) A—(iii), B—(i), C—(ii)      (d) A—(i), B—(iii), C—(ii)

174. For three different gases values of van der Waals' constant 'a' and 'b' are given. What is the correct order of liquefaction of gases?

Gases	<i>a</i>	<i>b</i>
$X_2$	1.3	0.090
$Y_2$	4.1	0.023
$Z_2$	2.2	0.075
(a) $X_2 > Y_2 > Z_2$	(b) $Y_2 > Z_2 > X_2$	
(c) $Z_2 > Y_2 > X_2$	(d) $X_2 > Z_2 > Y_2$	

175. Match the following:

List-I	List-II
(A) $P_c$	(i) $3b$
(B) $V_c$	(ii) $8a/27bR$
(C) $T_c$	(iii) $a/27b^2$

- (a) A—(i), B—(ii), C—(iii) (b) A—(iii), B—(ii), C—(i)  
 (c) A—(ii), B—(iii), C—(i) (d) A—(iii), B—(i), C—(ii)

176. By what factor does the average velocity of a gaseous molecule increases when the absolute temperature is doubled?  
 (DUMET 2010)

- (a) 1.4 (b) 2 (c) 2.8 (d) 4.0

177. The van der Waals' constant 'a' for different gases have been given as :

Gas	<i>a</i> (atm L <sup>2</sup> mol <sup>-2</sup> )
O <sub>2</sub>	1.36
N <sub>2</sub>	1.39
CH <sub>4</sub>	2.25
NH <sub>3</sub>	4.17

The gas that can be most easily liquefied is :

[JEE (Orissa) 2010]

- (a) O<sub>2</sub> (b) N<sub>2</sub> (c) CH<sub>4</sub> (d) NH<sub>3</sub>

178. Match the following:

List-I	List-II
(A) $U_{\text{rms}} / U_{\text{av}}$	(i) 1.22
(B) $U_{\text{av}} / U_{\text{mp}}$	(ii) 1.13
(C) $U_{\text{rms}} / U_{\text{mp}}$	(iii) 1.08

- (a) A—(iii), B—(ii), C—(i) (b) A—(i), B—(ii), C—(iii)  
 (c) A—(iii), B—(i), C—(ii) (d) A—(ii), B—(iii), C—(i)

179. Joule-Thomson coefficient is zero at:

- (a) critical temperature (b) inversion temperature  
 (c) absolute temperature (d) Boyle's temperature

180. At a constant pressure, what should be the percentage increase in temperature for a 10% increase in volume?

- (a) 10% (b) 11% (c) 8.9% (d) 12.5%

181. 5 g of unknown gas has pressure *P* at a temperature *T* K in a vessel. On increasing the temperature by 50°C, 1 g of the gas was given out to maintain the pressure *P*. The original temperature was:

- (a) 73 K (b) 100 K  
 (c) 200 K (d) none of these

182. Which of the following expressions correctly represents the relationship between the average molar kinetic energy, KE of CO and N<sub>2</sub> molecules at the same temperature?

[CBSE (PMT) 2000]

- (a)  $\overline{\text{KE}}_{\text{CO}} = \overline{\text{KE}}_{\text{N}_2}$   
 (b)  $\overline{\text{KE}}_{\text{CO}} > \overline{\text{KE}}_{\text{N}_2}$   
 (c)  $\overline{\text{KE}}_{\text{CO}} < \overline{\text{KE}}_{\text{N}_2}$

- (d) Cannot be predicted unless the volumes of the gases are given

183. Which of the following exhibits the weakest intermolecular forces?  
 (AIIMS 2000)

- (a) NH<sub>3</sub> (b) HCl (c) He (d) H<sub>2</sub>O

184. The compressibility of a gas is less than unity at STP. Therefore:  
 [IIT 2000; PMT (MP) 2004]

- (a)  $V_m > 22.4$  litre (b)  $V_m < 22.4$  litre  
 (c)  $V_m = 22.4$  litre (d)  $V_m = 44.8$  litre

185. The rms velocity of hydrogen is  $\sqrt{7}$  times the rms velocity of nitrogen. If *T* is the temperature of the gas:  
 (IIT 2000)

- (a)  $T(\text{H}_2) = T(\text{N}_2)$  (b)  $T(\text{H}_2) > T(\text{N}_2)$   
 (c)  $T(\text{H}_2) < T(\text{N}_2)$  (d)  $T(\text{H}_2) = \sqrt{7}T(\text{N}_2)$

186. The kinetic energy of any gas molecule at 0°C is:

- (a) zero (b) 3408 J  
 (c) 2 cal (d)  $5.66 \times 10^{-21}$  J

187. Densities of two gases are in the ratio 1 : 2 and their temperatures are in the ratio 2 : 1; then the ratio of their respective pressures is:  
 (BHU 2000)

- (a) 1 : 1 (b) 1 : 2 (c) 2 : 1 (d) 4 : 1

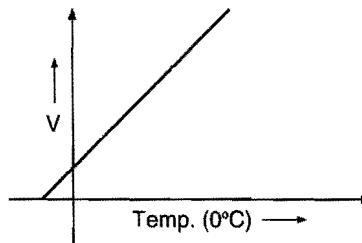
188. Gas equation  $PV = nRT$  is obeyed by:  
 (BHU 2000)

- (a) only isothermal process (b) only adiabatic process  
 (c) both (a) and (b) (d) none of these

189. An ideal gas will have maximum density when:  
 (CPMT 2000)

- (a)  $P = 0.5$  atm,  $T = 600$  K (b)  $P = 2$  atm,  $T = 150$  K  
 (c)  $P = 1$  atm,  $T = 300$  K (d)  $P = 1.0$  atm,  $T = 500$  K

190. The following graph illustrates:  
 (JIPMER 2000)



- (a) Dalton's law (b) Charles' law

- (c) Boyle's law (d) Gay-Lussac's law

191. 4.4 g of a gas at STP occupies a volume of 2.24 L. The gas can be:  
 [CET (Haryana) 2000]

- (a) O<sub>2</sub> (b) CO (c) NO<sub>2</sub> (d) CO<sub>2</sub>

192. At 0°C and one atm pressure a gas occupies 100 cc. If the pressure is increased to one and a half time and temperature is increased by one-third of absolute temperature, then final volume of the gas will be:  
 (DCE 2000)

- (a) 80 cc (b) 88.9 cc (c) 66.7 cc (d) 100 cc

193. Pressure of a mixture of 4 g of O<sub>2</sub> and 2 g of H<sub>2</sub> confined in a bulb of 1 litre at 0°C is:  
 (AIIMS 2000)

- (a) 25.215 atm (b) 31.205 atm  
 (c) 45.215 atm (d) 15.210 atm

194. Density ratio of O<sub>2</sub> and H<sub>2</sub> is 16 : 1. The ratio of their rms velocities will be:  
 (AIIMS 2000)

- (a) 4 : 1 (b) 1 : 16 (c) 1 : 4 (d) 16 : 1

195. The rate of diffusion of a gas having molecular weight just double of nitrogen gas is  $56 \text{ mL s}^{-1}$ . The rate of diffusion of nitrogen will be: [CPMT 2000]  
 (a)  $79.19 \text{ mL s}^{-1}$       (b)  $112.0 \text{ mL s}^{-1}$   
 (c)  $56 \text{ mL s}^{-1}$       (d)  $90.0 \text{ mL s}^{-1}$
196. The density of air is  $0.00130 \text{ g/mL}$ . The vapour density of air will be: [DCE 2000]  
 (a) 0.00065    (b) 0.65    (c) 14.4816    (d) 14.56
197. If  $300 \text{ mL}$  of a gas at  $27^\circ\text{C}$  is cooled to  $7^\circ\text{C}$  at constant pressure, its final volume will be: [AIIMS 2000]  
 (a)  $135 \text{ mL}$     (b)  $540 \text{ mL}$     (c)  $350 \text{ mL}$     (d)  $280 \text{ mL}$
198. For an ideal gas, number of moles per litre in terms of its pressure  $P$ , gas constant  $R$  and temperature  $T$  is: [AIEEE 2002]  
 (a)  $PT/R$     (b)  $PRT$     (c)  $P/RT$     (d)  $RT/P$
199. The van der Waals' equation reduces itself to the ideal gas equation at: [MEE (Kerala) 2001; CBSE (PMT) 2002]  
 (a) high pressure and low temperature  
 (b) low pressure and low temperature  
 (c) low pressure and high temperature  
 (d) high pressure alone
200. Which of the following volume ( $V$ ), temperature ( $T$ ) plots represents the behaviour of an ideal gas at one atmospheric pressure? [IIT (Screening) 2002; PET (Kerala) 2007]
- 
203. A crystal lattice with alternate +ve and -ve ions has radius ratio 0.524, its coordination number is: [PMT (Manipal) 2002]  
 (a) 4    (b) 3    (c) 6    (d) 12
204. The major binding force of diamond, silicon and quartz is: [MEE (Kerala) 2002]  
 (a) electrostatic force    (b) electrical attraction  
 (c) covalent bond force    (d) non-covalent bond force  
 (e) van der Waals' force
205. A compound is formed by elements  $A$  and  $B$ . This crystallizes in the cubic structure when atoms  $A$  are at the corners of the cube and atoms  $B$  are at the centre of the body. The simplest formula of the compound is: [DPMT 2009]  
 (a)  $AB$     (b)  $AB_2$     (c)  $A_2B$     (d)  $AB_4$
206. The coordination number of a metal crystallizing in a hexagonal close packed (hcp) structure is: [PET (MP) 2004]  
 (a) 6    (b) 12    (c) 8    (d) 4
207. The crystal system of a compound with unit cell dimensions  $a = 0.387$ ,  $b = 0.387$ ,  $c = 0.504 \text{ nm}$  and  $\alpha = \beta = 90^\circ$  and  $\gamma = 120^\circ$  is: [AIIMS 2004]  
 (a) cubic    (b) hexagonal  
 (c) orthorhombic    (d) rhombohedral
208. The maximum number of molecules is present in: [CBSE (PMT) 2004]  
 (a)  $15 \text{ L}$  of  $\text{H}_2$  gas at STP    (b)  $5 \text{ L}$  of  $\text{N}_2$  gas at STP  
 (c)  $0.5 \text{ g}$  of  $\text{H}_2$  gas    (d)  $10 \text{ g}$  of  $\text{O}_2$  gas
209. The root mean square velocity of one mole of a monoatomic gas having molar mass  $M$  is  $U_{\text{rms}}$ . The relation between average kinetic energy ( $E$ ) of the gas and  $U_{\text{rms}}$  is: [IIT (S) 2004]  
 (a)  $U_{\text{rms}} = \sqrt{\frac{3E}{2M}}$     (b)  $U_{\text{rms}} = \sqrt{\frac{2E}{3M}}$   
 (c)  $U_{\text{rms}} = \sqrt{\frac{2E}{M}}$     (d)  $U_{\text{rms}} = \sqrt{\frac{E}{3M}}$
210. Which of the following is not a property of liquid state? [BHU (Pre) 2005]  
 (a) Intermolecular force of attraction in a liquid is quite large  
 (b) All liquids accompanied by cooling on evaporation  
 (c) Lower the boiling point of a liquid, greater is its vapour pressure at room temperature  
 (d) A liquid boils at higher temperature at the top of a mountain than at the sea level
211. A certain sample of a gas has a volume of  $0.2 \text{ litre}$  measured at  $1 \text{ atm}$  pressure and  $0^\circ\text{C}$ . At the same pressure but  $273^\circ\text{C}$ , its volume will be: [BHU (Pre) 2005]  
 (a)  $0.4 \text{ L}$     (b)  $0.8 \text{ L}$     (c)  $27.8 \text{ L}$     (d)  $55.6 \text{ L}$
212. When electrons are trapped into the crystal in anion vacancy, the defect is known as: [BHU (Pre) 2005]  
 (a) Schottky defect    (b) Frenkel defect  
 (c) stoichiometric defect    (d)  $F$ -centres
213. In the equation of state of an ideal gas  $PV = nRT$ , the value of the universal gas constant  $R$  would depend only on the: [KCET 2005]  
 (a) nature of the gas    (b) pressure of the gas  
 (c) units of the measurement    (d) none of these
201. The following is a method to determine the surface tension of liquids: [CET (J&K) 2007]  
 (a) single capillary method    (b) refractometric method  
 (c) polarimetric method    (d) boiling point method
202. The crystalline structure of NaCl is: [CET (J&K) 2007]  
 (a) hexagonal close packing    (b) face-centred cubic  
 (c) square planar    (d) body-centred cubic

214. If  $Z$  is the number of atoms in the unit cell that represents the closest packing sequence  $ABC\ A\ B\ C\dots$ , the number of tetrahedral voids in the unit cell is equal to: [AIIMS 2005]

(a)  $Z$       (b)  $2Z$       (c)  $\frac{Z}{2}$       (d)  $\frac{Z}{4}$

215. Equation of Boyle's law is: [DPMT 2005]

(a)  $\frac{dP}{P} = -\frac{dV}{V}$       (b)  $\frac{dP}{P} = +\frac{dV}{V}$   
 (c)  $\frac{d^2P}{P} = -\frac{dV}{dT}$       (d)  $\frac{d^2P}{P} = +\frac{d^2V}{dt}$

[Hint:  $PV = \text{constant}$

$$P dV + V dP = 0 \\ \frac{dP}{P} = -\frac{dV}{V}$$

216. In a face-centred cubic unit cell, edge length is: [DPMT 2005]

(a)  $\frac{4}{\sqrt{3}}r$       (b)  $\frac{4}{\sqrt{2}}r$       (c)  $2r$       (d)  $\frac{\sqrt{3}}{2}r$

217. If  $v_{\text{rms}}$  is  $30R^{1/2}$  at  $27^\circ\text{C}$ , then calculate the molar mass of the gas in kilogram: [DPMT 2005]

(a) 1      (b) 2      (c) 4      (d) 0.001

[Hint:  $v_{\text{rms}} = \sqrt{\frac{3RT}{m}}$   
 $30R^{1/2} = \sqrt{\frac{3 \times R \times 300}{m}}$   
 $m = 0.001 \text{ kg}$ ]

218. The pressure exerted by 1 mole of methane in a 0.25 litre container at 300 K using van der Waals' equation (given  $a = 2.253 \text{ atm L}^2 \text{ mol}^{-2}$ ,  $b = 0.0428 \text{ L mol}^{-1}$ ) is: [JEE (Orissa) 2005]

(a) 82.82 atm      (b) 152.51 atm  
 (c) 190.52 atm      (d) 70.52 atm

219. An ionic compound has a unit cell consisting of 'A' ions at the corners of a cube and 'B' ions on the centres of the faces of the cube. The empirical formula for this compound would be: [AIEEE 2005; CET (Karnataka) 2009]

(a)  $AB$       (b)  $A_2B$   
 (c)  $AB_3$       (d)  $A_3B$

220. Which one of the following statements is not true about the effect of an increase in temperature on the distribution of molecular speeds in a gas?

(a) The most probable speed increases  
 (b) The fraction of the molecules with most probable speed increases  
 (c) The distribution becomes broader  
 (d) The area under the distribution curve remains the same as under the lower temperature

221. A gas can be liquefied: [AFMC 2005]

(a) above its critical temperature  
 (b) at its critical temperature  
 (c) below its critical temperature  
 (d) at any temperature

222. If the absolute temperature of a gas is doubled and the pressure is reduced to one-half, the volume of the gas will:

[PET (Kerala) 2005]

- (a) remain unchanged      (b) be doubled  
 (c) increase fourfold      (d) be halved  
 (e) be reduced to one-fourth

[Hint: Use  $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$ ]

223. To what temperature must a neon gas sample be heated to double the pressure, if the initial volume of a gas at  $75^\circ\text{C}$  is decreased by 15%? [PET (Kerala) 2005]

(a)  $319^\circ\text{C}$       (b)  $592^\circ\text{C}$       (c)  $128^\circ\text{C}$       (d)  $60^\circ\text{C}$   
 (e)  $90^\circ\text{C}$

[Hint:  $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$

$$\frac{PV}{348} = \frac{2P \times 85V}{T_2 \times 100}$$

$$T_2 = 591.6 \text{ K}$$

$$t_2 = 318.6^\circ\text{C}$$

224. The surface tension of which of the following liquids is maximum? [CBSE (Pre) 2005]

(a)  $\text{C}_2\text{H}_5\text{OH}$       (b)  $\text{CH}_3\text{OH}$       (c)  $\text{H}_2\text{O}$       (d)  $\text{C}_6\text{H}_6$

[Hint: (c) Due to hydrogen bonding,  $\text{H}_2\text{O}$  has the highest intermolecular force, hence its surface tension is also maximum.]

225. An element (with atomic mass = 250 g) crystallises in a simple cube. If the density of unit cell is  $7.2 \text{ g cm}^{-3}$ , what is the radius of the element? [JEE (Orissa) 2006]

(a)  $1.93 \times 10^{-6} \text{ cm}$       (b)  $1.93 \times 10^{-8} \text{ cm}$   
 (c)  $1.93 \times 10^{-8} \text{ \AA}$       (d)  $1.93 \times 10^{-8} \text{ m}$

[Hint:  $Z = \frac{l^3 \times \rho \times N_A}{M}$

$$1 = \frac{l^3 \times 7.2 \times 6.023 \times 10^{23}}{250}$$

$$l = 3.86 \times 10^{-8} \text{ cm}$$

$l = 2r$  (for simple cubic unit cell)

$$r = \frac{l}{2} = \frac{3.86 \times 10^{-8}}{2} = 1.93 \times 10^{-8} \text{ cm}$$

226. Dominance of strong repulsive forces among the molecules of the gas ( $Z$  = compressibility factor): [AIIMS 2006]

(a) depends on  $Z$  and indicated by  $Z = 1$   
 (b) depends on  $Z$  and indicated by  $Z > 1$   
 (c) depends on  $Z$  and indicated by  $Z < 1$   
 (d) is independent of  $Z$

[Hint: When  $Z > 1$ , the gas is less compressible than ideal gas and the repulsive forces dominate.]

227. Total volume of atoms present in a face-centred cubic unit cell of a metal is ( $r$  is atomic radius): [AIEEE 2006]

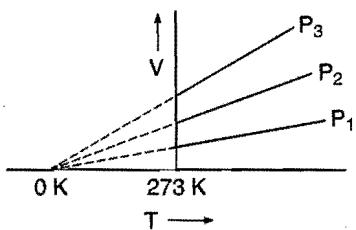
(a)  $\frac{20}{3} \pi r^3$       (b)  $\frac{24}{3} \pi r^3$       (c)  $\frac{12}{3} \pi r^3$       (d)  $\frac{16}{3} \pi r^3$

228. If we know the ionic radius ratio in a crystal of ionic solid, what can be known of the following? [CET (Gujarat) 2006]

(a) Magnetic property  
 (b) Nature of chemical bond  
 (c) Type of defect  
 (d) Geometrical shape of crystal

229. If a volume containing gas is compressed to half, how many moles of gas remained in the vessel? (DCE 2006)
- (a) Just double      (b) Just half  
 (c) Same      (d) More than double

230. The volume-temperature graphs of a given mass of an ideal gas at constant pressures are shown below. What is the correct order of pressures? (EAMCET 2006; AIIMS 2008)



- (a)  $P_1 > P_3 > P_2$       (b)  $P_1 > P_2 > P_3$   
 (c)  $P_2 > P_3 > P_1$       (d)  $P_2 > P_1 > P_3$
231. If NaCl is doped with  $10^{-4}$  mol % of SrCl<sub>2</sub>, the concentration of cation vacancies will be ( $N_A = 6.023 \times 10^{23}$ ): [CBSE (Medical) 2007]
- (a)  $6.02 \times 10^{16} \text{ mol}^{-1}$       (b)  $6.02 \times 10^{17} \text{ mol}^{-1}$   
 (c)  $6.02 \times 10^{14} \text{ mol}^{-1}$       (d)  $6.02 \times 10^{15} \text{ mol}^{-1}$

232. Coordination number of NaCl crystal will be: [PET (MP) 2007]
- (a) 8:8      (b) 6:6      (c) 4:4      (d) 2:2

233. The unit cell of Al (molar mass 27 g mol<sup>-1</sup>) has an edge length of 405 pm. Its density is 2.7 g / cm<sup>3</sup>. The cubic unit cell is: [PET (Kerala) 2007]

- (a) face-centred      (b) body-centred      (c) primitive  
 (d) edge-centred      (e) simple

[Hint:  $Z = \frac{a^3 \times d \times N_A}{M} = \frac{(405 \times 10^{-10})^3 \times 2.7 \times 6.023 \times 10^{23}}{27} = 4$

∴ It is a face-centred cubic unit cell.]

234. The 8:8 type packing is present in: (VITEEE 2007)
- (a) MgF<sub>2</sub>      (b) CsCl      (c) KCl      (d) NaCl

235. 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: [AIEEE 2007; EAMCET (Med.) 2010]

- (a)  $\frac{1}{2}$       (b)  $\frac{2}{3}$       (c)  $\frac{1}{3} \times \frac{273}{298}$       (d)  $\frac{1}{3}$

236. Percentage of free space in a body centred cubic unit cell is: [CBSE (PMT) 2008]
- (a) 34%      (b) 28%      (c) 30%      (d) 32%

237. Which of the following statement is not correct? [CBSE (PMT) 2008]

- (a) The number of carbon atoms in a unit cell of diamond is 4.  
 (b) The number of Bravais lattices in which a crystal can be categorized is 14.  
 (c) The fraction of the total volume occupied by the atoms in a primitive cell is 0.48.  
 (d) Molecular solids are generally volatile.
238. If  $a$  stands for the edge length of the cubic systems : simple cubic, body centred cubic and face centred cubic, then the ratio of radii of the spheres in these systems will be respectively: [CBSE (PMT) 2008]

- (a)  $\frac{1}{2}a : \frac{\sqrt{3}}{2}a : \frac{\sqrt{2}}{2}a$       (b)  $1a : \sqrt{3}a : \sqrt{2}a$   
 (c)  $\frac{1}{2}a : \frac{\sqrt{3}}{4}a : \frac{1}{2\sqrt{2}}a$       (d)  $\frac{1}{2}a : \sqrt{3}a : \frac{1}{\sqrt{2}}a$

[Hint : Simple unit cell,  $r = a/2$

Body centred unit cell,  $r = \frac{a\sqrt{3}}{4}$

Face centred unit cell,  $r = \frac{a}{2\sqrt{2}}$  ]

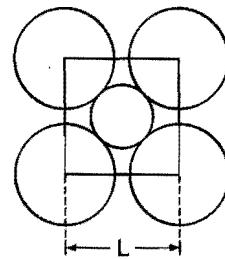
239. The term that corrects for the attractive forces present in a real gas in the van der Waals' equation is: (IIT 2009)

- (a)  $nb$       (b)  $\frac{an^2}{V^2}$       (c)  $\frac{-an^2}{V^2}$       (d)  $-nb$

240. Which is not the correct statement for ionic solids in which positive and negative ions are held by strong electrostatic attractive forces? (DCE 2009)

- (a) The ratio  $\frac{r^+}{r^-}$  increases as coordination number increases  
 (b) As the difference in size of ions increases coordination number increases  
 (c) When coordination number is eight, the  $\frac{r^+}{r^-}$  ratio lies between 0.225 – 0.414  
 (d) In ionic solid of the type AX (ZnS, Wurtzite) the coordination number of Zn<sup>2+</sup> and S<sup>2-</sup> respectively are 4 and 4

241. The packing efficiency of the two-dimensional square unit cell shown below is: (IIT 2010)



- (a) 39.27%      (b) 68.02%  
 (c) 74.05%      (d) 78.54%

[Hint :  $a\sqrt{2} = 4r$

$$a = 2\sqrt{2} r$$

$$\text{Packing fraction} = \frac{\text{Occupied area}}{\text{Total area}} \times 100$$

$$= \frac{2\pi r^2}{(2\sqrt{2}r)^2} \times 100 = 78.5\% ]$$

### Set-2: The questions given below may have more than one correct answers

1. If force of attraction between the molecules is negligible, van der Waals' equation (for one mole) will become:

- (a)  $PV = RT + Pb$       (b)  $P = \frac{RT}{V - b} - \frac{a}{V^2}$   
 (c)  $PV = RT + a/V$       (d)  $PV = RT - a/V$

2. van der Waals' equation for:

- |                                      |   |
|--------------------------------------|---|
| A. High pressure                     | (i) $PV = RT + Pb$                                |
| B. Low pressure                      | (ii) $PV = RT - a/V$                              |
| C. Force of attraction is negligible | (iii) $PV = RT + a/V$                             |
| D. Volume of molecules is negligible | (iv) $\left(P + \frac{a}{V^2}\right)(V - b) = RT$ |

- (a) A (iv), B (ii), C (i), D (iii)
- (b) A (i), B (ii), C (iii), D (iv)
- (c) A (iv), B (iii), C (ii), D (i)
- (d) A (iv), B (ii), C (iii), D (i)

3. van der Waals' constants for three different gases are given:

Gases	$a$	$b$
X	3.0	0.025
Y	10.0	0.030
Z	6.0	0.035

Which is correct?

- (a) Maximum critical temperature—Y
  - (b) Most ideal behaviour—X
  - (c) Maximum molecular volume—Z
  - (d) All are correct
4. What is the ratio of mean speed of an  $O_3$  molecule to the rms speed of an  $O_2$  molecule at the same  $T$ ?
- (a)  $(3\pi/7)^{1/2}$
  - (b)  $(16/9\pi)^{1/2}$
  - (c)  $(3\pi)^{1/2}$
  - (d)  $(4\pi/9)^{1/2}$

5. Boyle's law may be represented as:

- |   |  |
|---|--|
| (a) $\left(\frac{dP}{dV}\right)_T = K/V$          | (b) $\left(\frac{dP}{dV}\right)_T = -\frac{K}{V}$  |
| (c) $\left(\frac{dP}{dV}\right) = -\frac{K}{V^2}$ | (d) $\left(\frac{dP}{dV}\right)_T = \frac{K}{V^2}$ |

where,  $K$  = constant.

6. If pressure of a gas is increased by 1% when heated by  $1^\circ C$ , its initial temperature must be (if volume remains constant):
- (a) 100 K
  - (b) 100°C
  - (c) 250 K
  - (d) 250°C
7. Which of the following are not the units of gas constant,  $R$ ?
- (a) dyne  $K^{-1} mol^{-1}$
  - (b) erg  $deg^{-1} mol^{-1}$
  - (c)  $cm^3 K^{-1} mol^{-1}$
  - (d)  $kPa dm^3 K^{-1} mol^{-1}$

8. According to Charles' law:

- |  |  |
|--|--|
| (a) $V \propto \frac{1}{T}$            | (b) $\left(\frac{dV}{dT}\right)_P = K$               |
| (c) $\left(\frac{dT}{dV}\right)_P = K$ | (d) $\left(\frac{1}{T} - \frac{V}{T^2}\right)_P = 0$ |

9. In the following statements :

- (A) ideal gases are liquefied only at very low temperatures
- (B) ideal gases can not be liquefied
- (C) ideal gas behaviour is observed by real gases at low pressures
- (D) ideal gases do not exist

The correct statements are :

(ISAT 2010)

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

10. Which of the following relationships is/are not true?

- (a) Most probable velocity =  $\sqrt{\frac{2RT}{M}}$
- (b)  $PV = \frac{3}{2}kT$
- (c) Compressibility factor  $Z = \frac{PV}{nRT}$
- (d) Average kinetic energy of gas =  $\frac{1}{2}kT$

11. According to kinetic theory of gases:

(IIT 1991)

- (a) the pressure exerted by a gas is proportional to mean square velocity of the molecules
- (b) the pressure exerted by the gas is proportional to the root mean square velocity of the molecules
- (c) the root mean square velocity is inversely proportional to the temperature
- (d) the mean translational KE of the molecule is directly proportional to the absolute temperature

12. A gas described by van der Waals' equation :

(IIT 2008)

- (a) behaves similar to an ideal gas in the limit of large molar volume
- (b) behaves similar to an ideal gas in the limit of large pressures
- (c) is characterised by van der Waals' constant that are dependent on identity of the gas but are independent of the temperature.
- (d) has the pressure that is lower than the pressure exerted by the same behaving ideally.

## Assertion-Reason TYPE QUESTIONS

### Set-1

The questions given below consist of an 'Assertion' (A) and the 'Reason' (R). Use the following keys to choose the appropriate answer:

- (a) If both (A) and (R) are correct, and (R) is the correct explanation of (A).
- (b) If both (A) and (R) are correct, but (R) is not the correct explanation of (A).
- (c) If (A) is correct, but (R) is incorrect.

(d) If (A) is incorrect, but (R) is correct.

- (A) The heat absorbed during the isothermal expansion of an ideal gas against vacuum is zero.  
(R) The volume occupied by the molecules of an ideal gas is zero. (IIT 2000)
- (A) The pressure of a fixed amount of an ideal gas is proportional to its temperature.  
(R) Frequency of collisions and their impact both increase in proportion of the square root of temperature. (IIT 2000)

3. (A)  $C_P - C_V = R$  for an ideal gas.  
(R)  $\left(\frac{\partial E}{\partial V}\right)_T = 0$  for an ideal gas.
4. (A) A lighter gas diffuses more rapidly than a heavier gas.  
(R) At a given temperature, the rate of diffusion of a gas is inversely proportional to the square root of its density.
5. (A) On cooling, the brown colour of nitrogen dioxide disappears.  
(R) On cooling,  $\text{NO}_2$  undergoes dimerisation resulting in the pairing of the odd electrons in  $\text{NO}_2$ .
6. (A) The value of the van der Waals' constant ' $a$ ' is larger for ammonia than for nitrogen.  
(R) Hydrogen bonding is present in ammonia.
7. (A) The Joule-Thomson coefficient for the ideal gas is zero.  
(R) There are no intermolecular attractive forces in an ideal gas.
8. (A) At  $27^\circ\text{C}$ , the kinetic energy of 8 gram of methane is equal to the kinetic energy of 16 gram of oxygen.  
(R) The total heat change in a reaction is the same whether the chemical reaction takes place in one single step or in several steps. (EAMCET 2006)
9. (A) A closed cylinder containing high pressure gas tends to rise against gravity when the gas is allowed to escape through an orifice at the bottom.  
(R) The velocity of escaping gas develops an upward thrust proportional to the area of cross-section of the orifice. (SCRA 2007)
- [Hint: Assertion is correct but reason is wrong as the velocity of escaping gas is inversely proportional to the area of cross-section of orifice.]
10. (A) Meniscus of a liquid disappears at the critical temperature.  
(R) Density of liquid and its gaseous phase become equal at the critical temperature. [BHU (Screening) 2008]
11. (A) Graphite is soft while diamond is hard.  
(R) Graphite has three dimensional structure while diamond has planar. [BHU (Screening) 2008]
12. (A) White tin is an example of tetragonal system.  
(R) For tetragonal system  $a = b = c$  and  $\alpha = \beta = \gamma \neq 90^\circ$ .

## Set-2

The questions given below consist of two statements each printed as 'Assertion' (A) and 'Reason' (R). While answering these questions you are required to choose any one of the following four responses:

- (a) If both (A) and (R) are true and (R) is the correct explanation for (A).  
(b) If both (A) and (R) are true but (R) is not the correct explanation for (A).  
(c) If (A) is true but (R) is false.  
(d) If both (A) and (R) are false.
13. (A) Sulphur dioxide and chlorine are both bleaching agents.  
(R) Both are reducing agents. (AIIMS 1994)
14. (A) Nitrogen is unreactive at room temperature but becomes reactive at elevated temperatures (on heating or in the presence of catalysts).  
(R) In nitrogen molecule, there is extensive delocalisation of electrons. (AIIMS 1996)
15. (A) Noble gases can be liquefied.  
(R) Attractive forces can exist between non-polar molecules. (AIIMS 1998)

16. (A) Under similar conditions of temperature and pressure,  $\text{O}_2$  diffuses 1.4 times faster than  $\text{SO}_2$ .  
(R) Density of  $\text{SO}_2$  is 1.4 times greater than that of  $\text{O}_2$ .
17. (A) On compressing a gas to half the volume, the number of moles is halved.  
(R) The number of moles present decreases with decrease in volume.
18. (A) The plot of volume ( $V$ ) versus pressure ( $P$ ) at constant temperature is a hyperbola in the first quadrant.  
(R)  $V \propto 1/P$  at constant temperature.
19. (A) At constant temperature, if pressure on the gas is doubled, density is also doubled.  
(R) At constant temperature, molecular mass of a gas is directly proportional to the density and inversely proportional to the pressure.
20. (A) If  $\text{H}_2$  and  $\text{Cl}_2$  enclosed separately in the same vessel exert pressures of 100 and 200 mm respectively, their mixture in the same vessel at the same temperature will exert a pressure of 300 mm.  
(R) Dalton's law of partial pressures states that total pressure is the sum of partial pressures.
21. (A) Most probable velocity is the velocity possessed by maximum fraction of molecules at the same temperature.  
(R) On collision, more and more molecules acquire higher speed at the same temperature.
22. (A) Compressibility factor ( $Z$ ) for non-ideal gases is always greater than 1.  
(R) Non-ideal gases always exert higher pressure than expected.
23. (A) van der Waals' equation is applicable only to non-ideal gases.  
(R) Ideal gases obey the equation  $PV = nRT$ .
24. (A) Helium shows only positive deviations from ideal behaviour.  
(R) Helium is an inert gas.
25. (A) Gases are easily absorbed on the surface of metals, especially transition metals.  
(R) Transition metals have free valencies.
26. (A)  $\text{SO}_2$  gas is easily liquefied while  $\text{H}_2$  is not.  
(R)  $\text{SO}_2$  has low critical temperature while  $\text{H}_2$  has high critical temperature.
27. (A) Diffusion is used in the enrichment of  $\text{U}^{235}$ .  
(R) A lighter gas diffuses more rapidly than a heavier gas.
28. (A) Crystalline solids can cause X-rays to diffract.  
(R) Interatomic distance in crystalline solids is of the order of 0.1 nm. (AIIMS 2004)
29. (A) The effusion rate of oxygen is smaller than that of nitrogen.  
(R) Molecular size of nitrogen is smaller than that of oxygen. (AIIMS 2004)
30. (A) The compressibility factor for hydrogen varies with pressure with positive slope at all pressures.  
(R) Even at low pressures, the repulsive forces dominate in hydrogen gas. (AIIMS 2005)
31. (A) Graphite is an example of tetragonal crystal system.  
(R) For a tetragonal system  $a = b \neq c$ ,  $\alpha = \beta = 90^\circ$  and  $\gamma = 120^\circ$ . (AIIMS 2006)
32. (A) No compound has both Schottky and Frenkel defects.  
(R) Both defects change the density of the solid. (AIIMS 2008)

**Answers : OBJECTIVE QUESTIONS**

● Set-1

- |          |          |          |          |          |          |          |          |
|----------|----------|----------|----------|----------|----------|----------|----------|
| 1. (c)   | 2. (d)   | 3. (d)   | 4. (a)   | 5. (a)   | 6. (b)   | 7. (b)   | 8. (c)   |
| 9. (a)   | 10. (a)  | 11. (a)  | 12. (c)  | 13. (b)  | 14. (c)  | 15. (d)  | 16. (d)  |
| 17. (b)  | 18. (b)  | 19. (d)  | 20. (a)  | 21. (d)  | 22. (b)  | 23. (a)  | 24. (a)  |
| 25. (c)  | 26. (a)  | 27. (a)  | 28. (d)  | 29. (b)  | 30. (c)  | 31. (a)  | 32. (b)  |
| 33. (a)  | 34. (b)  | 35. (b)  | 36. (a)  | 37. (d)  | 38. (b)  | 39. (c)  | 40. (b)  |
| 41. (d)  | 42. (d)  | 43. (c)  | 44. (c)  | 45. (a)  | 46. (b)  | 47. (d)  | 48. (c)  |
| 49. (c)  | 50. (c)  | 51. (d)  | 52. (b)  | 53. (d)  | 54. (c)  | 55. (a)  | 56. (a)  |
| 57. (a)  | 58. (d)  | 59. (d)  | 60. (a)  | 61. (b)  | 62. (b)  | 63. (c)  | 64. (c)  |
| 65. (d)  | 66. (c)  | 67. (a)  | 68. (d)  | 69. (b)  | 70. (b)  | 71. (d)  | 72. (a)  |
| 73. (a)  | 74. (c)  | 75. (d)  | 76. (c)  | 77. (b)  | 78. (c)  | 79. (d)  | 80. (a)  |
| 81. (c)  | 82. (b)  | 83. (a)  | 84. (d)  | 85. (c)  | 86. (c)  | 87. (a)  | 88. (b)  |
| 89. (a)  | 90. (d)  | 91. (c)  | 92. (b)  | 93. (d)  | 94. (a)  | 95. (d)  | 96. (b)  |
| 97. (b)  | 98. (c)  | 99. (a)  | 100. (d) | 101. (a) | 102. (d) | 103. (b) | 104. (c) |
| 105. (c) | 106. (a) | 107. (d) | 108. (b) | 109. (b) | 110. (b) | 111. (d) | 112. (a) |
| 113. (c) | 114. (b) | 115. (a) | 116. (d) | 117. (a) | 118. (a) | 119. (b) | 120. (c) |
| 121. (d) | 122. (d) | 123. (c) | 124. (d) | 125. (b) | 126. (b) | 127. (c) | 128. (a) |
| 129. (a) | 130. (c) | 131. (b) | 132. (a) | 133. (d) | 134. (d) | 135. (a) | 136. (b) |
| 137. (d) | 138. (c) | 139. (b) | 140. (a) | 141. (a) | 142. (b) | 143. (c) | 144. (a) |
| 145. (b) | 146. (c) | 147. (c) | 148. (d) | 149. (d) | 150. (c) | 151. (b) | 152. (a) |
| 153. (c) | 154. (b) | 155. (d) | 156. (c) | 157. (c) | 158. (b) | 159. (d) | 160. (b) |
| 161. (d) | 162. (b) | 163. (b) | 164. (c) | 165. (b) | 166. (b) | 167. (a) | 168. (a) |
| 169. (b) | 170. (d) | 171. (c) | 172. (d) | 173. (c) | 174. (b) | 175. (d) | 176. (a) |
| 177. (d) | 178. (b) | 179. (a) | 180. (a) | 181. (b) | 182. (a) | 183. (c) | 184. (b) |
| 185. (c) | 186. (d) | 187. (a) | 188. (c) | 189. (b) | 190. (b) | 191. (d) | 192. (b) |
| 193. (a) | 194. (c) | 195. (a) | 196. (d) | 197. (d) | 198. (c) | 199. (c) | 200. (c) |
| 201. (a) | 202. (b) | 203. (c) | 204. (c) | 205. (a) | 206. (b) | 207. (b) | 208. (a) |
| 209. (b) | 210. (d) | 211. (a) | 212. (d) | 213. (c) | 214. (b) | 215. (a) | 216. (a) |
| 217. (d) | 218. (a) | 219. (c) | 220. (b) | 221. (c) | 222. (c) | 223. (a) | 224. (c) |
| 225. (b) | 226. (b) | 227. (d) | 228. (d) | 229. (c) | 230. (b) | 231. (b) | 232. (b) |
| 233. (a) | 234. (a) | 235. (d) | 236. (d) | 237. (c) | 238. (c) | 239. (b) | 240. (c) |
| 241. (d) |          |          |          |          |          |          |          |

● Set-2

- |        |         |            |            |        |        |           |              |
|--------|---------|------------|------------|--------|--------|-----------|--------------|
| 1. (a) | 2. (a)  | 3. (d)     | 4. (b)     | 5. (a) | 6. (a) | 7. (a, c) | 8. (b, c, d) |
| 9. (c) | 10. (d) | 11. (b, d) | 12. (a, c) |        |        |           |              |

**Answers : ASSERTION-REASON TYPE QUESTIONS**

- |         |         |         |         |         |         |         |         |
|---------|---------|---------|---------|---------|---------|---------|---------|
| 1. (b)  | 2. (c)  | 3. (b)  | 4. (a)  | 5. (a)  | 6. (a)  | 7. (a)  | 8. (b)  |
| 9. (c)  | 10. (a) | 11. (c) | 12. (c) | 13. (c) | 14. (c) | 15. (a) | 16. (c) |
| 17. (d) | 18. (a) | 19. (c) | 20. (d) | 21. (c) | 22. (d) | 23. (b) | 24. (b) |
| 25. (a) | 26. (c) | 27. (b) | 28. (c) | 29. (c) | 30. (a) | 31. (d) | 32. (d) |

## BRAIN STORMING PROBLEMS

### OBJECTIVE QUESTIONS for IIT ASPIRANTS

The following questions have single correct option:

1. Which of the following graphs is not a straight line for an ideal gas?

(a)  $V \rightarrow T$     (b)  $T \rightarrow P$     (c)  $n \rightarrow \frac{1}{T}$     (d)  $n \rightarrow \frac{1}{P}$

2. The quantity  $(PV / k_B T)$  represents the:

- (a) number of molecules in the gas
- (b) mass of the gas
- (c) number of moles of the gas
- (d) translational energy of the gas

[Hint:  $PV = nRT$

$$n = \frac{PV}{RT}$$

$$\begin{aligned} \text{Number of molecules} &= N_A \frac{PV}{RT} \\ &= \frac{PV}{(R/N_A)T} = \frac{PV}{k_B T} \end{aligned}$$

where,  $k_B$  = Boltzmann constant.]

3. 1 litre of  $N_2$  and  $7/8$  litre of  $O_2$  at the same temperature and pressure were mixed together. What is the relation between the masses of the two gases in the mixture?

- (a)  $M_{N_2} = 3M_{O_2}$
- (b)  $M_{N_2} = 8M_{O_2}$
- (c)  $M_{N_2} = M_{O_2}$
- (d)  $M_{N_2} = 16M_{O_2}$

[Hint:  $PV = \frac{M}{m} RT$

$$P \times 1 = \frac{M_{N_2}}{28} RT \quad \dots (i)$$

$$P \times \frac{7}{8} = \frac{M_{O_2}}{32} RT \quad \dots (ii)$$

Dividing eq. (i) by eq. (ii), we get

$$M_{N_2} = M_{O_2}$$

4. A box is divided into two equal compartments by a thin partition and they are filled with gases  $X$  and  $Y$  respectively. The two compartments have a pressure of 250 torr each. The pressure after removing the partition will be equal to:

- (a) 125 torr
- (b) 500 torr
- (c) 250 torr
- (d) 750 torr

5. The density of a gas  $A$  is twice that of a gas  $B$  at the same temperature. The molecular mass of gas  $B$  is thrice that of  $A$ . The ratio of the pressures acting on  $A$  and  $B$  will be:

- (a) 6 : 1
- (b) 7 : 8
- (c) 2 : 5
- (d) 1 : 4

[Hint:  $Pm = dRT$

$$\frac{P_A m_A}{P_B m_B} = \frac{d_A RT}{d_B RT}$$

$$\frac{P_A}{P_B} \times \frac{1}{3} = 2$$

$$P_A : P_B = 6 : 1$$

6. In the corrections made to the ideal gas equation for real gases, the reduction in pressure due to attractive forces is directly proportional to:

- (a)  $n/V$
- (b)  $nb$
- (c)  $\frac{n^2}{V^2} b$
- (d)  $\frac{n^2}{V^2}$

[Hint: Pressure correction =  $a \frac{n^2}{V^2}$

$\therefore$  Pressure correction  $\propto \frac{n^2}{V^2}$  ]

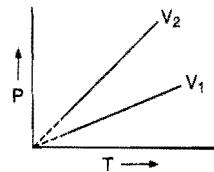
7. Which of the following conditions is favourable for liquefaction of gas?

- (a)  $T > T_c$ ,  $P > P_c$
- (b)  $T < T_c$ ,  $P > P_c$
- (c)  $T = T_c$ ,  $P = P_c$
- (d)  $T = T_c$ ,  $P < P_c$

8. An ideal gas of certain mass is heated in a small vessel and then in a large vessel, such that their volume remains unchanged. The  $P-T$  curves are:

- (a) parabolic with same curvature
- (b) parabolic with different curvatures
- (c) linear with same slope
- (d) linear with different slopes

[Hint:



Straight lines with different slopes will be obtained.]

9. A spherical air bubble is rising from the depth of a lake when pressure is  $P$  atm and temperature is  $T$  K. The percentage increase in its radius when it comes to the surface of a lake will be: (Assume temperature and pressure at the surface to be respectively  $2T$  K and  $P/4$ .)

- (a) 100%
- (b) 50%
- (c) 40%
- (d) 200%

[Hint:  $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$ ;  $V_1$  = initial volume,  $V_2$  = final volume

$$\frac{PV_1}{T} = \frac{P}{4} \times \frac{V_2}{2T}$$

$$V_1 = \frac{V_2}{8}$$

$$V_2 = 8V_1$$

$$V_2 = 8 \times \frac{4}{3} \pi r^3 = \frac{4}{3} \pi (8r)^3$$

New radius =  $2r$  ( $\therefore$  100% radius will increase)]

10. It is easier to liquefy oxygen than hydrogen because:

- (a) oxygen has a higher critical temperature and lower inversion temperature than hydrogen
- (b) oxygen has a lower critical temperature and higher inversion temperature than hydrogen

- (c) oxygen has a higher critical temperature and a higher inversion temperature than hydrogen  
 (d) the critical temperature and inversion temperature of oxygen is very low  
 11. 2 mole 'He' is mixed with 2 gm of H<sub>2</sub>. The molar heat capacity at constant pressure for the mixture is:

(a)  $\frac{17R}{6}$       (b)  $\frac{11R}{6}$       (c)  $4R$       (d)  $\frac{3R}{2}$

[Hint:  $C_P$  for 'He' =  $\frac{5}{2} R$ ;  $C_P$  for H<sub>2</sub> =  $\frac{7}{2} R$

$$n_{\text{He}} = 2; n_{\text{H}_2} = 1$$

$$C_P = \frac{n_1 C_{P_1} + n_2 C_{P_2}}{n_1 + n_2} = \frac{2 \times \frac{5}{2} R + 1 \times \frac{7}{2} R}{3} \\ = \frac{17R}{6}$$

12. The van der Waals' constant 'a' for the gases O<sub>2</sub>, N<sub>2</sub>, NH<sub>3</sub> and CH<sub>4</sub> are 1.36, 1.39, 4.17 and 2.253 respectively, the gas which can be most easily liquefied is:

(a) O<sub>2</sub>      (b) N<sub>2</sub>      (c) NH<sub>3</sub>      (d) CH<sub>4</sub>

[Hint: The van der Waals' constant 'a' is directly proportional to the intermolecular force; hence, the gas with greater value of 'a' can be most easily liquefied.]

13. At what temperature will the molar kinetic energy of 0.3 mole of 'He' be the same as that of 0.4 mole of argon at 400 K?

(a) 700 K      (b) 500 K      (c) 800 K      (d) 400 K

[Hint:  $KE = \frac{3}{2} nRT$

$n = 1$ , for molar kinetic energy

$$\left( \frac{3}{2} \times 1 \times R \times T \right)_{\text{Helium}} = \left( \frac{3}{2} \times 1 \times R \times 400 \right)_{\text{Argon}}$$

$$T = 400 \text{ K}$$

14. Let P<sub>s</sub> and P be the saturated partial pressure and partial pressure of water respectively. Then the relative humidity is given by:

(a)  $\frac{P_s + P}{P_s} \times 100$       (b)  $\frac{P}{P_s} \times 100$   
 (c)  $\frac{P_s}{P} \times 100$       (d)  $(P + P_s) \times 100$

15. Molar volume of a monoatomic gas at P<sub>0</sub> and T<sub>0</sub> is 0.5 times its molar volume at 10P<sub>0</sub> and at the same temperature. Ignoring the value of the van der Waals' constant 'a', the radius of the gas molecules is given by:

(a)  $\frac{0.8RT_0}{P_0}$       (b)  $\left( \frac{0.6RT_0}{P_0 N\pi} \right)^{1/3}$   
 (c)  $\left( \frac{3RT_0}{20P_0 N\pi} \right)^{1/3}$       (d)  $\left( \frac{3RT_0}{20P_0 \pi} \right)^{1/3}$

where, N = Avogadro's number

16. A vessel is filled with a mixture of oxygen and nitrogen. At what ratio of partial pressures will the mass of gases be identical?

(a)  $P(\text{O}_2) = 0.785P(\text{N}_2)$       (b)  $P(\text{O}_2) = 8.75P(\text{N}_2)$   
 (c)  $P(\text{O}_2) = 11.4P(\text{N}_2)$       (d)  $P(\text{O}_2) = 0.875P(\text{N}_2)$

[Hint:  $PV = nRT$

$$PV = \frac{w}{m} RT$$

$$P_{\text{O}_2} V = \frac{w}{32} RT \quad \dots (i)$$

$$P_{\text{N}_2} V = \frac{w}{28} RT \quad \dots (ii)$$

$$\frac{P_{\text{O}_2}}{P_{\text{N}_2}} = \frac{28}{32}$$

$$P_{\text{O}_2} = 0.875P_{\text{N}_2}]$$

17. KCl crystallises in the same type of lattice as does NaCl. Given that  $r_{\text{Na}^+}/r_{\text{Cl}^-} = 0.55$  and  $r_{\text{K}^+}/r_{\text{Cl}^-} = 0.74$ . Calculate the ratio of the side of the unit cell for KCl to that of NaCl

[PET (Kerala) 2008]

(a) 1.123      (b) 0.891      (c) 1.414      (d) 0.414  
 (e) 1.732

[Hint:  $\frac{r_{\text{Na}^+}}{r_{\text{Cl}^-}} = 0.55, \frac{r_{\text{K}^+}}{r_{\text{Cl}^-}} = 0.74$

$$\frac{\frac{r_{\text{Na}^+}}{r_{\text{Cl}^-}} + 1}{r_{\text{Cl}^-}} = 1.55 \quad \dots (1)$$

$$\frac{\frac{r_{\text{K}^+}}{r_{\text{Cl}^-}} + 1}{r_{\text{Cl}^-}} = 1.74 \quad \dots (2)$$

Dividing (2) by (1)

$$\frac{1.74}{1.55} = \frac{r_{\text{K}^+} + r_{\text{Cl}^-}}{r_{\text{Cl}^-}} \times \frac{r_{\text{Cl}^-}}{r_{\text{Na}^+} + r_{\text{Cl}^-}}$$

$$\frac{r_{\text{K}^+} + r_{\text{Cl}^-}}{r_{\text{Na}^+} + r_{\text{Cl}^-}} = 1.122]$$

18. 8:8 coordination of CsCl is found to change into 6:6 coordination:

(a) on increasing the pressure  
 (b) on increasing the temperature  
 (c) on decreasing the pressure  
 (d) on decreasing the temperature

19. An alloy of Cu, Ag and Au is found to have copper constituting ccp lattice. If silver atoms occupy the edge-centres and gold is present at body-centre, the alloy has the formula:

(a) Cu<sub>4</sub>Ag<sub>2</sub>Au      (b) Cu<sub>4</sub>Ag<sub>4</sub>Au  
 (c) Cu<sub>4</sub>Ag<sub>3</sub>Au      (d) CuAgAu

[Hint: In ccp arrangement, Cu atoms occupy the corners and face-centres.

$$\therefore \text{Number of Cu atoms} = 8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$$

$$\text{Number of silver atoms} = \text{Number of edge-centres} \times \frac{1}{4}$$

$$= 12 \times \frac{1}{4} = 3$$

Number of gold atoms = 1 (at body-centre)

$$\therefore \text{Formula of alloy} = \text{Cu}_4\text{Ag}_3\text{Au}]$$

20. The anions (A) form hexagonal closest packing and atoms (M) occupy only two-third of octahedral voids in it; then the general formula of the compound is:

(a) MA      (b) A<sub>2</sub>      (c) M<sub>2</sub>A<sub>3</sub>      (d) M<sub>3</sub>A<sub>2</sub>

21. In a face-centred cubic of  $A$  and  $B$ -atoms in which  $A$  atoms are at the corners of the unit cell and  $B$ -atoms at the face-centres, one of the  $A$ -atoms is missing from one corner in unit cell. The simplest formula of the compound is:

(a)  $A_7B_3$     (b)  $AB_3$     (c)  $A_7B_{24}$     (d)  $A_8B_{21}$

[Hint: Number of  $A$  atoms =  $\frac{1}{8} \times 7 = \frac{7}{8}$

Number of  $B$  atoms =  $6 \times \frac{1}{2} = 3$

$$A : B = \frac{7}{8} : 3 = 7 : 24$$

Molecular formula =  $A_7B_{24}$ ]

22. Select the incorrect statement(s):

- (a) Schottky defect is not shown by  $CsCl$   
 (b) Frenkel defect is shown by  $ZnS$   
 (c) hcp and ccp structures have different coordination numbers  
 (d) at high pressure, the coordination number increases

23. Select the incorrect statement:

(a) In  $CsCl$  unit cell,  $r_{Cs^+} + r_{Cl^-} = \frac{\sqrt{3}}{2} l$

(b) In  $NaCl$  unit cell,  $r_{Na^+} + r_{Cl^-} = \frac{l}{2}$

(c) In  $CsCl$  unit cell, 68% space is void

(d) In  $NaCl$  unit cell, 26% space is void

24. The ionic radii of  $Rb^+$  and  $I^-$  are 1.46 and 2.16 Å respectively. The most probable type of structure exhibited by it is:

- (a)  $CsCl$     (b)  $NaCl$     (c)  $ZnS$     (d)  $CaF_2$

25. Perovskite is a mineral with the formula  $CaTiO_3$ . Which of the positive ions in the crystal is more likely to be packed in the octahedral holes?

- (a)  $Ti^{4+}$     (b)  $Ti^{2+}$     (c)  $Ca^{2+}$     (d)  $O_2^+$

26. Which of the following is incorrect? [BHU (Screening) 2008]

- (a) A real gas behaves like ideal gas over a wide range of pressure (~ 100 atm) at Boyle point  
 (b) A real gas behaves like an ideal gas over a wide range of pressure (~ 100 atm) at critical temperature of the gas.

(c)  $\left(\frac{\partial U}{\partial V}\right)_T = 0$  for an ideal gas

(d)  $\left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{V^2}$  for a real gas obeying van der Waal's equation

[... : A real gas cannot behave like ideal gas at critical temperature.]

27. The number of atoms in 100 g of an fcc crystal with density  $d = 10 \text{ g/cm}^3$  and cell edge as 200 pm is equal to:

- (a)  $3 \times 10^{25}$     (b)  $5 \times 10^{24}$     (c)  $1 \times 10^{25}$     (d)  $2 \times 10^{25}$

28. In a ccp structure, the:

- (a) first and third layers are repeated  
 (b) first and fourth layers are repeated  
 (c) second and fourth layers are repeated  
 (d) first, third and sixth layers are repeated

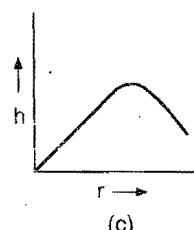
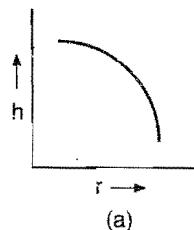
29. Which of the following compounds represents an inverse 2:3 spinel structure?

- (a)  $Fe^{III}[Fe^{II}Fe^{III}]O_4$     (b)  $PbO_2$   
 (c)  $Al_2O_3$     (d)  $Mn_3O_4$

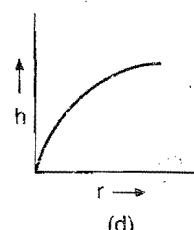
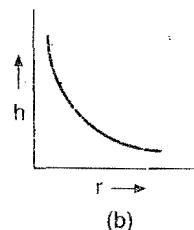
30. A solid solution of  $CdBr_2$  in  $AgBr$  contains:

- (a) Schottky defects  
 (b) Frenkel defects  
 (c) Colour centres  
 (d) Frenkel as well as Schottky defects

31. Which of the following correctly represents the relation between capillary rise ' $h$ ' and capillary radius ' $r$ '?



(a)



(b)

[Hint: Capillary rise decreases with increase in the radius of tube.]

32. There is a depression in the surface of the liquid in a capillary when:

- (a) the cohesive force is smaller than the adhesive force  
 (b) the cohesive force is greater than the adhesive force  
 (c) the cohesive and adhesive forces are equal  
 (d) none of the above is true

[Hint: Depression in the surface takes place when intermolecular attraction force of liquid called cohesive force dominates the force of attraction between the liquid and the capillary called adhesive force.]

33. Surface tension does not vary with:

- (a) temperature    (b) vapour pressure  
 (c) the size of surface    (d) concentration

34. Which among the following has the least surface tension?

- (a) Benzene    (b) Acetic acid  
 (c) Diethyl ether    (d) Chlorobenzene

35. The SI unit of the coefficient of viscosity is:

- (a)  $N \text{ s}^{-1} \text{ m}^{-1}$     (b)  $N \text{ s m}^{-2}$     (c)  $N \text{ s}^{-2} \text{ m}^{-2}$     (d)  $N \text{ s}^{-1} \text{ m}^{-2}$

36. Compressibility factor for a gas under critical condition is:

- (a) 3/8    (b) 8/3    (c) 1    (d) 1/4

[Hint:  $P_c V_c = \frac{3}{8} R T_c$

$$Z = \frac{P_c V_c}{R T_c} = \frac{3}{8}$$

37. Critical temperature of  $H_2O$  is greater than that of  $O_2$  because  $H_2O$  molecules have:  
 (a) greater dipole moment  
 (b) V-shape  
 (c) lesser number of electrons  
 (d) it has only sigma bonds

38. For van der Waals' constants 'a' and 'b', the unit of the ratio  $\frac{a}{b}$  will be:

- (a) atm litre<sup>-1</sup>  
 (b) litre-atm mol<sup>-1</sup>  
 (c) litre-atm mol<sup>-2</sup>  
 (d) litre mol<sup>-1</sup>

[Hint:  $P_{\text{correction}} = \frac{an^2}{V^2}$  Unit of  $a = \text{atm litre}^2 \text{ mol}^{-2}$

$V_{\text{correction}} = nb$  Unit of  $b = \text{litre mol}^{-1}$

Unit of  $\left(\frac{a}{b}\right) = \frac{\text{atm litre}^2 \text{ mol}^{-2}}{\text{litre mol}^{-1}}$   
 $= \text{atm litre mol}^{-1}$ ]

39. Select the correct order of the following temperatures:

Boyle temp. Critical temp. Inversion temp.  
 (A) (B) (C)

- (a)  $A > C > B$   
 (b)  $B > A > C$   
 (c)  $A > B > C$   
 (d)  $C > A > B$

[Hint:  $T_B$  (Boyle temp.) =  $\frac{a}{R_b}$ ;  $T_i$  (Inversion temp.) =  $\frac{2a}{R_b}$

$T_c$  (Critical temp.) =  $\frac{8a}{27Rb}$

$\therefore T_i > T_B > T_c$ ]

40. The gas equation for a real gas is:

$P(V - b) = RT$

Here, the parameter 'b' is van der Waals' constant. The graph of pressure against temperature (isochore) will give straight line of slope:

- (a) zero (b)  $\frac{R}{(V - b)}$  (c)  $R/P$  (d) negative

41. A crystalline solid is made of X, Y and Z elements. Atoms of X form fcc packing; atoms of Y occupy octahedral voids while atoms of Z occupy tetrahedral voids. What will be the simplest formula of solid if atoms along one body diagonal are removed?

- (a)  $X_5Y_4Z_8$  (b)  $XYZ$  (c)  $X_8Y_4Z_5$  (d)  $X_2YZ$

[Hint : Number of atoms of X (at packing site, i.e., at corners and face-centres)]

$$= 8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$$

Number of atoms of Y = 4

Number of atoms of Z = 8

Along one body diagonal there will be two X atoms, one Y atom and two Z atoms are found and are removed.

Number of atoms of X will be =  $4 - \frac{1}{8} \times 2 = \frac{15}{4}$

Number of atoms of Y will be =  $4 - 1 = 3$

Number of atoms of Z will be =  $8 - 2 = 6$

$X : Y : Z$

$$\frac{15}{4} : 3 : 6$$

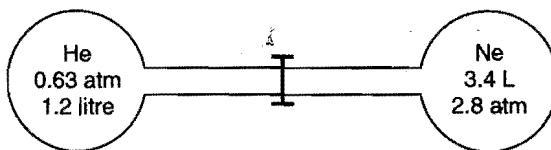
$$5 : 4 : 8$$

∴ Simplest formula will be  $X_5Y_4Z_8$ ]

42. Which of the following pattern has void fraction of 0.26?

- (a) AAAA... (b) ABABAB...  
 (c) ABCABCABC... (d) ABCCBAABC...

43. Two gas bulbs are connected by a thin tube. Calculate the partial pressure of helium after the connective valve is opened at a constant temperature of 27°C :



- (a) 1 atm (b) 0.328 atm (c) 1.64 atm (d) 0.166 atm

[Hint :  $n_{He} = \frac{PV}{RT} = \frac{0.63 \times 1.2}{0.0821 \times 300} = 0.03$

$$n_{Ne} = \frac{2.8 \times 3.4}{0.0821 \times 300} = 0.39$$

$$x_{He} = \frac{n_{He}}{n_{He} + n_{Ne}} = \frac{0.03}{0.03 + 0.39} = 0.0714$$

Total pressure after connecting the bulbs will be :

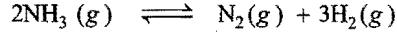
$$P_1V_1 + P_2V_2 = P_R(V_1 + V_2)$$

$$0.63 \times 1.2 + 2.8 \times 3.4 = P_R(1.2 + 3.4)$$

$$P_R = 2.33 \text{ atm}$$

$$P_{He} = x_{He} \times P_R = 0.0714 \times 2.33 = 0.166 \text{ atm}]$$

44. Ammonia gas at 76 cm Hg pressure was connected to a manometer. After sparking in the flask, ammonia is partially dissociated as follows:



the level in the mercury column of the manometer was found to show the difference of 18 cm. What is the partial pressure of  $\text{H}_2(g)$  at equilibrium?

- (a) 18 cm Hg (b) 9 cm Hg  
 (c) 27 cm Hg (d) 24 cm Hg.

[Hint :  $2\text{NH}_3(g) \rightleftharpoons \text{N}_2(g) + 3\text{H}_2(g)$

$t_0$	76	0	0
$t_{eq}$	76 - 2x	x	3x

$$\text{Total pressure after dissociation} = 76 - 2x + x + 3x = 76 + 2x$$

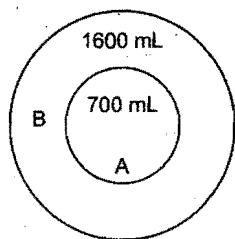
$$\text{Increase in pressure} = 2x = 18$$

$$x = 9 \text{ cm.}$$

$$\text{Partial pressure of H}_2 = 3x = 27 \text{ cm.}$$

45. Two balloons A and B are taken at 300K. Maximum capacity of balloon A and balloon B are 800 mL and 1800 mL respectively. When the balloon system is heated; which one will burst first?

- (a) Inner balloon (A)  
 (b) Outer balloon (B)  
 (c) Both balloons simultaneously  
 (d) Cannot be predicted



[Hint : For balloon A :

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$\frac{700}{300} = \frac{800}{T_2}$$

$$T_2 = 342.85 \text{ K}$$

For balloon B :

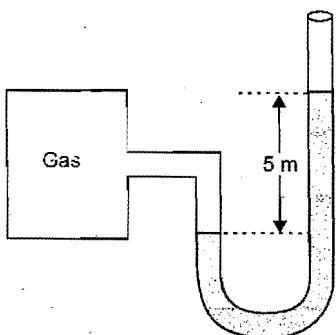
$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$\frac{1600}{300} = \frac{1800}{T_2}$$

$$T_2 = 337.5 \text{ K}$$

Thus, outer balloon B will burst first.]

46.



A gas jar of 10 litre volume filled with O<sub>2</sub> at 300 K is connected to glycerine manometer. The manometer shows 5 m difference in the level as shown in figure. What will be the number of moles of O<sub>2</sub> in the gas jar?

(Give d<sub>glycerine</sub> = 2.72 g/mL; d<sub>mercury</sub> = 13.6 g/mL).

- (a) 0.64 mol (b) 0.4 mol (c) 0.94 mol (d) 0.36 mol

[Hint : (h × d × g)<sub>Hg</sub> = (h × d × g)<sub>glycerine</sub>

$$(h \times 13.6)_{\text{Hg}} = (5 \times 2.72)_{\text{glycerine}}$$

$$h_{\text{Hg}} = 1 \text{ m}$$

$$P_{\text{gas}} = (1 + 0.76) \text{ m}$$

$$= 1760 \text{ mm Hg}$$

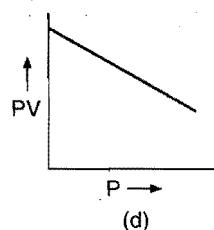
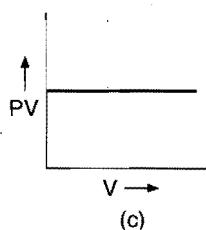
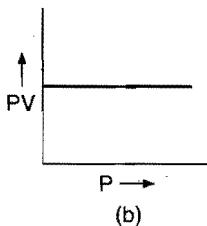
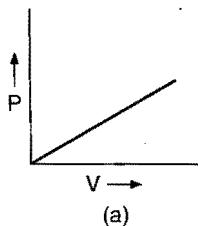
$$PV = nRT$$

$$\frac{1760}{760} \times 10 = n \times 0.0821 \times 300$$

$$n = 0.94 \text{ mol}]$$

**Following questions may have more than one correct options:**

1. Which of the following graphs represent Boyle's law?



2. Which of the following equation(s) is/are correct on the basis of ideal gas equation?

- (a)  $PV = \frac{N}{N_A} RT$  (b)  $PV = Nk_B T$   
 (c)  $PV = \frac{d}{m} RT$  (d)  $PV = dRT$

where,  $N$  = number of molecules,  $N_A$  = Avogadro's number,  $k_B$  = Boltzmann constant

3. A gas can be easily liquefied:

- (a) when its inversion temperature equals the Boyle's temperature  
 (b) under reversible adiabatic expansion  
 (c) under pressure when it is cooled below the critical temperature  
 (d) at low pressure and above critical temperature

[Hint: (i) Reversible adiabatic expansion lowers the temperature hence facilitates the liquefaction of gas. (ii) A gas can be liquefied below the critical temperature by increasing the pressure.]

4. Which of the following quantities are same for all ideal gases at the same temperature?

- (a) The kinetic energy of 1 mole  
 (b) The kinetic energy of 1 g  
 (c) The number of molecules in 1 mole  
 (d) The number of molecules in 1 g

[Hint: (i) 1 mole of a gas always contains  $6.023 \times 10^{23}$  molecules.

(ii) Kinetic energy of ideal gases depends only on temperature.]

5. Which of the following statements are correct?

- (a) Helium diffuses at a rate 8.65 times as much as CO does  
 (b) Helium diffuses at a rate 2.65 times as fast as CO does  
 (c) Helium diffuses at a rate of 4 times faster than CO<sub>2</sub>  
 (d) Helium diffuses at a rate 4 times as fast as SO<sub>2</sub> does

6. The viscosity of a liquid molecule depends on:

- (a) the volume of the liquid  
 (b) the temperature of the liquid  
 (c) the surface area of the liquid  
 (d) the structure of the molecule

7. Viscosity is the property of:

- (a) liquids (b) gases (c) solids (d) all of these

8. Which of the following crystals have 6:6 coordination?

- (a) NH<sub>4</sub>I (b) MgO (c) MnO (d) ZnS

9. Which of the following compounds represent a normal 2:3 spinel structure?

- (a) Mg<sup>II</sup> Al<sup>III</sup><sub>2</sub>O<sub>4</sub> (b) Co<sup>II</sup> (Co<sup>III</sup>)<sub>2</sub>O<sub>4</sub>  
 (c) Zn(TiZn) O<sub>4</sub> (d) Ni(CO)<sub>4</sub>

10. Which type of crystals contain only one Bravais lattice?

- (a) Hexagonal (b) Triclinic  
 (c) Rhombohedral (d) Monoclinic

11. At which temperature, is a ferrimagnetic solid converted to a ferromagnetic solid?

- (a) 850 K (b) 300 K (c) 400 K (d) 600 K
12. In NaCl structure, all the:  
 (a) octahedral sites are occupied  
 (b) tetrahedral sites are unoccupied  
 (c) octahedral as well as tetrahedral sites are unoccupied  
 (d) octahedral as well as tetrahedral sites are occupied
13. The density of a certain solid  $AB$  (formula mass = 119) is 2.75 g/cm<sup>3</sup>. The edge of the unit cell is 654 pm long. What is/are true about the solid  $AB$ ?  
 (a) It has bcc unit cell  
 (b) There are four constituents per unit cell  
 (c) Unit cell constituted by anion is fcc  
 (d) Structure is similar to ZnS

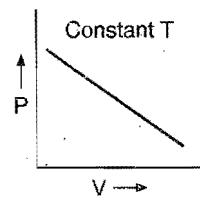
**[Hint:**

$$Z = \frac{a^3 \times d \times N}{M}$$

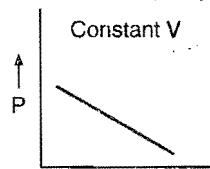
$$= \frac{(654 \times 10^{-10})^3 \times 2.75 \times 6.023 \times 10^{23}}{119} = 4$$

14. The unit cell of a crystalline solid is bounded by  $f$  (faces),  $e$  (edges) and  $c$  (interfacial angle). Which of the following relations is correct?  
 (a)  $f + e = c + 2$  (b)  $f + c = e + 2$   
 (c)  $c + e = f + 2$  (d) None of these

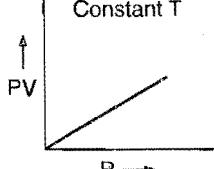
15. Which of the following diagrams correctly describes the behaviour of a fixed mass of an ideal gas? ( $T$  is measured in K)  
**[PMT (Kerala) 2007; CMS Vellore (Med.) 2008; CET (Punjab) 2008]**



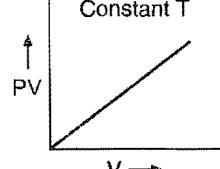
(a)



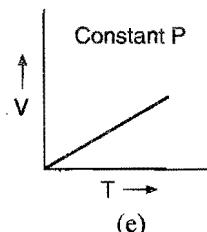
(b)



(c)



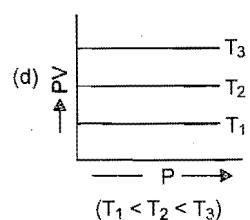
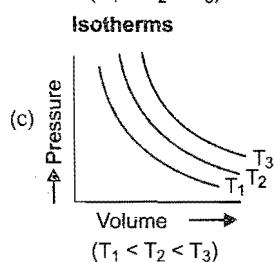
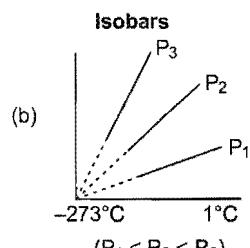
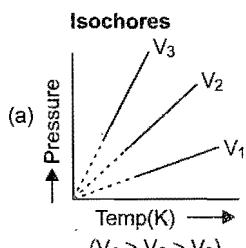
(d)



(e)

16. Molar mass of Ne atom is ten times of H<sub>2</sub> molecule. Which of the following statement is/are true?  
 (a) Both these gases have same Kinetic Energy at 27°C  
 (b) H<sub>2</sub> molecule will travel 10 times faster than Ne atom at same temperature  
 (c) Pressure of 1 mol Ne atom and 1 mole H<sub>2</sub> molecules will be same  
 (d) Ten mole of H<sub>2</sub> and 1 mole of Ne will have same volume at a temperature of 27°C

17. Select the correct conditions indicated below the following plots:



## Answers

### • Single correct option

- |         |         |         |         |         |            |         |         |
|---------|---------|---------|---------|---------|------------|---------|---------|
| 1. (d)  | 2. (a)  | 3. (c)  | 4. (c)  | 5. (a)  | 6. (d)     | 7. (b)  | 8. (d)  |
| 9. (a)  | 10. (c) | 11. (a) | 12. (c) | 13. (d) | 14. (b)    | 15. (c) | 16. (d) |
| 17. (a) | 18. (b) | 19. (c) | 20. (c) | 21. (c) | 22. (a, c) | 23. (c) | 24. (b) |
| 25. (a) | 26. (c) | 27. (b) | 28. (b) | 29. (a) | 30. (d)    | 31. (b) | 32. (b) |
| 33. (c) | 34. (c) | 35. (b) | 36. (a) | 37. (a) | 38. (b)    | 39. (d) | 40. (b) |
| 41. (a) | 42. (c) | 43. (d) | 44. (c) | 45. (b) | 46. (c)    |         |         |

### • One or more than one correct options

- |               |               |           |            |            |           |           |               |
|---------------|---------------|-----------|------------|------------|-----------|-----------|---------------|
| 1. (b, c)     | 2. (a, b)     | 3. (b, c) | 4. (a, c)  | 5. (a, d)  | 6. (b, d) | 7. (a, b) | 8. (a, b)     |
| 9. (a, b)     | 10. (a, b, c) | 11. (a)   | 12. (a, b) | 13. (b, c) | 14. (b)   | 15. (e)   | 16. (a, b, c) |
| 17. (a, c, d) |               |           |            |            |           |           |               |

## Integer Answer TYPE QUESTIONS

This section contains 14 questions. The answer to each of the questions is a single digit integer, ranging from 0 to 9. If the correct answers to question numbers X, Y, Z and W (say) are 6, 0, 9 and 2 respectively, then the correct darkening of bubbles will look like the given figure :

X	Y	Z	W
①	②	③	④
①	①	①	①
②	②	②	②
③	③	③	③
④	④	④	④
⑤	⑤	⑤	⑤
⑥	⑥	⑥	⑥
⑦	⑦	⑦	⑦
⑧	⑧	⑧	⑧
⑨	⑨	⑨	⑨

1. A substance  $AxBy$  crystallises in a face centred cubic lattice. Atoms 'A' occupy each corner of unit cell and atoms of 'B' occupy centre of each face of the cube. Total number of atoms of A and B in one unit cell will be .....
2. In KBr crystal structure, the number of second nearest neighbour of  $K^+$  ions are .....
3. Density of lithium atom is  $0.53 \text{ g/cm}^3$ . The edge length of Li is  $3.5 \text{ \AA}$ . The number of lithium atoms in a unit cell will be ..... (Atomic mass of lithium is 6.94)
4. A cubic solid is made up of two elements P and Q. Atoms of Q are present at the corners of the cube and atoms of P at the body centre. The coordination number of P and Q will be .....
5. If there are 3 moles of atoms present in the packing of pattern ABC ABC ABC ..... The number of moles of tetrahedral voids is equal to .....
6. The number of atoms in HCP unit cell is .....
7. How many effective  $\text{Na}^+$  ions are present in rock salt  $\text{NaCl}$ ? If ions along one axis joining opposite faces are removed?
8. How many moles of  $\text{SO}_2$  will occupy a volume of 10 litre at a pressure of 15 atm and temperature 624 K? ( $a = 6.71 \text{ atm L}^2 \text{ mol}^{-2}$ ;  $b = 0.0564 \text{ litre mol}^{-1}$ )

9. 3.2 g of oxygen and 0.2 g of hydrogen are placed in 1.12 litre flask at  $0^\circ\text{C}$ . The total pressure in atm of the gas mixture will be.....
10. A mixture of non reacting gases exert a pressure of 5 atm. If one of the gases occupy 40% volume of the mixture, what would be its partial pressure in atm?
11. A gas is found to have the formula  $(\text{C}_3\text{O}_2)_n$ . Its vapour density is 34. The value of  $n$  will be .....
12. The weight of hydrogen gas obtained from 42 g of  $\text{CaH}_2$  by treatment with water is ..... gm.
13. The stop cock containing two bulbs of volume 5 litre and 10 litre containing an ideal gas at 9 atm and 60 atm respectively is opened. What is the final pressure in atm if the temperature remains the same?
14. At 400 K, the root mean square (rms) speed of gas X (molecular mass = 40) is equal to the most probable speed of gas Y at 60 K. The molecular mass of the gas Y is .....

(IIT 2009)

[Hint :  $\left(\sqrt{\frac{3RT}{m}}\right)_X = \left(\sqrt{\frac{2RT}{m}}\right)_Y$

$$\sqrt{\frac{3R400}{40}} = \sqrt{\frac{2R60}{m}}$$

$$\sqrt{30} = \sqrt{\frac{4 \times 30}{m}}$$

$$m = 4 ]$$

### Answers

- |        |         |         |         |         |         |        |        |
|--------|---------|---------|---------|---------|---------|--------|--------|
| 1. (4) | 2. (12) | 3. (2)  | 4. (8)  | 5. (6)  | 6. (6)  | 7. (3) | 8. (3) |
| 9. (4) | 10. (2) | 11. (1) | 12. (4) | 13. (7) | 14. (4) |        |        |

## LINKED COMPREHENSION TYPE QUESTIONS

### ● Passage 1

The gases which strictly follow the general equation ( $PV = nRT$ ) are called ideal or perfect gases. Actually, there is no gas which is perfect or ideal. A real gas is one which actually exists, whether it obeys gas laws strictly or not. Under ordinary conditions, only those gases nearly behave as ideal or perfect which have very low boiling points such as nitrogen, hydrogen, etc. The most easily liquefiable and highly soluble gases such as ammonia, carbon dioxide, sulphur dioxide show large deviations.

A very convenient method of studying deviation of real gases from ideal behaviour is through a compressibility factor ( $Z$ ).

$$Z = \frac{PV}{nRT}$$

(i)  $Z = 1$ , for ideal gases.

(ii)  $Z \neq 1$ , for real gases.

### Answer the following questions:

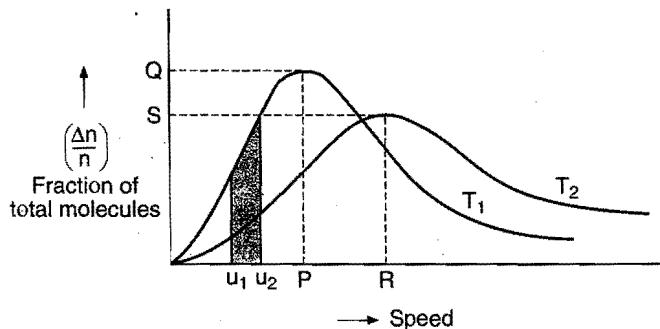
- Consider the equation  $Z = \frac{PV}{nRT}$ ; which of the following statements is correct?
  - When  $Z > 1$ , real gases are easier to compress than the ideal gas
  - When  $Z = 1$ , real gases get compressed easily
  - When  $Z > 1$ , real gases are difficult to compress
  - When  $Z = 1$ , real gases are difficult to compress
- The compressibility of a gas is less than unity at STP, therefore:
  - $V_m > 22.4 \text{ L}$
  - $V_m < 22.4 \text{ L}$
  - $V_m = 22.4 \text{ L}$
  - $V_m = 44.8 \text{ L}$
- At low pressure, the van der Waals' equation is reduced to:
  - $Z = \frac{PV_m}{RT} = 1 - \frac{aP}{RT}$
  - $Z = \frac{PV_m}{RT} = 1 + \frac{bP}{RT}$
  - $PV_m = RT$
  - $Z = \frac{PV_m}{RT} = 1 - \frac{a}{RT}$
- At Boyle's temperature, compressibility factor  $Z$  for a real gas is:
  - $Z = 1$
  - $Z = 0$
  - $Z > 1$
  - $Z < 1$

[Hint: At Boyle's temperature, the real gas behaves like an ideal gas.]
- The behaviour of a real gas is usually depicted by plotting compressibility factor  $Z$  versus pressure  $P$  at a constant temperature. At high temperature and pressure,  $Z$  is usually more than one. This fact can be explained by van der Waals' equation when:
  - the constant ' $a$ ' is negligible but not ' $b$ '
  - the constant ' $b$ ' is negligible but not ' $a$ '
  - both the constants ' $a$ ' and ' $b$ ' are negligible
  - both the constants ' $a$ ' and ' $b$ ' are not negligible
- The units of compressibility factor are:
  - $\text{atm L}^{-1}$
  - $\text{atm}^{-1}$
  - $\text{L}^{-1}$
  - unitless

### ● Passage 2

The gas molecules randomly move in all directions and collide with each other and with the wall of the container. It is difficult to determine the speed of an individual molecule but it has become possible to work out the distribution of molecules among different molecular speeds. This is known as Maxwell Boltzmann distribution.

Consider the following graph about Maxwell's distribution of speeds at two different temperatures  $T_1$  and  $T_2$ :



### Answer the following questions:

- In the above graph the point 'P' refers to:
  - root mean square speed at  $T_1$
  - average speed at  $T_1$
  - most probable speed at  $T_1$
  - highest possible speed at  $T_1$
- The shaded area represents:
  - number of molecules having speed between  $u_1$  and  $u_2$
  - number of molecules having speed less than the most probable speed
  - number of molecules having  $v_{rms}$  at  $T_1$
  - fraction of total molecules having average speed
- The point  $Q$  refers to:
  - number of molecules with speed at  $P$
  - fraction of total molecules with speed at  $P$
  - root mean square speed
  - total kinetic energy of molecules at  $P$
- Relation between  $T_1$  and  $T_2$  is:
  - $T_1 = T_2$
  - $T_1 > T_2$
  - $T_1 < T_2$
  - cannot be predicted
- Total area under the curve at  $T_1$  is:
  - equal to that under curve at  $T_2$
  - less than that under curve at  $T_2$
  - greater than that under curve at  $T_2$
  - can be greater or less than that under curve at  $T_2$ , depending on the nature of the gas
- Select the correct statement(s):
  - Most probable speed increases with increase in temperature
  - Fraction of total molecules with most probable velocity decreases with increase in temperature
  - Area under the curve increases with increase in the temperature
  - none of the above

7. The curve has which of the following characteristics?
- It has symmetrical distribution of molecules against molecular velocity.
  - The area under the curve gives the total number of molecules.
  - The maxima of the curve shifts towards right as the temperature is raised.
  - The area under the curve is independent of temperature.
- Select the correct statements from the codes given below:
- |                          |                         |
|--------------------------|-------------------------|
| (a) (i), (ii)            | (b) (i), (ii) and (iii) |
| (c) (ii), (iii) and (iv) | (d) all are correct     |

### ● Passage 3

The essential conditions for liquefaction of gases were discovered by Andrews in 1869 as a result of his study of pressure-volume-temperature relationship for  $\text{CO}_2$ . It was found that above a certain temperature, it was impossible to liquefy a gas whatever the pressure was applied. The temperature below which the gas can be liquefied by the application of pressure alone is called critical temperature ( $T_c$ ). The pressure required to liquefy a gas at this temperature is called the critical pressure ( $P_c$ ). The volume occupied by one mole of the substance at the critical temperature and pressure is called critical volume. Critical constants are related with van der Waals' constant as follows:

$$V_c = 3b, \quad P_c = \frac{a}{27b^2}, \quad T_c = \frac{8a}{27Rb}$$

#### Answer the following questions

- The relationship between  $P_c$ ,  $V_c$  and  $T_c$  is:
  - $P_c V_c = RT$
  - $P_c V_c = 3RT_c$
  - $P_c V_c = \frac{3}{5}RT_c$
  - $P_c V_c = \frac{3}{8}RT_c$
- Which of the following parameters is three times the van der Waals' constant ' $b$ '?
  - Critical volume
  - Critical temperature
  - Vapour density
  - Critical pressure
- The critical temperature of:
  - a substance means the temperature above which the substance is in vapour form
  - a gas is the temperature below which it can be liquefied by application of pressure
  - water is  $100^\circ\text{C}$
  - none of the above
- The pressure required to liquefy a gas at the critical temperature is called:
  - reduced pressure
  - critical pressure
  - vapour pressure
  - atmospheric pressure
- Gases **A** **B** **C** **D**  
 $P_c$  (atm) 2.2 14 35 45  
 $T_c$  (K) 5.1 33 127 140  
 Which of the above gases cannot be liquefied at 100 K and 50 atm?
  - $D$  only
  - $A$  only
  - $A$  and  $B$
  - $C$  and  $D$
- At critical point, the meniscus between liquid and vapour disappears due to:

- (a) zero refractive index      (b) zero surface tension  
 (c) zero viscosity      (d) zero critical temperature
- Gas  $A$  can be liquefied at room temperature by applying pressure but gas  $B$  cannot. This reflects:
  - critical temperature of  $B$  is less than that of  $A$
  - critical temperature of  $B$  is greater than that of  $A$
  - $A$  and  $B$  have critical temperature greater than room temperature
  - critical temperatures of both are equal
- The values of critical volumes of four gases  $A$ ,  $B$ ,  $C$  and  $D$  are 0.025 L, 0.312 L, 0.245 L and 0.432 L respectively. The gas with larger diameter will be:
 

(a) $A$	(b) $D$
(c) $B$	(d) $C$

[Hint:  $V_c = 3b = 3 \times 4N \times \frac{4}{3}\pi r^3$ ]

### ● Passage 4

Kinetic theory of gases is a generalization offered by Maxwell, Boltzmann, Clausius, etc., to explain the behaviour of ideal gases. This theory assumes that ideal gas molecules neither attract nor repel each other. Average kinetic energy of gas molecules is directly proportional to the absolute temperature. A gas equation called kinetic gas equation was derived on the basis of kinetic theory.

$$PV = \frac{1}{3}mnv^2$$

#### Answer the following questions

- |          |                         |
|----------|-------------------------|
| 1. Gas   | Density                 |
| <i>A</i> | $0.82 \text{ g L}^{-1}$ |
| <i>B</i> | $0.26 \text{ g L}^{-1}$ |
| <i>C</i> | $0.51 \text{ g L}^{-1}$ |
- Pick up the correct statement/statements:
- gas  $A$  will tend to lie at the bottom.
  - the number of atoms of various gases  $A$ ,  $B$  and  $C$  are same.
  - the gases will diffuse to form homogeneous mixture.
  - average kinetic energy of each gas is same.
  - (a) 2, 3      (b) 1, 4      (c) 1      (d) 3, 4
2. Select the incorrect statement(s) about the real gases:
- The molecules attract each other.
  - They show deviation from Boyle's and Charles' law.
  - Volume of gas molecules are negligible.
  - The molecules have negligible mass.
  - (a) 2, 3      (b) 1, 4      (c) 1      (d) 3, 4
3. The average kinetic energy per molecule of an ideal gas is equal to:
- $0.5 \text{ kJ}$
  - $0.5RT$
  - $1.5kT$
  - $1.5RT^2$
4. Which of the following do not pertain to the postulates of kinetic theory of gases?
- The gas molecules are perfectly elastic
  - Speed of gas molecules are ever changing
  - Pressure exerted by the gas is due to the collision of molecules with the walls of the container
  - Kinetic energy of a gas is given by the sum of 273 and temperature in Celsius scale

# SELF ASSESSMENT

## ASSIGNMENT NO. 4

### SECTION-I

#### Straight Objective Type Questions

This section contains 14 multiple choice questions. Each question has 4 choices (a), (b), (c) and (d), out of which only one is correct.

1. Boyle's temperature of four gases are given below:

Gases	A	B	C	D
$T_B$	120 K	25 K	500 K	410 K

which gas can be liquified most easily?

- (a) A      (b) B      (c) C      (d) D
2. A gas is enclosed in a vessel of volume  $V$  at temperature  $T_1$  and pressure  $P$ ; the vessel is connected to another vessel of volume  $V/2$  by a tube and a stop cock. The second vessel is initially evacuated. If the stop cock is opened, the temperature of second vessel becomes  $T_2$ . The first vessel is maintained at a temperature  $T_1$ . What is the final pressure  $P_1$  in the apparatus?
- (a)  $\frac{2PT_2}{2T_2 + T_1}$     (b)  $\frac{2PT_2}{T_2 + 2T_1}$     (c)  $\frac{PT_2}{2T_2 + T_1}$     (d)  $\frac{2PT_2}{T_1 + T_2}$
3. The ratio of rate of diffusion of gases A and B is 1 : 4. If the ratio of their masses present in the mixture is 2 : 3, what is the ratio of their mole fraction?

- (a)  $\frac{1}{8}$     (b)  $\frac{1}{12}$     (c)  $\frac{1}{16}$     (d)  $\frac{1}{24}$

4. Density of a gas at STP is 2 g / L while the expected density is 1.8 g / L assuming its ideal behaviour. Then:
- (a) gas behaves ideally  
 (b) forces of attraction are dominant among gas molecules  
 (c) forces of repulsion are dominant among gas molecules  
 (d) none of the above

5. In a crystalline solid, anions B are arranged in CCP lattice and cations A occupy 50% of the octahedral voids and 50% of the tetrahedral voids. What is the formula of the solid?
- (a) AB    (b)  $A_3B_2$     (c)  $A_2B_2$     (d)  $A_2B_3$

6. In a compound  $XY_2O_4$ , oxide ions are arranged in CCP and cations X are present in octahedral voids. Cations Y are equally distributed among octahedral and tetrahedral voids. The fraction of the octahedral voids occupied is:

- (a)  $\frac{1}{4}$     (b)  $\frac{1}{2}$     (c)  $\frac{1}{6}$     (d)  $\frac{1}{8}$

7. An ideal gas:
- (a) can be liquefied if its temperature is more than critical temperature  
 (b) can be liquefied if its pressure is more than critical pressure  
 (c) cannot be liquefied at any pressure and temperature  
 (d) can be liquefied if its temperature is more than Boyle's temperature

8. A mineral is made of calcium, titanium and oxygen  $Ca^{2+}$  ions located at corners,  $Ti^{4+}$  ions at the body-centre and  $O^{2-}$  ions at face-centres of the unit cell. The molecular formula of the mineral is.....

- (a)  $CaTi_3O_4$     (b)  $CaTiO_3$     (c)  $CaTiO_2$     (d)  $CaTi_2O_3$

9. If the graph is plotted for 1 mol gas in such a way that  $PV$  is plotted against  $P$  then intercept of the graph for real gas will be:

- (a)  $RT + Pb + a$     (b)  $RT$   
 (c)  $RT - Pb + a$     (d)  $RT + Pb + ab + a$

10. The ratio of Boyle's temperature and critical temperature for a gas is:

- (a)  $\frac{8}{27}$     (b)  $\frac{27}{8}$     (c)  $\frac{1}{2}$     (d)  $\frac{2}{1}$

11. With which of the following elements silicon should be doped so as to give p-type semiconductor? [CBSE (PMT) 2008]

- (a) Selenium    (b) Boron    (c) Germanium    (d) Arsenic

12. Total volume of atoms present in a face centred cubic unit cell of a metal is ( $r$  is atomic radius): [JIPMER 2008]

- (a)  $\frac{16}{3}\pi r^3$     (b)  $\frac{20}{3}\pi r^3$     (c)  $\frac{24}{3}\pi r^3$     (d)  $\frac{12}{3}\pi r^3$

13. How many effective  $Na^+$  and  $Cl^-$  ions are present respectively in the rocksalt ( $NaCl$ ). If ions along the axis joining opposite faces are removed?

- (a)  $4, \frac{7}{2}$     (b)  $\frac{7}{2}, \frac{7}{2}$     (c)  $\frac{7}{2}, 4$     (d) 3, 3

14. Kinetic energy and pressure of a gas of unit mole are related as :

- (a)  $P = 2E$     (b)  $P = \frac{2}{3}E$     (c)  $P = \frac{3}{2}E$     (d)  $P = \frac{E}{2}$

### SECTION-II

#### Multiple Answers Type Objective Questions

15. Which of the following measure the deviation from ideal behaviour of gas?

- (a) Collision diameter    (b) Collision frequency  
 (c) Compressibility factor    (d) van der Waals' constant 'a'

16. In face-centred cubic unit cell:

- (a) face diagonal of the cube is  $a\sqrt{2}$  or  $4r$   
 ( $a$  = edge length,  $r$  = radius of constituent units)  
 (b) effective number of atoms in the unit cell is 4  
 (c) 8 tetrahedral voids per unit cell  
 (d) rank of the unit cell is 3

17. Which of the following mixtures of gases at room temperature follow Dalton's law of partial pressures?

- (a) NO and O<sub>2</sub>    (b) CO and CO<sub>2</sub>  
 (c) NH<sub>3</sub> and HCl    (d) SO<sub>2</sub> and O<sub>2</sub>

18. A real gas can be liquefied:

- (a) under adiabatic expansion  
 (b) above critical temperature  
 (c) when cooled below critical temperature under applied pressure  
 (d) at temperature lower than critical temperature and pressure higher than critical pressure

19. Which of the following statements is (are) correct?

- (a) In body-centred cubic unit cell, the coordination number is 12  
 (b) The coordination number of each type of ion in CsCl is 8

- (c) A unit cell of an ionic crystal shares some of its ions with neighbouring unit cell  
 (d) If  $r_{\text{Na}^+} = 95 \text{ pm}$ ;  $r_{\text{Cl}^-} = 181 \text{ pm}$ ; then edge length of unit cell of NaCl is 552 pm

### SECTION-III

#### Assertion-Reason Type Questions

This section contains 6 questions. Each question contains **Statement-1** (Assertion) and **Statement-2** (Reason). Each question has following 4 choices (a), (b), (c) and (d), out of which only one is correct.

- (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.

- 20. Statement-1:** The pressure inside the LPG cylinder remains constant even when it is in use at room temperature.

**Because**

**Statement-2:** Vapour pressure of any liquid is independent of its amount; it depends only on temperature.

- 21. Statement-1:** If a gas has compressibility factor ( $Z$ ) greater than unity, then repulsive forces are dominant.

**Because**

**Statement-2:** Value of  $Z$  decreases with increase in pressure.

- 22. Statement-1:** The value of Boyle's temperature for a real gas is  $\left( T_B = \frac{a}{Rb} \right)$ .

**Because**

**Statement-2:** At Boyle's temperature,  $T_B$ , real gases behave ideally over a long range of pressure.

- 23. Statement-1:**  $\text{CaCO}_3$  shows polymorphism.

**Because**

**Statement-2:**  $\text{CaCO}_3$  exists in two forms called aragonite and calcite.

- 24. Statement-1:** Lead zirconate is piezoelectric solid.

**Because**

**Statement-2:** Lead zirconate crystals have no dipole moment.

- 25. Statement-1:** Band gap in germanium is small.

**Because**

**Statement-2:** The energy spread of each germanium atomic energy level is infinitesimally small. (IIT 2007)

### SECTION-IV

#### Matrix-Matching Type Questions

This section contains 3 questions. Each question contains statement given in two columns which have to be matched.

Statements (a, b, c and d) in Column-I have to be matched with statements (p, q, r and s) in Column-II. The answers to these questions have to be appropriately bubbled as illustrated in the following examples:

If the correct matches are (a-p,s); (b-q,r); (c-p,q) and (d-s); then correct bubbled  $4 \times 4$  matrix should be as follows:

	p	q	r	s
a	<input checked="" type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>
b	<input type="radio"/>	<input checked="" type="radio"/>	<input checked="" type="radio"/>	<input type="radio"/>
c	<input checked="" type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>
d	<input type="radio"/>	<input checked="" type="radio"/>	<input type="radio"/>	<input checked="" type="radio"/>

- 26. Match the Column-I with Column-II:**

**Column-I**

- (a) High temperature      (p)  $Z \neq 1$   
 (b) Extremely low pressure      (q)  $Pb < \frac{a}{V}$   
 (c) Very high pressure      (r)  $Z = 1$   
 (d) Low pressure      (s)  $Pb > \frac{a}{V}$

- 27. Match the Column-I with Column-II:**

**Column-I**

- (a) Constituent units occupy only corners      (p) 67.98%  
 (b) Constituent units occupy corners as well as face-centres      (q) 26.17%  
 (c) Constituent units occupy corners and body-centre      (r) 74.01%  
 (d) Constituent units occupy corners and edge-centres      (s) 52.33%

- 28. Match the Column-I with Column-II:**

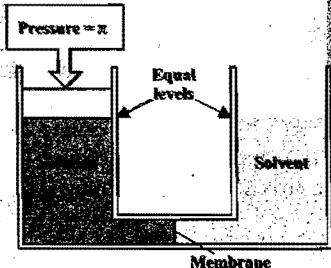
(IIT 2007)

**Column-I**

- (a) Simple cubic and face-centred cubic      (p) Have these cell parameters  $a = b = c$  and  $\alpha = \beta = \gamma$   
 (b) Cubic and rhombohedral      (q) Are two crystal systems  
 (c) Cubic and tetragonal      (r) Have only two crystallography angles of  $90^\circ$   
 (d) Hexagonal monoclinic      (s) Belong to same crystal system

## Answers

- |               |                                   |                             |                                      |         |         |            |               |
|---------------|-----------------------------------|-----------------------------|--------------------------------------|---------|---------|------------|---------------|
| 1. (c)        | 2. (a)                            | 3. (b)                      | 4. (b)                               | 5. (b)  | 6. (b)  | 7. (c)     | 8. (b)        |
| 9. (b)        | 10. (b)                           | 11. (b)                     | 12. (a)                              | 13. (d) | 14. (b) | 15. (c, d) | 16. (a, b, c) |
| 17. (a, b, d) | 18. (a, c, d)                     | 19. (b, c, d)               | 20. (c)                              | 21. (c) | 22. (b) | 23. (a)    | 24. (c)       |
| 25. (c)       | 26. (a-p) (b-p) (c-p, s) (d-p, q) | 27. (a-s) (b-r) (c-p) (d-q) | 28. (a-p, s) (b-p, q) (c-q) (d-q, r) |         |         |            |               |



# CHAPTER 5

## SOLUTIONS (General and Colligative Properties)

### 5.1 INTRODUCTION

When two or more chemically non-reacting substances are mixed, they form mixtures. A mixture may be **heterogeneous** or **homogeneous**. A heterogeneous mixture consists of distinct phases and the observed properties are just the sum of the properties of individual phases. However, a homogeneous mixture consists of a single phase which has properties that may differ drastically from those of the individual components.

**A homogeneous mixture whose composition can be varied within certain limits is termed a true solution.**

The constituents of a solution cannot be separated by filtration, settling or centrifugal action. All solutions are characterised by (i) homogeneity, (ii) absence of settling and (iii) the molecular or ionic state of sub-division of the components.

When the solution is composed of only two chemical substances, it is termed a **binary solution**. Similarly, it is called **ternary** and **quaternary** if it is composed of three and four components, respectively. Thus, a solution may be regarded as a single phase containing more than one component.

### 5.2 SOLVENT AND SOLUTE

Every solution consists of a solvent and one or more solutes. **Solvent in a solution is its constituent substance which has the same state of aggregation as that of the solution.** Generally, the component present in greater amount than any or all the other components is called the solvent. For the solubility of solids in liquids, where the liquid is present in large excess over the solid, there is no ambiguity in these terms, the solid being the solute and the liquid being the solvent. However, if the solution is such that the state of aggregation of the solution is the same as that of a component present in smaller amount, the latter is called the solvent. For example, in a syrup (liquid solution) containing 60% sugar (a solid) and 40% water (a liquid—same aggregation as solution), water is termed as the solvent. In a solution of alcohol and water, the substance present in a larger proportion by mass is called the solvent. But if both the liquids have same masses in solution, it becomes difficult to differentiate between solvent and solute.

### 5.3 TYPES OF SOLUTIONS

All the three states of matter (gas, liquid or solid) may behave either as solvent or solute. Depending on the state of solute or solvent, mainly there may be the following seven types of binary solutions:

S. No.	Solute	Solvent	Example
1.	Gas	Gas	Air
2.	Gas	Liquid	Aerated water ( $\text{CO}_2 + \text{H}_2\text{O}$ )
3.	Gas	Solid	Hydrogen in palladium
4.	Liquid	Liquid	Alcohol in water, benzene in toluene
5.	Liquid	Solid	Mercury in zinc amalgam
6.	Solid	Liquid	Sugar in water, common salt in water
7.	Solid	Solid	Various alloys

The solution of liquid in gas or solid in gas is not possible because the constituents cannot form a homogeneous mixture.

For a given solution, the amount of the solute dissolved in a unit volume of solution (or a unit amount of solvent) is termed as the concentration of the solute. Solutions containing relatively high concentration of solute are called **concentrated solutions** while those of relatively low concentration of solute are termed as **dilute solutions**.

In this chapter, we shall discuss only three types of solutions:

- (i) Gas in liquid.
- (ii) Liquid in liquid.
- (iii) Solid in liquid.

### 5.4 METHODS OF EXPRESSING THE CONCENTRATION OF A SOLUTION

The concentration of a solution can be expressed in a number of ways. The important methods are:

**(i) Mass percentage or Per cent by mass:** It is defined as the amount of solute in gram present in 100 gram of the solution.

$$\begin{aligned}\text{Mass percentage of solute} &= \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 100 \\ &= \frac{\text{Mass of solute}}{\text{Mass of solute} + \text{Mass of solvent}} \times 100 \\ &= \frac{\text{Mass of solute}}{\text{Volume of solution} \times \text{Density of solution}} \times 100\end{aligned}$$

The ratio  $\frac{\text{Mass of solute}}{\text{Mass of solution}}$  is termed as **mass fraction**.

Thus,

$$\text{Mass percentage of solute} = \text{Mass fraction} \times 100$$

10% solution of sugar means that 10 gram of sugar is present in 100 gram of the solution, i.e., 10 gram of sugar has been dissolved in 90 gram of water.

**(ii) Per cent by volume:** It is defined as the volume of solute in mL present in 100 mL solution.

$$\text{Per cent of solute by volume} = \frac{\text{Volume of solute}}{\text{Volume of solution}} \times 100$$

**(iii) Per cent mass by volume:** It is defined as the mass of solute present in 100 mL of solution.

Per cent of solute mass by volume

$$= \frac{\text{Mass of solute}}{\text{Volume of solution}} \times 100$$

**(iv) Strength or concentration (Gram per litre):** It is defined as the amount of the solute in gram present in one litre of the solution.

Concentration of solution

$$\begin{aligned}&= \frac{\text{Mass of solute in gram}}{\text{Volume of the solution in litres}} \\ &= \frac{\text{Mass of solute in gram}}{\text{Volume of the solution in mL}} \times 1000\end{aligned}$$

Concentration in gram per litre is also termed as strength of the solution. Let  $w$  g of the solute be present in  $V$  litre of solution; then

$$\text{Strength or concentration of the solution} = \frac{w}{V} \text{ gL}^{-1}$$

**Note:**  $V$  is not the volume of the solvent.  $V$  is actually the final volume after dissolving a definite quantity of solute in the solvent.]

**(v) Parts per million (ppm):** When the solute is present in trace quantities, it is convenient to express the concentration in parts per million (ppm). It is defined as the quantity of the solute in gram present in  $10^6$  gram of the solution.

$$\text{ppm} = \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 10^6$$

Atmospheric pollution in cities is also expressed in ppm by volume. It refers to the volume of the pollutant in  $10^6$  units of volume. 10 ppm of  $\text{SO}_2$  in air means 10 mL of  $\text{SO}_2$  is present in  $10^6$  mL of air.

**(vi) Mole fraction:** This method is used when the solution is constituted by mixing two or more components. It is defined as the ratio of number of moles of one component to the total number of moles of the solution (i.e., all the components). Taking three components  $A$ ,  $B$  and  $C$ .

Components	$A$	$B$	$C$
Mass (in gram)	$w_1$	$w_2$	$w_3$
Molecular mass	$m_1$	$m_2$	$m_3$
No. of g moles	$\frac{w_1}{m_1}$	$\frac{w_2}{m_2}$	$\frac{w_3}{m_3}$

$$\text{Total number of g moles} = \frac{w_1}{m_1} + \frac{w_2}{m_2} + \frac{w_3}{m_3}$$

$$\text{Thus, Mole fraction of } A = \frac{\frac{w_1}{m_1}}{\frac{w_1}{m_1} + \frac{w_2}{m_2} + \frac{w_3}{m_3}} = f_A$$

$$\text{Mole fraction of } B = \frac{\frac{w_2}{m_2}}{\frac{w_1}{m_1} + \frac{w_2}{m_2} + \frac{w_3}{m_3}} = f_B$$

$$\text{Mole fraction of } C = \frac{\frac{w_3}{m_3}}{\frac{w_1}{m_1} + \frac{w_2}{m_2} + \frac{w_3}{m_3}} = f_C$$

The sum of mole fractions of a solution is equal to 1, i.e.,  
 $f_A + f_B + f_C = 1$

In a binary solution,

$$\text{Mole fraction of solute} + \text{Mole fraction of solvent} = 1$$

Let  $n$  moles of solute ( $B$ ) and  $N$  moles of solvent ( $A$ ) be present in a solution.

$$\text{Mole fraction of solute} = \frac{n}{N+n} = X_B$$

$$\text{Mole fraction of solvent} = \frac{N}{N+n} = X_A$$

$$\text{Thus, } X_A + X_B = 1$$

Mole fraction is independent of temperature of the solution.

**(vii) Molality:** It is defined as the number of moles of the solute present in 1 kg of the solvent. It is denoted by  $m$ .

$$\text{Molality (} m \text{)} = \frac{\text{Number of moles of solute}}{\text{Number of kilo-grams of the solvent}}$$

Let  $w_B$  gram of the solute of molecular mass  $m_B$  be present in  $w_A$  gram of the solvent, then

$$\text{Molality (} m \text{)} = \frac{w_B}{m_B \times w_A} \times 1000$$

**Relation between mole fraction and molality:**

$$X_B = \frac{n}{N+n} \text{ and } X_A = \frac{N}{N+n}$$

$$\frac{X_B}{X_A} = \frac{n}{N} = \frac{\text{Moles of solute}}{\text{Moles of solvent}} = \frac{w_B \times m_A}{m_B \times w_A}$$

$$\frac{X_B \times 1000}{X_A \times m_A} = \frac{w_B \times 1000}{m_B \times w_A} = m$$

or  $\frac{X_B \times 1000}{(1 - X_B) m_A} = m$

**Note:** (i) Molality is the most convenient method to express the concentration because it involves the mass of liquids rather than their volumes. It is also independent of the variation in temperature.

(ii) Molality and solubility are related by the following relation :

$$\text{Molality} = \frac{\text{Solubility} \times 10}{\text{Molecular mass of the solute}}$$

$$\left[ \text{Solubility} = \frac{\text{Mass of solute in gram}}{\text{Mass of solvent in gram}} \times 100 \right]$$

(viii) **Molarity (Molar concentration):** It is defined as the number of moles of the solute per litre or per  $\text{dm}^3$  of the solution, i.e.,

$$\text{Molarity } (M) = \frac{\text{Number of moles of solute}}{\text{Number of litres of solution}}$$

or  $\text{Molarity} \times \text{Number of litres of solution}$   
 $= \text{Number of moles of solute}$

Let  $w_B$  g of the solute of molecular mass  $m_B$  be dissolved in  $V$  litre of solution.

$$\text{Molarity of the solution} = \frac{w_B}{m_B \times V}$$

or  $\text{Molarity} \times m_B = \frac{w_B}{V} = \text{Strength of the solution}$

If  $V$  is taken in mL ( $\text{cm}^3$ ), then

$$\text{Molarity of the solution} = \frac{w_B}{m_B \times V} \times 1000$$

The unit of molarity is mol litre<sup>-1</sup> or mol dm<sup>-3</sup>.

**Molarity (second method):** Let  $d$  = density of solution in g/mL and let it contains  $x\%$  solute by mass.

Then, mass of 1 litre solution =  $(1000 \times d)$  g

$$\text{Mass of solute in 1 litre} = \frac{x}{100} \times (1000 \times d) \text{ g}$$

$$= (x \times d \times 10) \text{ g}$$

Number of moles of solute in 1 litre

$$= \frac{\text{Mass of solute in gram}}{\text{Gram molecular mass of solute}} = \frac{x \times d \times 10}{m_B}$$

where  $m_B$  = molecular mass of solute

$$M = \frac{x \times d \times 10}{m_B}$$

**Molarity of dilution:**

$$\begin{array}{ll} \text{Before dilution} & \text{After dilution} \\ M_1 V_1 & = M_2 V_2 \end{array}$$

**Molarity of mixing:** Let there be three samples of solution (containing same solvent and solute) with their molarity  $M_1, M_2, M_3$  and volumes  $V_1, V_2, V_3$  respectively. These solutions are mixed; molarity of mixed solution may be given as:

$$M_1 V_1 + M_2 V_2 + M_3 V_3 = M_R (V_1 + V_2 + V_3)$$

where,  $M_R$  = Resultant molarity

$$V_1 + V_2 + V_3 = \text{Resultant volume after mixing}$$

**Note:** Molarity is dependent on volume; therefore, it depends on temperature.

1 M	Molar solution, i.e., molarity is 1
0.5 M or $M/2$	Semimolar
0.1 M or $M/10$	Decimolar
0.01 M or $M/100$	Centimolar
0.001 M or $M/1000$	Millimolar

#### Relationship between molality and molarity:

$$\frac{1}{m} = \frac{\rho}{M} - \frac{m_B}{1000}$$

where,  $\rho$  = density of solution

$m$  = molality

$M$  = molarity

$m_B$  = molar mass of solute

#### Relation between molarity ' $M$ ' and mole fraction:

Let  $M$  be the molarity of solution, and  $x_A, x_B$  be mole fractions of solvent and solute, respectively.

Suppose  $n_A$  and  $n_B$  moles of solvent and solute are mixed to form solution.

Mass of solution =  $n_A m_A + n_B m_B$  ... (i)  
 where,  $m_A$  and  $m_B$  are molar masses of solvent and solute, respectively.

$$\text{Volume of solution} = \frac{\text{Mass}}{\text{Density}} = \frac{(n_A m_A + n_B m_B)}{d}$$

$$\text{Molarity} = \frac{\text{Number of moles of solute} \times \frac{1000}{\text{Volume of solution}}}{\text{Number of litres of solution}}$$

$$M = n_B \times \frac{1000 \times d}{(n_A m_A + n_B m_B)}$$

Dividing both numerator and denominator by  $(n_A + n_B)$ ,

$$M = \left\{ \frac{n_B}{n_A + n_B} \right\} \times \frac{1000 \times d}{\frac{n_A}{n_A + n_B} \times m_A + \frac{n_B}{n_A + n_B} \times m_B}$$

$$M = \frac{x_B \times 1000 \times d}{x_A m_A + x_B m_B}$$

(ix) **Normality:** It is defined as the number of gram equivalents of solute present per litre of solution. It is denoted by ' $N$ '.

$$\text{Normality } (N) = \frac{\text{Number of gram equivalents of solute}}{\text{Number of litres of the solution}}$$

or  $\text{Normality} \times \text{Number of litres of the solution}$   
 $= \text{Number of gram equivalents of the solute}$

Let  $w_B$  gram of the solute of equivalent mass  $E_B$  be present in  $V$  litre of the solution, then,

$$\text{Normality} = \frac{w_B/E_B}{V} = \frac{w_B}{E_B \times V}$$

$$\begin{aligned}\text{Normality} \times \text{Equivalent mass} &= \frac{w_B}{V} \\ &= \text{Strength of the solution in g/L}\end{aligned}$$

Solutions are expressed as:

$$1 N, 2 N, \frac{N}{2}, \frac{N}{10}, \frac{N}{100}, \frac{N}{1000}, \text{etc.}$$

Like molarity, normality is also dependent on volume, therefore, it depends on temperature.

Normality of solution may be represented as,

$1 N$	Normal solution, i.e., normality is 1
$0.5 N$ or $\frac{N}{2}$	Seminormal
$0.1 N$ or $\frac{N}{10}$	Decinormal
$0.01 N$ or $\frac{N}{100}$	Centinormal
$0.001 N$ or $\frac{N}{1000}$	Millinormal

**Relationship between normality and molarity:** We know that,

$$\text{Molarity} \times \text{Molecular mass} = \text{Strength of the solution (g/L)}$$

Similarly,

$$\text{Normality} \times \text{Equivalent mass} = \text{Strength of the solution (g/L)}$$

Hence,

$$\text{Molarity} \times \text{Molecular mass} = \text{Normality} \times \text{Equivalent mass}$$

$$\text{or } \frac{\text{Normality}}{\text{Molarity}} = \frac{\text{Molecular mass}}{\text{Equivalent mass}} = n$$

$$\text{So, } \text{Normality} = n \times \text{Molarity}$$

[Normality (second method): Let 'd' is the density of solution in g/mL and 'x' is the percentage of the solute by mass.

Then,

$$N = \frac{x \times d \times 10}{\text{Equivalent mass of solute}} ]$$

(x) **Formality:** It is the number of formula mass in gram present per litre of solution. In case, formula mass is equal to molecular mass, formality is equal to molarity. Like molarity and normality, the formality is also dependent on temperature. It is used for ionic compounds in which there is no existence of a molecule. Mole of ionic compounds is called **formole** and molarity as **formality**.

### ::: SOME SOLVED EXAMPLES :::

**Example 1.** Calculate the masses of cane sugar and water required to prepare 250 g of 25% cane sugar solution.

**Solution:** Mass percentage of cane sugar = 25

We know that,

$$\text{Mass percentage} = \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 100$$

$$\text{So, } 25 = \frac{\text{Mass of cane sugar}}{250} \times 100$$

$$\text{or } \text{Mass of cane sugar} = \frac{25 \times 250}{100} = 62.5 \text{ g}$$

$$\text{Mass of water} = (250 - 62.5) = 187.5 \text{ g}$$

**Example 2.** Calculate the molarity of the following solutions:

(a) 4 g of caustic soda is dissolved in 200 mL of the solution.

(b) 5.3 g of anhydrous sodium carbonate is dissolved in 100 mL of solution.

(c) 0.365 g of pure HCl gas is dissolved in 50 mL of solution.

**Solution:** (a) Molecular mass of NaOH = 40

$$\text{No. of gram moles in 4 g of NaOH} = \frac{4}{40} = 0.1$$

$$\text{Volume of solution in litre} = \frac{200}{1000} = 0.2$$

$$\text{Molarity} = \frac{\text{No. of moles of solute}}{\text{Volume of solution in litre}} = \frac{0.1}{0.2} = 0.5 M$$

(b) Molecular mass of anhydrous  $\text{Na}_2\text{CO}_3$  = 106

$$\begin{aligned}\text{No. of gram moles in 5.3 g of anhydrous } \text{Na}_2\text{CO}_3 \\ = \frac{5.3}{106} = 0.05\end{aligned}$$

$$\text{Volume of solution in litre} = \frac{100}{1000} = 0.1$$

$$\begin{aligned}\text{Molarity} &= \frac{\text{No. of gram moles of solute}}{\text{Volume of solution in litre}} \\ &= \frac{0.05}{0.1} = 0.5 M\end{aligned}$$

(c) Molecular mass of HCl = 36.5

$$\text{No. of gram moles in 0.365 g of pure HCl} = \frac{0.365}{36.5}$$

$$\text{Volume of solution in litre} = \frac{50}{1000}$$

$$\begin{aligned}\text{Molarity} &= \frac{\text{No. of gram moles of solute}}{\text{Volume of solution in litre}} \\ &= \frac{0.365 \times 1000}{36.5 \times 50} = 0.2 M\end{aligned}$$

**Example 3.** The density of a solution containing 13% by mass of sulphuric acid is 1.09 g/mL. Calculate the molarity and normality of the solution.

**Solution:** Volume of 100 g of the solution

$$\begin{aligned} &= \frac{100}{d} = \frac{100}{1.09} \text{ mL} \\ &= \frac{100}{1.09 \times 1000} \text{ litre} \\ &= \frac{1}{1.09 \times 10} \text{ litre} \end{aligned}$$

Number of moles of  $\text{H}_2\text{SO}_4$  in 100 g of the solution =  $\frac{13}{98}$

$$\begin{aligned} \text{Molarity} &= \frac{\text{No. of moles of } \text{H}_2\text{SO}_4}{\text{Volume of soln. in litre}} = \frac{13}{98} \times \frac{1.09 \times 10}{1} \\ &= 1.445 M \end{aligned}$$

**Note:** In solving such numericals, the following formula can be applied:

$$\text{Molarity} = \frac{\% \text{ strength of soln.} \times \text{density of soln.} \times 10}{\text{Mol. mass}}$$

Similarly,

$$\text{Normality} = \frac{\% \text{ strength of soln.} \times \text{density of soln.} \times 10}{\text{Eq. mass}}$$

We know that,

$$\begin{aligned} \text{Normality} &= \text{Molarity} \times n \\ &= 1.445 \times 2 \quad \left[ n = \frac{\text{Mol. mass}}{\text{Eq. mass}} = \frac{98}{49} = 2 \right] \\ &= 2.89 N \end{aligned}$$

**Example 4.** Calculate the molarity of pure water ( $d = 1 \text{ g / mL}$ ).

**Solution:** Consider 1000 mL of water.

$$\text{Mass of 1000 mL of water} = 1000 \times 1 = 1000 \text{ g}$$

$$\text{No. of moles of water} = \frac{1000}{18} = 55.5$$

$$\begin{aligned} \text{Molarity} &= \frac{\text{No. of moles of water}}{\text{Volume in litre}} \\ &= \frac{55.5}{1} = 55.5 M \end{aligned}$$

**Example 5.** Calculate the quantity of sodium carbonate (anhydrous) required to prepare 250 mL  $\frac{M}{10}$  solution.

**Solution:** We know that,

$$\text{Molarity} = \frac{w}{M \times V}$$

where,  $w$  = mass of  $\text{Na}_2\text{CO}_3$  in g,

$$M = \text{molecular mass of } \text{Na}_2\text{CO}_3 \text{ in gram} = 106$$

$$V = \text{volume of solution in litre} = \frac{250}{1000} = 0.25$$

$$\text{Molarity} = \frac{1}{10}$$

$$\text{Hence, } \frac{1}{10} = \frac{w}{106 \times 0.25}$$

$$\text{or } w = \frac{106 \times 0.25}{10} = 2.65 \text{ g}$$

**Example 6.** 214.2 g of sugar syrup contains 34.2 g of sugar. Calculate (i) molality of the solution and (ii) mole fraction of sugar in the syrup.

**Solution:** (i) Mass of sugar = 34.2 g

$$\text{No. of moles of sugar} = \frac{34.2}{\text{Mol. mass}} = \frac{34.2}{342} = 0.1$$

$$\text{Mass of water} = (214.2 - 34.2)$$

$$= 180 \text{ g} = \frac{180}{1000} \text{ kg}$$

$$\text{No. of moles of water} = \frac{180}{18} = 10$$

$$\begin{aligned} \text{Molality} &= \frac{\text{No. of moles of sugar}}{\text{Mass of water in kg}} = \frac{0.1}{180} \times 1000 \\ &= 0.555 m \end{aligned}$$

$$(ii) \text{ Total number of moles} = 10.0 + 0.1 = 10.1$$

$$\begin{aligned} \text{Mole fraction of sugar} &= \frac{\text{No. of moles of sugar}}{\text{Total number of moles}} \\ &= \frac{0.1}{10.1} = 0.0099 \end{aligned}$$

**Example 7.** A solution contains 410.3 g of  $\text{H}_2\text{SO}_4$  per litre of solution at  $20^\circ\text{C}$ . If the density is 1.243 g/mL, what will be its molarity and molality?

**Solution:** Mol. mass of  $\text{H}_2\text{SO}_4$  = 98

$$\text{No. of moles of } \text{H}_2\text{SO}_4 = \frac{410.3}{98} = 4.186$$

$$\begin{aligned} \text{Molarity of } \text{H}_2\text{SO}_4 \text{ solution} &= \frac{\text{No. of moles of } \text{H}_2\text{SO}_4}{\text{Volume of soln. in litre}} \\ &= \frac{4.186}{1} = 4.186 M \end{aligned}$$

$$\text{Mass of 1 litre } \text{H}_2\text{SO}_4 \text{ solution} = 1000 \times 1.243 = 1243 \text{ g}$$

$$\text{Mass of water} = (1243 - 410.3) = 832.7 \text{ g} = \frac{832.7}{1000} \text{ kg}$$

$$\begin{aligned} \text{Molality of solution} &= \frac{\text{No. of moles of } \text{H}_2\text{SO}_4}{\text{Mass of water in kg}} \\ &= \frac{4.186}{832.7} \times 1000 \end{aligned}$$

$$= 5.027 m$$

**Example 8.** The density of a 2.03 M solution of acetic acid (molecular mass 60) in water is 1.017 g/mL. Calculate the molality of the solution.

**Solution:** Strength of the solution

$$\begin{aligned} &= \text{Molarity} \times \text{mol. mass} \\ &= 2.03 \times 60 = 121.8 \text{ g/L} \end{aligned}$$

Density of solution = 1.017 g/mL

$$\begin{aligned} \text{Mass of 1 litre of solution} &= 1000 \text{ mL} \times 1.017 \text{ g/mL} \\ &= 1017 \text{ g} \end{aligned}$$

$$\text{Mass of water} = 1017 - 121.8 = 895.2 \text{ g} = \frac{895.2}{1000} \text{ kg}$$

$$\text{Molality} = \frac{2.03}{895.2} \times 1000 = 2.267 \text{ m}$$

**Example 9.** The density of a 3 M sodium thiosulphate solution ( $\text{Na}_2\text{S}_2\text{O}_3$ ) is 1.25 g/mL. Calculate (i) the percentage by mass of sodium thiosulphate, (ii) the mole fraction of sodium thiosulphate and (iii) molalities of  $\text{Na}^+$  and  $\text{S}_2\text{O}_3^{2-}$  ions.

**Solution:** (i) Mass of 1000 mL of  $\text{Na}_2\text{S}_2\text{O}_3$  solution

$$= 1.25 \times 1000 = 1250 \text{ g}$$

Mass of  $\text{Na}_2\text{S}_2\text{O}_3$  in 1000 mL of 3 M solution

$$\begin{aligned} &= 3 \times \text{Mol. mass of } \text{Na}_2\text{S}_2\text{O}_3 \\ &= 3 \times 158 = 474 \text{ g} \end{aligned}$$

Mass percentage of  $\text{Na}_2\text{S}_2\text{O}_3$  in solution

$$= \frac{474}{1250} \times 100 = 37.92$$

Alternatively,  $M = \frac{x \times d \times 10}{m_A}$

$$3 = \frac{x \times 1.25 \times 10}{158}$$

$$x = 37.92$$

$$(ii) \text{ No. of moles of } \text{Na}_2\text{S}_2\text{O}_3 = \frac{474}{158} = 3$$

$$\text{Mass of water} = (1250 - 474) = 776 \text{ g}$$

$$\text{No. of moles of water} = \frac{776}{18} = 43.1$$

$$\text{Mole fraction of } \text{Na}_2\text{S}_2\text{O}_3 = \frac{3}{43.1 + 3} = \frac{3}{46.1} = 0.065$$

(iii) No. of moles of  $\text{Na}^+$  ions

$$\begin{aligned} &= 2 \times \text{No. of moles of } \text{Na}_2\text{S}_2\text{O}_3 \\ &= 2 \times 3 = 6 \end{aligned}$$

$$\begin{aligned} \text{Molality of } \text{Na}^+ \text{ ions} &= \frac{\text{No. of moles of } \text{Na}^+ \text{ ions}}{\text{Mass of water in kg}} \\ &= \frac{6}{776} \times 1000 \\ &= 7.73 \text{ m} \end{aligned}$$

$$\begin{aligned} \text{No. of moles of } \text{S}_2\text{O}_3^{2-} \text{ ions} &= \text{No. of moles of } \text{Na}_2\text{S}_2\text{O}_3 \\ &= 3 \end{aligned}$$

$$\text{Molality of } \text{S}_2\text{O}_3^{2-} \text{ ions} = \frac{3}{776} \times 1000 = 3.86 \text{ m}$$

**Example 10.** A solution is prepared by dissolving 5.64 g of glucose in 60 g of water. Calculate the following:

- (i) mass per cent of each of glucose and water,
- (ii) molality of the solution,
- (iii) mole fraction of each of glucose and water.

**Solution:** (i) Total mass of solution

$$= 5.64 + 60 = 65.64 \text{ g}$$

$$\text{Mass per cent of glucose} = \frac{5.64}{65.64} \times 100 = 8.59\%$$

$$\begin{aligned} \text{Mass per cent of water} &= (100 - \text{Mass per cent of glucose}) \\ &= (100 - 8.59) = 91.41\% \end{aligned}$$

$$(ii) \text{ No. of moles of glucose} = \frac{5.64}{180}$$

$$\text{Mass of water in kg} = \frac{60}{1000}$$

$$\text{Molality} = \frac{5.64}{180} \times \frac{1000}{60} = 0.522 \text{ m}$$

$$(iii) \text{ No. of moles of glucose} = \frac{5.64}{180} = 0.0313$$

$$\text{No. of moles of water} = \frac{60}{18} = 3.333$$

$$\text{Mole fraction of glucose} = \frac{0.0313}{3.333 + 0.0313} = 0.0093$$

$$\text{Mole fraction of water} = \frac{3.333}{3.333 + 0.0313} = 0.9907$$

**Example 11.** What would be the molality of a solution made by mixing equal volumes of 30.0% by mass of  $\text{H}_2\text{SO}_4$  (density 1.218 g  $\text{cm}^{-3}$ ) and 70% by mass of  $\text{H}_2\text{SO}_4$  (density 1.610 g  $\text{cm}^{-3}$ )?

**Solution:** Let 100 mL of one solution be mixed with 100 mL of the other solution.

$$\text{Mass of 100 mL of 30\% } \text{H}_2\text{SO}_4 = 100 \times 1.218 = 121.8 \text{ g}$$

$$\text{Mass of } \text{H}_2\text{SO}_4 \text{ in } 121.8 \text{ g of 30\% } \text{H}_2\text{SO}_4$$

$$= \frac{30}{100} \times 121.8 \text{ g} = 36.54 \text{ g}$$

$$\text{Mass of water} = (121.8 - 36.54) = 85.26 \text{ g}$$

$$\text{Mass of 100 mL of 70\% } \text{H}_2\text{SO}_4 = 100 \times 1.61 = 161.0 \text{ g}$$

$$\text{Mass of } \text{H}_2\text{SO}_4 \text{ in } 161.0 \text{ g of 70\% } \text{H}_2\text{SO}_4$$

$$= \frac{70}{100} \times 161.0 \text{ g} = 112.7 \text{ g}$$

$$\text{Mass of water} = (161.0 - 112.7) = 48.30 \text{ g}$$

$$\text{Total } \text{H}_2\text{SO}_4 \text{ in solution} = 36.54 + 112.7 = 149.24 \text{ g}$$

$$\text{No. of moles of H}_2\text{SO}_4 = \frac{149.24}{98}$$

Total mass of water in solution =  $(85.26 + 48.30)$

$$= 133.56 \text{ g} = \frac{133.56}{1000} \text{ kg}$$

$$\text{Molality} = \frac{\text{No. of moles of H}_2\text{SO}_4}{\text{Mass of water in kg}} = \frac{149.24}{98} \times \frac{1000}{133.56}$$

$$= 1.14 \text{ m}$$

**Example 12.** The mole fraction of  $\text{CH}_3\text{OH}$  in an aqueous solution is 0.02 and its density is  $0.994 \text{ g cm}^{-3}$ . Determine its molarity and molality.

**Solution:** Let  $x$  mole of  $\text{CH}_3\text{OH}$  and  $y$  mole of water be present in solution.

$$\text{Mole fraction of CH}_3\text{OH} = \frac{x}{x+y} = 0.02$$

$$\text{So, } \frac{y}{x} = 49 \quad \text{or} \quad \frac{x}{y} = \frac{1}{49}$$

$$\text{Molality} = \frac{x}{18 \times y} \times 1000 = \frac{1000}{18 \times 49} = 1.13 \text{ m}$$

$$\text{Volume of solution} = \frac{\text{Total mass}}{\text{density}} = \frac{32x + 18y}{0.994} \text{ mL}$$

$$= \frac{32x + 18y}{0.994 \times 1000} \text{ litre} = \frac{32x + 18y}{994} \text{ litre}$$

$$\text{Molarity} = \frac{x}{32x + 18y} \times 994$$

$$= \frac{994}{32 + 18 \times y/x} = \frac{994}{32 + 18 \times 49} = 1.0875 \text{ M}$$

**Example 13.** Calculate the concentration of  $\text{NaOH}$  solution in g/mL, which has the same normality as that of a solution of  $\text{HCl}$  of concentration 0.04 g/mL.

$$\text{Solution: } N_{\text{HCl}} = \frac{w_B \times 1000}{E_B \times V} = \frac{0.04 \times 1000}{36.5 \times 1} = 1.095$$

$$N_{\text{NaOH}} \equiv N_{\text{HCl}}$$

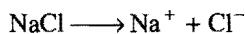
$$\therefore 1.095 = \frac{w_B \times 1000}{40 \times 1}$$

$$w_B = 0.0438 \text{ g/mL}$$

**Example 14.** How many  $\text{Na}^+$  ions are present in 50 mL of a 0.5 M solution of  $\text{NaCl}$ ?

$$\text{Solution: Number of moles of NaCl} = \frac{MV}{1000}$$

$$= \frac{0.5 \times 50}{1000} = 0.025$$



$$\text{Number of Na}^+ = \text{Number of moles of NaCl}$$

$$= 0.025$$

$$\text{Number of ions of Na}^+ = 0.025 \times 6.023 \times 10^{23}$$

$$= 1.505 \times 10^{22}$$

**Example 15. Reaction,**



is used for commercial preparation of bromine from its salts. Suppose we have 50 mL of a 0.06 M solution of  $\text{NaBr}$ . What volume of a 0.05 M solution of  $\text{Cl}_2$  is needed to react completely with the  $\text{Br}^-$ ?

**Solution:**  $2\text{Br}^- (\text{aq}) + \text{Cl}_2 (\text{aq}) \longrightarrow 2\text{Cl}^- (\text{aq}) + \text{Br}_2 (\text{aq})$

$$\frac{M_1 V_1 (\text{Br}^-)}{n_1} = \frac{M_2 V_2 (\text{Cl}_2)}{n_2}$$

where,  $n_1$  and  $n_2$  are corresponding coefficients.

$$\frac{0.06 \times 50}{2} = \frac{0.05 \times V_2}{1}$$

$$\therefore V_2 = 30 \text{ mL}$$

**Example 16.** Calculate the molarity, molality and mole fraction of ethyl alcohol in a solution of total volume 95 mL prepared by adding 50 mL of ethyl alcohol (density =  $0.789 \text{ mL}^{-1}$ ) to 50 mL water (density =  $1.00 \text{ g mL}^{-1}$ ).

**Solution:**

$$\text{No. of moles of ethyl alcohol} = \frac{\text{Vol.} \times \text{density}}{\text{Mol. mass}}$$

$$= \frac{50 \times 0.789}{46} = 0.8576$$

$$\text{No. of moles of water} = \frac{\text{Vol.} \times \text{density}}{\text{Mol. mass}} = \frac{50 \times 1}{18}$$

$$= 2.7777$$

$$\text{Molarity} = \frac{\text{No. of moles}}{\text{Vol. of sol. in mL}} \times 1000$$

$$= \frac{0.8576}{95} \times 1000 = 9.027 \text{ M}$$

$$\text{Molality} = \frac{\text{No. of moles of}}{\text{Mass of solvent}} \times 1000$$

$$= \frac{0.8576}{50} \times 1000 = 52 \text{ m}$$

$$\text{Mole fraction} = \frac{0.8576}{0.8576 + 2.7777} = \frac{0.8576}{3.6353} = 0.236$$

## 5.5 SOLUTIONS OF GASES IN LIQUIDS (Solubility of Gases)

All gases are soluble in water as well as in other liquids to a greater or lesser extent. Solutions of gases in water play an important role in our daily life. The common examples are carbonated beverages, i.e., soft drinks, household cleaners containing aqueous solutions of ammonia, formalin—an aqueous solution of formaldehyde, etc. The natural waters contain dissolved  $\text{O}_2$  which is vital for the existence of aquatic life in sea, rivers and lakes.

The solubility of a gas in a liquid is expressed in terms of **absorption coefficient**. It is defined as the volume of the gas in mL that can be dissolved by 1 mL of a liquid solvent at the

temperature of the experiment at one atmospheric pressure. The volume of the gas is measured at STP. Thus, if  $v$  is the volume of the gas dissolved, reduced to STP,  $V$  is the volume of the solvent and  $P$  is pressure of the gas in atmospheres, then the absorption coefficient,  $\alpha$ , is given by

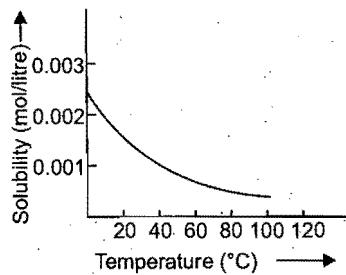
$$\alpha = \frac{v}{VP}$$

The following factors affect the solubilities of gases in liquids:

(i) **Nature of the gas and solvent**: Generally, the gases which can be easily liquefied are more soluble in common solvents. For example,  $\text{CO}_2$  is more soluble in water than oxygen or hydrogen. The gases which react with the solvent possess higher solubility. For example,  $\text{HCl}$  and  $\text{NH}_3$  are highly soluble in water.

Oxygen, nitrogen and carbon dioxide are much more soluble in ethyl alcohol than in water at the same temperature and pressure.

(ii) **Temperature**: The solubility of most of the gases in liquids decreases with increase of temperature as the dissolution is an exothermic process. When water is heated in a beaker, bubbles of air are formed on the sides of the glass before the water boils. As the temperature rises, the dissolved air molecules begin to "boil out" of the solution long before the water itself boils.



**Fig. 5.1 Temperature dependence of  $\text{O}_2$  gas solubility in water**

The reduced solubility of molecular oxygen in hot water has a direct bearing on **thermal pollution**, i.e., the heating of the environment—usually waterways—to temperatures that are harmful to its living inhabitants.

(iii) **Pressure**: The most important factor which influences the solubility of a gas in a liquid is the **pressure**. The effect of pressure on the solubility of the gas in the liquid is given by Henry's law, which states that *the solubility of a gas in a liquid is directly proportional to the pressure of the gas over the solution at a definite temperature*. The solubility is taken as the mass of the gas dissolved per unit volume of the liquid. Thus, if  $m$  is the mass of the gas dissolved per unit volume of the solvent and  $P$  is the pressure of the gas in equilibrium with the solution, then

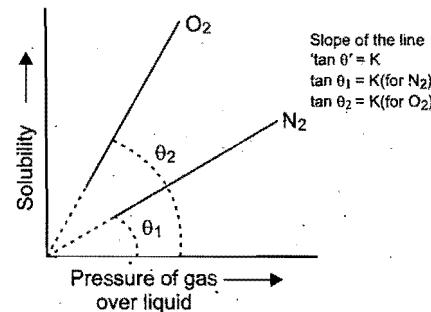
$$m \propto P$$

$$\text{or} \quad m = KP \quad \dots(i)$$

where,  $K$  is the proportionality constant.

When  $P = 1$ ,  $m = K$ , i.e., the solubility of the gas at unit pressure is equal to constant  $K$ . The value of  $K$  is different for each gas at a particular temperature. The magnitude of  $K$  depends upon the nature of the gas, nature of solvent, temperature and the units of pressure. Equation (i) represents equation of straight line

$(y = mx)$  passing through origin. Fig. 5.2 shows the variation of solubility of some gases against equilibrium pressure. The straight line graphs show the validity of Henry's law.



**Fig. 5.2 Variation of solubility of a gas with pressure**

If solubility of the gas is known at one particular pressure, then it can be calculated at other pressures using the following relation,

$$\frac{m_1}{m_2} = \frac{P_1}{P_2} \quad \dots(ii)$$

where ' $m_1$ ' is the solubility of the gas at pressure ' $P_1$ ' and ' $m_2$ ' is the solubility of the gas at pressure ' $P_2$ '.

When a mixture of two or more non-reacting gases is brought in contact with a solvent, each constituent gas dissolves in proportion to its own partial pressure. Henry's law can be applied to each individual gas independent of the presence of other gas. If we use the mole fraction of the gas in the solution as a measure of its solubility, then the law can be stated as, "*mole fraction of the gas in a solution is proportional to the partial pressure of the gas*."

$$x \propto P$$

where,  $x$  = mole fraction of the gas in solution  
and  $p$  = partial pressure of the gas.

$$\text{or} \quad x = K' p$$

$$\text{or} \quad p = \frac{1}{K'} x = K_H x \quad \left( K_H = \frac{1}{K'} \right) \dots(iii)$$

$K_H$  is called Henry's law constant. Different gases have different values of  $K_H$  at a definite temperature for a given solvent.

**Table 5.1 Values of Henry's Law Constant ( $K_H$ ) for Some Common Gases in Water**

Gas	Temperature (K)	$K_H$ (k bar)
He	293	144.97
$\text{H}_2$	293	69.16
$\text{N}_2$	293	76.48
$\text{N}_2$	303	88.84
$\text{O}_2$	293	34.86
$\text{O}_2$	393	46.82

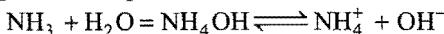
From equation (iii), it can be inferred that higher is the value of Henry's law constant, the lower is the solubility of the gas in the liquid.

### Limitations of Henry's Law

Henry's law holds good if the following conditions are fulfilled :

- (i) The pressure is not too high,
- (ii) The temperature is not very low,
- (iii) The gas does not chemically combine with the solvent.

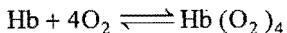
The gas molecules do not either dissociate or associate in the solvent. In case the dissolved gas reacts with the solvent, higher solubilities can result. The solubility of ammonia in water is much higher than expected because of the following reaction :



Carbon dioxide also reacts with water.



Another interesting example concerns the dissolution of oxygen in blood. Normally, oxygen gas is only sparingly soluble in water. However, its solubility in blood is abnormally high because of the high content of haemoglobin (Hb) molecules, which are eventually delivered to the tissues for use in metabolism.



Due to these processes, Henry's law is not strictly followed.

### Applications of Henry's Law

1. Soft drink bottles are sealed at high pressure, to increase the solubility of  $\text{CO}_2$  in the soft drink.
2. At high altitude, partial pressure of oxygen is low, it leads to low concentration of oxygen in blood of people living there. Low concentration of oxygen develops **anoxia**, i.e., unable to think and act properly.
3. When scuba divers go deep in the sea, solubility of atmospheric gases increases in blood. When the divers come up, there is release of dissolved gases and it leads to the formation of bubbles of nitrogen in our blood capillaries and hence there is painful sensation called **bends**. To avoid bends; the tanks of scuba divers are filled with 11.7% He, 56.2%  $\text{N}_2$  and 32.1% oxygen.

**Note :** (i) Gases are less soluble in aqueous solutions of electrolytes than in pure water. It is called *salting out effect*.  
(ii) Non-electrolytes such as sugar if present in a solution also reduce the solubility of gases in water.]

**Example 17.** Calculate the concentration of  $\text{CO}_2$  in a soft drink that is bottled at partial pressure of  $\text{CO}_2$  of 4 atm over the liquid at  $25^\circ\text{C}$ . The Henry's Law constant for  $\text{CO}_2$  in water at  $25^\circ\text{C}$  is  $3.1 \times 10^{-2}$  mol/litre-atm.

**Solution:** According to Henry's Law:

$$S = KP \neq 3.1 \times 10^{-2} \times 4 = 0.12 \text{ mol litre}^{-1}$$

**Example 18.** The partial pressure of ethane over a saturated solution containing  $6.56 \times 10^{-2}$  g of ethane is 1 bar. If the solution contains  $5 \times 10^{-2}$  g of ethane, then what shall be the partial pressure of the gas?

**Solution:**

$$\frac{S_1}{S_2} = \frac{P_1}{P_2}$$

$$\frac{6.56 \times 10^{-2}}{5 \times 10^{-2}} = \frac{1}{P_2}$$

$$P_2 = 0.762 \text{ bar}$$

### ILLUSTRATIONS OF OBJECTIVE QUESTIONS

1.  $0.5 \text{ M H}_2\text{SO}_4$  is diluted from 1 litre to 10 litre, normality of the resulting solution is: (AFMC 2005)

- (a) 1 N      (b) 0.1 N      (c) 10 N      (d) 11 N

[Ans. (b)]

[Hint:  $M_1V_1 = M_2V_2$

$$0.5 \times 1 = M_2 \times 10$$

$$M_2 = 0.05$$

$$N = M \times \text{basicity of acid} = 0.05 \times 2 = 0.1 \text{ N}$$

2. Molar solution means 1 mole of solute present in:

|BCECE (Medical) 2005|

- (a) 1000 g of solvent      (b) 1 litre of solvent  
(c) 1 litre of solution      (d) 1000 g of solution

[Ans. (c)]

3. The molarity of a solution containing 50 g of NaCl in 500 g of a solution and having a density of  $0.936 \text{ g/cm}^3$  is:

- (a) 1.5 M      (b) 1.6 M      (c) 1.8 M      (d) 1.2 M

[Ans. (b)]

[Hint:  $M = \frac{x \times d \times 10}{m_B}$  ... (i)

$$x = \frac{50}{500} \times 100 = 10$$

$$\therefore M = \frac{10 \times 0.936 \times 10}{58.5} = 1.6 \text{ M}$$

4. 20 mL of 0.5 M HCl is mixed with 30 mL of 0.3 M HCl, the molarity of the resulting solution is:

- (a) 0.8 M      (b) 0.53 M      (c) 0.38 M      (d) 0.83 M

[Ans. (c)]

[Hint:  $M_1V_1 + M_2V_2 = M_R(V_1 +$

$$0.5 \times 20 + 0.3 \times 30 = M_R \times 5$$

$$M_R = 0.38 \text{ M}$$

where,  $M_R$  = resultant molarity of mixture.]

5. How many moles and how many grams of NaCl are present in 250 mL of a 0.5 M NaCl solution?

- (a) 0.125 mol; 7.32 g      (b) 7.32 mol; 0.125 g  
(c) 0.125 mol; 0.125 g      (d) 7.32 mol; 7.32 g

[Ans. (a)]

[Hint: Number of moles =  $\frac{MV}{1000} = \frac{0.5 \times 250}{1000} = 0.125$

$$\text{Mass of NaCl} = 58.5 \times 0.125 = 7.32 \text{ g}$$

6. Density of a 2.05 M solution of acetic acid in water is 1.02 g/mL. The molality of the solution is: (AIEEE 2006)

- (a)  $1.14 \text{ mol kg}^{-1}$       (b)  $3.28 \text{ mol kg}^{-1}$   
(c)  $2.28 \text{ mol kg}^{-1}$       (d)  $0.44 \text{ mol kg}^{-1}$

[Ans. (c)]

[Hint:  $m = \frac{M \times 1000}{1000d - Mm_B} = \frac{2.05 \times 1000}{1000 \times 1.02 - 2.05 \times 60} = 2.28 \text{ mol kg}^{-1}$ ]

7. The hardness of water sample containing 0.002 mol of magnesium sulphate dissolved in a litre of water is expressed as:

[PMT (Kerala) 2007]

- (a) 20 ppm (b) 200 ppm (c) 2000 ppm (d) 120 ppm  
(e) 240 ppm

[Ans. (b)]

[Hint:  $10^6$  g water contains  $(0.002 \times 1000)$  mol  $\text{MgSO}_4$ 

$$1 \text{ mol } \text{MgSO}_4 \approx 1 \text{ mol } \text{CaCO}_3$$

$$\therefore 2 \text{ mol } \text{MgSO}_4 \approx 2 \text{ mol } \text{CaCO}_3, \text{ i.e., } 2 \times 100 \text{ g } \text{CaCO}_3$$

$$\therefore \text{Hardness of water} = 200 \text{ ppm}$$

8. The density (in  $\text{g mL}^{-1}$ ) of a  $3.6 M$  sulphuric acid solution, i.e., 29%  $\text{H}_2\text{SO}_4$  (molar mass =  $98 \text{ g mol}^{-1}$ ) by mass will be:

(AIEEE 2007)

- (a) 1.45 (b) 1.64 (c) 1.88 (d) 1.22

[Ans. (d)]

$$[\text{Hint: } M = \frac{x \times d \times 10}{m_B}]$$

$$d = \frac{M \times m_B}{x \times 10} = \frac{3.6 \times 98}{29 \times 10} \approx 1.22 \text{ g mL}^{-1}$$

9. 1 litre solution containing 490 g of sulphuric acid is diluted to 10 litre with water. What is the normality of the resulting solution?

(SCRA 2007)

- (a) 0.5 N (b) 1.0 N (c) 5.0 N (d) 10.0 N

[Ans. (b)]

$$[\text{Hint: } N = \frac{w_B \times 1000}{E_B \times V} = \frac{490 \times 1000}{49 \times 1000} = 10]$$

$$N_1 V_1 = N_2 V_2$$

$$10 \times 1 = N_2 \times 10$$

$$N_2 = 1$$

10. 250 mL of a  $\text{Na}_2\text{CO}_3$  solution contains 2.65 g of  $\text{Na}_2\text{CO}_3$ . 10 mL of this solution is added to  $x$  mL of water to obtain 0.001  $M$   $\text{Na}_2\text{CO}_3$  solution. The value of  $x$  is....

(Molecular mass of  $\text{Na}_2\text{CO}_3$  = 106 amu) [BHU (Mains) 2008]

- (a) 1000 (b) 990 (c) 9990 (d) 90

[Ans. (b)]

[Hint : Molarity of solution.

$$M = \frac{w_B \times 1000}{m_B \times V} = \frac{2.65 \times 1000}{106 \times 250} = 0.1$$

$$M_1 V_1 = M_2 V_2$$

$$0.1 \times 10 = 0.001 (10 + x)$$

$$x = 990 \text{ mL}$$

11. The volumes of two HCl solutions  $A$  (0.5 N) and  $B$  (0.1 N) to be mixed for preparing 2 L of 0.2 N HCl are:

(EAMCET (Med) 2008)

- (a) 0.5 L of  $A$  + 1.5 L of  $B$   
(b) 1.5 L of  $A$  + 0.5 L of  $B$   
(c) 1 L of  $A$  + 1 L of  $B$   
(d) 0.75 L of  $A$  + 1.25 L of  $B$

[Ans. (a)]

[Hint : Let  $x$  L of  $A$  and  $(2 - x)$  L of  $B$  are mixed.

$$M_1 V_1 + M_2 V_2 = M_R (V_1 + V_2)$$

$$0.5 \times x + 0.1 (2 - x) = 0.2 \times 2$$

$$(0.5 - 0.1)x = 0.4 - 0.2$$

$$0.4x = 0.2$$

$$x = 0.5 \text{ L}$$

∴ 0.5 L of  $A$  and 1.5 L of  $B$  should be mixed.]

## 5.6 SOLUTIONS OF LIQUIDS IN LIQUIDS

When one liquid dissolves in another, the molecules of the solvent are caused to move apart so as to accommodate the solute molecules. Similarly, the solute molecules must also be separated so that they can take their places in the mixture. In both these processes, energy is required. Finally, as the solute and solvent molecules are brought together, energy is released because of the attractive forces between them. When solute and solvent molecules are strongly attracted to each other, more energy is released in the final step. Three cases may arise under these circumstances. The overall dissolution process results either in evolution of heat or absorption of heat, or energy released in the final step is the same as the energy absorbed in the first two, i.e., net change is zero.

### Examples:

1. Benzene and carbon

tetrachloride:

No evolution or absorption of heat.

2. Acetone and water:

Evolution of heat.

3. Ethyl alcohol and water:

Absorption of heat.

A liquid may or may not be soluble in another liquid. Depending upon the relative solubility of a liquid in another, the following three cases are possible:

### Liquid-Liquid Systems

1. Liquids that are completely miscible.

Examples:  
Benzene and toluene;  
Ethyl alcohol and water;  
Carbon tetrachloride and benzene.

2. Liquids that are partially miscible.

Examples:  
Ether and water;  
Phenol and water;  
Nicotine and water.

3. Liquids that are practically immiscible.

Examples:  
Benzene and water;  
Carbon tetrachloride and water;  
Benzene and alcohol.

Miscible liquids form three types of solutions, which can be ideal or non-ideal solutions.

**Ideal solution:** An ideal solution is one in which the molecules attract one another with equal force irrespective of their nature. Thus, a solution composed of two components  $A$  and  $B$  will be an ideal one if the forces between  $A$  and  $A$ ,  $A$  and  $B$  and  $B$  should be the same. An ideal solution possesses the following characteristics:

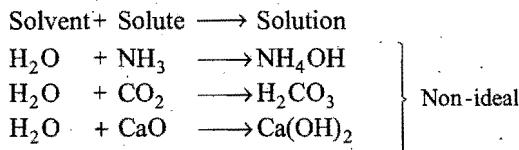
- (i) Volume change of mixing should be zero.

$$\Delta V_{\text{mix}} = 0; V_{\text{solvent}} + V_{\text{solute}} = V_{\text{solution}}$$

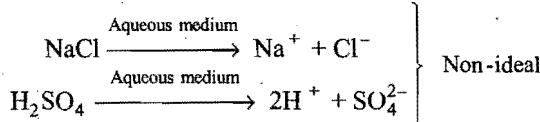
- (ii) Heat change on mixing should be zero.

$$\Delta H_{\text{mix}} = 0 \text{ (Heat is neither absorbed nor evolved.)}$$

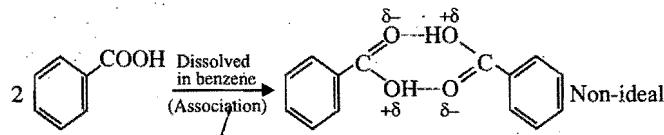
- (iii) There should be no chemical reaction between solvent and solute.



(iv) Solute molecules should not dissociate in the ideal solution.



(v) Solute molecules should not associate in ideal solution.



(vi) Ideal solutions must obey Raoult's law at all concentrations.

The following are some of the binary mixtures which show the properties of ideal solutions:

- (a) Benzene and toluene,
- (b) Carbon tetrachloride and silicon tetrachloride,
- (c) *n*-Hexane and *n*-heptane,
- (d) Ethylene dibromide and ethylene dichloride.

### Raoult's Law

According to this law, the partial pressure of any volatile constituent of a solution at a constant temperature is equal to the vapour pressure of pure constituent multiplied by the mole fraction of that constituent in the solution.

Let a mixture (solution) be prepared by mixing  $n_A$  mole of liquid *A* and  $n_B$  mole of liquid *B*. Let  $p_A$  and  $p_B$  be the partial pressures of two constituents *A* and *B* in solution and  $p_A^0$  and  $p_B^0$  the vapour pressures in pure state respectively.

Table 5.2 Comparison between Ideal and Non-ideal Solutions

Ideal solutions	Non-ideal solutions	
	Positive deviation from Raoult's law	Negative deviation from Raoult's law
<ol style="list-style-type: none"> <li>Obey Raoult's law at every range of concentration.</li> <li><math>\Delta H_{\text{mix}} = 0</math>; neither heat is evolved nor absorbed during dissolution.</li> <li><math>\Delta V_{\text{mix}} = 0</math>; total volume of solution is equal to sum of volumes of the components.</li> <li><math>P = p_A + p_B = p_A^0 X_A + p_B^0 X_B</math> i.e., <math>p_A = p_A^0 X_A</math>; <math>p_B = p_B^0 X_B</math></li> <li><math>A - A</math>, <math>A - B</math>, <math>B - B</math> interactions should be same, i.e., '<i>A</i>' and '<i>B</i>' are identical in shape, size and character.</li> <li>Escaping tendency of '<i>A</i>' and '<i>B</i>' should be same in pure liquids and in the solution.</li> </ol>	<p>Do not obey Raoult's law.</p> <p><math>\Delta H_{\text{mix}} &gt; 0</math>. Endothermic dissolution; heat is absorbed.</p> <p><math>\Delta V_{\text{mix}} &gt; 0</math>. Volume is increased after dissolution.</p> <p><math>p_A &gt; p_A^0 X_A</math>; <math>p_B &gt; p_B^0 X_B</math>  <math>\therefore p_A + p_B &gt; p_A^0 X_A + p_B^0 X_B</math></p> <p><i>A</i> — <i>B</i> attractive force should be weaker than <i>A</i> — <i>A</i> and <i>B</i> — <i>B</i> attractive forces. '<i>A</i>' and '<i>B</i>' have different shape, size and character.</p> <p>'<i>A</i>' and '<i>B</i>' escape easily showing higher vapour pressure than the expected value.</p> <p><b>Examples:</b>          dilute solutions;          benzene + toluene;  <i>n</i>-hexane + <i>n</i>-heptane;          chlorobenzene + bromobenzene;          ethyl bromide + ethyl iodide;  <i>n</i>-butyl chloride + <i>n</i>-butyl bromide.</p>	<p>Do not obey Raoult's law.</p> <p><math>\Delta H_{\text{mix}} &lt; 0</math>. Exothermic dissolution; heat is evolved.</p> <p><math>\Delta V_{\text{mix}} &lt; 0</math>. Volume is decreased during dissolution.</p> <p><math>p_A &lt; p_A^0 X_A</math>; <math>p_B &lt; p_B^0 X_B</math>  <math>\therefore p_A + p_B &lt; p_A^0 X_A + p_B^0 X_B</math></p> <p><i>A</i> — <i>B</i> attractive force should be greater than <i>A</i> — <i>A</i> and <i>B</i> — <i>B</i> attractive forces. '<i>A</i>' and '<i>B</i>' have different shape, size and character.</p> <p>Escaping tendency of both components '<i>A</i>' and '<i>B</i>' is lowered showing lower vapour pressure than expected ideally.</p> <p><b>Examples:</b>          acetone + ethanol;          acetone + CS<sub>2</sub>;          water + methanol;          water + ethanol;          CCl<sub>4</sub> + toluene;          CCl<sub>4</sub> + CHCl<sub>3</sub>;          acetone + benzene;          CCl<sub>4</sub> + CH<sub>3</sub>OH;          cyclohexane + ethanol.</p>

Thus, according to Raoult's law,

$$p_A = \frac{n_A}{n_A + n_B} p_A^0 = \text{mole fraction of } A \times p_A^0 = X_A \cdot p_A^0$$

$$\text{and } p_B = \frac{n_B}{n_A + n_B} p_B^0 = \text{mole fraction of } B \times p_B^0 = X_B \cdot p_B^0$$

If the total pressure be  $P$ , then

$$\begin{aligned} P &= p_A + p_B \\ &= \frac{n_A}{n_A + n_B} p_A^0 + \frac{n_B}{n_A + n_B} p_B^0 \end{aligned}$$

$$= X_A \cdot p_A^0 + X_B \cdot p_B^0$$

This law, in fact, is the major deciding factor, whether a solution will be ideal or non-ideal. Ideal solutions obey Raoult's law at every range of concentration. Non-ideal solutions do not obey Raoult's law. They show either **positive** or **negative** deviation from Raoult's law. For comparison between ideal and non-ideal solutions a table has been given below. (Only binary combinations of miscible liquids have been considered.)

### Graphical Representation of Ideal and Non-ideal Solutions

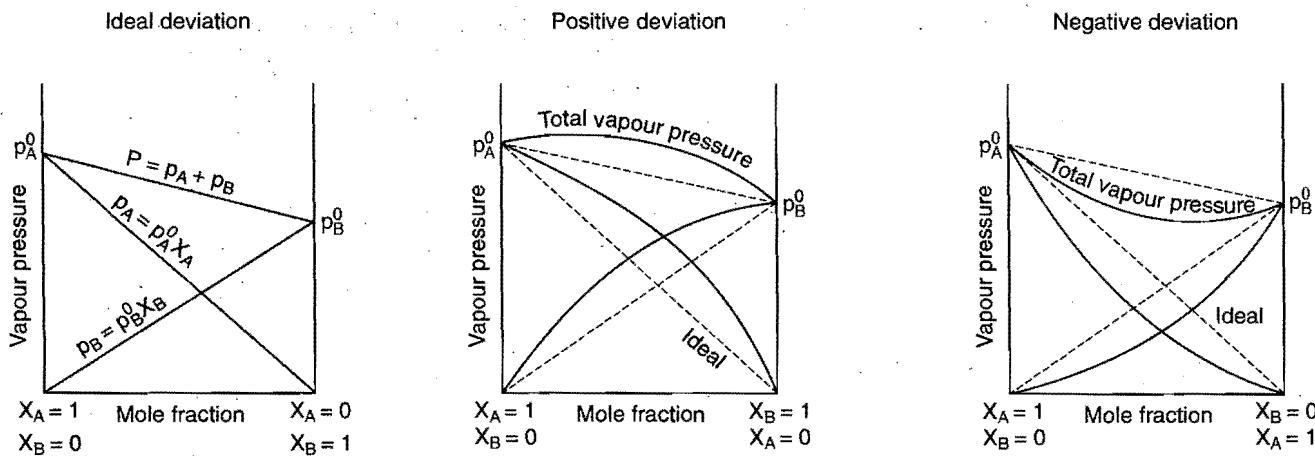


Fig. 5.3

#### Relation between Dalton's Law and Raoult's Law:

The composition of the vapour in equilibrium with the solution can be calculated applying Dalton's law of partial pressures. Let the mole fractions of vapours  $A$  and  $B$  be  $Y_A$  and  $Y_B$  respectively. Let  $p_A$  and  $p_B$  be the partial pressures of vapours  $A$  and  $B$  respectively and total pressure  $P$ .

$$p_A = Y_A \cdot P \quad \dots (i)$$

$$p_B = Y_B \cdot P \quad \dots (ii)$$

$$p_A = X_A \cdot p_A^0 \quad \dots (iii)$$

$$p_B = X_B \cdot p_B^0 \quad \dots (iv)$$

Equating eqs. (i) and (iii),

$$Y_A \cdot P = X_A \cdot p_A^0$$

or

$$Y_A = \frac{X_A \cdot p_A^0}{P} = \frac{p_A}{P}$$

Similarly, equating eqs. (ii) and (iv),

$$Y_B = \frac{X_B \cdot p_B^0}{P} = \frac{p_B}{P}$$

Thus, in case of ideal solution the vapour phase is richer with more volatile component, i.e., the one having relatively greater vapour pressure.

**Example 19.** The vapour pressures of ethanol and methanol are 44.5 mm and 88.7 mm Hg respectively. An ideal solution is formed at the same temperature by mixing 60 g of ethanol with 40 g of methanol. Calculate the total vapour

pressure of the solution and the mole fraction of methanol in the vapour.

**Solution:** Mol. mass of ethyl alcohol =  $C_2H_5OH = 46$

$$\text{No. of moles of ethyl alcohol} = \frac{60}{46} = 1.304$$

Mol. mass of methyl alcohol =  $CH_3OH = 32$

$$\text{No. of moles of methyl alcohol} = \frac{40}{32} = 1.25$$

$$\text{"} X_A \text{"}, mole fraction of ethyl alcohol} = \frac{1.304}{1.304 + 1.25} = 0.5107$$

$$\text{"} X_B \text{"}, mole fraction of methyl alcohol} = \frac{1.25}{1.304 + 1.25} = 0.4893$$

$$\begin{aligned} \text{Partial pressure of ethyl alcohol} &= X_A \cdot p_A^0 = 0.5107 \times 44.5 \\ &= 22.73 \text{ mm Hg} \end{aligned}$$

$$\begin{aligned} \text{Partial pressure of methyl alcohol} &= X_B \cdot p_B^0 = 0.4893 \times 88.7 \\ &= 43.40 \text{ mm Hg} \end{aligned}$$

$$\begin{aligned} \text{Total vapour pressure of solution} &= 22.73 + 43.40 \\ &= 66.13 \text{ mm Hg} \end{aligned}$$

Mole fraction of methyl alcohol in the vapour

$$= \frac{\text{Partial pressure of } CH_3OH}{\text{Total vapour pressure}} = \frac{43.40}{66.13} = 0.6563$$

**Example 20.** Two liquids A and B form an ideal solution. At 300 K, the vapour pressure of a solution containing 1 mole of A and 3 mole of B is 550 mm of Hg. At the same temperature, if one more mole of B is added to this solution, the vapour pressure of the solution increases by 10 mm of Hg. Determine the vapour pressure of A and B in their pure states.

**Solution:** Let the vapour pressure of pure A be =  $p_A^0$ ; and the vapour pressure of pure B be =  $p_B^0$ .

Total vapour pressure of solution (1 mole A + 3 mole B)

$$= X_A \cdot p_A^0 + X_B \cdot p_B^0 \quad [X_A \text{ is mole fraction of A and } X_B \text{ is mole fraction of B}]$$

$$550 = \frac{1}{4} p_A^0 + \frac{3}{4} p_B^0$$

or  $2200 = p_A^0 + 3p_B^0 \quad \dots \text{(i)}$

Total vapour pressure of solution (1 mole A + 4 mole B)

$$= \frac{1}{5} p_A^0 + \frac{4}{5} p_B^0$$

$$560 = \frac{1}{5} p_A^0 + \frac{4}{5} p_B^0$$

or  $2800 = p_A^0 + 4p_B^0 \quad \dots \text{(ii)}$

Solving eqs. (i) and (ii),

$$p_B^0 = 600 \text{ mm of Hg} = \text{vapour pressure of pure B}$$

$$p_A^0 = 400 \text{ mm of Hg} = \text{vapour pressure of pure A}$$

**Example 21.** An aqueous solution containing 28% by mass of a liquid A (mol. mass = 140) has a vapour pressure of 160 mm at 37°C. Find the vapour pressure of the pure liquid A (The vapour pressure of water at 37°C is 150 mm).

**Solution:** For two miscible liquids,

$$P_{\text{total}} = \text{Mole fraction of A} \times p_A^0 + \text{Mole fraction of B} \times p_B^0$$

$$\text{No. of moles of A} = \frac{28}{140} = 0.2$$

Liquid B is water. Its mass is (100 - 28), i.e., 72.

$$\text{No. of moles of B} = \frac{72}{18} = 4.0$$

$$\text{Total no. of moles} = 0.2 + 4.0 = 4.2$$

$$\text{Given, } P_{\text{total}} = 160 \text{ mm}$$

$$p_B^0 = 150 \text{ mm}$$

$$\text{So, } 160 = \frac{0.2}{4.2} \times p_A^0 + \frac{4.0}{4.2} \times 150$$

$$p_A^0 = \frac{17.15 \times 4.2}{0.2} = 360.15 \text{ mm}$$

**Example 22.** Heptane and octane form ideal solution. At 373 K, the vapour pressures of the two liquids are 105.2 kPa and 46.8 kPa respectively. What will be the vapour pressure, in bar, of a mixture of 25 g of heptane and 35 g of octane?

**Solution:** (A) Heptane  $C_7H_{16} \quad m_A = 100$

(B) Octane  $C_8H_{18} \quad m_B = 114$

$$n_A = \frac{w_A}{m_A} = \frac{25}{100} = 0.25; \quad n_B = \frac{35}{114} = 0.3$$

$$x_A = \frac{0.25}{0.25 + 0.30}; \quad x_B = \frac{0.3}{0.25 + 0.30} \\ = 0.45 \quad = 0.55$$

$$p = p_A^0 x_A + p_B^0 x_B \\ = 105.2 \times 0.45 + 46.8 \times 0.55 \\ = 47.34 + 25.74 = 73.08 \text{ kPa}$$

### ILLUSTRATIONS OF OBJECTIVE QUESTIONS

12. Mole fraction of the component A in vapour phase is  $x_1$  and the mole fraction of component A in liquid mixture is  $x_2$ , then ( $p_A^0$  = vapour pressure of pure A;  $p_B^0$  = vapour pressure of pure B), the total vapour pressure of liquid mixture is:

- (a)  $p_A^0 \frac{x_2}{x_1}$       (b)  $p_A^0 \frac{x_1}{x_2}$       (c)  $p_B^0 \frac{x_1}{x_2}$       (d)  $p_B^0 \frac{x_2}{x_1}$

[Ans. (a)]

[Hint:  $p_A = p_A^0 x_2$ , vapour pressure of 'A'

Mole fraction of A in vapour =  $\frac{p_A}{P_{\text{total}}}$

$$x_1 = \frac{p_A^0 x_2}{P}$$

$$P = \frac{p_A^0 x_2}{x_1}$$

13. Vapour pressure of pure A ( $p_A^0$ ) = 100 mm Hg

Vapour pressure of pure B ( $p_B^0$ ) = 150 mm Hg

2 mole of liquid A and 3 mole of liquid B are mixed to form an ideal solution. The vapour pressure of solution will be:

- (a) 135 mm    (b) 130 mm    (c) 140 mm    (d) 145 mm

[Ans. (b)]

[Hint:  $x_A = \frac{2}{5}, x_B = \frac{3}{5}$

$$P = p_A^0 x_A + p_B^0 x_B$$

$$= 100 \times \frac{2}{5} + 150 \times \frac{3}{5} = 40 + 90 = 130]$$

14. The vapour pressure of a certain pure liquid A at 298 K is 40 m bar. When a solution of B is prepared in A at the same temperature, the vapour pressure is found to be 32 m bar. The mole fraction of A in the solution is:

- (a) 0.5    (b) 0.2    (c) 0.1    (d) 0.8

[Ans. (d)]

[Hint:  $P = p_A^0 x_A$

$$32 = 40 \times x_A \text{ or } x_A = 0.8]$$

15. 100 mL of liquid A and 25 mL of liquid B are mixed to form a solution of volume 125 mL. Then the solution is:

- (a) ideal

- (b) non-ideal with positive deviation

- (c) non-ideal with negative deviation

- (d) cannot be predicted

[Ans. (a)]

[Hint:  $\Delta V_{\text{mix}} = 0$ , hence the solution is ideal.]

16. The vapour pressure of pure benzene at 88°C is 957 mm and that of toluene at the same temperature is 379.5 mm. Calculate the composition of benzene-toluene mixture boiling at 88°C:

- (a)  $x_{\text{benzene}} = 0.66$ ;  $x_{\text{toluene}} = 0.34$   
 (b)  $x_{\text{benzene}} = 0.34$ ;  $x_{\text{toluene}} = 0.66$   
 (c)  $x_{\text{benzene}} = x_{\text{toluene}} = 0.5$   
 (d)  $x_{\text{benzene}} = 0.75$ ;  $x_{\text{toluene}} = 0.25$

[Ans. (a)]

[Hint:  $p = p_{\text{benzene}}^0 x_{\text{benzene}} + p_{\text{toluene}}^0 x_{\text{toluene}}$   
 $760 = 957 \cdot x_{\text{benzene}} + 379.5(1 - x_{\text{benzene}})$   
 $x_{\text{benzene}} = 0.66$   
 and  $x_{\text{toluene}} = 1 - 0.66 = 0.34]$

17. At 25°C, the total pressure of an ideal solution obtained by mixing 3 mole of A and 2 mole of B, is 184 torr. What is the vapour pressure (in torr) of pure B at the same temperature (Vapour pressure of pure A at 25°C is 200 torr.)?

[CET (J&K) 2006]

- (a) 180      (b) 160      (c) 16      (d) 100

[Ans. (b)]

[Hint:  $x_A = \frac{n_A}{n_A + n_B} = \frac{3}{3+2} = \frac{3}{5} = 0.6$   
 $x_B = 0.4$   
 $p = p_A^0 x_A + p_B^0 x_B$   
 $184 = 200 \times 0.6 + p_B^0 \times 0.4$   
 $184 = 120 + p_B^0 \times 0.4$   
 $p_B^0 = \frac{64}{0.4} = 160 \text{ torr}]$

18. The mass of glucose that would be dissolved in 50 g of water in order to produce the same lowering of vapour pressure as is produced by dissolving 1 g of urea in the same quantity of water is:

(KCET 2006)

- (a) 1 g      (b) 3 g      (c) 6 g      (d) 18 g

[Ans. (b)]

[Hint:  $(\Delta p)_{\text{glucose}} = (\Delta p)_{\text{urea}}$   
 $(x_B)_{\text{glucose}} = (x_B)_{\text{urea}}$   
 i.e.,  $\left(\frac{n_B}{n_A}\right)_{\text{glucose}} = \left(\frac{n_B}{n_A}\right)_{\text{urea}}$   
 $\frac{w_B}{50} \times \frac{18}{180} = \frac{1 \times 18}{50 \times 60}$   
 $w_B = 3 \text{ g}]$

## 5.7 THEORY OF FRACTIONAL DISTILLATION

The process of separation of one liquid from another liquid (binary mixture) having different boiling points by distillation is termed fractional distillation. The information, whether a particular solution of two liquids can be separated by distillation or not, is provided by the study of liquid-vapour equilibrium diagrams at constant pressure, say atmospheric pressure. **The separation is possible only when the vapour phase has a composition different from that of the boiling liquid mixture.**

**Liquid pairs of type-I (Ideal solutions):** The boiling temperature-composition curves for liquid and vapour phases in the case of binary solutions of first type are represented in Fig. 5.4.

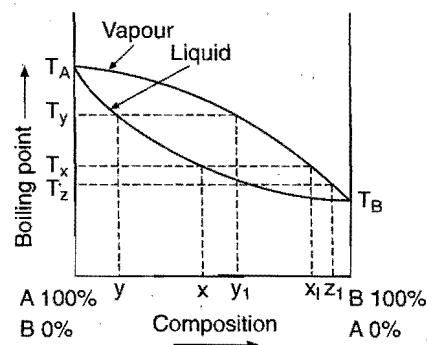


Fig. 5.4 Liquid-vapour equilibrium diagram of a solution of type-I

Suppose a solution of composition  $x$  is heated. When the temperature  $T_x$  is reached, the boiling will start. At this temperature, the vapour coming off from  $x$  will have the composition  $x_1$ . Since,  $x_1$  is richer in  $B$  than  $x$ , the composition of the residual liquid will become richer in  $A$ . Let the new composition be  $y$ . This liquid cannot boil at temperature  $T_x$  but will require higher temperature  $T_y$ . The vapour coming off at temperature  $T_y$  will also be richer in  $B$  as represented by  $y_1$ . Hence, the composition of the residue will again be enriched in  $A$ . Thus, if the process is allowed to continue, the boiling point of solution will go on increasing towards  $T_A$ , the boiling point of pure liquid  $A$ . At the same time the solution becomes more and more rich in  $A$ . If the process is continued for a sufficiently long time, pure liquid  $A$  can be obtained.

Now, if the initial vapours are condensed, the solution obtained will have the composition  $x_1$  and boils at temperature  $T_z$ . Evidently, the distillate is richer in  $B$  than before. If the process of condensation and redistilling is continued, the final distillate will be pure  $B$  component.

Thus, the two liquids forming a solution of type-I can be separated by fractional distillation.

**Solution of type-II (Positive deviations from Raoult's law):** The boiling temperature-composition curves for the liquid and vapour phases have been shown in Fig. 5.5. The two curves meet at a minimum point  $C$  where the liquid and vapour phases have the same composition. The liquid mixture at point  $C$  will boil at constant temperature  $T$  without undergoing any

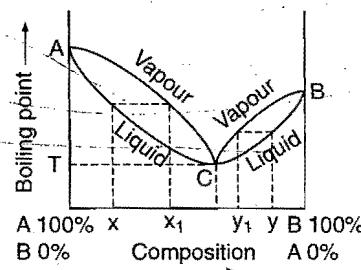


Fig. 5.5 Boiling point-composition curves in binary solution of type-II

change in composition. Such a mixture which boils at constant temperature and distils over completely at the same temperature without any change in composition, is called **constant boiling mixture or azeotropic mixture**.

Consider the distillation of a mixture of composition  $x$ . The vapour given off has the composition  $x_1$ . The composition of residual liquid will shift towards  $A$ . In the mean time the composition of the distillate shifts towards  $C$ . Ultimately by repeated fractional distillation, the mixture of composition  $C$  will be obtained as distillate and pure liquid  $A$  will be left as residue. It will never be possible to have pure  $B$ .

When a mixture of composition  $y$  is distilled, the vapour given off has the composition  $y_1$ , i.e., the composition of residual liquid will shift towards  $B$ . Ultimately the mixture of composition  $C$  will be obtained as distillate and pure liquid  $B$  will be left as residue. It will never be possible to have pure  $A$ .

There are several liquid pairs which form minimum boiling point azeotropes. Some examples are given in the table:

Table 5.3 Some Azeotropic Mixtures

Mixture	% Composition of azeotrope	Boiling point (pressure = 1 atm)
1. Water-Ethanol	95.97 Ethanol	78.15°C
2. Pyridine-Water	57.00 Pyridine	92.60°C
3. Ethanol-Benzene	32.40 Ethanol	67.80°C
4. Acetic acid-Toluene	28.00 Acetic acid	105.40°C

**Solutions of type-III (Negative deviations from Raoult's law):** The boiling temperature-composition curves for the liquid and vapour phases have been shown in Fig. 5.6. The curves meet at point  $C$ . At this point, both liquid and vapour phases have same composition. The constant-boiling mixture has maximum boiling point.

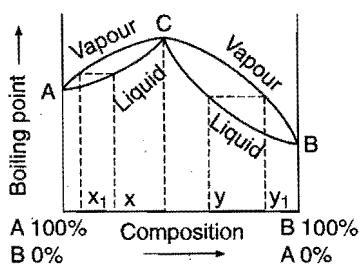


Fig. 5.6 Boiling temperature-composition curves in binary solution of type-III

Consider the distillation of a mixture of composition  $x$ . The vapour coming off is richer in  $A$  as indicated by composition  $x_1$ . The composition of the residual liquid shifts towards  $C$ . As the distillation proceeds, the composition of the distillate moves towards  $A$  and that of residue towards  $C$ .

Similarly, a mixture of composition lying between  $B$  and  $C$ , say  $y$ , on distillation will give vapour richer in  $B$  as indicated by composition  $y_1$ . The composition of residual liquid shifts towards  $C$  and distillate towards  $A$  on repeated distillation.

It is never possible to separate a mixture completely into the pure components  $A$  and  $B$ . It mainly gives a constant boiling mixture (azeotropes) which can never be separated by distillation.

There are several liquid pairs which form maximum boiling point azeotrope. Some examples are tabulated below:

Mixture	% Composition of azeotrope	Boiling point (pressure = 1 atm)
1. Nitric acid-Water	68% Nitric acid	125.5°C
2. Acetic acid-Pyridine	65% Pyridine	139.0°C
3. Chloroform-Acetone	80% Chloroform	65.0°C
4. Hydrogen chloride-Water	79.8% Water	108.6°C

## 5.8 SOLUTIONS OF SOLIDS IN LIQUIDS

Solutions of this type are most common. In solutions of solids in liquids, the liquid is invariably referred to as a solvent and the solid dissolved in it as the solute. If a solute is added in small amounts at a time to a given amount of a solvent at a constant temperature, with vigorous stirring of the solvent after each addition, a stage is reached when the added solute no more disappears, i.e., goes into solution but remains undissolved. The solution is then said to be saturated. A solution which remains in contact with undissolved solute is termed as saturated. It can also be defined as one which is in equilibrium with the excess of solid at a particular temperature.

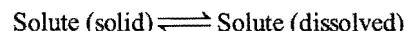
The amount of solute dissolved in 100 g of a solvent to form a saturated solution at a given temperature is termed the **solubility** of the solute in the given solvent at that temperature. Each substance has a characteristic solubility in a given solvent at a definite temperature.

When a solid is added to the solvent, the particles from the solid diffuse into it. The solute and solvent molecules move constantly in the solution phase. Some of the particles of the solute return to the solid state due to collisions. Thus, two opposite processes operate simultaneously.

(a) *Dissolution*: Particles of solute leaving the solid and dissolving in the solvent.

(b) *Recrystallisation*: Solute particles returning to the solid form.

When these two processes move with same speed, an equilibrium stage is reached,



Thus, a dynamic equilibrium exists in a saturated solution.

When a saturated solution prepared at a higher temperature is cooled, it gives a solution which contains usually more of solute than required for the saturated solution at that temperature. Such a solution is referred to as a **supersaturated solution**. It is usually unstable and changes to saturated solution when excess of solute comes out in solid state.

The following factors influence the solubility of a solute in a liquid:

- (1) Nature of solute,
- (2) Nature of solvent,
- (3) Temperature.

**1. Nature of solute:** The solutes (solids) can be classified as ionic and non-ionic solids. The ionic solids consist of positively and negatively charged ions. It is the force of attraction between the ions, i.e., lattice energy which opposes the tendency of a solute to dissolve. This force of attraction is different in different ionic solids depending on the charges present on the ions and distance between ions (ionic radii). The ionic solutes having high lattice energy like  $\text{BaSO}_4$  are less soluble while those having less lattice energy have more solubility. The ions are solvated by the solvent molecules and in this process energy (known as hydration energy) is released. When the hydration energy is high, the ionic solid is more soluble.

Many non-ionic substances dissolve in polar solvents due to hydrogen bonding. Generally, if the solute and solvent have similar characteristics, i.e., both are polar or both non-polar, the solubility is high and if both are dissimilar, the solubility is found low.

**2. Nature of solvent:** Ionic solids dissolve to a larger extent in a solvent having a high dielectric constant as compared to solvents of low dielectric constants. Dielectric constant of water is 80 while that of methyl alcohol is 33.5. An ionic solid, therefore, dissolves more readily in water than in methyl alcohol. Benzene has a very low dielectric constant of 2.3 and, hence, ionic solids do not dissolve in benzene.

For non-ionic solids, the guiding principle is '*like dissolves like*', i.e., if the solvent is polar, it will dissolve the polar solutes and if it is non-polar, it will dissolve the non-polar solutes in it.

**3. Temperature:** The solubility of a solute in a given solvent varies appreciably with temperature. A few curves drawn between solubility in water and temperature are given in Fig. 5.7.

It is observed that the solubility of  $\text{NaCl}$  increases very slightly with an increase in temperature whereas those of  $\text{KNO}_3$ ,  $\text{NaNO}_3$ ,  $\text{AgNO}_3$  and  $\text{KI}$ , etc., increase greatly. A sharp break in a solubility curve indicates the formation of a compound whose solubility is different from that of the substance from which it has been formed as in the case of  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ . It loses its water of crystallisation at  $32.3^\circ\text{C}$  and is converted into anhydrous form. There are few substances like calcium acetate, cerium sulphate, calcium chromate, etc., which show a decrease in solubility with rise in temperature.

Generally, solubility depends on heat of solution. If a substance dissolves with absorption of heat, the solubility increases with rise of temperature. On the other hand, if a substance dissolves with evolution of heat, the solubility decreases with rise of temperature.

**Determination of solubility:** The solubility of salts is generally determined by gravimetric method. First of all a saturated solution is prepared. Some part of this saturated solution is weighed out in a porcelain dish. The solution is evaporated slowly to dryness on a sand bath. The dish is cooled and weighed again. The observations are recorded as follows:

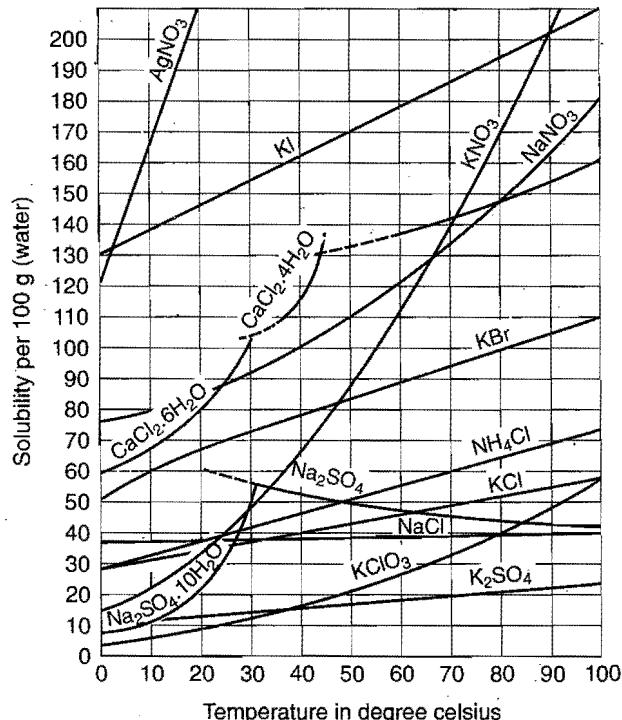


Fig. 5.7 Solubility curves of some compounds

1. Mass of empty dish =  $w$  g
2. Mass of dish + solution =  $w_1$  g
3. So, Mass of solution =  $(w_1 - w)$  g
4. Mass of dish + residue =  $w_2$  g  
So, Mass of residue =  $(w_2 - w)$  g =  $x$  g  
and Mass of solvent = (Mass of solution) – Mass of residue  

$$= (w_1 - w) - (w_2 - w)$$

$$= (w_1 - w_2) = y$$

Thus, the solubility of salt =  $\frac{x}{y} \times 100$  g per 100 g of solvent.

**Example 23:** 50 g of a saturated aqueous solution of potassium chloride at  $30^\circ\text{C}$  is evaporated to dryness, when 13.2 g of dry  $\text{KCl}$  was obtained. Calculate the solubility of  $\text{KCl}$  in water at  $30^\circ\text{C}$ .

**Solution:** Mass of water in solution =  $(50 - 13.2) = 36.8$  g

$$\text{Solubility of } \text{KCl} = \frac{\text{Mass of } \text{KCl}}{\text{Mass of water}} \times 100 = \frac{13.2}{36.8} \times 100 = 35.87 \text{ g}$$

**Example 24.** How much copper sulphate will be required to saturate 100 g of a dilute aqueous solution of  $\text{CuSO}_4$  at  $25^\circ\text{C}$  if 10 g of the dilute solution leave on evaporation and drying 1.2 g of anhydrous  $\text{CuSO}_4$ ? The solubility of  $\text{CuSO}_4$  in water at  $25^\circ\text{C}$  is 25.

**Solution:** 100 g of dilute solution of  $\text{CuSO}_4$  contain  

$$= 1.2 \times 10 = 12.0 \text{ g CuSO}_4$$

$$\begin{aligned} \text{Mass of water present in dilute solution} \\ = (100 - 12) = 88 \text{ g} \end{aligned}$$

To saturate 100 g of water,  $\text{CuSO}_4$  required = 25 g

$$\text{So, to saturate } 88 \text{ g of water, CuSO}_4 \text{ required} = \frac{25}{100} \times 88 \\ = 22 \text{ g}$$

Thus, the mass of CuSO<sub>4</sub> to be added to 100 g of dilute solution to saturate it = (22 - 12) = 10 g

## 5.9 COLLIGATIVE PROPERTIES OF DILUTE SOLUTIONS

A dilute solution is one in which the amount of the solute is very small in comparison to the amount of the solvent. The dilute solutions show more or less ideal behaviour as the heat and volume changes, accompanying the mixing of solute and solvent, are negligible for all practical purposes. Dilute solutions obey Raoult's law.

Dilute solutions containing non-volatile solute exhibit some special properties which depend only upon the number of solute particles present in the solution irrespective of their nature. These properties are termed as **colligative properties**. The colligative properties are:

- (i) Lowering in the vapour pressure,
- (ii) Elevation in the boiling point,
- (iii) Depression in the freezing point and
- (iv) Osmotic pressure.

Colligative properties are the properties of dilute solutions, that is why these are termed as *colligative properties of dilute solutions*. These properties are related to one another. Thus, if one is measured, the other can be calculated. The importance of these properties lies in the fact that they provide methods for the determination of molecular masses of dissolved solutes. The results are excellent if the following three conditions are satisfied:

- (i) The solution should be very dilute.
- (ii) The solute should be non-volatile.
- (iii) The solute does not dissociate or associate in solution.

## 5.10 LOWERING IN THE VAPOUR PRESSURE

When a non-volatile solute is added to a solvent, the vapour pressure is lowered due to the following reasons:

(i) Percentage surface area occupied by the solvent decreases. Thus, the rate of evaporation and vapour pressure decreases. The solute molecules occupy the surface, and so the per cent surface area occupied by the solvent decreases.

(ii) According to Graham's law of evaporation,

$$\text{Rate of evaporation} \propto \frac{1}{\sqrt{\text{density}}}$$

When a non-volatile solute is dissolved in a liquid, its density increases. Thus, both rate of evaporation and vapour pressure are lowered.

If  $p_0$  is the vapour pressure of pure solvent and  $p_s$  is the vapour pressure of the solution, the difference ( $p_0 - p_s$ ) is

**Note : Isopiestic solutions :** Two solutions having same vapour pressure at same temperature are known as isopiestic solutions.

termed **lowering in vapour pressure** and the ratio  $\left[ \frac{p_0 - p_s}{p_0} \right]$  is termed **relative lowering in vapour pressure**.

Raoult, in 1886, established a relationship between relative lowering in vapour pressure and composition of the solution after a series of experiments in various solvents. The relationship is known as **Raoult's law**. It states that **the relative lowering in vapour pressure of a dilute solution is equal to mole fraction of the solute present in the solution**.

If  $n$  moles of solute be dissolved in  $N$  moles of the solvent, the mole fraction of the solute will be  $\frac{n}{n + N}$ .

$$\text{According to Raoult's law, } \frac{p_0 - p_s}{p_0} = \frac{n}{n + N}$$

This is the mathematical expression for Raoult's law.

**[Modified form of Raoult's law:** The above relationship can be written as,

$$\frac{p_0}{p_0 - p_s} = \frac{n + N}{n} = 1 + \frac{N}{n}$$

$$\text{or } \frac{p_0}{p_0 - p_s} - 1 = \frac{N}{n} \text{ or } \frac{p_s}{p_0 - p_s} = \frac{N}{n}$$

$$\text{or } \frac{p_0 - p_s}{p_s} = \frac{n}{N} = \frac{w_A}{m_A} \times \frac{m_B}{w_B}$$

This equation gives accurate results and is easy to apply.]

### Derivation of Raoult's Law for a Dilute Solution

When a non-volatile solute is dissolved in a volatile solvent, a fraction of the surface of solvent is blocked by solute molecules where no evaporation occurs. Thus, under similar conditions, the vapour pressure is decreased. The vapour pressure of the solution, thus, depends upon the number of molecules of the solvent present on the surface of the solution. The number of such molecules is proportional to mole fraction of the solvent.

So, the vapour pressure of solution,

$$p_s' \propto \frac{N}{n + N}$$

$$\text{or } p_s = k \cdot \frac{N}{n + N} \quad \dots \text{(i)}$$

( $k$  is proportionality factor)

For pure solvent,  $n = 0$

$$\text{and hence, } p_0 = k \cdot \frac{N}{0 + N} = k \quad \dots \text{(ii)}$$

Putting the value of  $k$  in eq. (i)

$$p_s = p_0 \cdot \frac{N}{n + N}$$

$$\text{or} \quad \frac{p_s}{p_0} = \frac{N}{n + N}$$

$$\text{or} \quad 1 - \frac{p_s}{p_0} = 1 - \frac{N}{n + N}$$

$$\text{or} \quad \frac{p_0 - p_s}{p_0} = \frac{n}{n + N} \quad \dots (\text{iii})$$

This is Raoult's equation.

If a solution is made by dissolving  $w_B$  g of solute (molecular mass  $m_B$ ) in  $w_A$  g of the solvent (molecular mass  $m_A$ ), the mole fraction of the solute will be

$$\frac{\frac{w_B}{m_B}}{\frac{w_A}{m_A} + \frac{w_B}{m_B}}$$

If the solution is very dilute,  $\frac{w_B}{m_B}$  can be neglected in the denominator as compared to  $\frac{w_A}{m_A}$ . The eq. (iii), thus, becomes

$$\frac{p_0 - p_s}{p_0} = \frac{w_B \times m_A}{m_B \times w_A} \quad \dots (\text{iv})$$

This relationship is useful in the determination of the molecular mass of dissolved solute by measuring relative lowering of vapour pressure.

### Measurement of Relative Lowering in Vapour Pressure (Ostwald and Walker Method)

The apparatus used is shown in Fig. 5.8. It consists of two sets of bulbs. The first set of three bulbs is filled with solution to half of their capacity and second set of another three bulbs is filled with the pure solvent. Each set is separately weighed accurately. Both sets are connected to each other and then with the accurately weighed set of guard tubes filled with anhydrous calcium chloride or some other dehydrating agents like  $P_2O_5$ , conc.  $H_2SO_4$  etc. The bulbs of solution and pure solvent are kept in a thermostat maintained at a constant temperature.

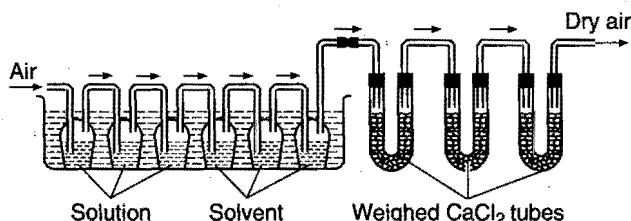


Fig. 5.8 Ostwald and Walker method

A current of pure dry air is bubbled through the series of bulbs as shown in Fig. 5.8. The air gets saturated with the vapours in each set of bulbs. The air takes up an amount of vapours proportional to the vapour pressure of the solution first and then it takes up more amount of vapours from the solvent which is proportional to the difference in the vapour pressure of the solvent and the vapour pressure of solution, i.e.,  $p_0 - p_s$ . The two sets of bulbs are weighed again. The guard tubes are also weighed.

Loss in mass in the solution bulbs  $\propto p_s$

Loss in mass in the solvent bulbs  $\propto (p_0 - p_s)$

Total loss in both sets of bulbs  $\propto [p_s + (p_0 - p_s)]$   
 $\propto p_0$

Total loss in mass of both sets of bulbs is equal to gain in mass of guard tubes.

$$\text{Thus, } \frac{p_0 - p_s}{p_0} = \frac{\text{Loss in mass in solvent bulbs}}{\text{Total loss in mass in both sets of bulbs}} \\ = \frac{\text{Loss in mass in solvent bulbs}}{\text{Gain in mass of guard tubes}}$$

Further, we know from Raoult's law,

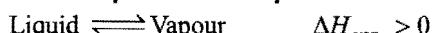
$$\frac{p_0 - p_s}{p_0} = \frac{w_B / m_B}{w_A / m_A + w_B / m_B} \\ \therefore \frac{\text{Loss in mass of solvent bulbs}}{\text{Gain in mass of guard tubes}} = \frac{w_B / m_B}{w_A / m_A + w_B / m_B}$$

The above relationship is used for calculation of molecular masses of non-volatile solutes.

For very dilute solutions, the following relationship can be applied:

$$\frac{p_0 - p_s}{p_0} = \frac{\text{Loss in mass of solvent bulbs}}{\text{Gain in mass of guard tubes}} = \frac{w_B \times m_A}{m_B \times w_A}$$

### Vapour Pressure of Liquid and Temperature



Vapour pressure of liquid increases with temperature. Here,  $\Delta H$  is enthalpy of vaporisation. A graphical representation of vapour pressure versus temperature is given below :

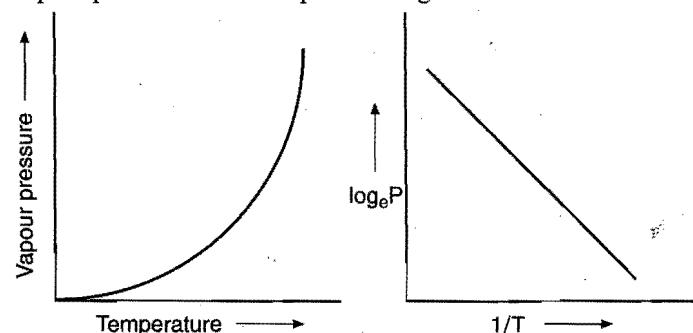


Fig. 5.9 Variation of vapour pressure with temperature

If vapour pressure of a liquid is known at a temperature; it can be calculated at another temperature using Clausius-Clapeyron equation :

$$\log_{10} \left( \frac{P_2}{P_1} \right) = \frac{\Delta H_{\text{vap.}}}{2.303 R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]$$

Here,  $P_1$  = Vapour pressure at temperature  $T_1$

$P_2$  = Vapour pressure at temperature  $T_2$

### SOME SOLVED EXAMPLES

**Example 25.** Calculate the vapour pressure lowering caused by addition of 50 g of sucrose (molecular mass = 342) to 500 g of water if the vapour pressure of pure water at 25°C is 23.8 mm Hg.

**Solution:** According to Raoult's law,

$$\frac{P_0 - P_s}{P_0} = \frac{n}{n + N}$$

or

$$\Delta p = \frac{n}{n + N} \cdot P_0$$

Given:  $n = \frac{50}{342} = 0.146$ ;  $N = \frac{500}{18} = 27.78$  and  $P_0 = 23.8$

Substituting the values in the above equation,

$$\Delta p = \frac{0.146}{0.146 + 27.78} \times 23.8 = 0.124 \text{ mm Hg}$$

**Example 26.** The vapour pressure of pure benzene at a certain temperature is 640 mm Hg. A non-volatile solid weighing 2.175 g is added to 39.0 g of benzene. The vapour pressure of the solution is 600 mm Hg. What is the molecular mass of the solid substance? (IIT 1990; MLNR 1992)

**Solution:** According to Raoult's law,

$$\frac{P_0 - P_s}{P_0} = \frac{n}{n + N}$$

Let  $m$  be the molecular mass of the solid substance.

$$n = \frac{2.175}{m}; N = \frac{39}{78} = 0.5$$

(molecular mass of benzene = 78)

$$P_0 = 640 \text{ mm}; P_s = 600 \text{ mm}$$

Substituting the values in above equation,

$$\frac{640 - 600}{640} = \frac{\frac{2.175}{m}}{\frac{2.175}{m} + 0.5} = \frac{2.175}{2.175 + 0.5m}$$

$$m = \frac{2.175 \times 16 - 2.175}{0.5} = 65.25$$

**Example 27.** A solution containing 30 g of a non-volatile solute in exactly 90 g of water has a vapour pressure of 21.85 mm of Hg at 25°C. Further, 18 g of water is then added to the solution; the new vapour pressure becomes 22.15 mm of Hg at 25°C. Calculate (a) molecular mass of the solute and (b) vapour pressure of water at 25°C. (MLNR 1990)

**Solution:** Let the vapour pressure of water at 25°C be  $P_0$  and molecular mass of the solute be  $m$ .

Using Raoult's law in the following form,

$$\frac{P_0 - P_s}{P_s} = \frac{wM}{Wm}$$

$$\text{For solution (I), } \frac{(P_0 - 21.85)}{21.85} = \frac{30 \times 18}{90 \times m} \quad \dots (i)$$

$$\text{For solution (II), } \frac{(P_0 - 22.15)}{22.15} = \frac{30 \times 18}{108 \times m} \quad \dots (ii)$$

Dividing eq. (i) by eq. (ii),

$$\frac{(P_0 - 21.85)}{21.85} \times \frac{22.15}{(P_0 - 22.15)} = \frac{108}{90} = \frac{6}{5}$$

$$P_0 = 23.87 \text{ mm of Hg}$$

Substituting the value of  $P_0$  in eq. (i)

$$m = 67.9$$

**Example 28.** What mass of non-volatile solute (urea) needs to be dissolved in 100 g of water in order to decrease the vapour pressure of water by 25%. What will be the molality of solution? (IIT 1993)

**Solution:** Using Raoult's law in the following form,

$$\frac{P_0 - P_s}{P_s} = \frac{wM}{Wm}$$

If  $P_0 = 100 \text{ mm}$ , then  $P_s = 75 \text{ mm}$

$$\frac{100 - 75}{75} = \frac{w \times 18}{100 \times 60}$$

$$w = 111.1$$

$$\text{Molality} = \frac{w \times 1000}{m \times W} = \frac{111.1 \times 1000}{60 \times 100} = 18.52 \text{ m}$$

**Example 29.** A current of dry air was bubbled through a bulb containing 26.66 g of an organic compound in 200 g of water, then through a bulb at the same temperature, containing water and finally through a tube containing anhydrous calcium chloride. The loss of mass in bulb containing water was 0.087 g and gain in mass of the calcium chloride tube was 2.036 g. Calculate the molecular mass of the organic substance.

**Solution:**  $\frac{P_0 - P_s}{P_0} = \frac{\text{Loss in mass of solvent bulb}}{\text{Gain in mass of CaCl}_2 \text{ tube}}$

$$= \frac{0.087}{2.036}$$

Let the molecular mass of the organic substance be  $m$ . According to Raoult's law,

$$\frac{P_0 - P_s}{P_0} = \frac{w/m}{\frac{w}{m} + \frac{W}{M}}$$

$$\frac{0.087}{2.036} = \frac{\frac{26.66}{m}}{\frac{26.66}{m} + \frac{200}{18}} = \frac{26.66}{26.66 + \frac{200}{18}m}$$

$$m = 53.75$$

**Example 30.** The vapour pressure of a dilute aqueous solution of glucose is 750 mm Hg at 373 K. Calculate (i) molality, (ii) mole fraction of the solute.

**Solution:**  $P_0 = \text{Vapour pressure of water at } 373 \text{ K} = 760 \text{ mm Hg}$

Using Raoult's law in the following form,

$$\frac{P_0 - P_s}{P_s} = \frac{wM}{Wm}$$

$$\text{or} \quad \frac{760 - 750}{750} = \frac{w}{Wm} \times 18$$

$$\text{or} \quad \frac{w}{W \times m} = \frac{10}{750 \times 18}$$

$$\text{Molality} = \frac{w}{W \times m} \times 1000 = \frac{10 \times 1000}{750 \times 18} = 0.74 \text{ m}$$

$p_s$  = Mole fraction of solvent  $\times p_0$ ;

$$\text{Mole fraction of solvent} = \frac{750}{760}$$

$$\text{So, Mole fraction of solute} = \left(1 - \frac{750}{760}\right) = 0.0132$$

**Example 31.** Calculate the vapour pressure of an aqueous solution which contains 5 mass per cent of urea. The vapour pressure of pure water is 23.5 mm Hg. Molar mass of urea is 60.

**Solution:** Mass of urea = 5 g

Mass of water = (100 - 5) = 95 g

$$\text{No. of moles of urea} = \frac{5}{60} = 0.083$$

$$\text{No. of moles of water} = \frac{95}{18} = 5.278$$

$$\begin{aligned} \text{Total number of moles} &= 5.278 + 0.083 \\ &= 5.361 \end{aligned}$$

$$\text{Mole fraction of solvent} = \frac{5.278}{5.361}$$

$$\begin{aligned} p_s &= \text{Mole fraction of solvent} \times p_0 \\ &= \frac{5.278}{5.361} \times 23.5 = 23.14 \text{ mm} \end{aligned}$$

**Example 32.** 10 g of glucose (molar mass 180) and 20 g of sucrose (molar mass 342) are dissolved in 100 g of water. What will be the vapour pressure of the resultant solution if the vapour pressure of water is 35 mm Hg?

**Solution:** Mass of glucose = 10 g

$$\text{No. of moles of glucose} = 0.0556$$

$$\text{Mass of sucrose} = 20 \text{ g}$$

$$\text{No. of moles of sucrose} = 0.0585$$

$$\text{Mass of water} = 100 \text{ g}$$

$$\text{No. of moles of water} = 5.556$$

$$\begin{aligned} \text{Total number of moles} &= 5.556 + 0.0585 + 0.0556 \\ &= 5.67 \end{aligned}$$

$$\text{Mole fraction of water} = \frac{5.556}{5.67}$$

Vapour pressure of solution = Mole fraction of water  $\times p_0$

$$= \frac{5.556}{5.67} \times 35 = 34.3 \text{ mm Hg}$$

**Example 33.** Calculate the vapour pressure of an aqueous solution of 1.0 molal glucose solution at 100°C.

**Solution:** Molality =  $\frac{w}{m \times W} \times 1000$

where,  $w$  = mass of solute in grams;

$W$  = mass of solvent in grams

$$1.0 = \frac{w}{m \times W} \times 1000$$

or

$$\frac{w}{m \times W} = \frac{1.0}{1000} = 0.001$$

Applying Raoult's law for dilute solution,

$$\frac{p_0 - p_s}{p_0} = \frac{w}{m \times W} \times M \quad (M = 18)$$

$$\frac{760 - p_s}{760} = 0.001 \times 18 \quad (p_0 = 760 \text{ mm at } 100^\circ\text{C})$$

or

$$\begin{aligned} p_s &= 760 - 760 \times 0.001 \times 18 \\ &= 760 - 13.68 \\ &= 746.32 \text{ mm} \end{aligned}$$

**Example 34.** The vapour pressure of pure benzene at 50°C is 268 mm of Hg. How many moles of non-volatile solute per mole of benzene are required to prepare a solution of benzene having a vapour pressure 167 mm of Hg at 50°C?

**Solution:** Applying Raoult's law in the following form:

$$\frac{p_0 - p_s}{p_s} = \frac{wM}{Wm} = \frac{w/m}{W/M}$$

= No. of moles of solute per mole of benzene

$$\text{or } \frac{n}{N} = \frac{(268 - 167)}{167} = 0.6047 \approx 0.605$$

**Alternative method:** We know that,  $p_s$  = Mole fraction of solvent  $\times p_0$

or  $167 = \text{Mole fraction of solvent} \times 268$

$$\text{So, Mole fraction of solvent} = \frac{167}{268} = 0.623$$

$$\text{Mole fraction of solute} = 1 - 0.623 = 0.377$$

$$\frac{n}{N} = \frac{\text{Mole fraction of solute}}{\text{Mole fraction of solvent}} = \frac{0.377}{0.623} = 0.605$$

### ILLUSTRATIONS OF OBJECTIVE QUESTIONS

19. The vapour pressure of water at 23°C is 19.8 mm. 0.1 mole glucose is dissolved in 178.2 g of water. What is the vapour pressure (in mm) of the resultant solution?

- (a) 19      (b) 19.602      (c) 19.402      (d) 19.202

[Ans. (b)]

$$\text{Hint: } n_B = 0.1, n_A = \frac{178.2}{18} = 9.9$$

$$x_A = \frac{n_A}{n_A + n_B} = \frac{9.9}{9.9 + 0.1} = 0.99$$

$$\begin{aligned} p &= p_0 x_A \\ &= 19.8 \times 0.99 = 19.602 \text{ mm} \end{aligned}$$

20. What is the vapour pressure of the solution containing 34.2 g of sucrose per 100 g of water at 25°C? The vapour pressure of water at 25°C is 23.75 mm.

- (a) 20.3 mm      (b) 23.10 mm  
 (c) unpredictable      (d) 23.33 mm

[Ans. (d)]

[Hint:  $n_A = \frac{w_A}{m_A} = \frac{100}{18} = 5.55$

$$n_B = \frac{34.2}{342} = 0.1$$

$$x_A = \frac{5.55}{5.55 + 0.1} = \frac{5.55}{5.65} = 0.982$$

$$p = p_0 x_A$$

$$= 23.75 \times 0.982 = 23.33 \text{ mm}$$

21. Lowering of vapour pressure due to a solute in 1 molal aqueous solution at 100°C is:

- (a) 13.44 mm Hg                  (b) 14.12 mm Hg  
 (c) 31.2 mm Hg                  (d) 35.2 mm Hg

[Ans. (a)]

[Hint:  $m = \frac{x_B \times 1000}{(1 - x_B)m_A}$        $x_B$  = mole fraction of solute  
 $m_A$  = molar mass of solvent

$$1 = \frac{x_B \times 1000}{(1 - x_B) \times 18}$$

$$x_B = 0.0176$$

$$x_A = 1 - 0.0176 = 0.9824$$

$$p = p_0 x_A$$

$$= 760 \times 0.9824 = 746.62$$

$$\Delta p = p_0 - p = 760 - 746.62$$

$$\approx 13.4 \text{ mm Hg}$$

22. The mass of a non-volatile solute (molecular mass = 40) which should be dissolved in 114 g octane to reduce its vapour pressure to 80% will be:

- (a) 20 g                  (b) 30 g                  (c) 10 g                  (d) 40 g

[Ans. (c)]

[Hint: If  $p_0 = 100$ , then  $p = 80$

$$p = p_0 x_A$$

$$80 = 100 \times x_A$$

$$x_A = 0.80$$

$$x_A = \frac{n_A}{n_A + n_B} = \frac{114/114}{114/114 + w_B/40}$$

$$0.8 = \frac{1}{1 + w_B/40}$$

$$1 + \frac{w_B}{40} = \frac{1}{0.8}$$

$$w_B = 10 \text{ g}$$

23. 3g urea is dissolved in 45g of water. The relative lowering of vapour pressure is :                  [Comed (Karnataka) 2008]

- (a) 0.05                  (b) 0.04                  (c) 0.02                  (d) 0.01

[Ans. (c)]

[Hint:  $n_B = \frac{3}{60} = 0.05$ ;       $n_A = \frac{45}{18} = 2.5$

$$\frac{\Delta p}{p_0} = x_B = \frac{0.05}{2.5 + 0.05} = 0.0196 = 0.02$$

24. When 25g of a non-volatile solute is dissolved in 100g of water, the vapour pressure is lowered by 0.225 mm. If the

vapour pressure of water at 25°C is 17.5 mm, what is the molecular mass of the solute?                  [EAMCET (Engg) 2008]

- (a) 206                  (b) 302                  (c) 318                  (d) 276

[Ans. (c)]

[Hint :  $p = p_0 x_A$

$$(17.5 - 0.225) = 17.5 \times \frac{100/18}{100/18 + \frac{25}{m_B}}$$

$$\frac{17.275}{17.5} \left( \frac{100}{18} + \frac{25}{m_B} \right) = \frac{100}{18}$$

$$0.987 \left( \frac{100}{18} + \frac{25}{m_B} \right) = 5.55$$

$$5.55 + \frac{25}{m_B} = 5.628$$

$$m_B \approx 318 \text{ mm}$$

## 5.11 ELEVATION OF BOILING POINT (Ebullioscopy)

The boiling point of a liquid is the temperature at which its vapour pressure is equal to the atmospheric pressure. The vapour pressure of a liquid is lowered when a non-volatile solute is added to it. Hence, the temperature of the solution when its vapour pressure will be equal to atmospheric pressure will be higher than the temperature of the pure solvent. In other words, the boiling point of the solvent is elevated by the addition of non-volatile solute. The difference in the boiling point of the solution and the boiling point of the pure solvent is termed elevation of boiling point.

Elevation of boiling point,

$(\Delta T) = \text{Boiling point of the solution} - \text{Boiling point of pure solvent}$

This can be better understood by plotting a graph of vapour pressure against temperature for a pure solvent and two solutions of different concentrations. The curves of the solutions always lie below the curve of the pure solvent. The line  $P_0 C$  represents the atmospheric pressure.  $T_0$ ,  $T_1$  and  $T_2$  represent the boiling points of pure solvent, solution I and solution II respectively. The vapour pressure of pure solvent, solution I and solution II at temperature  $T_0$  are  $P_0$ ,  $P_1$  and  $P_2$  respectively.

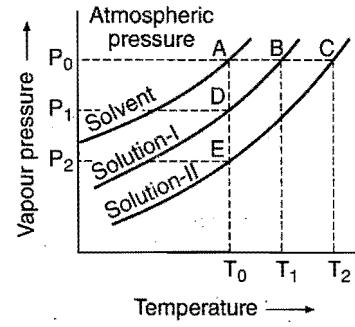


Fig. 5.10

Assuming that the solutions are very dilute, these curves may be approximately taken as straight lines near the boiling point. Thus,  $\Delta ACE$  and  $\Delta ABD$  are similar.

Therefore,

$$\frac{AC}{AB} = \frac{AE}{AD}$$

or

$$\frac{T_2 - T_0}{T_1 - T_0} = \frac{P_0 - P_2}{P_0 - P_1}$$

or

$$\frac{\Delta T_2}{\Delta T_1} = \frac{\Delta P_2}{\Delta P_1}$$

or

$$\Delta T \propto \Delta P$$

From Raoult's law for dilute solution,

$$\frac{P_0 - p_s}{P_0} = \frac{w_B \times m_A}{m_B \times w_A}$$

( $p_s$  = vapour pressure of solution)

or

$$P_0 - p_s = \frac{w_B \times m_A}{m_B \times w_A} \cdot P_0$$

For the pure solvent,  $P_0$  (its vapour pressure at the boiling point) and  $m_A$  (its molecular mass) are constant. Therefore,

$$P_0 - p_s \propto \frac{w_B}{m_B \times w_A}$$

or

$$\Delta p \propto \Delta T \propto \frac{w_B}{m_B \times w_A}$$

or

$$\Delta T = K \cdot \frac{w_B}{m_B \times w_A} \quad \dots (i)$$

where  $K$  is a constant, called as elevation constant.

When,  $\frac{w_B}{m_B} = 1$ , (one mole of solute) and  $w_A = 1$  g, then

$$\Delta T = K$$

Thus, boiling point constant is equal to the elevation in boiling point which would be theoretically produced when 1 mole of a non-volatile solute is dissolved in 1 g of the solvent.

If  $\frac{w_B}{m_B} = 1$  and  $w_A = 100$  g,

Then,

$$\Delta T = \frac{K}{100} = K'$$

$K'$  is called **molecular elevation constant**. It is defined as the elevation in boiling point produced when 1 mole of the solute is dissolved in 100 g of the solvent.

Thus,

$$K = 100K'$$

Putting this value in eq. (i),

$$\Delta T = 100K' \cdot \frac{w_B}{m_B w_A} \quad \dots (ii)$$

If  $\frac{w_B}{m_B} = 1$  and  $w_A = 1000$  g,

\* This relation may also be written as:

$$\Delta T = \frac{1000 K_b \times w}{m \times W}$$

where,  $w$  and  $W$  are masses of solute and solvent respectively and  $m$  = molecular mass of solute.

Then,

$$\Delta T = \frac{K}{1000} = K_b$$

$K_b$  is called **molal elevation constant**. It is defined as the elevation in boiling point produced when 1 mole of the solute is dissolved in 1000 g of the solvent.

Thus,

$$K = 1000 K_b$$

Putting this value in eq. (i),

$$\Delta T = \frac{1000 K_b w_A}{m_A w_B} \quad \dots (iii)$$

or

$$\Delta T = \text{Molality} \times K_b$$

$$\left( \text{since } \frac{w_B}{m_B \times w_A} \times 1000 = \text{molality} \right)$$

The elevation in boiling point of a solution of non-electrolyte is proportional to its molality and equimolar solutions of all the substances in the same solvent will show equal elevation in boiling points. These are known as Raoult's laws of elevation of boiling point.

Molal elevation constant is characteristic of a particular solvent and can be calculated from the thermodynamical relationship.

$$K_b = \frac{RT_b^2}{1000 L_v}$$

where,  $R$  is molar gas constant,  $T_b$  is the boiling point of the solvent on kelvin scale and  $L_v$ , the latent heat of vaporisation of solvent in calories per gram.

$$\text{For water} \quad K_b = \frac{2 \times (373)^2}{1000 \times 540} = 0.515$$

The molal elevation constants for some common solvents are given in the following table:

**Table 5.4 Molal Elevation Constants of Some Solvents**

Solvent	B.pt. (°C)	Molal elevation constant (K kg mol⁻¹)
Water	100.0	0.52
Acetone	56.0	1.70
Chloroform	61.2	3.67
Carbon tetrachloride	76.8	5.02
Benzene	80.0	2.70
Ethyl alcohol	78.4	1.15

If  $K_b$ ,  $w_A$ ,  $\Delta T$  and  $w_B$  are known, molecular mass of a non-volatile solute can be determined. The most convenient method for the determination of  $\Delta T$  in the laboratory is the Landsberger method.

## 5.12 DEPRESSION OF FREEZING POINT (Cryoscopy)

Freezing point of a substance is defined as the temperature at which the vapour pressure of its liquid is equal to the vapour pressure of the corresponding solid. Since, the addition of a non-volatile solute always lowers the vapour pressure of a solvent, therefore, it will be in equilibrium with solid phase at a lower pressure and hence at a lower temperature. The difference between the freezing points of the pure solvent and its solution is called depression of freezing point.

Depression of freezing point

$$(\Delta T) = \text{Freezing point of the solvent}$$

$$- \text{Freezing point of the solution}$$

This can be better understood by plotting a graph of vapour pressure against temperature for a pure solvent and two solutions, solution I and solution II. *CFB* is a curve for a solid solvent. The solvent, solution I and solution II vapour pressure curves meet *CFB* curve at points *B*, *F* and *C* respectively. Thus,  $T_0$ ,  $T_1$  and  $T_2$  are the freezing points of pure solvent, solution I and solution II respectively. The vapour pressures at temperatures  $T_0$ ,  $T_1$  and  $T_2$  for solvent, solution I and solution II are, thus,  $P_0$ ,  $P_1$  and  $P_2$  respectively.

For very dilute solutions, the curves *FD* and *CE* are almost straight lines and *CB* is also nearly a straight line. The  $\Delta BEC$  and  $\Delta BDF$  are similar.

So,

$$\frac{EC}{DF} = \frac{BE}{BD}$$

or

$$\frac{T_0 - T_2}{T_0 - T_1} = \frac{P_0 - P_2}{P_0 - P_1}$$

or

$$\frac{\Delta T_2}{\Delta T_1} = \frac{\Delta P_2}{\Delta P_1}$$

or

$$\Delta T \propto \Delta P$$

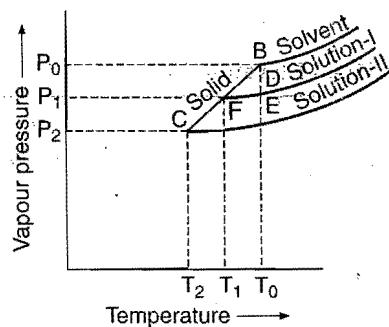


Fig. 5.11

From Raoult's law for dilute solutions,

$$\frac{P_0 - P_s}{P_0} = \frac{w_B}{m_B} \cdot \frac{m_A}{w_A}$$

\* This relation may also be written as:

$$\Delta T = \frac{1000 K_f \times w}{m \times W}$$

where  $w$  and  $W$  are the masses of solute and solvent respectively and  $m$  = molecular mass of solute.

or

$$P_0 - P_s = \frac{w_B}{m_B} \cdot \frac{m_A}{w_A} \cdot P_0$$

For the pure solvent,  $P_0$  and  $m_B$  are constants. Therefore,

$$P_0 - P_s \propto \frac{w_B}{m_B w_A}$$

or

$$\Delta p \propto \frac{w_B}{m_B w_A}$$

or

$$\Delta p \propto \Delta T \propto \frac{w_B}{m_B w_A}$$

or

$$\Delta T = K \cdot \frac{w_B}{m_B w_A} \quad \dots (i)$$

where,  $K$  is a constant, called depression constant.

$$\text{When, } \frac{w_B}{m_B} = 1 \text{ (one mole of solute)} \text{ and } w_A = 1 \text{ g}$$

$$\Delta T = K$$

Thus, depression constant is equal to the depression of the freezing point which would be theoretically produced when one mole of a non-volatile solute is dissolved in 1 g of the solvent.

$$\text{If } \frac{w_B}{m_B} = 1 \text{ and } w_B = 100 \text{ g,}$$

$$\Delta T = \frac{K}{100} \\ = K'$$

$K'$  is called molecular depression constant.

**It is defined as the depression of freezing point produced when 1 mole of the solute is dissolved in 100 g of the solvent.**

Thus,

$$K = 100K'$$

Putting this value in eq. (i),

$$\Delta T = \frac{100K' \times w_B}{m_B \times w_A} \quad \dots (ii)$$

$$\text{If } \frac{w_B}{m_B} = 1 \text{ and } w_A = 1000 \text{ g}$$

$$\Delta T = \frac{K}{1000} \\ = K_f$$

$K_f$  is called molal depression constant.

**It is defined as the depression of freezing point produced when 1 mole of solute is dissolved in 1000 g of the solvent.**

Thus,

$$K = 1000 K_f$$

Putting this value in eq. (i),

$$\Delta T = 1000 K_f \cdot \frac{w_B}{m_B w_A} \quad \dots (iii)$$

or

$$\Delta T = \text{molality} \times K_f$$

$K_f$  is characteristic of a particular solvent and can be calculated from the thermodynamical relationship

$$K_f = \frac{0.002 T_f^2}{L_f}$$

where,  $T_f$  is the freezing point of solvent in absolute scale and  $L_f$  the latent heat of fusion in calories per gram of the solvent. For water,

$$K_f = \frac{0.002 \times (273)^2}{80}$$

$$= 1.86 \text{ K kg mol}^{-1}$$

The molal depression constants for some common solvents are given in the following table:

**Table 5.5 Molal Depression Constants of Some Solvents**

Solvent	F.pt. (°C)	Molal elevation constant (K kg mol <sup>-1</sup> )
Water	0.0	1.86
Ethyl alcohol	-114.6	1.99
Chloroform	-63.5	4.70
Carbon tetrachloride	-22.8	29.80
Benzene	5.5	5.12
Camphor	179.0	39.70

If  $K_f$ ,  $w_A$ ,  $\Delta T$  and  $w_B$  are known, molecular mass of a non-volatile solute can be determined.  $\Delta T$  is measured by Beckmann's method in the laboratory.

The molecular mass of non-volatile and non-ionisable solute can be calculated using following formula:

$$m_B = \frac{K_f}{\Delta T} \times \frac{w_B}{w_A} \times 1000$$

where,  $w_B$  and  $w_A$  are the masses of solute and solvent respectively.

**Anti-freeze solutions :** Water is used in radiators of cars and other automobilcs. In cold countries where the atmospheric temperature becomes less than zero degree, the water in the radiators would freeze. Anti-freeze solutions are useful under these conditions when the vehicles are used in the regions of sub-zero temperature so that the water does not freeze in radiators. Such solutions are made by dissolving ethylene glycol in water. Freezing point can be lowered to the desired extent by varying the concentration of ethylene glycol. Glycerol can also be used as anti-freeze.

**Freezing mixture :** It is a mixture of ice and common salt (NaCl). It is used in the making of ice-cream and in the laboratories to create low temperatures. With the help of this mixture, a temperature as low as -33°C (240 K) can be achieved.

**Note:** Ebullioscopic and cryoscopic methods are effective when :

- (i) Solutions are dilute. Solutions obey Raoult's law.
- (ii) The solute is non-volatile.
- (iii) There is no association or dissociation of solute molecules in the solution.

- (iv) Solute does not form a solid solution with solvent in frozen state, i.e., only solvent separates in solid state on freezing the solution.
- (v) Equimolar quantities of different substances dissolved in the same quantity of solvent bring out the same depression in freezing point of the solvent under identical conditions.

### ::: SOME SOLVED EXAMPLES :::

**Example 35.** On dissolving 10.8 g glucose (m.wt. = 180) in 240 g of water, its boiling point increases by 0.13°C. Calculate the molecular elevation constant of water.

**Solution:**  $\Delta T = \frac{100K_b \times w}{W \times m}$

or  $K' = \frac{\Delta T \times W \times m}{100 \times w}$

Given,  $\Delta T = 0.13^\circ\text{C}$ ,  $W = 240\text{ g}$ ,  $m = 180$  and  $w = 10.8\text{ g}$

$$K' = \frac{0.13 \times 240 \times 180}{100 \times 10.8} = 5.2^\circ$$

**Example 36.** A solution of 2.5 g of a non-volatile solid in 100 g benzene is boiled at 0.42°C higher than the boiling point of pure benzene. Calculate the molecular mass of the substance. Molal elevation constant of benzene is 2.67 K kg mol<sup>-1</sup>.

**Solution:**  $m = \frac{1000K_b \times w}{W \times \Delta T}$

Given,  $K_b = 2.67$ ,  $w = 2.5\text{ g}$ ,  $W = 100\text{ g}$ ,  $\Delta T = 0.42^\circ\text{C}$

$$m = \frac{1000 \times 2.67 \times 2.5}{100 \times 0.42} = 158.9$$

The molecular mass of substance is 158.9.

**Example 37.** The molal elevation constant for water is 0.56 K kg mol<sup>-1</sup>. Calculate the boiling point of a solution made by dissolving 6.0 g of urea ( $\text{NH}_2\text{CONH}_2$ ) in 200 g of water.

**Solution:**  $\Delta T = \frac{1000K_b \times w}{m \times W}$

Given,  $K_b = 0.56 \text{ K kg mol}^{-1}$ ,  $w = 6.0 \text{ g}$ ,  $W = 200 \text{ g}$ ,  $m = 60$

$$\Delta T = \frac{1000 \times 0.56 \times 6.0}{200 \times 60} = 0.28^\circ\text{C}$$

Thus, the boiling point of solution = b.pt. of water +  $\Delta T$

$$= (100^\circ\text{C} + 0.28^\circ\text{C}) = 100.28^\circ\text{C}$$

**Example 38.** By dissolving 13.6 g of a substance in 20 g of water, the freezing point decreased by 3.7°C. Calculate the molecular mass of the substance. 'Molal depression constant for water = 1.863 K kg mol<sup>-1</sup>)

**Solution:**  $m = \frac{1000K_f \times w}{W \times \Delta T}$

Given,  $K_f = 1.863 \text{ K kg mol}^{-1}$

$$w = 13.6 \text{ g}, W = 20 \text{ g}, \Delta T = 3.7^\circ\text{C}$$

$$m = \frac{1000 \times 1.863 \times 13.6}{20 \times 3.7} = 342.39$$

**Example 39.** On dissolving 0.25 g of a non-volatile substance in 30 mL benzene (density 0.8 g/mL), its freezing point decreases by 0.40°C. Calculate the molecular mass of non-volatile substance ( $K_f = 5.12 \text{ K kg mol}^{-1}$ ).

**Solution:** Mass of benzene,  $W = \text{volume} \times \text{density}$

$$= 30 \times 0.8 = 24 \text{ g}$$

Given,  $K_f = 5.12 \text{ K kg mol}^{-1}$ ,  $w = 0.25 \text{ g}$ ,  $\Delta T = 0.40^\circ\text{C}$ .

We know that,

$$\begin{aligned} m &= \frac{1000 K_f \times w}{W \times \Delta T} \\ &= \frac{1000 \times 5.12 \times 0.25}{24 \times 0.40} = 133.33 \end{aligned}$$

**Example 40.** A solution of 1.25 g of a certain non-volatile substance in 20 g of water freezes at 271.94 K. Calculate the molecular mass of the solute ( $K_f = 1.86 \text{ K kg mol}^{-1}$ ).

**Solution:** Freezing point of solution = 271.94 K

Freezing point of water = 273.0 K

$$\Delta T = (273 - 271.94) = 1.06 \text{ K}$$

$$\text{We know that, } m = \frac{1000 K_f \times w}{W \times \Delta T}$$

Given,  $K_f = 1.86 \text{ K kg mol}^{-1}$ ,  $w = 1.25 \text{ g}$ ,  $W = 20 \text{ g}$  and  $\Delta T = 1.06 \text{ K}$ .

$$m = \frac{1000 \times 1.86 \times 1.25}{20 \times 1.06} = 109.66$$

**Example 41.** Two elements A and B form compounds having molecular formulae  $AB_2$  and  $AB_4$ . When dissolved in 20.0 g of benzene, 1.0 g of  $AB_2$  lowers the freezing point by 2.3°C, whereas 1.0 g of  $AB_4$  lowers the freezing point by 1.3°C. The molal depression constant for benzene in 1000 g is 5.1. Calculate the atomic masses of A and B.

**Solution:** We know that,

$$m = \frac{1000 K_f \times w}{W \times \Delta T}$$

$$\begin{aligned} \text{Molecular mass of } AB_2 \text{ (from given data)} &= \frac{1000 \times 5.1 \times 1}{20 \times 2.3} \\ &= 110.86 \end{aligned}$$

$$\begin{aligned} \text{and Molecular mass of } AB_4 \text{ (from given data)} &= \frac{1000 \times 5.1 \times 1}{1.3 \times 20} \\ &= 196.15 \end{aligned}$$

$$\text{Further, } AB_4 = A + 4B = 196.15 \quad \dots \text{(i)}$$

$$AB_2 = A + 2B = 110.86 \quad \dots \text{(ii)}$$

Subtracting eq. (ii) from (i),

$$2B = 85.29$$

$$B = 42.645$$

Putting the value of B in eq. (ii),

$$A + 85.29 = 110.86$$

$$\text{or } A = (110.86 - 85.29) = 25.57$$

Thus, the atomic masses of A and B are 25.57 and 42.645 respectively.

**Example 42.** 1.355 g of a substance dissolved in 55 g of  $\text{CH}_3\text{COOH}$  produced a depression in the freezing point of 0.618°C. Calculate the molecular weight of the substance ( $K_f = 3.85$ ). [CECE (Mains) Bihar 2005]

$$\text{Solution: } \Delta T = K_f \times \frac{w_B \times 1000}{m_B \times w_A}$$

where,  $w_B$  = mass of solute,  $m_B$  = molar mass of solute,  $w_A$  = mass of solvent

$$\begin{aligned} 0.618 &= 3.85 \times \frac{1.355 \times 1000}{m_B \times 55} \\ m_B &= 153.47 \end{aligned}$$

**Example 43.** An aqueous solution of a non-volatile solute boils at 100.17°C. At what temperature will the solution freeze? (Given:  $K_b = 0.512 \text{ K kg mol}^{-1}$  and  $K_f = 1.86 \text{ K kg mol}^{-1}$ )

**Solution:** We know that,

$$\begin{aligned} \Delta T_b &= \text{molality} \times K_b \\ 0.17 &= \text{molality} \times 0.512 \end{aligned}$$

$$\text{Molality of the solution} = \frac{0.17}{0.512} \text{ m}$$

Let depression in freezing point be  $\Delta T_f$

$$\begin{aligned} \Delta T_f &= \text{molality} \times K_f \\ &= \frac{0.17}{0.512} \times 1.86 = 0.62^\circ\text{C} \end{aligned}$$

Thus, the freezing point of the solution is

$$0.00 - 0.62 = -0.62^\circ\text{C}$$

**Example 44.** 18 g of glucose,  $\text{C}_6\text{H}_{12}\text{O}_6$ , is dissolved in 1 kg of water in a saucepan. At what temperature will the water boil (1.013 bar pressure)?  $K_b$  for water is  $0.52 \text{ K kg mol}^{-1}$ .

$$\text{Solution: } \Delta T = K_b \times \frac{w_B \times 1000}{m_B \times w_A}$$

$$\Delta T = 0.52 \times \frac{18 \times 1000}{180 \times 1000}$$

$$T - T_0 = 0.052$$

$$T - 373 = 0.052$$

$$T = 373.052 \text{ K}$$

**Example 45.** A solution of urea in water has boiling point of 100.15°C. Calculate the freezing point of the same solution if  $K_f$  and  $K_b$  for water are  $1.87 \text{ K kg mol}^{-1}$  and  $0.52 \text{ K kg mol}^{-1}$  respectively.

$$\text{Solution: } \Delta T_b = (100.15 - 100) = 0.15^\circ\text{C}$$

We know that,  $\Delta T_b = \text{molality} \times K_b$

$$\text{Molality} = \frac{\Delta T_b}{K_b} = \frac{0.15}{0.52} = 0.2884$$

$$\Delta T_f = \text{molality} \times K_f \\ = 0.2884 \times 1.87 = 0.54^\circ\text{C}$$

Thus, the freezing point of the solution =  $-0.54^\circ\text{C}$

**Example 46.** In a cold climate, water gets frozen causing damage to radiator of a car. Ethylene glycol is used as antifreezing agent. Calculate the amount of ethylene glycol to be added to 4 kg of water to prevent it from freezing at  $-6^\circ\text{C}$  ( $K_f$  for water =  $1.85 \text{ K kg mol}^{-1}$ ). (IIT 1992)

**Solution:** Given,

$$\Delta T = 6^\circ\text{C}, W = 4 \text{ kg} = 4000 \text{ g}, m = 62, K_f = 1.85$$

$$w = \frac{m \times W \times \Delta T}{1000 \times K_f} \\ = \frac{62 \times 4000 \times 6}{1000 \times 1.85} = 804.32 \text{ g}$$

**Example 47.** A solution containing 0.2563 g of naphthalene (molecular mass = 128) in 50 g of carbon tetrachloride yields a boiling point elevation of  $0.201^\circ\text{C}$  while a solution of 0.6216 g of an unknown solute in the same mass of the solvent gives a boiling point elevation of  $0.647^\circ\text{C}$ . Find the molecular mass of the unknown solute.

**Solution:** We know that,

$$K_b = \frac{\Delta T_b \times W \times m}{1000 \times w}$$

$$\text{For CCl}_4, K_b = \frac{0.201 \times 50 \times 128}{1000 \times 0.2563} = 5.019$$

$K_b$  is now used in the second part of the problem.

$$m = \frac{1000 \times K_b \times w}{\Delta T_b \times W} \\ = \frac{1000 \times 5.019 \times 0.6216}{0.647 \times 50} = 96.44$$

**Example 48.** Calculate the molal depression constant of a solvent which has freezing point  $16.6^\circ\text{C}$  and latent heat of fusion  $180.75 \text{ J g}^{-1}$ .

$$\text{Solution: } K_f = \frac{RT_f^2}{1000 \times L_f}$$

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1},$$

$$T_f = 16.6^\circ\text{C} = 273 + 16.6 = 289.6 \text{ K},$$

$$L_f = 180.75 \text{ J g}^{-1}$$

Substituting the values in the above equation,

$$K_f = \frac{8.314 \times (289.6)^2}{1000 \times 180.75} = 3.86$$

### ILLUSTRATIONS OF OBJECTIVE QUESTIONS

25. Calculate the molal depression constant of a solvent which has freezing point  $16.6^\circ\text{C}$  and latent heat of fusion  $180.75 \text{ J g}^{-1}$ . [JEE (Orissa) 2005]

- (a) 2.68      (b) 3.86      (c) 4.68      (d) 2.86

[Ans. (b)]

$$[\text{Hint: } K_f = \frac{RT_0^2}{1000L} \\ = \frac{8.314 \times (289.6)^2}{1000 \times 180.75} \\ = 3.86]$$

26. The elevation in boiling point for 13.44 g of  $\text{CuCl}_2$  dissolved in 1 kg of water as solvent will be ( $K_b = 0.52 \text{ K kg mol}^{-1}$ ; molar mass of  $\text{CuCl}_2 = 134.4 \text{ g/mol}$ ): (IIT 2005)

- (a) 0.05      (b) 0.10      (c) 0.16      (d) 0.20

[Ans. (c)]

[Hint:  $i = 3$ , assuming complete ionization of  $\text{CuCl}_2$

$$\Delta T = i \times K_b \times \frac{w_B \times 1000}{m_B \times w_A} \\ = 3 \times 0.52 \times \frac{13.44 \times 1000}{134.4 \times 1000} = 0.156 \approx 0.16$$

27. A solution containing 7 g of a solute (molar mass  $210 \text{ g mol}^{-1}$ ) in 350 g of acetone raised the boiling point of acetone from  $56^\circ\text{C}$  to  $56.3^\circ\text{C}$ . The value of ebullioscopic constant of acetone in  $\text{K kg mol}^{-1}$  is:

- (a) 2.66      (b) 3.15      (c) 4.12      (d) 2.86

[Ans. (b)]

$$[\text{Hint: } \Delta T = K_b \times \frac{w_B \times 1000}{m_B \times w_A} \\ 0.3 = K_b \times \frac{7 \times 1000}{210 \times 350} \\ K_b = \frac{0.3 \times 210 \times 350}{7 \times 1000} = 3.15 \text{ K kg mol}^{-1}]$$

28. The normal boiling point of toluene is  $110.7^\circ\text{C}$  and its boiling point elevation constant is  $3.32 \text{ K kg mol}^{-1}$ . The enthalpy of vaporization of toluene is nearly:

- (a)  $17 \text{ kJ mol}^{-1}$       (b)  $21 \text{ kJ mol}^{-1}$   
(c)  $51 \text{ kJ mol}^{-1}$       (d)  $68 \text{ kJ mol}^{-1}$

[Ans. (b)]

$$[\text{Hint: } K_b = \frac{RT_0^2}{1000L}; 3.32 = \frac{(8.314 \times 10^{-3}) \times (383.7)^2}{1000 \times L}$$

$$L = 0.368 \text{ kJ/g}$$

Latent heat per mol =  $0.368 \times$  molar mass of acetone  
=  $0.368 \times 58 = 21.344 \text{ kJ mol}^{-1}$

29. An aqueous solution freezes at  $-0.186^\circ\text{C}$  ( $K_f = 1.86 \text{ K kg mol}^{-1}$ ,  $K_b = 0.512 \text{ K kg mol}^{-1}$ ). The elevation of b. pt. of the solution is:

$$(a) 0.186 \quad (b) 0.512 \quad (c) \frac{0.512}{1.86} \quad (d) 0.0512$$

[Ans. (d)]

[Hint:  $\Delta T = K_f \times m$

$$0.186 = 1.86 \times m$$

$$m = 0.1$$

$$\Delta T = K_b \times m = 0.512 \times 0.1 = 0.0512]$$

30. The amount of urea to be dissolved in 500 cc of water ( $K_f = 1.86$ ) to produce a depression of  $0.186^\circ\text{C}$  in the freezing point is: [UGET (Manipal) 2006]

$$(a) 9 \text{ g} \quad (b) 6 \text{ g} \quad (c) 3 \text{ g} \quad (d) 0.3 \text{ g}$$

[Ans. (c)]

[Hint:  $\Delta T = K_f \times \frac{w_B \times 1000}{m_B \times w_A}$

$$0.186 = 1.86 \times \frac{w_B \times 1000}{60 \times 500}$$

$$w_B = 3 \text{ g}]$$

31. What should be the freezing point of aqueous solution containing 17 g of  $\text{C}_2\text{H}_5\text{OH}$  in 1000 g of water ( $K_f$  for water =  $1.86 \text{ deg kg mol}^{-1}$ )?

$$(a) -0.69^\circ\text{C} \quad (b) 0.34^\circ\text{C} \\ (c) 0.0^\circ\text{C} \quad (d) -0.34^\circ\text{C}$$

[Ans. (a)]

[Hint:  $\Delta T = K_f \times \frac{w_B \times 1000}{m_B \times w_A} = 1.86 \times \frac{17 \times 1000}{46 \times 1000} = 0.69$

$$\therefore \text{Freezing point of solution} = 0 - 0.69 = -0.69^\circ\text{C}]$$

## 5.13 OSMOSIS AND OSMOTIC PRESSURE

**Osmosis:** When a semipermeable membrane is placed between a solution and a solvent, it is observed that solvent molecules enter the solution and the volume of solution increases. It is also observed that if two solutions of unequal concentrations are separated by a semipermeable membrane, the solvent molecules from a solution of lower concentration move towards a solution of higher concentration. This phenomenon was first observed by **Abbe Nollet** (1748) and termed as **Osmosis** (Greek, *osmos* = to push). Osmosis is defined as the spontaneous flow of solvent molecules through semipermeable membrane from a pure solvent to a solution or from a dilute to a concentrated solution.

The phenomenon of osmosis can be demonstrated by the following experiment:

Two eggs of same size are taken and their outer hard shell is removed by dissolving in dilute hydrochloric acid. One of the eggs is placed in distilled water and the other in saturated salt solution.

After sufficient time, it is noticed that the egg placed in water swells up and that placed in salt solution shrinks. In the first case, water enters the concentrated egg fluid while in the second case, water comes out of the egg as salt solution is more concentrated than the egg fluid.

\* Membranes which allow the passage of only solvent molecules through them are called semipermeable membranes. Egg membrane, goat's bladder and cell membranes can serve as semipermeable membranes but these are not perfect for laboratory measurements. Artificial membranes of gelatinous inorganic substances such as copper ferrocyanide are used these days as semipermeable membranes.

### Difference between Osmosis and Diffusion

The two processes, diffusion and osmosis, can be distinguished in terms of the following aspects:

(i) In diffusion, solute as well as solvent molecules flow in opposite directions while in osmosis the flow of solvent molecules occurs in one direction only.

(ii) For osmosis, a semipermeable membrane\* is required while for diffusion it is not required.

### Semipermeable membrane

"A membrane which allows the solvent molecules to pass through it but prevents the passage of solute molecules through it is called a semipermeable membrane."

Examples of semipermeable membranes are too many. Parchment paper, membranes covering the animal and plant cells and many gelatinous inorganic substances such as calcium phosphate and copper ferrocyanide, etc., act as semipermeable membranes. Animal and plant membranes are not all completely semipermeable. The best semipermeable membrane used is prepared by deposition of copper ferrocyanide,  $\text{Cu}_2[\text{Fe}(\text{CN})_6]$ , in the pores of a porous pot.

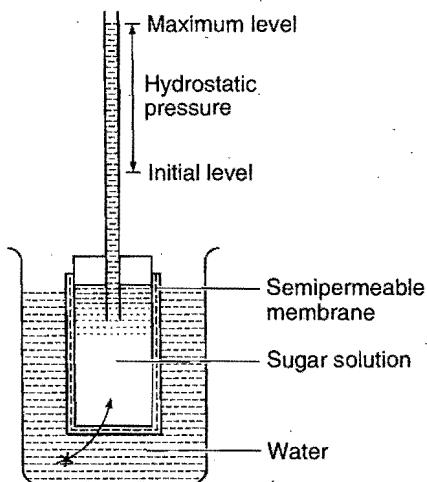
**Working of semipermeable membrane :** Several theories have been put forward to explain the working of semipermeable membrane. These are :

**(a) The sieve theory :** The theory was suggested by Traube. According to this theory, a semipermeable membrane contains a large number of small pores which act like a sieve. The pores allow the smaller molecules of solvent to pass through it but does not allow the larger molecules of solute to do so. However, this theory fails in those cases of semipermeability where the solute molecules are smaller than the solvent molecules.

**(b) The solution theory :** According to this theory, a membrane is permeable to those substances which dissolve in it and is impermeable to those which are insoluble in it. Thus, a layer of phenol acts as a semipermeable membrane when placed between a solution of  $\text{Ca}(\text{NO}_3)_2$ . Phenol allows water to pass through it because water is soluble in phenol. It is impermeable to  $\text{Ca}(\text{NO}_3)_2$  because  $\text{Ca}(\text{NO}_3)_2$  is insoluble in phenol.

**(c) Vapour pressure theory :** According to this theory, a solvent can pass through a semipermeable membrane because the vapour pressure of the pure solvent is higher than the vapour pressure of the solution. This theory is widely accepted because it explains the phenomenon of osmosis.

**Osmotic pressure:** A porous pot is taken and a semipermeable membrane of copper ferrocyanide is deposited in its walls. It is fitted with a long glass tube with the help of a rubber stopper. It is filled with concentrated aqueous sugar solution and placed in distilled water. Osmosis occurs and the level of the solution in glass tube rises over a period of time. After a few days, the level becomes stationary. At this equilibrium state the hydrostatic pressure of the liquid column exactly balances the tendency which enables the water molecules to pass through semipermeable membrane.



**Fig. 5.12 Hydrostatic pressure determination**

The hydrostatic pressure developed as a result of osmosis is a measure of osmotic pressure of the solution. Osmotic pressure is also defined as the hydrostatic pressure built up on the solution which just stops the osmosis.

$$\text{Osmotic pressure} = \text{hydrostatic pressure}$$

$$\pi = hgd$$

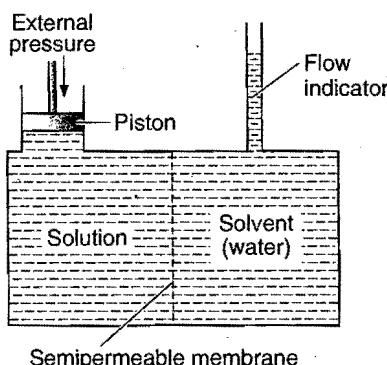
where,  $h$  = increase in level in the tube of unit cross section,  $d$  = density of solution and  $g$  = acceleration due to gravity.

Actually, this will not be an exact measure of osmotic pressure of the solution originally taken because sufficient dilution has taken place with time.

If osmosis takes place due to concentration gradient i.e., when two solutions of different concentration are separated by semipermeable membrane then,

$$\pi = hdg = \Delta CRT$$

**Alternative definition:** An apparatus as shown in Fig. 5.13 consists of a water-tight chamber which is divided into two halves by a semipermeable membrane and fitted with a water-tight piston and a flow indicator in separate compartments. The compartment having a piston is filled with solution and the other compartment is filled with a pure solvent. Water (solvent) tries to flow into the solution side. To check this tendency, a certain pressure shall have to be applied by the piston. This external pressure is thus a measure of osmotic pressure of the solution. **The external pressure which must be applied on the**

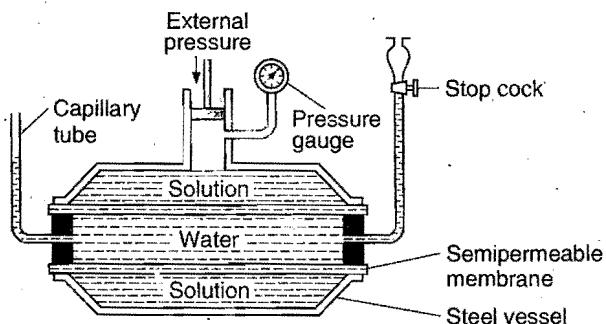


**Fig. 5.13**

solution in order to stop the flow of the solvent into the solution through semipermeable membrane is equal to osmotic pressure.

#### Determination of Osmotic Pressure: Berkeley and Hartley's Method

Various methods are employed for the measurement of osmotic pressure but the best known method was suggested by Berkeley and Hartley. The apparatus used is shown in Fig. 5.14. A porcelain tube having copper ferrocyanide membrane in its walls is enclosed in a metallic jacket. The porcelain tube is fitted with a reservoir of pure solvent at one end and a capillary tube at the other end. In a metallic jacket, there is an arrangement for applying external pressure which is measured with the help of pressure gauge.



**Fig. 5.14 Berkeley and Hartley's method**

**Procedure:** The porcelain tube is filled with pure solvent and the metallic jacket with solution. The level in the capillary tube will tend to move down as the solvent flows towards solution due to osmosis. External pressure is now applied on the solution by the piston so that level in capillary remains stationary. The reading of pressure gauge is recorded. This is the osmotic pressure of the solution.

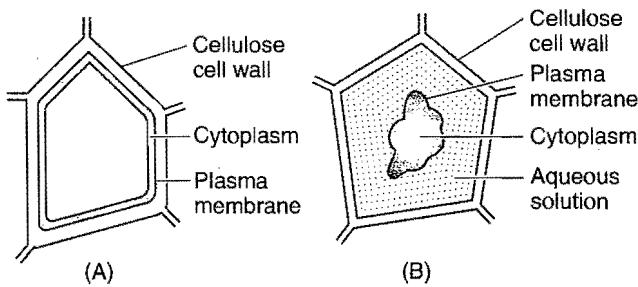
**Advantages:** (i) It is a quick and accurate method.

(ii) The concentration of the solution does not change because flow of solvent is not permitted into solution; so the results obtained by this method are reliable.

(iii) As the osmotic pressure is balanced by external pressure, there is no strain on membrane and the danger of its bursting is eliminated. So, this method can be used to measure high osmotic pressures also.

**Comparison of osmotic pressures:** de-Vries developed an approximate method for comparing the relative osmotic pressures of aqueous solutions. A solution of low osmotic pressure is termed **hypotonic** and solution of high osmotic pressure is termed **hypertonic**. The protoplasmic layer, lining the cell walls of plant cells is easily penetrated by water but is almost impermeable to the substances dissolved in the cellular fluid. When a plant cell is placed in hypotonic solution, the water is drawn in and the cell swells. If the cell is placed in a hypertonic solution, water will diffuse out of the cell fluid and partial collapse of the cell will take place when hypotonic solution is separated from hypertonic solution using semipermeable membrane, then osmosis takes place from hypotonic to

hypertonic because solvent concentration is greater in hypotonic solution. This phenomenon is known as **plasmolysis**. The change in cell can be observed under a microscope. When the plant cell is placed in the solution of same osmotic pressure as that of the cell fluid, no change in the structure of the cell is observed. Such solutions having same osmotic pressures are termed **isotonic**. By putting, therefore, cells of the same kind into solutions of different concentrations, it can be ascertained whether the solution is hypertonic or hypotonic or isotonic.



**Fig. 5.15 Plasmolysis**

Some biological explanation on the basis of osmosis are given below:

- (i) In animals, circulation of water to all parts of body takes place due to osmosis.
- (ii) Plant roots absorb water from soil due to osmosis. Concentration of cell sap inside the root hair cells is higher than that of water present in the soil. Water enters the root cells due to endosmosis.
- (iii) Water absorbed by plant roots is circulated in the entire plant body and reaches to the top of a tall tree due to osmosis.
- (iv) Osmosis helps in plant growth and germination of seeds.
- (v) Red blood cells burst when placed in water; it is due to endosmosis.
- (vi) Various functions of plants are controlled by osmosis, e.g., stretching of leaves and flowers, opening and closing of flowers.
- (vii) Use of salt and sugar in pickles and jams acts as preservatives. It prevents growth of bacteria and fungi by osmosis.
- (viii) Dead bodies swell under water due to endosmosis.
- (ix) When dried fruits and vegetables are placed in water, they slowly swell and return to the original form. It is again due to endosmosis of water into the fruits and vegetables.

**Intravenous drip of saline water :** Saline drip to the patients is also based on the principle of osmosis.

- (i) A 0.91% solution of NaCl in water is isotonic to human blood. Hence, in this solution red blood cells neither swell nor shrink.
- (ii) Aqueous solution of NaCl with concentration less than 0.91% is hypotonic to blood. On placing red blood cells in this solution, endosmosis results into bursting of RBCs.
- (iii) Aqueous solution of NaCl with concentration more than 0.91% is **hypertonic** to blood. On placing red blood cells in it exosmosis or plasmolysis results into shrinking of cells.

## 5.14 VAN'T HOFF THEORY OF DILUTE SOLUTIONS

van't Hoff realised that an analogy exists between gases and solutions provided osmotic pressure of solutions is used in place of ordinary gas pressure. He showed that for dilute solutions of non-electrolytes the following laws hold good:

**1. Boyle-van't Hoff law:** The osmotic pressure ( $P$  or  $\pi$ ) of a solution is directly proportional to its concentration ( $C$ ) when the temperature is kept constant. The concentration of the solution containing one gram mole in  $V$  litre is equal to  $\frac{1}{V} \left( C = \frac{1}{V} \right)$ .

Thus,

$$P \propto C \text{ (when temperature is constant)}$$

$$\text{or } P \propto \frac{1}{V}$$

$$\text{or } PV = \text{constant} \quad \text{or} \quad \pi V = \text{constant}$$

van't Hoff presumed that the osmotic pressure is due to the bombardment of solute molecules against the semipermeable membrane as the gas pressure is due to hits recorded by gas molecules against the walls of its container.

**2. Pressure-Temperature law (Gay-Lussac-van't Hoff law):** Concentration remaining same, the osmotic pressure of a dilute solution is directly proportional to its absolute temperature ( $T$ ), i.e.,

$$P \propto T$$

$$\text{or } \frac{P}{T} = \text{constant} \quad \text{or} \quad \frac{\pi}{T} = \text{constant}$$

Combining the two laws, i.e., when concentration and temperature both are changing, the osmotic pressure will be given by:

$$P \propto C T$$

$$\text{or } P = k C T$$

$$\text{or } P = k \cdot \frac{1}{V} \cdot T \quad \left( \text{since, } C = \frac{1}{V} \right)$$

$$\text{or } PV = ST \text{ or } \pi V = ST$$

$S$  is called molar solution constant.

Here,  $V$  is the volume of solution containing one gram mole of the solute. The value of  $S$  comes out to  $0.082 \text{ litre atm K}^{-1} \text{ mol}^{-1}$  which is in agreement with the value of  $R$ , the molar gas constant. In case, the solution contains  $n$  gram moles in  $V$  litre, the general equation would become:

$$PV = nST \text{ or } \pi V = nST$$

**3. Third law:** Equimolecular solutions of different solutes exert equal osmotic pressure under identical conditions of temperature. Such solutions which have the same osmotic pressure are termed **isotonic or iso-osmotic**. When two isotonic solutions are separated by a semipermeable membrane, no flow of solvent molecules is observed on either side.

The law is similar to Avogadro's hypothesis. It can be stated as, "Equal volumes of dilute solutions of different solutes, having the same temperature and osmotic pressure, contain equal number of molecules".

$$\text{For solution I, } PV = n_1 ST$$

$$\text{For solution II, } PV = n_2 ST$$

Thus,  $n_1$  must be equal to  $n_2$  when  $P, V$  and  $T$  are same.

The analogy of dilute solutions with gases is thus perfect. This led van't Hoff to suggest that a solute in dissolved state (i.e., in solution) behaves as a gas and the osmotic pressure of the solution is equal to the pressure which the solute would exert if it were a gas at the same temperature and occupying the same volume as that of the solution. This statement is known as van't Hoff theory of dilute solutions.

## 5.15 DETERMINATION OF MOLECULAR MASSES

In the case of dilute solutions, it has been stated that the equation  $PV = nST$  holds good. Instead of one gram mole of the solute present in  $V$  litre of solution, let  $w_B$  gram of solute (mol. mass  $m_B$ ) be present in  $V'$  litre of solution; then

$$n = \frac{w_B}{m_B} \text{ and } V = V'$$

Thus, the equation  $PV = nST$  becomes:

$$PV' = \frac{w_B}{m_B} \cdot ST$$

$$\text{or } m_B = \frac{w_B \times S \times T}{PV'}$$

Knowing the value of  $P$  experimentally, the value of  $m_B$ , i.e., molecular mass of the solute can be determined.

Consider two solutions I and II having  $n_1$  and  $n_2$  moles of the solute in  $V_1$  and  $V_2$  litres of solution respectively. Let  $P_1$  and  $P_2$  be their osmotic pressures at the same temperature ( $T$ ).

$$\text{From the equation } PV = nST,$$

$$\text{For solution I, } P_1 V_1 = n_1 ST$$

$$\text{or } P_1 = \frac{n_1}{V_1} ST$$

$$\text{For solution II, } P_2 V_2 = n_2 ST$$

$$\text{or } P_2 = \frac{n_2}{V_2} ST$$

If both solutions are isotonic, i.e.,  $P_1 = P_2$ , obviously,

$$\frac{n_1}{V_1} ST = \frac{n_2}{V_2} ST$$

$$\text{or } \frac{n_1}{V_1} = \frac{n_2}{V_2}$$

$$\text{or } \frac{w_1/m_1}{V_1} = \frac{w_2/m_2}{V_2}$$

$$\text{or } \frac{w_1}{m_1 \times V_1} = \frac{w_2}{m_2 \times V_2}$$

This is the condition for isotonic solutions.

If molecular mass of one solute is known, the molecular mass of the other can be determined without using osmotic pressure values.

### Osmotic pressure of mixture of two solutions:

**Case I:** Let two solutions of same substance having different osmotic pressures  $\pi_1$  and  $\pi_2$  are mixed. Osmotic pressure of the resultant solution can be calculated as,

$$\pi_1 V_1 + \pi_2 V_2 = \pi_R (V_1 + V_2)$$

where,  $V_1$  and  $V_2$  are the volumes of two solutions and  $\pi_R$  is the resultant osmotic pressure.

**Case II:** Let  $n_1$  and  $n_2$  are the number of moles of two different solutes present in  $V_1$  and  $V_2$  volumes respectively.

Osmotic pressure of the mixture can be calculated as,

$$\begin{aligned} \pi &= \pi_1 + \pi_2 = \frac{n_1 i_1 RT}{(V_1 + V_2)} + \frac{n_2 i_2 RT}{(V_1 + V_2)} \\ \pi &= \frac{(n_1 i_1 + n_2 i_2) RT}{(V_1 + V_2)} \end{aligned}$$

Here,  $i_1$  and  $i_2$  are van't Hoff factor for the two solutes.

### SOME SOLVED EXAMPLES

**Example 49.** 200 cm<sup>3</sup> of an aqueous solution contains 1.26 g of a polymer. The osmotic pressure of such solution at 300 K is found to be  $2.57 \times 10^{-3}$  bar. Calculate the molar mass of the polymer.

$$\begin{aligned} \text{Solution: } \pi V &= \frac{w_B}{m_B} RT \\ m_B &= \frac{w_B}{V} \times \frac{RT}{\pi} \\ &= \frac{1.26}{0.2} \times \frac{0.083 \times 300}{2.57 \times 10^{-3}} = 61038 \text{ g mol}^{-1} \end{aligned}$$

**Example 50.** A solution is prepared by dissolving 1.08 g of human serum albumin, a protein obtained from blood plasma, in 50 cm<sup>3</sup> of aqueous solution. The solution has an osmotic pressure of 5.85 mm Hg at 298 K:

(a) What is molar mass of albumin?

(b) What is height of water column placed in solution?

$$d(H_2O) = 1 \text{ g cm}^{-3}$$

**Solution:** (a) Molar mass of albumin can be calculated using following relation:

$$m_B = \frac{w_B \times RT}{\pi V} \quad \dots(i)$$

Given,  $w_B = 1.08 \text{ g}$ ;  $R = 0.0821 \text{ litre atm K}^{-1} \text{ mol}^{-1}$

$$T = 298 \text{ K}, \pi = \frac{5.85}{760} \text{ atm}; V = \frac{50}{1000} = 0.05 \text{ litre}$$

Substituting these values in eq. (i)

$$m_B = \frac{1.08 \times 0.0821 \times 298}{(5.85/760) \times 0.05} = 68655 \text{ g/mol}$$

$$(b) \quad \pi = h \cdot d \cdot g$$

$$\frac{5.85}{760} \times 101325 = h \times 1 \times 10^{-3} \times 9.8$$

$$\therefore h = 7.958 \times 10^4 \text{ m} = 7.958 \times 10^6 \text{ cm}$$

**Example 51.** Calculate osmotic pressure of 5% solution of cane sugar (sucrose) at 15°C.

**Solution:**  $m$  = mol. mass of sucrose ( $C_{12}H_{22}O_{11}$ ) = 342

$$w = 5 \text{ g}, \quad V = 100 \text{ mL} = 0.1 \text{ litre}$$

$$S = 0.082, \quad T = (15 + 273) = 288 \text{ K}$$

Applying the equation  $PV = \frac{w}{m} \cdot ST$ ,

$$P = \frac{5}{342} \times \frac{1}{0.1} \times 0.082 \times 288 \\ = 3.453 \text{ atm}$$

**Example 52.** The solution containing 10 g of an organic compound per litre showed an osmotic pressure of 1.18 atmosphere at 0°C. Calculate the molecular mass of the compound ( $S = 0.0821 \text{ litre atm per degree per mol}$ ).

**Solution:** Applying the equation,

$$m = \frac{w}{PV}$$

Given,  $w = 10 \text{ g}$ ,  $P = 1.18 \text{ atm}$ ,  $V = 1 \text{ litre}$ ,  $S = 0.0821$  and  $T = 273 \text{ K}$ .

$$m = \frac{10}{1.18 \times 1} \times 0.0821 \times 273 = 189.94$$

**Example 53.** The osmotic pressure of a solution containing 30 g of a substance in 1 litre solution at 20°C is 3.2 atmosphere. Calculate the value of  $S$ . The molecular mass of solute is 228.

**Solution:** Applying the equation,

$$PV = \frac{w}{m} \cdot ST$$

$$S = \frac{m \times P \times V}{w \times T}$$

or

Given,  $m = 228$ ,  $P = 3.2 \text{ atm}$ ,  $V = 1 \text{ litre}$ ,  $w = 30 \text{ g}$  and

$$T = 20 + 273 = 293 \text{ K}$$

$$S = \frac{228 \times 3.2 \times 1}{30 \times 293}$$

$$= 0.083 \text{ litre atm per degree per mol}$$

**Example 54.** What is the volume of solution containing 1g mole of sugar that will give rise to an osmotic pressure of 1 atmosphere at 0°C?

**Solution:** Applying the equation  $PV = n \cdot ST$ ,

$$V = \frac{n}{P} \times S \times T$$

Given,  $n = 1$ ,  $P = 1 \text{ atm}$ ,  $S = 0.0821$  and  $T = 273 \text{ K}$

$$V = \frac{1}{1} \times 0.0821 \times 273 = 22.4 \text{ litre}$$

**Example 55.** Find the osmotic pressure of M/20 solution of urea at 27°C ( $S = 0.0821 \text{ litre atm K}^{-1} \text{ mol}^{-1}$ ).

**Solution:** Applying the equation  $PV = n \cdot ST$ ,

$$P = \frac{n}{V} \cdot ST$$

$$\text{or } P = \text{Molarity} \times S \times T$$

Given,

$$\text{molarity} = \frac{1}{20} = 0.05, S = 0.0821 \text{ and } T = 27 + 273 = 300 \text{ K}$$

Substituting values,

$$P = 0.05 \times 0.0821 \times 300 = 1.2315 \text{ atm}$$

**Example 56.** The osmotic pressure of a solution of an organic substance containing 18g in one litre of solution at 293K is  $2.414 \times 10^5 \text{ Nm}^{-2}$ . Find the molecular mass of the substance if  $S = 8.3 \text{ JK}^{-1} \text{ per mol}$ .

**Solution:** Applying the equation,

$$PV = \frac{w}{m} \cdot ST$$

$$\text{or } m = \frac{w}{PV} \cdot ST$$

$$\text{Given, } P = 2.414 \times 10^5 \text{ Nm}^{-2}, V = 1.0 \text{ lit} = 1 \times 10^{-3} \text{ m}^3,$$

$$S = 8.3 \text{ JK}^{-1} \text{ per mol}, w = 18 \text{ g and } T = 293 \text{ K}$$

$$m = \frac{18}{2.414 \times 10^5 \times 1 \times 10^{-3}} \times 8.3 \times 293 = 181.33$$

**Example 57.** A 5% solution of cane sugar is isotonic with 0.877% solution of urea. Calculate the molecular mass of urea if the molecular mass of cane sugar is 342.

**Solution:** Let the molecular mass of urea be  $m_2$ .

$$\text{Molar concentration of sugar} = \frac{w_1}{m_1 \times V_1} = \frac{5}{342 \times 0.1}$$

$$\text{and Molar concentration of urea} = \frac{w_2}{m_2 \times V_2} = \frac{0.877}{m_2 \times 0.1}$$

For isotonic solutions,

$$\frac{w_1}{m_1 V_1} = \frac{w_2}{m_2 V_2}$$

$$\frac{5}{342 \times 0.1} = \frac{0.877}{m_2 \times 0.1}$$

$$m_2 = \frac{0.877 \times 342}{5} = 59.987$$

### ILLUSTRATIONS OF OBJECTIVE QUESTIONS

32. Find out the osmotic pressure of 0.25 M aqueous solution of urea at 27°C ( $R = 0.082 \text{ litre atm K}^{-1} \text{ mol}^{-1}$ ,  $R = 1.987 \text{ cal K}^{-1} \text{ mol}^{-1}$ ). [I CET (Gujarat) 2008]  
 (a) 6.15 atm (b) 0.615 atm (c) 0.0615 atm (d) 61.5 atm  
 [Ans. (a)]

[Hint :  $\pi = CRT$   
 $= 0.25 \times 0.0821 \times 300$   
 $= 6.157 \text{ atm}$ ]

33. Two solutions of glucose have osmotic pressures 1.5 and 2.5 atm. 1 litre of first solution is mixed with 2 litre of second solution. The osmotic pressure of the resultant solution will be:  
(a) 1.62 atm (b) 6.12 atm (c) 1.26 atm (d) 2.16 atm  
[Ans. (d)]

[Hint:  $\pi_1 V_1 + \pi_2 V_2 = \pi_R (V_1 + V_2)$

$$1.5 \times 1 + 2.5 \times 2 = \pi_R \times 3$$

$$\pi_R = \frac{6.5}{3} = 2.16 \text{ atm}]$$

34. 18 g glucose and 6 g urea are dissolved in 1 litre aqueous solution at 27°C. The osmotic pressure of the solution will be:  
(a) 3.826 atm (b) 4.926 atm  
(c) 2.92 atm (d) 9.42 atm  
[Ans. (b)]

[Hint:  $\pi V = (n_1 + n_2)RT$

$$\pi V = \left( \frac{w_1}{m_1} + \frac{w_2}{m_2} \right) RT$$

$$\pi \times 1 = \left( \frac{18}{180} + \frac{6}{60} \right) \times 0.0821 \times 300$$

$$\pi = 4.926 \text{ atm}]$$

35. A solution containing 10 g per dm<sup>3</sup> of urea (m.w. = 60) is isotonic with a 5% solution of a non-volatile solute. The molecular mass of this non-volatile solute is:

[CBSE (Medical) 2006]

- (a) 250 g mol<sup>-1</sup> (b) 300 g mol<sup>-1</sup>  
(c) 350 g mol<sup>-1</sup> (d) 200 g mol<sup>-1</sup>  
[Ans. (b)]

[Hint:  $\pi_1 (\text{urea}) = \pi_2 (\text{unknown solute})$

$$C_1 (\text{urea}) = C_2 (\text{unknown solute})$$

$$\left[ \frac{w_B \times 1000}{m_B \times V} \right]_{\text{urea}} = \left[ \frac{w_B \times 1000}{m_B \times V} \right]_{\text{unknown solute}}$$

$$\frac{10 \times 1000}{60 \times 1000} = \frac{5 \times 1000}{m_B \times 100}$$

$$m_B = 300 \text{ g mol}^{-1}]$$

36. The osmotic pressure of a solution at 0°C is 4 atm. What will be its osmotic pressure at 546 K under similar conditions?

- (a) 4 atm (b) 2 atm (c) 8 atm (d) 1 atm

[Ans. (c)]

[Hint:  $\frac{\pi_1}{\pi_2} = \frac{CRT_1}{CRT_2}$

$$\frac{\pi_1}{\pi_2} = \frac{T_1}{T_2}$$

$$\frac{4}{\pi_2} = \frac{273}{546}$$

$$\pi_2 = 8 \text{ atm}]$$

37. The temperature at which 10% aqueous solution  $\left( \frac{W}{V} \right)$  of glucose will exhibit the osmotic pressure of 16.4 atm, is :  
 $(R = 0.082 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1})$

- (a) 360°C (b) 180 K (c) 90 K (d) 300 K

(e) 360 K

[Ans. (e)]

[Hint:  $\pi V = nRT$

$$\pi V = \frac{W}{m} RT$$

$$16.4 \times \left( \frac{100}{1000} \right) = \frac{10}{180} \times 0.082 \times T$$

$$T = 360 \text{ K}]$$

## 5.16 REVERSE OSMOSIS

When a solution is separated from pure water by a semipermeable membrane, water moves towards the solution on account of osmosis. This process continues till osmotic pressure becomes equal to hydrostatic pressure or osmosis can be stopped by applying external pressure equal to osmotic pressure on solution. If external pressure greater than osmotic pressure is applied, the flow of solvent molecules can be made to proceed from solution towards pure solvent, i.e., in reverse direction of the ordinary osmosis. This type of osmosis is termed **reverse osmosis**. Reverse osmosis is used for the desalination of sea water for getting fresh drinking water.

## 5.17 ABNORMAL COLLIGATIVE PROPERTIES

The colligative properties of solutions depend on the number of solute particles present in solution. Various relations derived for colligative properties hold good in dilute solutions only when there is no change in molecular state of solute. In case, the total number of particles of the solute changes in solution, the colligative property shall also change accordingly. The number of particles in solution may change in two ways:

(i) **By dissociation:** When the substance is an electrolyte, i.e., the substance undergoes ionisation and number of particles increases in solution, the ions act as particles. The number of particles, thus, increases on ionisation and the value of colligative property increases accordingly.

(ii) **By association:** When the substance undergoes association, i.e., two or more molecules of the solute associate to form a single giant particle, the number of particles decreases and consequently the value of colligative property decreases. Thus,

Normal value of colligative property

∞ No. of particles of solute taken

Abnormal value of colligative property

∞ No. of particles of solute after ionisation or association

Abnormal colligative property

Thus, the ratio,  $\frac{\text{Abnormal colligative property}}{\text{Normal colligative property}}$ , may have the value either more than 1 or less than 1. The ratio is termed **van't Hoff factor** which is represented by '*i*'. Thus,

Table 5.6 Illustrations of van't Hoff Factor 'i' for Different Solutes

S. No.	Solute type	Example	Ionisation or association	No. of particles in the solution from 1 mole solute	van't Hoff factor 'i'	Abnormal molecular mass
1.	Non-electrolyte	Urea, sucrose, glucose	—	1	1	$m_{\text{normal}}$
2.	Binary electrolyte AB type	NaCl, KCl CH <sub>3</sub> COOH, etc.	$AB \rightleftharpoons A^+ + B^-$ $1-\alpha \quad \alpha \quad \alpha$	2	$1+\alpha$	$\frac{m_{\text{normal}}}{1+\alpha}$
3.	Ternary electrolyte AB <sub>2</sub> type or A <sub>2</sub> B type	CaCl <sub>2</sub> , BaCl <sub>2</sub> H <sub>2</sub> SO <sub>4</sub> , K <sub>2</sub> [PtCl <sub>6</sub> ]	$AB_2 \rightleftharpoons A^{2+} + 2B^-$ $1-\alpha \quad \alpha \quad 2\alpha$ $A_2B \rightleftharpoons 2A^+ + B^{2-}$ $1-\alpha \quad 2\alpha \quad \alpha$	3	$1+2\alpha$	$\frac{m_{\text{normal}}}{1+2\alpha}$
4.	Quaternary electrolyte AB <sub>3</sub> or A <sub>3</sub> B type	AlCl <sub>3</sub> , K <sub>3</sub> [Fe(CN) <sub>6</sub> ] FeCl <sub>3</sub> , K <sub>3</sub> PO <sub>4</sub>	$AB_3 \rightleftharpoons A^{3+} + 3B^-$ $1-\alpha \quad \alpha \quad 3\alpha$ $A_3B \rightleftharpoons 3A^+ + B^{3-}$ $1-\alpha \quad 3\alpha \quad \alpha$	4	$1+3\alpha$	$\frac{m_{\text{normal}}}{1+3\alpha}$
5.	Association of solute	Benzoic acid forming dimer in benzene	$nA \rightleftharpoons An$ $1-\alpha \quad \frac{\alpha}{n}$	$\frac{1}{n}$	$\left[1 - \left(1 - \frac{1}{n}\right)\alpha\right]$	$\frac{m_{\text{normal}}}{\left[1 - \left(1 - \frac{1}{n}\right)\alpha\right]}$
6.	General electrolyte AB <sub>n-1</sub>	One mole of solute giving n ions in the solution	$AB_{n-1} \rightleftharpoons A^{+(n-1)} + (n-1)B^-$ $1-\alpha \quad \alpha \quad (n-1)\alpha$	n	$[1 + (n-1)\alpha]$	$\frac{m_{\text{normal}}}{[1 + (n-1)\alpha]}$

$$\begin{aligned} i &= \frac{P_{\text{obs.}}}{P_{\text{normal}}} = \frac{(\Delta p)_{\text{obs.}}}{(\Delta p)_{\text{normal}}} \\ &= \frac{(\Delta T_b)_{\text{obs.}}}{(\Delta T_b)_{\text{normal}}} = \frac{(\Delta T_f)_{\text{obs.}}}{(\Delta T_f)_{\text{normal}}} \\ &= \frac{\text{Actual no. of particles in solution}}{\text{No. of particles taken}} \end{aligned}$$

(i) Suppose one molecule of an electrolyte gives 'n' ions on dissociation and 'α' is its degree of ionisation. Obviously,

$$\text{Number of ions produced} = n\alpha$$

$$\text{and} \quad \text{Number of unionised molecules} = 1 - \alpha$$

$$\begin{aligned} \text{Total number of particles in solution} &= 1 - \alpha + n\alpha \\ &= 1 + (n-1)\alpha \end{aligned}$$

Thus,

$$\text{van't Hoff factor } i = \frac{1 + (n-1)\alpha}{1} > 1 \text{ if } n \text{ is 2 or more}$$

$$\text{and} \quad \alpha = \frac{i-1}{n-1}$$

(ii) Suppose 'n' molecules associate to form one giant molecule and 'α' is the degree of association; then



$$\text{Total number of particles in solution} = 1 - \alpha + \alpha/n$$

$$= 1 + \left(\frac{1}{n} - 1\right)\alpha$$

$$\text{Thus, van't Hoff factor } i = \frac{1 + \left(\frac{1}{n} - 1\right)\alpha}{1} < 1 \text{ if } n \text{ is 2 or more}$$

$$\alpha = \frac{1-i}{1-1/n}$$

$$\text{As, Colligative property} \propto \frac{1}{\text{mol. mass}}$$

$$\text{So, } \frac{\text{Observed colligative property}}{\text{Normal colligative property}} = \frac{\text{Normal mol. mass}}{\text{Observed mol. mass}}$$

$$\text{Thus, } i = \frac{\text{Normal mol. mass}}{\text{Observed mol. mass}}$$

In case of dissociation,

$$i = \frac{\text{Normal mol. mass}}{\text{Observed mol. mass}} = 1 + (n-1)\alpha > 1$$

Observed mol. mass will always be less than normal mol. mass.

In case of association,

$$i = \frac{\text{Normal mol. mass}}{\text{Observed mol. mass}} = 1 + \left(\frac{1}{n} - 1\right)\alpha < 1$$

Observed mol. mass will always be higher than normal mol. mass.

#### Relation between osmotic pressure and vapour pressure

Let an aqueous dilute solution filled in a capillary tube is closed at one end by a semipermeable membrane. The tube is placed in pure solvent (water). Entire apparatus is closed by a belljar. At osmotic equilibrium, the belljar is saturated with water

vapour. At equilibrium osmotic pressure ( $\pi$ ) becomes equal to hydrostatic pressure.

$$\pi = h \times d \quad \dots (i)$$

where ' $h$ ' is height in the column,  $\pi$  is osmotic pressure.

Let,  $p_0$  = Vapour pressure of pure solvent

$p$  = Vapour pressure of solution

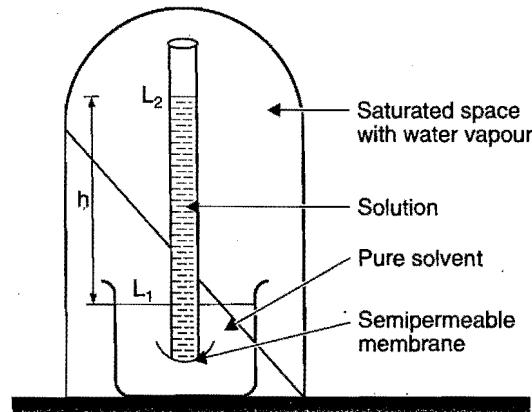


Fig. 5.16

Pressure at level  $L_1$  =  $p_0$ ; Pressure at level  $L_2$  =  $p$ . Pressure at  $L_1$  will be greater than pressure at  $L_2$ . Then

$$p_0 - p = hD \quad \dots (ii)$$

where ' $D$ ' is density of solvent vapour at pressure  $p_0$ .

Dividing eq. (i) by eq. (ii), we have,

$$\frac{\pi}{p_0 - p} = \frac{hd}{hD} = \frac{d}{D}$$

at a fixed temperature  $d/D$  is constant.

$$\therefore \pi = \text{constant} (p_0 - p) \quad \dots (iii)$$

$$\text{i.e., } \pi \propto (p_0 - p) \text{ or } \Delta p \quad \dots (iv)$$

Thus, osmotic pressure is directly proportional to the lowering of vapour pressure.

We know that,

$$p_0 V = nRT$$

$$p_0 V = \frac{W}{M} RT$$

$$\text{i.e., } p_0 M = \frac{W}{V} RT = DRT$$

$$\therefore p_0 = \frac{RTD}{M} \quad \dots (v)$$

Dividing eq. (iii) by eq. (v), we get

$$\frac{p_0 - p}{p_0} = \pi \times \frac{D}{d} \times \frac{M}{RTD}$$

$$\frac{\Delta p}{p_0} = \pi \frac{M}{dRT}$$

At a fixed temperature,  $\pi$  and  $\frac{M}{dRT}$  is constant.

Thus,  $\frac{\Delta p}{p_0} \propto \pi$ , i.e., osmotic pressure is proportional to relative lowering of vapour pressure.

### Partial pressure of immiscible liquids

Let 'A' and 'B' be the two volatile and immiscible liquids;  $p_A$  and  $p_B$  be the partial pressures of 'A' and 'B' respectively.

Then,

$$\frac{p_A}{p_B} = \frac{n_A}{n_B}$$

where,  $M_A$  and  $M_B$  are molar concentrations of 'A' and 'B' respectively.

$$\frac{p_A}{p_B} = \frac{W_A / m_A}{W_B / m_B}$$

where,  $W_A$  and  $W_B$  are weights of 'A' and 'B',  $m_A$  and  $m_B$  are molecular weights of 'A' and 'B' respectively.

**Example 58.** Phenol associates in benzene to a certain extent for a dimer. A solution containing  $20 \times 10^{-3}$  kg of phenol in 1.0 kg of benzene has its freezing point decreased by 0.69 K. Calculate the fraction of the phenol that has dimerised ( $K_f$  of benzene is  $5.12^\circ\text{K kg mol}^{-1}$ ).

**Solution:** Observed mol. mass

$$\begin{aligned} &= \frac{1000 \times K_f \times w}{W \times \Delta T} \\ &= \frac{1000 \times 5.12 \times 20 \times 10^{-3}}{1 \times 0.69} = 148.4 \end{aligned}$$

Normal mol. mass of phenol ( $\text{C}_6\text{H}_5\text{OH}$ ) = 94

$$\text{So, } \frac{\text{Normal mol. mass}}{\text{Observed mol. mass}} = \frac{94}{148.4}$$

$$= 1 + \left( \frac{1}{n} - 1 \right) \alpha = 1 + \left( \frac{1}{2} - 1 \right) \alpha$$

$$\frac{94}{148.4} = 1 - \frac{\alpha}{2}$$

$$\text{or } \alpha = 0.733 \text{ or } 73.3\%$$

**Example 59.** The freezing point depression of 0.001 m  $K_x[\text{Fe}(\text{CN})_6]$  is  $7.10 \times 10^{-3}$  K. Determine the value of  $x$ . Given,  $K_f = 1.86 \text{ K kg mol}^{-1}$  for water.

**Solution:**

$$\Delta x = i \times K_f \times m$$

$$7.10 \times 10^{-3} = i \times 1.86 \times 0.001$$

$$i = 3.817$$

$$\alpha = \frac{i-1}{n-1}$$

$$1 = \frac{3.817 - 1}{(x+1) - 1}$$

$$x = 2.817 \approx 3$$

$\therefore$  Molecular formula of the compound is  $\text{K}_3[\text{Fe}(\text{CN})_6]$ .

**Example 60.** A  $\frac{M}{10}$  solution of potassium ferrocyanide is 46% dissociated at  $18^\circ\text{C}$ . What will be its osmotic pressure?

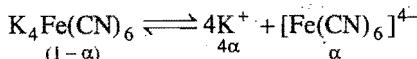
**Solution:** Normal osmotic pressure =  $\frac{w}{m \times V} \times S \times T$

(when no dissociation has taken place)

$$\frac{w}{m} = 0.1, V = 1 \text{ litre}, S = 0.0821, T = 18 + 273 = 291 \text{ K}$$

$$\text{Normal osmotic pressure} = \frac{0.1}{1} \times 0.0821 \times 291 = 2.389 \text{ atm}$$

Potassium ferrocyanide is an electrolyte. It dissociates as:



$$\text{Total number of particles} = 1 - \alpha + 4\alpha + \alpha = 1 + 4\alpha$$

$$\alpha = 0.46; \text{ so, } 1 + 4\alpha = 1 + 4 \times 0.46 = 2.84$$

$$\frac{\text{Observed osmotic pressure}}{\text{Normal osmotic pressure}} = \frac{2.84}{1}$$

$$\text{Observed osmotic pressure} = 2.84 \times 2.389 \\ = 6.785 \text{ atm}$$

**Example 61.** A 0.5% aqueous solution of  $\text{KCl}$  was found to freeze at  $-0.24^\circ\text{C}$ . Calculate the van't Hoff factor and degree of dissociation of the solute at this concentration ( $K_f$  for water =  $1.86 \text{ K kg mol}^{-1}$ ).

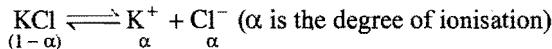
**Solution:** Observed mol. mass of  $\text{KCl}$  =  $\frac{1000 \times K_f \times w}{\Delta T \times W}$

Given,  $K_f = 1.86 \text{ K kg mol}^{-1}$ ,  $w = 0.5 \text{ g}$ ,  $W = 100 \text{ g}$ ,  $\Delta T = 0.24$

So, Observed mol. mas. of  $\text{KCl}$  =  $\frac{1000 \times 1.86 \times 0.5}{0.24 \times 100} = 38.75$

Normal mol. mass of  $\text{KCl}$  =  $39 + 35.5 = 74.5$

$$\text{van't Hoff factor} = \frac{\text{Normal mol. mass}}{\text{Observed mol. mass}} \\ = \frac{74.5}{38.75} = 1.92$$



$$\text{Total number of particles} = 1 - \alpha + \alpha + \alpha = 1 + \alpha$$

$$i = 1 + \alpha$$

$$1.92 = 1 + \alpha$$

$$\text{So, } \alpha = 1.92 - 1 = 0.92$$

i.e., 92% dissociated.

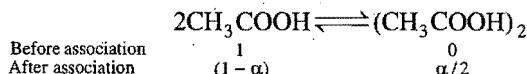
**Example 62.** The freezing point of a solution containing  $0.2 \text{ g}$  of acetic acid in  $20 \text{ g}$  of benzene is lowered by  $0.45^\circ\text{C}$ . Calculate the degree of association of acetic acid in benzene ( $K_f$  for benzene is  $5.12 \text{ K kg mol}^{-1}$ ). (IIT 1994)

**Solution:** Let the observed molecular mass of acetic acid be  $m_{\text{obs}}$ .

$$m_{\text{obs.}} = \frac{1000 \times K_f \times w}{W \times \Delta T}$$

$$= \frac{1000 \times 5.12 \times 0.2}{20 \times 0.45} = 113.78$$

Normal molecular mass of acetic acid = 60



$$\text{van't Hoff factor} = \frac{\text{Normal mol. mass}}{\text{Obs. mol. mass}} \\ = \frac{1 - \alpha + \alpha / 2}{1}$$

$$\frac{60}{113.78} = 1 - \frac{\alpha}{2}$$

$$\text{or } \alpha = 0.945$$

or 94.5% associated.

### ILLUSTRATIONS OF OBJECTIVE QUESTIONS

38. 0.002 molar solution of  $\text{NaCl}$  having degree of dissociation of 90% at  $27^\circ\text{C}$  has osmotic pressure equal to:

- (a) 0.94 bar (b) 9.4 bar  
(c) 0.094 bar (d)  $9.4 \times 10^{-4}$  bar

[Ans. (c)]

$$[\text{Hint: } \alpha = \frac{i-1}{n-1}]$$

$$0.9 = \frac{i-1}{2-1}; i = 1.9$$

$$\pi = iCRT$$

$$= 1.9 \times 0.002 \times 0.082 \times 300 \\ = 0.094 \text{ bar}]$$

39. A 0.2 molal solution of  $\text{KCl}$  freezes at  $-0.68^\circ\text{C}$ . If  $K_f$  for  $\text{H}_2\text{O}$  is 1.86, the degree of dissociation of  $\text{KCl}$  is:

- (a) 75% (b) 83% (c) 65% (d) 92%

[Ans. (b)]

$$[\text{Hint: } \Delta T = i \times K_f \times m]$$

$$0.68 = i \times 1.86 \times 0.2 \\ i = 1.83$$

$$\alpha = \frac{i-1}{n-1}$$

$$= \frac{1.83-1}{2-1} = 0.83$$

Ionization = 83%]

40. A certain substance ' $A$ ' tetramerises in water to the extent of 80%. A solution of  $2.5 \text{ g}$  of  $A$  in  $100 \text{ g}$  of water lowers the freezing point by  $0.3^\circ\text{C}$ . The molar mass of  $A$  is:

- (a) 122 (b) 31 (c) 244 (d) 62

[Ans. (d)]

$$[\text{Hint: } \alpha = \frac{1-i}{1-\frac{1}{n}}]$$

$$0.8 = \frac{1-i}{1-\frac{1}{4}}; i = 0.4$$

$$\Delta T = iK_f \times m$$

$$0.3 = 0.4 \times 1.86 \times \frac{w_B \times 1000}{m_B \times w_A}$$

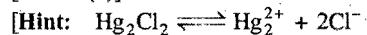
$$0.3 = 0.4 \times 1.86 \times \frac{2.5 \times 1000}{m_B \times 100}$$

$$m_B = 62]$$

41. van't Hoff factor of  $\text{Hg}_2\text{Cl}_2$  in its aqueous solution will be ( $\text{Hg}_2\text{Cl}_2$  is 80% ionized in the solution):

(a) 1.6      (b) 2.6      (c) 3.6      (d) 4.6

[Ans. (b)]



$$n = 3$$

$$\alpha = \frac{i - 1}{n - 1}$$

$$0.8 = \frac{i - 1}{3 - 1}$$

$$i = 2.6]$$

42. 0.1 M aqueous solution of  $\text{MgCl}_2$  at 300 K is 4.92 atm. What will be the percentage ionization of the salt?

(a) 49%      (b) 29%      (c) 39%      (d) 69%

[Ans. (a)]

[Hint:  $\pi = iCRT$

$$4.92 = i \times 0.1 \times 0.0821 \times 300$$

$$i = 1.99$$

$$\alpha = \frac{i - 1}{n - 1}$$

$$= \frac{1.99 - 1}{3 - 1} = \frac{0.99}{2} = 0.49$$

Percentage ionization = 49%]

43. Which of the following solutions will exhibit highest boiling point? (KCET 2006)

(a) 0.01 M  $\text{Na}_2\text{SO}_4$       (b) 0.01 M  $\text{KNO}_3$   
 (c) 0.015 M urea      (d) 0.015 M glucose

[Ans. (a)]

[Hint:  $\Delta T = i \times k_b \times m$

$i \times m$  of  $\text{Na}_2\text{SO}_4$  is highest, hence its boiling point will also be highest.

$\text{Na}_2\text{SO}_4 \quad i \times m = 3 \times 0.01 = 0.03$

$\text{KNO}_3 \quad i \times m = 2 \times 0.01 = 0.02$

Urea  $i \times m = 1 \times 0.015 = 0.015$

Glucose  $i \times m = 1 \times 0.015 = 0.015$ ]

## MISCELLANEOUS NUMERICAL EXAMPLES

**Example 1.** Calculate the freezing point of an aqueous solution of a non-electrolyte having an osmotic pressure of 2.0 atm at 300 K.

$$(K_f = 1.86 \text{ K kg mol}^{-1}, R = 0.0821 \text{ litre-atm K}^{-1} \text{ mol}^{-1})$$

(IIT 1993)

**Solution:** We know that,

$$P = CRT$$

$$\text{or, } C = \frac{P}{RT} = \frac{2}{0.0821 \times 300} \text{ mol lit}^{-1}$$

In dilute solution, the density of water can be taken as 1.0 g cm<sup>-3</sup>.

$$\text{Hence, } \frac{2}{0.0821 \times 300} \text{ mol lit}^{-1} = \frac{2}{0.0821 \times 300} \text{ mol kg}^{-1}$$

Let  $\Delta T$  be the depression in freezing point.

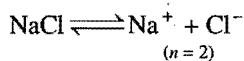
$$\begin{aligned} \Delta T &= K_f \times \text{molality} \\ &= 1.86 \times \frac{2}{0.0821 \times 300} = 0.151 \text{ K} \end{aligned}$$

$$\text{Freezing point} = (273 - 0.151) = 272.749 \text{ K or } -0.151^\circ \text{C}$$

**Example 2.** Calculate the amount of NaCl which must be added to 100 g water so that freezing point is depressed by 2 K. For water,  $K_f = 1.86 \text{ K kg mol}^{-1}$ .

**Solution:** NaCl is a strong electrolyte. It is completely dissociated in solution.

Degree of dissociation,  $\alpha = 1$



$$\text{No. of particles after dissociation} = 1 + (n - 1)\alpha$$

$$= 1 + (2 - 1) \times 1 = 2$$

$$\frac{\Delta T_{\text{obs}}}{\Delta T_{\text{theo}}} = \frac{\text{No. of particles after dissociation}}{\text{No. of particles when there is no dissociation}}$$

$$\frac{2}{\Delta T_{\text{theo}}} = 2$$

$$\text{or } \Delta T_{\text{theo.}} = 1$$

Let  $w$  g of NaCl be dissolved in 100 g of water.

$$\text{So, } \Delta T_{\text{theo.}} = \frac{1000 \times K_f \times w}{W \times m}$$

$$\text{or } w = \frac{\Delta T_{\text{theo.}} \times W \times m}{1000 \times K_f} = \frac{1 \times 100 \times 58.5}{1000 \times 1.86}$$

$$= 3.145 \text{ g}$$

**Example 3.** The degree of dissociation of  $\text{Ca}(\text{NO}_3)_2$  in a dilute solution containing 14 g of the salt per 200 g of water at 100°C is 70%. If the vapour pressure of water is 760 mm, calculate the vapour pressure of solution. (IIT 1991)

**Solution:**

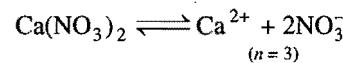
$\Delta p_{\text{theo.}}$  = Lowering in vapour pressure when there is no dissociation

$$= p_0 \times \frac{wM}{Wm}$$

(given,  $p_0 = 760 \text{ mm}$ ,  $w = 14 \text{ g}$ ,  $W = 200 \text{ g}$ ,  $M = 18$ ,  $m = 164$ )

$$= \frac{760 \times 14 \times 18}{200 \times 164} = 5.84 \text{ mm}$$

$$\text{Degree of dissociation} = \frac{70}{100} = 0.7$$



$$\frac{\Delta p_{\text{obs.}}}{\Delta p_{\text{theo.}}} = \frac{\text{No. of particles after dissociation}}{\text{No. of particles when there is no dissociation}}$$

$$= \frac{1 + (n - 1)\alpha}{1} = \frac{1 + (3 - 1) \times 0.7}{1} = 2.4$$

$$\text{So, } \Delta p_{\text{obs.}} = 2.4 \times \Delta p_{\text{theo.}} = 2.4 \times 5.84$$

$$= 14.02 \text{ mm}$$

$$p_0 - p_s = \Delta p_{\text{obs.}} = 14.02$$

$$p_s = p_0 - 14.02 = 760 - 14.02 = 745.98 \text{ mm}$$

**Example 4.** Calculate the osmotic pressure of solution obtained by mixing 100 mL of 3.4% solution of urea (molecular mass = 60) and 100 mL of 1.6% solution of cane sugar (molecular mass = 342) at 20°C.

**Solution:** No. of moles of urea =  $\frac{3.4}{60} = 0.0567$

No. of moles of cane sugar =  $\frac{1.6}{342} = 0.0047$

Total number of moles =  $(0.0567 + 0.0047) = 0.0614$

Total volume of solution =  $(100 + 100) = 200 \text{ mL}$

$$= 0.2 \text{ litre}$$

$PV = (\text{Total number of moles}) \times S \times T$

$$P = \frac{0.0614}{0.2} \times 0.0821 \times 293 = 7.385 \text{ atm}$$

**Example 5.** Calculate the normal boiling point of a sample of sea water found to contain 3.5% of NaCl and 0.13% of  $\text{MgCl}_2$  by mass. The normal boiling point of water is 100°C and  $K_b$  (water) =  $0.51 \text{ K kg mol}^{-1}$ . Assume that both the salts are completely ionised.

**Solution:** Mass of NaCl = 3.5 g

$$\text{No. of moles of NaCl} = \frac{3.5}{58.5}$$

Number of ions furnished by one molecule of NaCl is 2.

So, actual number of moles of particles furnished by sodium chloride =  $2 \times \frac{3.5}{58.5}$

Similarly, actual number of moles of particles furnished by

magnesium chloride =  $3 \times \frac{0.13}{95}$

$$\text{Total number of moles of particles} = \left( 2 \times \frac{3.5}{58.5} + 3 \times \frac{0.13}{95} \right) \\ = 0.1238$$

$$\text{Mass of water} = (100 - 3.5 - 0.13) = 96.37 \text{ g} = \frac{96.37}{1000} \text{ kg}$$

$$\text{Molality} = \frac{0.1238}{96.37} \times 1000 = 1.2846$$

$$\Delta T_b = \text{Molality} \times K_b \\ = 1.2846 \times 0.51 = 0.655 \text{ K}$$

Hence, boiling point of sea water = 373.655 K or 100.655°C.

**Example 6.** A solution of a non-volatile solute in water has a boiling point of 375.3 K. Calculate the vapour pressure of water above this solution at 338 K. Given,  $p_0$  (water) = 0.2467 atm at 338 K and  $K_b$  for water = 0.52.

$$\text{Solution: } \Delta T_b = (375.3 - 373.15) = 2.15 \text{ K}$$

We know that,

$$\Delta T_b = \text{Molality} \times K_b$$

$$2.15 = \text{Molality} \times 0.52$$

$$\text{Molality} = \frac{2.15}{0.52} = 4.135$$

i.e., 4.135 moles of the solute present in 1000 g of water (55.5 moles).

$$\text{Mole fraction of water} = \frac{55.5}{4.135 + 55.5} = \frac{55.5}{59.635}$$

Vapour pressure of water above solution

$$= \text{Mole fraction} \times p_0 \\ = \frac{55.5}{59.635} \times 0.2467 = 0.23 \text{ atm}$$

**Example 7.** Sea water is 3.5% by mass of a salt and has a density 1.04 g cm<sup>-3</sup> at 293 K. Assuming the salt to be sodium chloride, calculate the osmotic pressure of sea water. Assume complete ionisation of the salt.

$$\text{Solution: Mass of NaCl} = 3.5 \text{ g}$$

$$\text{No. of moles} = \frac{3.5}{58.5}$$

Actual number of moles of particles of solute in solution

$$= \frac{2 \times 3.5}{58.5}$$

$$\text{Volume of solution} = \frac{100}{1.04 \times 1000} \text{ litre}$$

$$\pi = \frac{2 \times 3.5}{58.5} \times \frac{1.04 \times 1000}{100} \times 0.0821 \times 293 = 29.93 \text{ atm}$$

**Example 8.** Molality of a solution in aqueous medium is 0.8. Calculate its mole fraction and the percentage by mass of solute if molar mass of solute is 60.

**Solution:** We know that,

$$m = \frac{x_B \times 1000}{(1 - x_B) \times m_A} \quad \dots (i)$$

where,  $x_B$  = mole fraction of solute

$m_A$  = molar mass of solvent

$$0.8 = \frac{x_B \times 1000}{(1 - x_B) \times 18}$$

$$x_B = 0.014$$

Let  $w_B = x$  g,  $w_A = 100$  g

$$m = \frac{w_B \times 1000}{m_B \times w_A}$$

$$0.8 = \frac{x \times 1000}{60 \times 100}$$

$$x = 4.8\%$$

**Example 9.** Calculate the boiling point of a solution containing 0.61 g of benzoic acid in 50 g of CS<sub>2</sub> (l) assuming 84% dimerisation of the acid. The boiling point and  $K_b$  of CS<sub>2</sub> are 46.2°C and 2.3 K kg mol<sup>-1</sup> respectively. (IIT 1997)

**Solution:**  $\Delta T = i \times K_b \times \text{Molality}$

$$= i \times K_b \times \frac{w \times 1000}{m \times W}$$

$$\alpha = \frac{1-i}{1-1/n}$$

$$0.84 = \frac{1-i}{1-1/2}$$

$$i = 0.58$$

$$\Delta T = 0.58 \times 2.3 \times \frac{0.61 \times 1000}{122 \times 50} = 0.1334$$

$$T - T_0 = 0.1334$$

$$T = T_0 + 0.1334 = 46.2 + 0.1334 = 46.3334$$

**Example 10.** A very small amount of a non-volatile solute (that does not dissociate) is dissolved in 56.8 cm<sup>3</sup> of benzene (density 0.889 g cm<sup>-3</sup>). At room temperature, vapour pressure of this solution is 98.8 mm Hg while that of benzene is 100 mm Hg. Find the molality of the solution. If the freezing temperature of this solution is 0.73 degree lower than that of benzene, what is the value of molal freezing point depression constant of benzene?

(IIT 1997)

**Solution:**  $\frac{\Delta p}{p_0} = X_A$

$$\frac{100 - 98.8}{100} = X_A$$

$$X_A = 0.012$$

$$\text{Molality} = \frac{X_A \times 1000}{(1 - X_A) m_B} = \frac{0.012 \times 1000}{0.988 \times 78} = 0.1557$$

$$\Delta T = K_f \times \text{Molality}$$

$$0.73 = K_f \times 0.1557$$

$$K_f = 4.688$$

**Example 11.** The solution of a non-volatile solute in water freezes at  $-0.30^\circ\text{C}$ . The vapour pressure of pure water at  $298\text{ K}$  is  $23.51\text{ mm Hg}$  and  $K_f$  for water is  $1.86\text{ degree/molal}$ . Calculate the vapour pressure of this solution at  $298\text{ K}$ .

(IIT 1998)

**Solution:**  $\Delta T = K_f \times \text{Molality}$

$$0.3 = 1.86 \times \text{Molality}$$

$$\text{Molality} = 0.161$$

$$\text{Molality} = \frac{X_A \times 1000}{(1 - X_A) \times m_B}$$

$$0.161 = \frac{X_A \times 1000}{(1 - X_A) \times 18}$$

$$X_A = 0.00289$$

$$\frac{\Delta p}{p_0} = X_A$$

$$\frac{23.51 - p_s}{23.51} = 0.00289$$

$$p_s = 23.442\text{ mm}$$

**Example 12.**  $x\text{ g}$  of a non-electrolytic compound (molar mass = 200) is dissolved in 1.0 litre of  $0.05\text{ M NaCl}$  solution. The osmotic pressure of this solution is found to be  $4.92\text{ atm}$  at  $27^\circ\text{C}$ . Calculate the value of  $x$ . Assume complete dissociation of  $\text{NaCl}$  and ideal behaviour of this solution.

(IIT 1998)

**Solution:**

(i) For  $\text{NaCl}$ :  $\pi = iCRT = 2 \times 0.05 \times 0.0821 \times 300 = 2.463\text{ atm}$

(ii) For unknown compound:

$$\pi = CRT = \frac{x}{200} \times 0.0821 \times 300 = 0.1231x\text{ atm}$$

$$\text{Total osmotic pressure } \pi = \pi_1 + \pi_2$$

$$4.92 = 2.463 + 0.1231x$$

$$x = 19.959\text{ g}$$

**Example 13.** The freezing point of a solution containing  $50\text{ cm}^3$  of ethylene glycol in  $50\text{ g}$  of water is found to be  $-34^\circ\text{C}$ . Assuming ideal behaviour, calculate the density of ethylene glycol ( $K_f$  for water =  $1.86\text{ K kg mol}^{-1}$ ).

(IIT 1999)

**Solution:**  $\Delta T = K_f \times \frac{w \times 1000}{m \times W}$

$$34 = 1.86 \times \frac{w \times 1000}{62 \times 50}$$

$$w = 56.66\text{ g}$$

$$V = \frac{w}{d}$$

$$50 = \frac{56.66}{d}$$

$$d = 1.13\text{ g/cm}^3$$

**Example 14.** A  $1.2\%$  solution of  $\text{NaCl}$  is isotonic with  $7.2\%$  solution of glucose. Calculate the van't Hoff factor of  $\text{NaCl}$ . (MLNR 1997)

**Solution:**  $\text{NaCl}$  glucose

$$\pi_{(\text{NaCl})} = \pi_{(\text{glucose})}$$

$$iC_1RT = C_2RT$$

$$iC_1 = C_2$$

$$i \left( \frac{1.2 / 58.5}{V} \right) = \frac{7.2 / 180}{V}$$

$$i = \frac{7.2 \times 58.5}{1.2 \times 180} = 1.95$$

**Example 15.**  $1.4\text{ g}$  of acetone dissolved in  $100\text{ g}$  of benzene gave a solution which freezes at  $277.12\text{ K}$ . Pure benzene freezes at  $278.4\text{ K}$ .  $2.8\text{ g}$  of solid  $(A)$  dissolved in  $100\text{ g}$  of benzene gave a solution which froze at  $277.76\text{ K}$ . Calculate the molecular mass of  $(A)$ .

(IIT 2000)

**Solution:** We know that,

$$\Delta T = K_f \times \frac{w \times 1000}{m \times W}$$

where,  $\Delta T$  = Depression in freezing point $K_f$  = Molal depression constant of benzene $w$  = Mass of solute $m$  = Molecular mass of solute $W$  = Mass of solvent

Case I:  $(278.4 - 277.12) = K_f \times \frac{1.4 \times 1000}{58 \times 100}$

$$1.28 = K_f \times \frac{14}{58} \quad \dots (1)$$

Case II:  $(278.4 - 277.76) = K_f \times \frac{2.8 \times 1000}{m_{(A)} \times 100}$

$$0.64 = K_f \times \frac{28}{m_{(A)}} \quad \dots (2)$$

Dividing eq. (1) by eq. (2), we get

$$m_{(A)} = 232$$

**Example 16.** To  $500\text{ cm}^3$  of water,  $3.0 \times 10^{-3}\text{ kg}$  of acetic acid is added. If  $23\%$  of acetic acid is dissociated, what will be the depression in freezing point?  $K_f$  and density of water are  $1.86\text{ K kg}^{-1}\text{ mol}^{-1}$  and  $0.997\text{ g cm}^{-3}$  respectively.

(IIT 2000)

**Solution:** Mass of solute =  $3.0 \times 10^{-3}\text{ kg} = 3.0\text{ g}$ 

Molecular mass of solute = 60

$$\text{Mass of solvent} = 500 \times 0.997 = 498.5 \text{ g}$$

We know that,

$$\text{Degree of dissociation } (\alpha) = \frac{i-1}{n-1}$$

$$0.23 = \frac{i-1}{2-1}$$

or

$$i = 1.23$$

$$\begin{aligned}\Delta T &= i \times K_f \times \text{molality} \\ &= 1.23 \times 1.86 \times \frac{3 \times 1000}{60 \times 498.5} = 0.229\end{aligned}$$

i.e., depression in freezing point = 0.229

**Example 17.** Osmotic pressure of a solution is 1.3 atm. The density of solution is  $1.1 \text{ g/cm}^3$ . Calculate osmotic rise.

$$(1 \text{ atm} = 76 \text{ cm Hg}, d_{\text{Hg}} = 13.6 \text{ g/cm}^3)$$

$$\text{Solution: } \pi = h d g$$

$$\begin{aligned}1.3 \times 76 \times 13.6 \times g &\equiv h \times 1.1 \times g \\ h &= \frac{1.3 \times 76 \times 13.6}{1.1} \text{ cm} \\ &= 1221 \text{ cm}\end{aligned}$$

**Example 18.** (a) 10 g of a certain non-volatile solute were dissolved in 100 g water at  $20^\circ\text{C}$ . The vapour pressure was lowered from 17.3555 mm to 17.2350 mm; calculate the m.wt. of the solute.

(b) The vapour pressure of pure water at  $25^\circ\text{C}$  is 23.62 mm. What will be the vapour pressure of a solution of 1.5 g urea in 50 g of water? (IIT 2001)

$$\text{Solution: (a)} \text{ We know that, } \frac{P_0 - P}{P} = \frac{w_B \times m_A}{m_B \times w_A}$$

$$\frac{17.3555 - 17.2350}{17.2350} = \frac{10 \times 18}{m_B \times 100}$$

$$m_B = 258.5$$

$$(b) p = p_0 \times x_A$$

$$p = p_0 \frac{n_A}{n_A + n_B} = 23.62 \times \frac{\frac{50}{18}}{\frac{50}{18} + \frac{1.5}{60}}$$

$$p = 23.41 \text{ mm Hg}$$

**Example 19.** Match the boiling point with  $K_b$  for x, y and z if molecular weight of x, y and z are same:

	b. pt.	$K_b$
x	100	0.68
y	27	0.53
z	253	0.98

(IIT 2003)

**Solution:** Molal elevation constant may be calculated as,

$$\begin{aligned}K_{b1000} &= \frac{RT_0^2}{1000 L_V} && (\text{where, } T_0 = \text{boiling point of pure solvent} \\ &= \frac{RT_0^2}{1000 \frac{\Delta H_V}{m_B}} && L_V = \text{latent heat of vaporization} \\ &= \frac{RT_0^2 m_B}{1000 \Delta H_V} && \text{per gram} \\ K_{b1000} &= \frac{RT_0 m_B}{1000 \Delta S_V} && (\text{here, } \Delta H_V = \text{molar latent heat of} \\ &&& \text{vaporization}) \\ &&& m_B = \text{molar mass of solute}) \\ \text{Since, } \Delta S_V &= \frac{\Delta H_V}{T_0} && \text{here, } \Delta S_V = \text{entropy of vaporization}\end{aligned}$$

By considering  $\Delta S_V$  as almost constant,  $K_b \propto T_0$ .

$$\therefore K_b(x) = 0.68; K_b(y) = 0.53 \text{ and } K_b(z) = 0.98$$

**Example 20.** 1.22 g  $C_6H_5COOH$  is added into two solvents and data of  $\Delta T_b$  and  $K_b$  are given as:

(a) In 100g  $CH_3COCH_3$ ;  $\Delta T_b = 0.17$ ;  $K_b = 1.7 \text{ kg kelvin/mol}$

(b) In 100g benzene;  $\Delta T_b = 0.13$ ;  $K_b = 2.6 \text{ kg kelvin/mol}$

Find out the molecular weight of  $C_6H_5COOH$  in both cases and interpret the result. (IIT 2004)

$$\begin{aligned}\text{Solution: (a)} \quad \Delta T &= K_b \times \frac{w_B \times 1000}{m_B \times w_A} \\ 0.17 &= 1.7 \times \frac{1.22 \times 1000}{m_B \times 100} \\ m_B &= 122\end{aligned}$$

(normal molecular mass of benzoic acid)

$$\begin{aligned}\text{(b)} \quad \Delta T &= \frac{K_b \times w_B \times 1000}{m_B \times w_A} \\ 0.13 &= \frac{2.6 \times 1.22 \times 1000}{m_B \times 100} \\ m_B &= 244\end{aligned}$$

(Abnormally double molecular mass of benzoic acid, it shows association of benzoic acid in benzene.)

**Example 21.** How much  $C_2H_5OH$  should be added to 1 litre  $H_2O$  so that it will not freeze at  $-20^\circ\text{C}$ ?

$$K_f = 1.86^\circ\text{C/m}$$

**Solution:** Mass of 1 litre water = 1000 g

$$\begin{aligned}\therefore \Delta T &= K_f \times \frac{w_B \times 1000}{m_B \times w_A} \\ 20 &= 1.86 \times \frac{w_B \times 1000}{46 \times 1000} \\ w_B &= 494.6 \text{ g}\end{aligned}$$

**Example 22.** Depression in freezing point of 0.1 molal solution of HF is  $-0.201^\circ\text{C}$ . Calculate percentage degree of dissociation of HF. ( $K_f = 1.86 \text{ K kg mol}^{-1}$ )

[AIPMT (Mains) 2008]

**Solution :** We know

$$\Delta T = i \times k_f \times m$$

$$0.201 = i \times 1.86 \times 0.1$$

$$i = 1.0806$$

The degree of dissociation HF may be calculated as.

$$\alpha = \frac{i-1}{n-1} = \frac{1.0806 - 1}{2 - 1} = 0.0806$$

$$\text{Percentage dissociation} = \alpha \times 100 = 0.0806 \times 100 \\ = 8.06$$

**Example 23.** There is KI and sucrose solution with 0.1 M concentration, if the osmotic pressure of KI and sucrose solution is 0.465 atm and 0.245 atm respectively. Then find the van't Hoff factor of KI and its degree of dissociation. [AIPMT (Mains) 2008]

**Solution :** For KI

$$\pi = i CRT$$

$$0.465 = i \times 0.1 \times RT \quad \dots(i)$$

For Sucrose

$$\pi = CRT$$

$$0.245 = 0.1 \times RT \quad \dots(ii)$$

Dividing eq. (i) by (ii)

$$\frac{0.465}{0.245} = i$$

$$i = 1.897$$

$$\text{We know, } \alpha = \frac{i-1}{n-1} = \frac{1.897 - 1}{2 - 1} \\ = 0.897$$

$$\therefore \text{Percentage ionization} = 0.897 \times 100 \\ = 89.7$$

**Example 24.** 102% solution of glycerine and 2% solution of glucose are isotonic. Molecular mass of glucose is 180 then find out the molecular mass of glycerine. [AIPMT (Mains) 2009]

**Solution :**  $\pi_{\text{glycerine}} = \pi_{\text{glucose}}$

$$\therefore C_{(\text{glycerine})} = C_{(\text{glucose})}$$

$$\frac{120 \times 1000}{m_{\text{glycerine}} \times 100} = \frac{2 \times 1000}{180 \times 100}$$

$$m_{\text{glycerine}} = 91.8$$

## SUMMARY AND IMPORTANT POINTS TO REMEMBER

**1. Solution:** It is a homogeneous mixture of two or more components whose concentration can be varied within certain limits. A solution containing only two components is termed a binary solution. One component is called the solute while other as solvent. The component having the same physical state as the solution is called the solvent. In solutions, in which the two components have the same physical state, the component present in larger proportion is termed the solvent and the other component is called solute.

**2. Solubility:** A solution is said to be saturated when it contains as much solute as it can dissolve at a particular temperature in presence of the undissolved solute. A super-saturated solution contains more quantity and an unsaturated solution contains less quantity of the solute than a saturated solution.

The amount of the solute in grams which can dissolve at a particular temperature in 100 grams of the solvent when the solution is saturated is termed solubility of the solute.

**3. Solubility of a gas in a liquid:** Gases which can be easily liquified are more soluble in common solvents. The gases which form ions in water are highly soluble in water. The solubility of a gas generally decreases with rise in temperature and increases with increase in pressure.

Mass of gas dissolved per unit volume of a solvent is directly proportional to the pressure of the gas at a given temperature. This is Henry's law.

$$m = KP \quad (\text{at constant temperature})$$

where,  $m$  is the mass of gas dissolved per unit volume of solvent,  $P$  is pressure of the gas in equilibrium with the solution and  $K$  is proportionality constant.

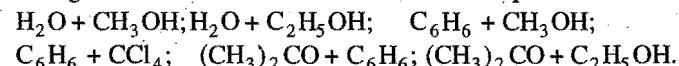
**4. Solutions of liquids in liquids:** Miscible liquids form three types of solutions which may be ideal or non-ideal solutions.

Ideal solution is that in which the attractive forces among the solute and solvent molecules are of the same order as that of solute intramolecular and solvent intramolecular forces. The  $\Delta H$  mixing and  $\Delta V$  mixing in such solutions is zero. Ideal solutions obey Raoult's law.

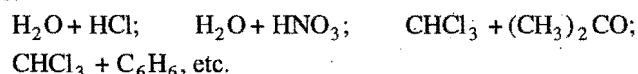
The solutions in which solute-solvent interactions are different from solute-solute and solvent-solvent interactions are called non-ideal solutions. The non-ideal solutions do not obey Raoult's law for all concentrations.

$\Delta H_{\text{mix}} \neq 0$  and  $\Delta V \neq 0$  in these solutions. There are two types of deviations from the ideal behaviour.

(i) If  $\Delta V_{\text{mix}} > 0$  and  $\Delta H_{\text{mix}} > 0$ , then non-ideal solutions show positive deviations. Such solutions form a constant boiling mixture of definite composition (azeotropic mixture) having boiling point less than either of both the liquids. In these solutions solvent-solvent and solute-solute interactions are stronger than solvent-solute interactions. Examples are:



(ii) If  $\Delta V_{\text{mix}} < 0$  and  $\Delta H_{\text{mix}} < 0$ , then non-ideal solutions show negative deviations. In these solutions, solvent-solvent and solute-solute interactions are weaker than solvent-solute interactions. Such solutions also form azeotropic mixture having boiling point higher than either of the two solvents. Examples are:



**5. Methods of expressing the concentration of a solution:** Some of the methods are given in the table.

Name	Symbol	Formula	Definition	Effect of temperature
1. Mass percentage	% (W/W)	$\frac{\text{Mass of solute}}{\text{Mass of solution}} \times 100$	Number of parts by mass of solute per hundred parts of the solution.	No effect
2. Gram per litre	g/L	$\frac{\text{Mass of solute in grams}}{\text{Volume of solution in litres}}$	Amount of the solute in grams present in one litre of solution.	Changes with change of temperature.
3. Parts per million	ppm	$\frac{\text{Mass of solute}}{\text{Mass of solution}} \times 10^6$	Number of parts by mass of solute per $10^6$ parts of solution.	No effect
4. Molarity	M	$\frac{\text{Number of moles of solute}}{\text{Number of litres of solution}}$	Number of moles of solute per litre of solution.	Changes with change of temperature.
5. Molality	m	$\frac{\text{Number of moles of solute}}{\text{Number of kilograms of the solvent}}$	Number of moles of solute present in 1 kg of the solvent.	No effect
6. Normality	N	$\frac{\text{Number of gram equivalents of solute}}{\text{Number of litres of solution}}$	Number of gram equivalents of the solute present in one litre of the solution.	Changes with change of temperature.
7. Mole fraction	X	$\frac{n_A}{n_A + n_B}$	Ratio of number of moles of one component to the total number of moles of solution.	No effect
8. Formality	F	$\frac{\text{Number of formula mass}}{\text{Number of litres of solution}}$	Number of formula mass in grams present per litre of solution.	Changes with change of temperature.

**6. Raoult's law:** The partial pressure of any volatile constituent of a solution at a constant temperature is equal to the vapour pressure of pure constituent multiplied by mole fraction of that constituent in the solution.

$$p_A = \text{mole fraction of } A \times p_A^0 = X_A \times p_A^0$$

In the case of binary solution of two volatile liquids, the total vapour pressure of such solution can be given as:

$$\begin{aligned} \text{Total vapour pressure of solution} &= p_A^0 \times X_A + p_B^0 \times X_B \\ &= p_A + p_B \end{aligned}$$

Mole fraction of component A in vapour phase,

$$\text{i.e., } Y_A = \frac{p_A}{p} = \frac{p_A^0 X_A}{p_A^0 X_A + p_B^0 X_B}$$

$$\text{similarly, } Y_B = \frac{p_B^0 X_B}{p_A^0 X_A + p_B^0 X_B}$$

**7. Colligative properties:** The properties of dilute solutions containing non-volatile solutes, which depend upon the number of solute particles in solution are called colligative properties. These properties do not depend upon the nature of solutes and solvents. The four colligative properties are:

- (i) Relative lowering in vapour pressure
- (ii) Elevation in the boiling point
- (iii) Depression in the freezing point
- (iv) Osmotic pressure.

All these properties are dependent on the concentration of solutes in solution.

**8. Relative lowering in vapour pressure:** When a non-volatile solute is dissolved in a solvent, its vapour pressure decreases. ( $p_0 - p_s$ ) is known as lowering in vapour

pressure.  $\left( \frac{p_0 - p_s}{p_0} \right)$  is called relative lowering in vapour pressure.

The relative lowering in vapour pressure of a solution containing non-volatile solute is equal to the mole fraction of the solute present in the solution. This is Raoult's law. Mathematically,

$$\frac{p_0 - p_s}{p_0} = X_{\text{solute}} = \frac{n}{n + N}$$

Let  $w$  g of the solute (mol. mass =  $m$ ) be dissolved in  $W$  g of solvent (molecular mass =  $M$ ).

$$\frac{p_0 - p_s}{p_0} = \frac{w/m}{w/m + W/M}$$

If the solution is very dilute  $w/m$  in denominator can be neglected.

$$\frac{p_0 - p_s}{p_0} = \frac{w/m}{W/M} = \frac{wM}{mW} \quad \text{or} \quad \frac{\Delta p}{p_0} = \frac{w_A m_B}{m_A w_B}$$

**9. Elevation of boiling point:** The boiling point of a solution containing non-volatile solute is always higher than the boiling point of a pure solvent. The increase in boiling point is termed elevation and represented as  $\Delta T_b$ .

$$\Delta T_b \propto \text{Molality of the solution}$$

$$\text{or } \Delta T_b = m \times K_b \quad (K_b \text{ is a molal elevation constant})$$

$$\text{or } \Delta T_b = \frac{1000 \times K_b \times w}{W \times m} \quad \text{or } \Delta T_b = \frac{1000 \times K_b \times w_A}{w_B \times m_A}$$

where,  $w$  = mass of solute;  $m$  = molecular mass of solute;

$W$  = mass of solvent

$$K_b \text{ is equal to } \frac{RT_0^2}{1000L}$$

where,  $T_0$  = boiling point of solvent in absolute scale;

$L$  = latent heat of vaporization

The units of  $K_b$  are  $\text{K kg mol}^{-1}$ .

**10. Depression in freezing point:** The freezing point of a solution containing non-volatile solute is always less than the freezing point of a pure solvent. The decrease in freezing point is termed depression and represented as  $\Delta T_f$ .

$$\Delta T_f \propto \text{molality of the solution}$$

$$\text{or } \Delta T_f = m \times K_f \quad (K_f \text{ is a molal depression constant})$$

$$\text{or } \Delta T_f = \frac{1000 \times K_f \times w}{W \times m} \text{ or } \Delta T_f = \frac{1000 \times K_f \times w_A}{w_B \times m_A}$$

where,  $w$  = mass of solute;  $m$  = molecular mass of solute;

$W$  = mass of solvent

$$K_f \text{ is equal to } \frac{RT_0^2}{1000L}$$

where,  $T_0$  = freezing point of solvent in absolute scale;

$L$  = latent heat of fusion.

The units of  $K_f$  are  $\text{K kg mol}^{-1}$ .

**11. Osmosis and osmotic pressure:** When a solution is separated from the pure solvent with the help of a semipermeable membrane, the solvent molecules from the pure solvent move towards the solution. The movement of solvent molecules from low concentration to higher concentration through semipermeable membrane is termed as osmosis.

As a result of osmosis, a pressure is developed which is termed as osmotic pressure, i.e., the hydrostatic pressure which develops on account of osmosis is called osmotic pressure. It is equal to  $h \cdot d \cdot g$ . It is also found that if an equal and opposite force is applied on the solution, the osmosis stops. Thus, the excess pressure that must be applied on the solution as to prevent osmosis is also the measure of osmotic pressure.

Osmotic pressure of a dilute solution is given by van't Hoff equation,  $P = CRT$ , where  $C$  = concentration,  $R$  = solution constant and  $T$  = absolute temperature.

$$C = \frac{n}{V} = \frac{w}{m \times V}$$

where,  $w$  = mass of solute in grams

$V$  = volume of solution in litres

$m$  = molecular mass of solute

$$\text{i.e., } P = \frac{w}{m \times V} \cdot RT$$

Best method for the determination of osmotic pressure is Berkeley and Hartley's method.

The term hypertonic and hypotonic are applied to compare the osmotic pressures of two solutions. The solution having lower

osmotic pressure is termed hypotonic and the solution having higher osmotic pressure is termed hypertonic solution. The two solutions having equal osmotic pressures are termed as isotonic. Condition for isotonic solutions is

$$\frac{w_1}{m_1 V_1} = \frac{w_2}{m_2 V_2}$$

A 0.91% solution of pure NaCl is isotonic with human blood cells (RBC). An NaCl solution with concentration less than 0.91% is called hypotonic and RBC will swell and burst in the solution. An NaCl solution with concentration greater than 0.91% is called hypertonic and RBC will shrink in this solution, i.e., will undergo plasmolysis or crenation.

**12. van't Hoff factor:** When the solute undergoes dissociation or association in solution, the number of particles in solution increases or decreases and thus, the colligative property changes accordingly. In 1886, van't Hoff introduced a factor ' $i$ ' known as van't Hoff factor to express the extent of dissociation or association of the solute in solution.

van't Hoff factor,  $i$

$$= \frac{\text{Observed colligative property}}{\text{Theoretical or normal colligative property}}$$

$$= \frac{\text{No. of particles after dissociation or association}}{\text{No. of particles when there is no dissociation or association}}$$

$$= \frac{\text{Normal molecular mass of the solute}}{\text{Observed molecular mass of the solute}}$$

From the value of ' $i$ ' it is possible to determine the degree of dissociation or association.

In case of dissociation ' $i$ ' is greater than 1.

$$i = \frac{1 + (n - 1)\alpha}{1}$$

where,  $n$  is the number of particles per molecule and  $\alpha$  is the degree of dissociation.

$$\text{or } \alpha = \frac{i - 1}{(n - 1)}$$

Similarly, in case of association, ' $i$ ' is less than 1.

$$i = \frac{1 + \left(\frac{1}{n} - 1\right) \alpha}{1}$$

where,  $n$  is the number of molecules which are associated to form one giant molecule and  $\alpha$  is the degree of association.

$$\text{or } \alpha = \frac{i - 1}{\left(\frac{1}{n} - 1\right)}$$

Molecular masses of electrolytes observed by the methods based on colligative properties are always less than normal molecular masses.

13. Calculation of osmotic pressure from lowering of vapour pressure:

$$\frac{P_0 - P}{P_0} = \frac{\pi m_B}{RdT}$$

where,  $P_0$  = vapour pressure of pure solvent

$P$  = vapour pressure of solution

$\pi$  = osmotic pressure

$m_B$  = molecular mass of solvent

$d$  = density of solution in  $\text{g mL}^{-1}$

$R$  = gas constant in  $\text{atm mL / deg / mol}$ , i.e., 82.1.

14. Variation of vapour pressure with temperature (Clausius-Clapeyron equation):

$$\log_{10} \left( \frac{P_2}{P_1} \right) = \frac{\Delta H}{2.303R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]$$

where,  $P_1$  = vapour pressure at  $T_1$

$P_2$  = vapour pressure at  $T_2$

$\Delta H$  = latent heat of vaporization per mole

15. Variation of vapour pressure of a liquid with external pressure:

$$\log_{10} \left( \frac{P_2}{P_1} \right) = \frac{V_l}{2.303RT} (P_2 - P_1)$$

where,  $p_1$  = vapour pressure at external pressure  $P_1$

$p_2$  = vapour pressure at external pressure  $P_2$

$V_l$  = molar volume of liquid.

16. Molecular masses of polymers are best determined by osmotic pressure method because other colligative properties give so low value that they cannot be measured accurately.

17. To avoid the freezing of water in a car radiator, in the sub-zero weather, ethylene glycol is added to lower the freezing point of water.

18. Freezing point is same as melting point. Hence, instead of depression in freezing point, depression in melting point can be determined. For this purpose camphor is used as solvent because it has high molal depression constant, i.e.,  $40 \text{ K m}^{-1}$ .

19. Relationship between different colligative properties:

(i) Osmotic pressure  $\pi$  and boiling point elevation  $\Delta T_b$ :

$$\pi = \Delta T_b \times \frac{dRT}{1000K_b}$$

(ii) Osmotic pressure  $\pi$  and freezing point depression  $\Delta T_f$ :

$$\pi = \Delta T_f \times \frac{dRT}{1000K_f}$$

(iii) Elevation in boiling point and relative lowering of vapour pressure:

$$\Delta T_b = \frac{1000K_b}{m_A} \times \frac{\Delta P}{P_0}; \quad m_A = \text{molar mass of solvent}$$

(iv) Depression in freezing point and relative lowering of vapour pressure:

$$\Delta T_f = \frac{1000K_f}{m_A} \times \frac{\Delta P}{P_0}$$

20. Hygroscopic and deliquescent substances both absorb moisture from the air. The former do not change their state, e.g., glycerol, whereas the latter dissolve into it, e.g., NaOH. They absorb moisture because the vapour pressure of their saturated solution is less than that of water vapours present in surroundings at that temperature.

The substances like  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$  which lose their water of crystallisation are called efflorescent.

# Questions

**1.** Match the following:

Set-I	Set-II
(A) 10 vol H <sub>2</sub> O <sub>2</sub>	1. Perhydrol
(B) 20 vol H <sub>2</sub> O <sub>2</sub>	2. 5.358 N
(C) 30 vol H <sub>2</sub> O <sub>2</sub>	3. 1.785 N
(D) 100 vol H <sub>2</sub> O <sub>2</sub>	4. 3.03 %

The correct match is :

- (a) A - 4, B - 3, C - 2, D - 1
- (b) A - 1, B - 2, C - 3, D - 4
- (c) A - 1, B - 3, C - 2, D - 4
- (d) A - 4, B - 2, C - 3, D - 1

[CPMT (UP) 2008]

**2.** Matrix Matching Problems (For IIT aspirants):

[A] Match the solutes in Column-I with the van't Hoff factors in Column-II:

Column-I	Column-II
(a) K <sub>4</sub> [Fe(CN) <sub>6</sub> ]	(p) 1 + $\alpha$
(b) Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	(q) Greater than 1
O 	
(c) NH <sub>2</sub> —C—NH <sub>2</sub>	(r) (1 + 4 $\alpha$ )
(d) CaCl <sub>2</sub>	(s) 1

$\alpha$  = Degree of ionization.

[B] Match the solutions in Column-I with their nature in Column-II:

Column-I	Column-II
(a) Benzene + toluene	(p) Non-ideal solution
(b) Ethanol + water	(q) Ideal solution
(c) Benzene + chloroform	(r) $\Delta H_{mix} > 0$
(d) Carbon tetrachloride + chloroform	(s) $\Delta H_{mixing} = 0$

[C] Match the solutions in Column-I with their nature in Column-II:

Column-I	Column-II
(a) <i>n</i> -hexane + <i>n</i> heptane	(p) Can be perfectly separated by distillation
(b) Acetone + chloroform	(q) Maximum boiling azeotrope
(c) Acetone + aniline	(r) Cannot be perfectly separated by distillation
(d) Ethanol + water	(s) Nearly ideal

[D] Match the solutions in Column-I with their osmotic properties in Column-II:

Column-I	Column-II
(a) S <sub>1</sub> : 0.1 M glucose, S <sub>2</sub> : 0.1 M urea	(p) S <sub>1</sub> and S <sub>2</sub> are isotonic
(b) S <sub>1</sub> : 0.1 M NaCl, S <sub>2</sub> : 0.1 M Na <sub>2</sub> SO <sub>4</sub>	(q) No migration of solvent across the membrane
(c) S <sub>1</sub> : 0.1 M NaCl, S <sub>2</sub> : 0.1 M KCl	(r) S <sub>1</sub> is hypertonic to S <sub>2</sub>
(d) S <sub>1</sub> : 0.1 M CuSO <sub>4</sub> , S <sub>2</sub> : 0.1 M sucrose	(s) S <sub>1</sub> is hypotonic to S <sub>2</sub>

[Note: Assume that the electrolytes are completely ionised.]

[E] Match the solutions in Column-I with their colligative properties in Column-II:

Column-I	Column-II
(a) 0.1 M Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	(p) Solution with highest boiling point
(b) 0.1 M NaCl	(q) Solution with van't Hoff factor greater than 1
(c) 0.1 M glucose	(r) Solution with lowest osmotic pressure
(d) 0.1 M CaCl <sub>2</sub>	(s) Solution with lowest freezing point

[Note: Assume that the electrolytes are completely ionised.]

[F] Match the concentration terms of List-I with their informations in List-II:

List-I	List-II
(a) Molarity	(p) Number of gram formula mass of solute dissolved per litre of solution
(b) Molality	(q) Number of moles of solute dissolved per kg of solvent
(c) Formality	(r) Depends on temperature
(d) Strength of solution	(s) Number of moles of solute dissolved per litre of solution

**1.** (a) A-4, B-3, C-2, D-1.

**2.** [A] (a—q, r); (b—q, r); (c—s); (d—p, q)

[B] (a—q, s); (b—p, r); (c—p); (d—s)

[C] (a—p, s); (b—q, r); (c—q, r); (d—r)

[D] (a—p, q); (b—s); (c—p, q); (d—r)

[E] (a—p, q, s); (b—q); (c—r); (d—q)

[F] (a—r, s); (b—q); (c—p, r); (d—r)

## PRACTICE PROBLEMS

1. 15 g of methyl alcohol is present in 100 mL of solution. If the density of solution is  $0.96 \text{ g mL}^{-1}$ , calculate the mass percentage of methyl alcohol in solution.

[Ans. 15.625%]

2. A solution is prepared by dissolving 15 g of cane sugar in 60 g water. Compute the mass per cent of each component of solution.

[Ans. Mass percentage of sugar 20%, Mass percentage of water 80%]

3. The density of the solution of a salt  $X$  is  $1.15 \text{ g mL}^{-1}$ . 20 mL of the solution when completely evaporated gave a residue of 4.6 g of the salt. Calculate the mass percentage of the solute in solution.

[Ans. 20%]

4. (a) 5.85 g of NaCl is dissolved in 200 mL of water. What will be the molarity of this solution?

[Ans. 0.5 M]

- (b) Calculate the molarity of the solution obtained by dissolving 20.6 g NaBr in 500 mL of water.

[Ans. 0.4 M]

5. The density of a solution containing 40% by mass of HCl is  $1.2 \text{ g/mL}$ . Calculate the molarity of the solution.

[Ans. 13.15 M]

6. Concentrated sulphuric acid has density of  $1.9 \text{ g/mL}$  and 99%  $\text{H}_2\text{SO}_4$  by mass. Calculate the molarity of the acid.

[Ans. 19.19 M]

7. A mixture of alcohol and water contains 54% water by mass. Calculate the mole fraction of alcohol in this solution.

[Ans. 0.25]

8. What amount of oxalic acid is required to prepare 250 mL  $0.1 \text{ N}$  solution (Given: molecular mass of oxalic acid = 126)?

[Ans. 1.575 g]

9. 7.45 g of potassium chloride is dissolved in 100 g of water. What will be the molality of the solution?

[Ans. 1 m]

10. A solution is prepared by mixing 50 g sugar in 100 g of water at  $25^\circ\text{C}$ . Calculate the following:

(i) Mass per cent of water.

(ii) Mole fraction of sugar.

(iii) Molality of the solution.

[Ans. (i) 66.6 (ii) 0.0256 (iii) 1.46 m]

11. A solution contains 25% water, 50% ethanoic acid and 25% ethanol by mass. Compute the mole fraction of each component.

[Ans. Mole fraction of water = 0.5022;

Mole fraction of ethanoic acid = 0.3013;

Mole fraction of ethanol = 0.1965]

12. Find the amount of 98% pure  $\text{Na}_2\text{CO}_3$  required to prepare 5 litres of  $2 \text{ N}$  solution.

[Ans. 540.8 g impure  $\text{Na}_2\text{CO}_3$ ]

13. Calculate the final molarity when 2.0 litre of  $3.0 \text{ M}$  sugar solution and 3.0 litre of  $2.5 \text{ M}$  sugar solution are mixed and then diluted to 10 litres with water.

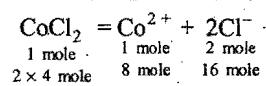
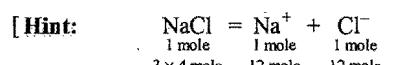
[Hint: After mixing number of moles of sugar present  $= 2 \times 3 + 3 \times 2.5 = 13.5$ ; Final molarity  $= \frac{13.5}{10} = 1.35 \text{ M}$  ]

14. If 20.0 mL of  $1.0 \text{ M}$  calcium chloride and 60 mL of  $0.2 \text{ M}$   $\text{CaCl}_2$  are mixed, what will be the molarity of the final solution?

[Ans. 0.40 M]

15. Calculate the molarity of each of the ions in a solution when 3.0 litre of  $4.0 \text{ M}$   $\text{NaCl}$  and 4.0 litre of  $2.0 \text{ M}$   $\text{CoCl}_2$  are mixed and diluted to 10 litre.

[Ans. Molarity  $\text{Na}^+ = 1.2 \text{ M}$ ; Molarity  $\text{Co}^{2+} = 0.8 \text{ M}$ ; Molarity  $\text{Cl}^- = 2.8 \text{ M}$  ]



Total  $\text{Cl}^-$  ions = 28 mole]

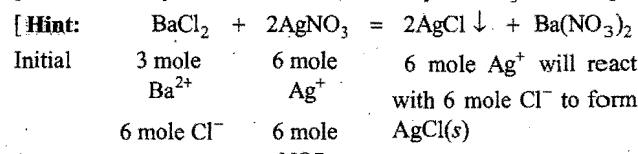
16. What volume of 96%  $\text{H}_2\text{SO}_4$  solution (density  $1.83 \text{ g/mL}$ ) is required to prepare 4 litre of  $3.0 \text{ M}$   $\text{H}_2\text{SO}_4$  solution?

[Ans. 670 mL]

[Hint: First determine the molarity of 96%  $\text{H}_2\text{SO}_4$  and then dilute to get the desired solution.]

17. Calculate the molarity of each ion in solution after 2.0 litre of  $3.0 \text{ M}$   $\text{AgNO}_3$  is mixed with 3.0 litre of  $1.0 \text{ M}$   $\text{BaCl}_2$ .

[Ans. Molarity of  $\text{Ba}^{2+} = 0.6 \text{ M}$ ; Molarity of  $\text{NO}_3^- = 1.2 \text{ M}$  ]



After reaction  $\text{Ba}^{2+}$   $\text{NO}_3^-$

Total volume  $3.0 + 2.0 = 5$  litre.]

18. The density of a 10.0% by mass of KCl solution in water is  $1.06 \text{ g/mL}$ . Calculate molarity, molality and mole fraction of KCl in this solution.

[Ans. Molarity =  $1.42 \text{ M}$ ; Molality =  $1.489 \text{ m}$ ; mole fraction of KCl = 0.026]

19. Calculate the molality and mole fraction of the solute in an aqueous solution containing 6 g of urea per 500 g of water (Mol. mass of urea = 60).

[Ans. Molality =  $0.2 \text{ M}$ ; Mole fraction = 0.00359]

20. Calculate the molality of 1 litre solution of 93%  $\text{H}_2\text{SO}_4$  (mass/volume). The density of the solution is  $1.84 \text{ g/mL}$ .

(MLNR 1993)

[Ans. 10.428 m]

21. Molarity of  $\text{H}_2\text{SO}_4$  is 0.8 and its density is  $1.06 \text{ g/cm}^3$ . What will be its concentration in terms of molality and mole fraction.

[CBSE (Mains) 2005]

[Ans.  $m = 0.814$ ;  $x_{\text{H}_2\text{SO}_4} = 0.014$  ]

22. A 6.90 M solution of KOH in water contains 30% by mass of KOH. Calculate the density of the solution.  
 [Ans. 1.288 g mL<sup>-1</sup>]
23. How many kilograms of wet NaOH containing 10% water are required to prepare 60 litre of a 0.5 M solution?  
 [Ans. 1.33 kg]
24. In an experiment, 18.0 g of mannitol was dissolved in 100 g of water. The vapour pressure of solution at 20°C was 17.226 mm of mercury. Calculate the molecular mass of mannitol. The vapour pressure of water at 20°C is 17.535 mm of mercury.  
 [Ans. Molecular mass of mannitol = 181.02]
25. The vapour pressure of water at 20°C is 17.53 mm. Calculate the vapour pressure of a solution at 20°C containing 6 g of urea in 100 g of water (molecular mass of urea = 60).  
 [Ans. Vapour pressure of solution = 17.22 mm]
26. The vapour pressure of ether (molecular mass = 74) is 442 mm Hg at 293 K. If 3 g of a compound A are dissolved in 50 g of ether at this temperature, the vapour pressure falls to 426 mm Hg. Calculate the molecular mass of A assuming that the solution of A is very dilute.  
 [Ans. m = 123]
27. 18.2 g of urea is dissolved in 100 g of water at 50°C. The lowering of vapour pressure produced is 5 mm Hg. Calculate the molecular mass of urea. The vapour pressure of water at 50°C is 92 mm Hg.  
 [Ans. 57.05]  
 [Hint: Use  $\frac{P_0 - P_s}{P_0} = \frac{n}{n + N}$ , as the solution is not very dilute]
28. Calculate the vapour pressure of a solution at 100°C containing 3 g of cane sugar in 33 g of water.  
 [Ans. 756.36 mm of Hg]  
 [Hint: Apply  $\frac{P_0 - P_s}{P_0} = \frac{wM}{Wm}$  as the solution is very dilute.  
 $p_0 = 760 \text{ mm of Hg at } 100^\circ\text{C and } m = 342$ ]
29. An aqueous solution containing 28% by mass of a liquid A (molecular mass = 140) has a vapour pressure of 160 mm at 37°C. Find the vapour pressure of pure liquid A (the vapour pressure of water at 37°C is 150 mm).  
 [Ans.  $p_A = 358.3 \text{ mm}$ ]  
 [Hint: Apply  $P_{\text{total}} = \text{mole fraction of liquid } A \times p_A + \text{mole fraction of water} \times p_w$ . Mass of water = 100 - 28 = 72 g]
30. At 25°C, the vapour pressure of pure benzene is 100 torr, while that of pure ethyl alcohol is 44 torr. Assuming ideal behaviour, calculate the vapour pressure at 25°C of a solution which contains 10 g of each substance.  
 [Ans. 64.775 torr]
31. Estimate the lowering of the vapour pressure due to solute in a 1.0 molal aqueous solution at 100°C.  
 [Ans. 14 mm of Hg or 14 torr]
32. Find the molality of a solution containing a non-volatile solute if the vapour pressure is 2% below the vapour pressure of pure water.  
 [Ans. 1.133 m] (Dhanbad 1990)
33. Calculate the mass of a non-volatile solute of molecular mass 40, which should be dissolved in 114 g of octane to reduce the vapour pressure to 80%.  
 [Ans. 10 g]
34. 10 g of a certain non-volatile solute was dissolved in 100 g of water at 20°C. The vapour pressure was lowered from 17.3555 to 17.235 mm. Calculate the molecular mass of the solute.  
 [Ans. 257.45]
35. 0.534 g of solute is dissolved in 15 g of water then freezing point temperature changes from 0°C to -1.57°C. Molal depression constant of water,  $K_f = 1.85 \text{ K kg mol}^{-1}$ . Find out:  
 (i) Molal concentration  
 (ii) Molecular mass of solute [AIPMT (Mains) 2009]  
 [Ans. (i) 0.848 (ii) 41.98 amu]
36. Addition of 0.643 g of a compound to 50 mL of benzene (density 0.879 g/mL) lowers the freezing point from 5.51°C to 5.03°C. If  $K_f$  for benzene is 5.12, calculate the molecular mass of the compound. (IIT 1992)  
 [Ans. 156]
37. A solution made by dissolving 0.32 g of a new compound in 25 g of water has freezing point -0.201°C. Calculate the molecular mass of the new compound.  
 [Ans. 118.4]
38. The boiling point of a solution of 0.1050 g of a substance in 15.84 g of ether was found to be 0.1°C higher than that of pure ether. What is the molecular mass of the substance (Molecular elevation constant of ether per 100 g is 21.6)? (MLNR 1991)  
 [Ans. 143.18]
39. Calculate the freezing point and the boiling point at 1 atmosphere of a solution containing 30 g cane sugar (molecular mass 342) and 150 g water.  
 Given:  $K_b = 0.513$  and  $K_f = 1.86$ .  
 [Ans. Boiling point = 100.3; Freezing point = -1.09°C]
40. When 36.0 g of a solute having the empirical formula CH<sub>2</sub>O is dissolved in 1.20 kg of water, the solution freezes at -0.93°C. What is the molecular formula of the compound?  
 [Ans. C<sub>2</sub>H<sub>4</sub>O<sub>2</sub>]
41. In winter, the normal temperature in Kullu valley was found to be -11°C. Is a 28% (by mass) aqueous solution of ethylene glycol suitable for a car radiator?  
 $K_f$  for water = 1.86 K kg mol<sup>-1</sup>.  
 [Ans. Yes. The given solution freezes at -11.66°C]
42. Latent heat of fusion of water is 80 cal/g and its normal freezing point is 0°C. Calculate molal depression constant for water. ( $R = 1.987 \text{ cal}$ )  
 [Ans. 1.86 K kg mol<sup>-1</sup>]
43. A solution containing 7.5 g of urea (molecular mass = 60) in 1 kg of water freezes at the same temperature as another solution containing 15 g of solute 'A' in the same amount of water. Calculate molar mass of 'A'.  
 [Ans. 120]
44. Calculate the osmotic pressure of a decinormal solution of NaCl which is ionised to 80% at 27°C.  
 [Ans. 4.43 atm]
45. What is the volume of a solution containing 2 g mole of sugar that will give rise to an osmotic pressure of 1 atmosphere at STP?  
 [Ans. 44.8 litre]

46. If the osmotic pressure of 5 g per litre solution of a compound at 27°C is 0.025 atm, calculate the molecular mass of the compound.

[Ans. 4926]

47. The osmotic pressure of blood is 7.65 atmosphere at 37°C. How much glucose should be used per litre for an intravenous injection that is to have same osmotic pressure as blood?

[Ans. 54.18 g of glucose per litre]

48. 10 g of cane sugar (molecular mass = 342) in  $1 \times 10^{-3}$  m<sup>3</sup> of solution produces an osmotic pressure of  $6.68 \times 10^4$  Nm<sup>-2</sup> at 273 K. Calculate the value of S in SI units.

[Hint:  $S = \frac{PV}{n \times T}$

Given:  $V = 1 \times 10^{-3}$  m<sup>3</sup>;  $P = 6.68 \times 10^4$  Nm<sup>-2</sup>;

$$n = \frac{10}{342}, T = 273$$

$$S = \frac{6.68 \times 10^4 \times 1 \times 10^{-3} \times 342}{10 \times 273} = 8.3684 \text{ J K}^{-1} \text{ mol}^{-1}$$

49. A 250 mL water solution containing 48 g of sucrose (molecular mass = 342) at 300 K is separated from pure water by means of a semipermeable membrane. What pressure must be applied on solution as to prevent osmosis?

[Ans. 13.8 atm]

50. What would be the osmotic pressure of 0.05 M solution of sucrose at 5°C? Find out the concentration of a solution of glucose which would be isotonic with this solution of sucrose. (Molecular mass of sucrose = 342, Molecular mass of glucose = 180)

[Ans. 1.14 atm; Concentration of glucose soln. = 9.0 g/L]

51. Calculate the osmotic pressure of 0.5% solution of glucose (molecular mass 180) at 18°C. The value of solution constant is 0.0821 litre-atm K<sup>-1</sup> mol<sup>-1</sup>.

[Ans. 0.6628 atm]

52. At 10°C, the osmotic pressure of urea solution is 500 mm. The solution is diluted and the temperature is raised to 25°C, when the osmotic pressure is found to be 105.3 mm. Determine extent of dilution.

[Hint: Original solution  $\frac{500}{760} \times V_1 = \frac{w}{m} \times S \times 283$  ... (i)]

After dilution  $\frac{105.3}{760} \times V_2 = \frac{w}{m} \times S \times 298$  ... (ii)

or  $\frac{V_2}{V_1} \times \frac{105.3}{500} = \frac{298}{283}$

or  $\frac{V_2}{V_1} = \frac{298}{283} \times \frac{500}{105.3} = 5$

i.e., the solution is diluted to the extent that  $V_2$  is five times the original volume ( $V_1$ ).

53. Two solutions containing respectively 0.75 g of urea (molecular mass 60) and 1.5 g compound X in 100 g of water boil at the same temperature. Calculate the molecular mass of X.

[Ans. 120]

54. A 5% solution of glucose is isotonic with 1.1% solution of KCl at 30°C. Calculate the degree of ionisation of KCl.

[Ans. 0.88 or 88%]

55. What should be the osmotic pressure of a solution of urea in water at 30°C which has boiling point 0.052 K higher than pure water? Assume molarity and molality to be the same.  $K_b$  for water is 0.52 K kg mol<sup>-1</sup>.

[Ans. 2.487 atm]

56. 4.0 g of a substance A dissolved in 100 g H<sub>2</sub>O depressed the freezing point of water by 0.1°C while 4.0 g of another substance B depressed the freezing point by 0.2°C. Which one has higher molecular mass and what is the relation?

[Ans.  $M_A = 2M_B$ ]

57. A solution containing 28 g of phosphorus in 315 g of CS<sub>2</sub> (boiling point 46.3°C) boils at 47.98°C. The molal elevation constant for CS<sub>2</sub> is 2.34 K kg mol<sup>-1</sup>. Calculate the molecular mass of phosphorus and deduce its formula in CS<sub>2</sub>.

[Ans. 123.8, P<sub>4</sub>]

58. A solution of two volatile liquids A and B obeys Raoult's law. At a certain temperature it is found that when the pressure above the mixture in equilibrium is 402.5 mm of Hg, the mole fraction of A in the vapour is 0.35 and in the liquid it is 0.65. What are the vapour pressures of two liquids at this temperature?

[Hint: Let  $p_A$  and  $p_B$  be the partial pressures of vapours and  $p_A^0$  and  $p_B^0$  be the vapour pressures of two liquids respectively.

$$p_A = 0.65 p_A^0 \quad \text{and} \quad p_B = 0.35 p_B^0$$

$$p_A + p_B = 402.5 \quad (\text{given})$$

In vapour phase,

$$\frac{p_A}{p_A + p_B} = 0.35 \quad \text{or} \quad p_A = 0.35 \times 402.5 = 140.875 \text{ mm}$$

So,  $p_A^0 = 216.72 \text{ mm}$  and  $p_B^0 = 747.5 \text{ mm}$

59. Calculate the amount of ice that will separate out on cooling a solution containing 50 g of ethylene glycol in 200 g water to -9.3°C ( $K_f$  for water = 1.86 K kg mol<sup>-1</sup>). (IIT 1995)

[Hint:  $\Delta T = K_f \times m$

$$9.3 = 1.86 \times m$$

or  $m = 5$

Thus, solution of 5.0 molality will have freezing point of -9.3°C.

Let  $W$  g water be needed to prepare 5.0 molal solution containing  $\frac{50}{62}$  mole of ethylene glycol.

$$\text{So, } \frac{50 \times 1000}{62 \times W} = 5.0$$

$$\text{or } W = \frac{50 \times 1000}{62 \times 5} = 161.3 \text{ g}$$

Hence, ice separating out =  $(200 - 161.3) = 38.7 \text{ g}$

60. At 293.2 K, the density of a 60% aqueous solution of methanol is 0.8946 g/mL. Calculate volume of 1 mole of the solution.

[Ans. 28.46 mL/mol]

[Hint: Let volume of solution be 100 mL

$$W = 100 \times 0.8946 = 89.46 \text{ g}$$

$$n_{\text{CH}_3\text{OH}} = \frac{60}{32} = 1.875$$

$$n_{\text{H}_2\text{O}} = \frac{29.46}{18} = 1.636$$

$$\text{Total moles} = 1.875 + 1.636 = 3.511$$

$$\text{Volume per mole} = \frac{100}{3.511} = 28.48 \text{ mL/mol}$$

61. 1.2 kg ethylene glycol  $\left( \begin{array}{c} \text{CH}_2\text{OH} \\ | \\ \text{CH}_2\text{OH} \end{array} \right)$  was added in a car radiator

containing 9 litre water. The freezing of water was just prevented when car was running in the Himalayan valley at temperature  $-4^\circ\text{C}$ . Sudden thunderstorm in the valley lowered the temperature to  $-6^\circ\text{C}$ . Calculate the amount of ice separated.

[Ans. 3 kg ice]

[Hint:  $\Delta T = K_f \times \frac{w_A \times 1000}{m_A \times w_B}$  A  $\rightarrow$  Solute; B  $\rightarrow$  Solvent]

$$6 = 1.86 \times \frac{1200 \times 1000}{62 \times w_B}$$

$$w_B = 6000 \text{ g}$$

$$\begin{aligned} I_{\text{Weight of ice}} &= \text{Total weight of H}_2\text{O} - \text{wt. of H}_2\text{O at } -6^\circ\text{C} \\ &= 9000 - 6000 = 3000 \text{ g} = 3 \text{ kg} \end{aligned}$$

62. 2 g mixture of glucose and sucrose is dissolved in 1 litre water at 298 K to develop osmotic pressure of 0.207 atm. Calculate percentage composition of glucose and sucrose by mole as well as by mass.

[Ans.

Percentage by mole: glucose = 65.194, sucrose = 34.806;

Percentage by mass: glucose = 50, sucrose = 50.]

63. If benzoic acid (mol. mass = 122) is associated into double molecules when dissolved in benzene and the osmotic pressure of a solution of 5 g of benzoic acid in 100 mL benzene is 5.73 atm at  $10^\circ\text{C}$ , what is the percentage association of benzoic acid?

[Ans. 80%]

[Hint:  $\pi = iCRT = i \frac{n}{V} RT$

$$5.73 = i \times \frac{5/122}{0.1} \times 0.0821 \times 283$$

$$i = 0.6017$$

$$\alpha = \frac{1-i}{1-1/n} = \frac{1-0.6017}{1-1/2} \approx 0.8$$

% association = 80%]

64. 0.1 formal solution of NaCl is found to be isotonic with 1.10% solution of urea. Calculate the apparent degree of ionization of NaCl.

[Ans. 0.83]

[Hint:  $\pi_{\text{NaCl}} = \pi_{\text{urea}}$

$$= n \times \frac{1}{V} RT$$

$$i \times 0.1 \times RT = \frac{1.1}{60 \times 0.1} \times RT \quad (\pi = \frac{n}{V} RT)$$

$$i = 1.83$$

$$\alpha = \frac{i-1}{n-1} = \frac{1.83-1}{2-1} = 0.83]$$

65. The vapour pressure of water at  $100^\circ\text{C}$  is 760 mm. What will be the vapour pressure at  $95^\circ\text{C}$ ? The latent heat of water at this temperature range is 548 cal/g.

[Ans. 634.3 mm]

[Hint: Use Clausius-Clapeyron equation.

$$\log_{10} \left( \frac{P_2}{P_1} \right) = \frac{\Delta H}{2.303R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

66. Calculate the increase in vapour pressure of water per atmosphere rise in external pressure at  $10^\circ\text{C}$ . The vapour pressure of water at  $10^\circ\text{C}$  and 1 atm is equal to 9.2 mm.

[Ans. 0.1%]

[Hint: Use  $\log_{10} \left( \frac{P_2}{P_1} \right) = \frac{V_l}{2.303RT} (P_2 - P_1)$

$V_l$  = molar volume of liquid]

67. An aqueous solution of  $\text{H}_2\text{SO}_4$  has density 1.84 g/mL.

Solution contains 98%  $\text{H}_2\text{SO}_4$  by mass. Calculate:

- (i) molarity of solution
- (ii) overall molarity of solution
- (iii) molar volume
- (iv) specific volume

(v) relative decrease in vapour pressure with respect to water, assuming  $\text{H}_2\text{SO}_4$  as non-electrolyte at this high concentration.

[Hint: (i)  $M = \frac{x \times d \times 10}{m_B}$

$$= \frac{98 \times 1.84 \times 10}{98} = 18.4$$

(ii) Weight of solution (1 litre) =  $1000 \times 1.84 = 1840 \text{ g}$

$$w_B \text{ (weight of H}_2\text{SO}_4) = \frac{98}{100} \times 1840 = 1803.2 \text{ g}$$

$$w_A \text{ (weight of water)} = 1840 - 1803.2 = 36.8 \text{ g}$$

$$\begin{aligned} \text{Total number of moles} &= \frac{w_A}{m_A} + \frac{w_B}{m_B} = \frac{36.8}{18} + \frac{1803.2}{98} \\ &= 2.044 + 18.4 = 20.444 \end{aligned}$$

Overall molarity = 20.444

(iii) Molar volume =  $\frac{\text{Volume}}{\text{Total moles}} = \frac{1000}{20.444} = 48.914 \text{ mL/mol}$

(iv) Specific volume =  $\frac{1}{\text{density}} = \frac{1}{1.84} \text{ mL/g} = 0.543 \text{ mL/g}$

(v) Molality ( $m$ ) =  $\frac{w_B \times 1000}{m_B \times w_A} = \frac{98 \times 1000}{98 \times 2} = 500$

$$m = \frac{x_B \times 1000}{(1-x_B)m_A}$$

$$500 = \frac{x_B \times 1000}{(1-x_B) \times 18}$$

$$x_B = 0.9$$

According to Raoult's law:  $\frac{\Delta p}{P_0} = x_B = 0.9$

68. You are given two samples of HCl with molarity 0.341 and 0.143; volume of each sample being 1 litre. What will be the maximum volume of 0.243 M HCl that can be obtained by mixing the given samples in the following two conditions?

- (i) When water is added for dilution.
- (ii) When no water is added.

[Ans. (i) 2.0204 litre; (ii) 1.98 litre]

**Hints:** (i) Let  $x$  litre of  $0.341\text{ M HCl}$  and 1 litre of  $0.143\text{ M HCl}$  be mixed to obtain  $0.243\text{ M HCl}$ .

$$M_1V_1 + M_2V_2 = M_R(V_1 + V_2)$$

$$0.341 \times x + 0.143 \times 1 = 0.243(1+x)$$

$$(0.341 - 0.243)x = 0.243 - 0.143$$

$$0.098x = 0.1$$

$$x = 1.0204 \text{ litre}$$

$$\text{Total volume} = 1 + x = 2.0204 \text{ litre}$$

Since, volume is greater than 2 litre, hence water is to be added.

(ii) Let  $x$  litre of  $0.143\text{ M HCl}$  and 1 litre of  $0.341\text{ M HCl}$  are mixed to obtain  $0.243\text{ M HCl}$ .

$$M_1V_1 + M_2V_2 = M_R(V_1 + V_2)$$

$$0.143 \times x + 0.341 \times 1 = 0.243(1+x)$$

$$0.1x = 0.098$$

$$x = 0.98 \text{ litre}$$

$$\text{Total volume} = 1 + x = 1.98 \text{ litre}$$

Since, volume is less than two litres, no water is to be added.]

69. What is the vapour pressure of a solution of glucose which has an osmotic pressure of 3 atmosphere at  $20^\circ\text{C}$ ? The vapour pressure of water at  $20^\circ\text{C}$  is 17.39 mm. Consider the density of solution equal to that of solvent.

[Ans. 17.35 mm]

$$\text{Hint: Use: } \frac{\Delta p}{p_0} = \frac{\pi m}{dRT}$$

70. The osmotic pressure of an aqueous solution of a non-electrolyte is 18.8 atm at  $15^\circ\text{C}$ . What will be the vapour pressure of this solution at  $100^\circ\text{C}$  (Density of water at  $100^\circ\text{C} \approx 1\text{ g/cc}$ )?

[Ans. 0.958 atm]

[Hint: Use,  $\frac{\pi_1}{T_1} = \frac{\pi_2}{T_2}$  to calculate osmotic pressure at  $100^\circ\text{C}$ .

$$\frac{18.8}{278} = \frac{\pi_2}{373}$$

$$\pi_2 = 25.224 \text{ atm}$$

$$\text{Use, } \frac{p_0 - p}{p_0} = \frac{\pi m}{dRT}$$

$$\frac{1 - p}{1} = \frac{25.224 \times 18}{(1 \times 10^3) \times 0.0821 \times 373}$$

$$p = 0.958 \text{ atm}]$$

71. Calculate the osmotic pressure at  $25^\circ\text{C}$  of a solution containing 1 g of glucose and 1 g of sucrose in 1 litre of solution.

If it were not known that the solute was a mixture of glucose and sucrose, what would be the molecular weight of solute corresponding to the calculated osmotic pressure?

[Ans. 0.207 atm, 236.384]

**Hint:** Use;  $\pi V = (n_1 + n_2)RT$  to calculate osmotic pressure

$$\pi \times 1 = \left( \frac{1}{180} + \frac{1}{342} \right) \times 0.0821 \times 298 \\ = 0.207 \text{ atm}$$

$$\text{Use; } \pi V = \frac{w}{m} RT \text{ to calculate molar mass of solute.}$$

$$0.207 \times 1 = \frac{2}{m} \times 0.0821 \times 298 \\ m = 236.384]$$

72. 100 mL aqueous solution of glucose with osmotic pressure 1.2 atm at  $25^\circ\text{C}$  is mixed with 300 mL aqueous solution of urea at 2.4 atm at  $25^\circ\text{C}$ . Calculate the osmotic pressure of mixture.

[Ans. 1.68 atm]

**Hint:** Use:  $\pi_1V_1 + \pi_2V_2 = \pi_R(V_1 + V_2)$

$$\pi_R = \frac{\pi_1V_1 + \pi_2V_2}{V_1 + V_2} \\ = \frac{1.2 \times 100 + 2.4 \times 300}{500} = 1.68 \text{ atm}]$$

## OBJECTIVE QUESTIONS

### Set-1: Questions with single correct answer

- A solution is defined as a:
  - homogeneous mixture of two or more substances
  - heterogeneous mixture of two or more substances
  - homogeneous mixture of liquid and solid components only
  - homogeneous mixture consisting of water as one of the components
- Ideal solution is formed when its components:
  - have zero heat of mixing only
  - have zero volume change on mixing only
  - have zero heat of mixing and zero volume change
  - can be converted into gases
- Solutions which distil without change in composition or temperature are called:
  - amorphous
  - azeotropic mixture
  - supersaturated
  - ideal
- Azeotropic mixtures are:
  - mixture of two solids
  - those which boil at different temperatures
  - those which can be fractionally distilled
  - constant boiling mixtures
- The solubility of a gas in a liquid is directly proportional to the pressure of the gas. This statement is:
  - Raoult's law
  - Henry's law
  - van't Hoff's law
  - None of these
- Which of the following is not correct for an ideal solution?
  - Raoult's law is obeyed for entire concentration range and temperatures
  - $\Delta H_{\text{mix}} = 0$
  - $\Delta V_{\text{mix}} = 0$
  - $\Delta S_{\text{mix}} = 0$

7. The solubility of a gas in liquid increases with:  
 (a) increase in temperature  
 (b) reduction of gas pressure  
 (c) decrease in temperature and increase of gas pressure  
 (d) amount of liquid taken
8. Saturated solution of NaCl on heating becomes:  
 (a) supersaturated      (b) unsaturated  
 (c) remains saturated    (d) none of these
9. A supersaturated solution is a metastable solution whose concentration:  
 (a) is equal to the solubility of the substance in solvent  
 (b) is less than the solubility  
 (c) exceeds the solubility  
 (d) continuously changes
10. When a crystal of a solute is introduced into a supersaturated solution of the solute:  
 (a) the solute dissolves  
 (b) the solution becomes unsaturated  
 (c) the solution remains supersaturated  
 (d) the excess of solute crystallises out
11. An electrolyte dissolves in water if:  
 (a) lattice energy is less than hydration energy  
 (b) lattice energy is greater than hydration energy  
 (c) lattice energy is equal to hydration energy  
 (d) dissolution is endothermic
12. The solubility of a substance is defined as the amount of solute in grams:  
 (a) present in 100 g of the solvent  
 (b) present in 100 g of the solution  
 (c) present in 100 mL of the solution  
 (d) present in 1 litre of the solution
13. Which of the following will form an ideal solution?  
 (a) C<sub>2</sub>H<sub>5</sub>OH and water    (b) HNO<sub>3</sub> and water  
 (c) CHCl<sub>3</sub> and CH<sub>3</sub>COCH<sub>3</sub>    (d) C<sub>6</sub>H<sub>6</sub> and C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>
14. Which of the following shows positive deviation from Raoult's law?  
 (a) C<sub>6</sub>H<sub>6</sub> and C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>    (b) C<sub>6</sub>H<sub>6</sub> and CCl<sub>4</sub>  
 (c) CHCl<sub>3</sub> and C<sub>2</sub>H<sub>5</sub>OH    (d) CHCl<sub>3</sub> and CH<sub>3</sub>COCH<sub>3</sub>
15. Which of the following shows negative deviation from Raoult's law?  
 (a) CHCl<sub>3</sub> and acetone    (b) C<sub>6</sub>H<sub>6</sub> and C<sub>2</sub>H<sub>5</sub>OH  
 (c) C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub> and C<sub>6</sub>H<sub>6</sub>    (d) C<sub>6</sub>H<sub>6</sub> and CCl<sub>4</sub>
16. An azeotropic mixture of two liquids boils at a lower temperature than either of them when:  
 (a) it is saturated  
 (b) it does not deviate from Raoult's law  
 (c) it shows negative deviation from Raoult's law  
 (d) it shows positive deviation from Raoult's law
17. A maxima or minima obtained in the temperature composition curve of a mixture of two liquids indicates:  
 (a) an azeotropic mixture  
 (b) an eutectic formation  
 (c) that the liquids are immiscible with one another  
 (d) that the liquids are partially miscible at the maximum or minimum
18. Among the following, that does not form an ideal solution is:  
 (a) C<sub>6</sub>H<sub>6</sub> and C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>    (b) C<sub>2</sub>H<sub>5</sub>Cl and C<sub>2</sub>H<sub>5</sub>OH  
 (c) C<sub>6</sub>H<sub>5</sub>Cl and C<sub>6</sub>H<sub>5</sub>Br    (d) C<sub>2</sub>H<sub>5</sub>Br and C<sub>2</sub>H<sub>5</sub>I
19. Which of the following solution pairs can be separated by fractional distillation?  
 (a) Water-HNO<sub>3</sub>      (b) Water-HCl  
 (c) Benzene-toluene    (d) C<sub>2</sub>H<sub>5</sub>OH-water
20. When two liquids *A* and *B* are mixed, their boiling points become greater than both of them. The mixture is:  
 (a) ideal solution  
 (b) non-ideal solution with negative deviation from Raoult's law  
 (c) non-ideal solution with positive deviation from Raoult's law  
 (d) normal solution
21. The azeotropic mixture of water (b.pt. 100°C) and HCl (b.pt. 85°C) boils at 108.5 °C. When this mixture is distilled, it is possible to obtain:  
 (a) pure HCl  
 (b) pure water  
 (c) pure water as well as HCl  
 (d) neither HCl nor H<sub>2</sub>O in their pure states
22. Pressure cooker reduces cooking time because: (CPMT 1990)  
 (a) the heat is more evenly distributed inside the cooker  
 (b) a large flame is used  
 (c) boiling point of water is elevated  
 (d) whole matter is converted into steam
23. A molal solution is one that contains one mole of a solute in:  
 (a) 1000 g of the solvent    (b) one litre of the solution  
 (c) one litre of the solvent    (d) 22.4 litre of the solution
24. In which mode of expression, the concentration of the solution remains independent of temperature?  
 (a) Normality    (b) Molality    (c) Molarity    (d) Formality
25. 8 g NaOH is dissolved in one litre of solution. Its molarity is:  
 (a) 0.8 M    (b) 0.4 M    (c) 0.2 M    (d) 0.1 M
26. If 18 g of glucose is present in 1000 g of solvent, the solution is said to be:  
 (a) 1 molar    (b) 0.1 molar    (c) 0.5 molal    (d) 0.1 molal
27. The molarity of pure water is: [CMC (Vellore) 1991]  
 (a) 100 M    (b) 55.6 M    (c) 50 M    (d) 18 M
28. For preparing 0.1 M solution of H<sub>2</sub>SO<sub>4</sub> in one litre, we need H<sub>2</sub>SO<sub>4</sub>:  
 (a) 9.8 g    (b) 4.9 g    (c) 49.0 g    (d) 0.98 g
29. Mole fraction of C<sub>3</sub>H<sub>5</sub>(OH)<sub>3</sub> in a solution of 36 g of water and 46 g of glycerine is: (CPMT 1991)  
 (a) 0.46    (b) 0.36    (c) 0.20    (d) 0.40
30. H<sub>2</sub>O<sub>2</sub> solution used for hair bleaching is sold as a solution of approximately 5.0 g H<sub>2</sub>O<sub>2</sub> per 100 mL of the solution. The molecular mass of H<sub>2</sub>O<sub>2</sub> is 34. The molarity of this solution is approximately:  
 (a) 0.15 M    (b) 1.5 M    (c) 3.0 M    (d) 3.4 M
31. The number of moles of solute per kg of a solvent is called its:  
 (a) molarity      (b) normality  
 (c) mole fraction    (d) molality
32. 1000 g aqueous solution of CaCO<sub>3</sub> contains 10 g of calcium carbonate. Concentration of the solution is:

$$\text{Octane } B, n_B = \frac{35}{114} = 0.31$$

$$x_A = \frac{n_A}{n_A + n_B} = \frac{0.25}{0.25 + 0.31} = 0.45$$

$$x_B = 0.55$$

$$p = p_A^0 x_A + p_B^0 x_B$$

$$= 105 \times 0.45 + 45 \times 0.55$$

$$= 72 \text{ kPa} ]$$

52. If the various terms in the following expressions have usual meanings, the van't Hoff factor ' $i$ ' cannot be calculated by which of the following expression?  
 (a)  $\pi V = \sqrt{i} nRT$   
 (b)  $\Delta T_f = i \times K_f \times m$   
 (c)  $\Delta T_b = i \times K_b \times m$   
 (d) 
$$\frac{P_{\text{solvent}}^o - P_{\text{solution}}}{P_{\text{solvent}}^o} = i \left[ \frac{n}{N+n} \right]$$
53. Semipermeable membrane is that which permits the passage of:  
 (CPMT 1990)  
 (a) solute molecules only  
 (b) solvent molecules only  
 (c) solvent and solute molecules both  
 (d) neither solute nor solvent molecules
54. Which inorganic precipitate acts as semipermeable membrane?  
 (a) Calcium sulphate      (b) Barium oxalate  
 (c) Nickel phosphate      (d) Copper ferrocyanide
55. During osmosis, flow of water through a semipermeable membrane is:  
 [CBSE (Medical) 2006]  
 (a) from solution having higher concentration only  
 (b) from both sides of semipermeable membrane with equal flow rates  
 (c) from both sides of semipermeable membrane with unequal flow rates  
 (d) from solution having lower concentration only
56. At constant temperature, the osmotic pressure of a solution is:  
 (a) directly proportional to the concentration  
 (b) inversely proportional to the concentration  
 (c) directly proportional to the square of concentration  
 (d) directly proportional to the square root of concentration
57. Osmotic pressure observed when benzoic acid is dissolved in benzene, is less than that expected from theoretical considerations. This is because : [MGIMS (Wardha) 2008]  
 (a) benzoic acid is organic solute  
 (b) benzoic acid has higher molar mass than benzene  
 (c) benzoic acid gets associated in benzene  
 (d) benzoic acid gets dissociated in benzene
58. Blood cells do not shrink in blood because blood is:  
 [PMT (Med) 2007]  
 (a) hypertonic      (b) isotonic  
 (c) equimolar      (d) hypotonic
59. Isotonic solutions have the same:  
 (a) density      (b) molar concentration  
 (c) normality      (d) strength
60. The osmotic pressure of solution increases if: (CPMT 1991)  
 (a) temperature is decreased  
 (b) concentration is decreased  
 (c) number of solute particles is increased  
 (d) volume is increased
61. The osmotic pressure of a 5% solution of cane sugar (molecular mass 342) at 15°C is:  
 (a) 3.46 atm      (b) 3.64 atm      (c) 4.0 atm      (d) 2.45 atm
62. A solution has an osmotic pressure of 0.821 atm at 300 K. Its concentration would be:  
 (IIT 1990)
- (a) 0.66 M      (b) 0.32 M      (c) 0.066 M      (d) 0.033 M
63. If 3 g of glucose (molecular mass 180) is dissolved in 60 g of water at 15°C, then the osmotic pressure of this solution will be:  
 (a) 0.34 atm      (b) 0.65 atm      (c) 6.57 atm      (d) 5.57 atm
64. The relationship between the values of osmotic pressure of 0.1 M solutions of  $\text{KNO}_3$  ( $P_1$ ) and  $\text{CH}_3\text{COOH}$  ( $P_2$ ) is:  
 (a)  $P_1 = P_2$       (b)  $P_2 > P_1$   
 (c) 
$$\frac{P_1}{P_1 + P_2} = \frac{P_2}{P_1 + P_2}$$
      (d)  $P_1 > P_2$
65. An electrolyte  $A$  gives 3 ions and  $B$  is a non-electrolyte. If 0.1 M solution of  $B$  produces an osmotic pressure  $P$ , then 0.05 M solution of  $A$  will produce an osmotic pressure, assuming that the electrolyte is completely ionised:  
 (a)  $1.5P$       (b)  $P$       (c)  $0.5P$       (d)  $0.75P$
66. 1 molar solution of a non-volatile and non-electrolyte compound will produce an osmotic pressure ..... at 0°C.  
 (a) 1 atm      (b) 44.8 atm      (c) 10.0 atm      (d) 22.4 atm
67. If 0.1 M solution of glucose and 0.1 M urea solution are placed on two sides of a semipermeable membrane to equal heights, then it will be correct to say that: (CBSE 1992)  
 (a) there will be no net movement across the membrane  
 (b) glucose will flow towards urea solution  
 (c) urea will flow towards glucose solution  
 (d) water will flow from urea solution towards glucose solution
68. Which solution will exert highest osmotic pressure?  
 (a) 1 M glucose solution      (b) 1 M urea solution  
 (c) 1 M alum solution      (d) 1 M  $\text{NaCl}$  solution
69. Which is the correct relation between osmotic pressure of 0.1 M  $\text{NaCl}$  solution and 0.1 M  $\text{Na}_2\text{SO}_4$  solution?  
 (a) The osmotic pressure of  $\text{Na}_2\text{SO}_4$  is less than  $\text{NaCl}$  solution  
 (b) The osmotic pressure of  $\text{Na}_2\text{SO}_4$  is more than  $\text{NaCl}$  solution  
 (c) Both have same osmotic pressure  
 (d) None of the above
70. A 0.6% urea solution would be isotonic with:  
 [CET (Karnataka) 2009]  
 (a) 0.1 M glucose solution      (b) 0.1 M  $\text{KCl}$  solution  
 (c) 0.6% glucose solution      (d) 0.6%  $\text{NaCl}$  solution
71. Which one of the following solutions will have highest osmotic pressure? (Assume that all the salts are equally dissociated.)  
 (a) 0.1 M  $\text{Al}_2(\text{SO}_4)_3$   
 (b) 0.1 M  $\text{BaCl}_2$   
 (c) 0.1 M  $\text{Na}_2\text{SO}_4$   
 (d) The solution obtained by mixing equal volumes of (b) and (c)
72. The following solutions have equal concentrations. Which one will show minimum osmotic pressure?  
 (a)  $\text{BaCl}_2$       (b)  $\text{AgNO}_3$   
 (c)  $\text{Na}_2\text{SO}_4$       (d)  $(\text{NH}_4)_3\text{PO}_4$
73. A solution of a substance containing 1.05 g per 100 mL was found to be isotonic with 3% glucose solution. The molecular mass of the substance is:  
 (a) 31.5      (b) 6.3      (c) 630      (d) 63

74. The osmotic pressure of equimolar solutions of  $\text{BaCl}_2$ ,  $\text{NaCl}$  and glucose will be in the order:  
 (a) glucose >  $\text{NaCl}$  >  $\text{BaCl}_2$  (b)  $\text{BaCl}_2$  >  $\text{NaCl}$  > glucose  
 (c)  $\text{NaCl}$  >  $\text{BaCl}_2$  > glucose (d)  $\text{NaCl}$  > glucose >  $\text{BaCl}_2$
75. At  $25^\circ\text{C}$ , the highest osmotic pressure is exhibited by  $0.1 \text{ M}$  solution of: (CBSE 1994)  
 (a)  $\text{CaCl}_2$  (b)  $\text{KCl}$  (c) glucose (d) urea
76. The plant cell will shrink when placed in:  
 (a) water (b) a hypotonic solution  
 (c) a hypertonic solution (d) an isotonic solution
77. The osmotic pressure of a solution at  $273 \text{ K}$  is  $2.5 \text{ atm}$ . Its osmotic pressure at  $546 \text{ K}$  under similar conditions will be:  
 (a)  $0.5 \text{ atm}$  (b)  $1.0 \text{ atm}$  (c)  $2.5 \text{ atm}$  (d)  $5.0 \text{ atm}$
78. Which one of the following pairs of solutions will be expected to be isotonic under the same temperature?  
 [CET (Gujarat) 2006; AMU (Medical) 2009]  
 (a)  $0.1 \text{ M}$  urea and  $0.1 \text{ M}$   $\text{NaCl}$   
 (b)  $0.1 \text{ M}$  urea and  $0.2 \text{ M}$   $\text{MgCl}_2$   
 (c)  $0.1 \text{ M}$   $\text{NaCl}$  and  $0.1 \text{ M}$   $\text{Na}_2\text{SO}_4$   
 (d)  $0.1 \text{ M}$   $\text{Ca}(\text{NO}_3)_2$  and  $0.1 \text{ M}$   $\text{Na}_2\text{SO}_4$
79. An aqueous solution of methanol in water has vapour pressure:  
 (a) less than that of water (b) equal to that of water  
 (c) more than that of water (d) equal to that of methanol
80. An aqueous solution is  $1 \text{ molal}$  in  $\text{KI}$ . Which change will cause the vapour pressure of the solution to increase?  
 [CBSE (PMT) 2010]  
 (a) Addition of  $\text{NaCl}$  (b) Addition of  $\text{Na}_2\text{SO}_4$   
 (c) Addition of  $1 \text{ molal}$   $\text{KI}$  (d) Addition of water
81. Osmotic pressure of a solution containing  $0.1$  mole of solute per litre at  $273 \text{ K}$  is (in atm):  
 (a)  $\frac{0.1 \times 273}{0.0821}$  (b)  $\frac{0.1}{1} \times 0.0821 \times 273$   
 (c)  $\frac{1}{0.1} \times 0.0821 \times 273$  (d)  $\frac{0.1}{1} \times \frac{0.0821}{273}$
82. A solution of urea contains  $8.6 \text{ g}$  per litre. It is isotonic with a  $5\%$  solution of a non-volatile solute. The molecular mass of the solute will be:  
 (a) 349 (b) 34.9 (c) 3490 (d) 861
83. The hard shell of an egg was dissolved in  $\text{HCl}$ . The egg was then placed in a concentrated solution of  $\text{NaCl}$ . What will happen?  
 (a) The egg will shrink  
 (b) The egg will swell  
 (c) The egg will become harder  
 (d) There will be hardly any visible change
84. Blood has been found isotonic with:  
 (a) saturated solution of  $\text{NaCl}$   
 (b) saturated solution of  $\text{KCl}$   
 (c) saturated solution of  $1 : 1$  mixture of  $\text{NaCl}$  and  $\text{KCl}$   
 (d) normal sodium chloride solution
85. When a solute is dissolved in a solvent:  
 (a) vapour pressure of the solvent is decreased  
 (b) freezing point of the solution becomes less than that of solvent  
 (c) boiling point of the solution becomes higher than that of solvent  
 (d) all are correct
86. The molal elevation constant is the ratio of the elevation in boiling point to:  
 (a) molarity (b) molality  
 (c) mole fraction of solute (d) mole fraction of solvent
87. In cold countries, ethylene glycol is added to water in the radiators of cars during winters. It results in:  
 (a) reducing viscosity (b) reducing specific heat  
 (c) reducing freezing point (d) reducing boiling point
88. The best colligative property used for the determination of molecular masses of polymers is:  
 (a) relative lowering in vapour pressure  
 (b) osmotic pressure  
 (c) elevation in boiling point  
 (d) depression in freezing point
89. Ebullioscopy is concerned with:  
 (a) osmotic pressure of a solution  
 (b) elevation of boiling point of a solution  
 (c) depression in freezing point of a solution  
 (d) relative lowering in vapour pressure of a solution
90. Cryoscopy is concerned with:  
 (a) osmotic pressure of a solution  
 (b) elevation of boiling point of a solution  
 (c) depression in freezing point of a solution  
 (d) relative lowering in vapour pressure of a solution
91. Molecular mass of a non-volatile solute can be determined by:  
 (a) Cryoscopic method (b) Victor-Meyer's method  
 (c) Graham's method (d) Duma's method
92. Beckmann's thermometer measures:  
 (a) boiling point of the solution  
 (b) freezing point of the solution  
 (c) any temperature  
 (d) elevation in boiling point or depression in freezing point
93. The freezing point of  $1\%$  of lead nitrate solution in water will be: [UGET (Manipal) 2006]  
 (a)  $2^\circ\text{C}$  (b)  $1^\circ\text{C}$  (c)  $0^\circ\text{C}$  (d) below  $0^\circ\text{C}$
94. A solution of  $1.25 \text{ g}$  of non-electrolyte in  $20 \text{ g}$  of water freezes at  $271.94 \text{ K}$ . If  $K_f$  is  $1.86 \text{ K kg mol}^{-1}$  then molecular mass of the solute will be:  
 (a) 207.8 (b) 179.79 (c) 209.6 (d) 109.5
95. The ratio of the value of colligative property for  $\text{KCl}$  solution to that of sugar solution at the same concentration is nearly:  
 (a) 1 (b) 2 (c) 0.5 (d) 2.5
96. The freezing point order of the solution of glucose is:  
 (a)  $10\% > 3\% > 2\% > 1\%$  (b)  $1\% > 2\% > 3\% > 10\%$   
 (c)  $1\% > 3\% > 10\% > 2\%$  (d)  $10\% > 1\% > 3\% > 2\%$
97. Which one of the following solutions has the highest b.p.? [UGET (Manipal) 2006]  
 (a)  $0.1 \text{ M}$   $\text{NaCl}$  (b)  $0.1 \text{ M}$  urea  
 (c)  $0.1 \text{ M}$   $\text{BaCl}_2$  (d)  $0.1 \text{ M}$  glucose
98. The freezing point of  $1 \text{ molal}$   $\text{NaCl}$  solution assuming  $\text{NaCl}$  to be  $100\%$  dissociated in water is:

- (a)  $-1.86^{\circ}\text{C}$  (b)  $-3.72^{\circ}\text{C}$   
 (c)  $+1.86^{\circ}\text{C}$  (d)  $+3.72^{\circ}\text{C}$
99. Which of the following  $0.1\text{ M}$  aqueous solutions will have the lowest freezing point? (MLNR 1990)  
 (a)  $\text{K}_2\text{SO}_4$  (b)  $\text{NaCl}$  (c) Urea (d) Glucose
100. The freezing point of a  $0.05\text{ molal}$  solution of a non-electrolyte in water is: (MLNR 1990)  
 (a)  $-1.86^{\circ}\text{C}$  (b)  $-0.93^{\circ}\text{C}$  (c)  $-0.093^{\circ}\text{C}$  (d)  $0.93^{\circ}\text{C}$
101. The freezing point of equimolar aqueous solution will be highest for: (IIT 1990)  
 (a)  $\text{C}_6\text{H}_5\text{NH}_3\text{Cl}$  (b)  $\text{Ca}(\text{NO}_3)_2$   
 (c)  $\text{La}(\text{NO}_3)_3$  (d)  $\text{C}_6\text{H}_{12}\text{O}_6$  (glucose)
102. Elevation in boiling point was  $0.52^{\circ}\text{C}$  when  $6\text{ g}$  of a compound  $X$  was dissolved in  $100\text{ g}$  of water. Molecular mass of the compound  $X$  is: ( $K_b$  for water is  $0.52$  per  $1000\text{ g}$  of water.)  
 (a)  $120$  (b)  $60$  (c)  $600$  (d)  $180$
103. The molal freezing point constant for water is  $1.86$ . If  $342\text{ g}$  of cane sugar is dissolved in  $1000\text{ g}$  of water, the solution will freeze at:  
 (a)  $1.86^{\circ}\text{C}$  (b)  $-1.86^{\circ}\text{C}$  (c)  $-3.92^{\circ}\text{C}$  (d)  $3.92^{\circ}\text{C}$
104. The molal elevation constant of water is  $0.51$ . The boiling point of  $0.1\text{ molal}$  aqueous  $\text{NaCl}$  solution is nearly: (IIT 1991)  
 (a)  $100.05^{\circ}\text{C}$  (b)  $100.1^{\circ}\text{C}$  (c)  $100.2^{\circ}\text{C}$  (d)  $101.0^{\circ}\text{C}$
105. The molal elevation of an unknown solution is equal to the molal elevation of  $0.1\text{ M}$  solution of urea. The concentration of unknown solution is:  
 (a)  $1\text{ M}$  (b)  $0.01\text{ M}$  (c)  $0.1\text{ M}$  (d) none of these
106. Benzoic acid dissolved in benzene will show a molecular mass of:  
 (a)  $122$  (b)  $61$  (c)  $244$  (d)  $366$
107. If the observed and normal osmotic pressures of a  $\text{KCl}$  solution are  $5.85$  and  $3.20\text{ atm}$ , the degree of dissociation of  $\text{KCl}$  is:  
 (a)  $1$  (b)  $0.082$  (c)  $0.82$  (d)  $0.28$
108. The van't Hoff factor of a  $0.005\text{ M}$  aqueous solution of  $\text{KCl}$  is  $1.95$ . The degree of ionisation of  $\text{KCl}$  is:  
 (a)  $0.95$  (b)  $0.97$  (c)  $0.94$  (d)  $0.96$
109. If the observed and normal osmotic pressures of  $1\%$   $\text{NaCl}$  solution are  $5.7$  and  $3.0\text{ atm}$ , the degree of dissociation of  $\text{NaCl}$  is:  
 (a)  $0.9$  (b)  $1.0$  (c)  $0.57$  (d)  $0.3$
110. Which one of the following salts would have the same value of the van't Hoff factor as that of  $\text{K}_3\text{Fe}(\text{CN})_6$ ? (CBSE 1994)  
 (a)  $\text{Al}_2(\text{SO}_4)_3$  (b)  $\text{NaCl}$   
 (c)  $\text{Na}_2\text{SO}_4$  (d)  $\text{Al}(\text{NO}_3)_3$
111. Equimolar solutions of  $A$  and  $B$  show depression in freezing point in the ratio of  $2 : 1$ .  $A$  remains in normal state in solution.  $B$  will be in... state in solution.  
 (a) normal (b) associated  
 (c) hydrolysed (d) dissociated
112. The values of observed and calculated molecular mass of  $\text{Ca}(\text{NO}_3)_2$  are  $65.4$  and  $164$  respectively. The degree of ionisation of the salt will be:  
 (a)  $0.25$  (b)  $0.50$  (c)  $0.60$  (d)  $0.75$
113. Which of the following compounds corresponds to van't Hoff factor to be equal to  $2$  in dilute solution?
- (a)  $\text{KCl}$  (b)  $\text{BaCl}_2$  (c)  $\text{K}_2\text{SO}_4$  (d)  $\text{C}_6\text{H}_{12}\text{O}_6$
114. A solution containing  $3.3\text{ g}$  of a substance in  $125\text{ g}$  of benzene ( $b.p. = 80^{\circ}\text{C}$ ) boils at  $80.66^{\circ}\text{C}$ . If  $K_b$  for benzene is  $3.28\text{ K kg mol}^{-1}$  the molecular mass of the substance will be: (CPMT 1992)  
 (a)  $130.20$  (b)  $129.20$  (c)  $132.20$  (d)  $131.20$
115. The elevation in boiling point of a solution of  $10\text{ g}$  of a binary electrolyte (molecular mass  $100$ ) in  $100\text{ g}$  of water is  $\Delta T_b$ . The value of  $K_b$  for water is:  
 (a)  $\frac{\Delta T_b}{2}$  (b)  $10$  (c)  $10\Delta T_b$  (d)  $\frac{\Delta T_b}{10}$
116. The molal freezing point constant for water is  $1.86\text{ K kg mol}^{-1}$ . Therefore, the freezing point of  $0.1\text{ M}$   $\text{NaCl}$  solution in water is expected to be: (MLNR 1994)  
 (a)  $-1.86^{\circ}\text{C}$  (b)  $-0.186^{\circ}\text{C}$  (c)  $-0.372^{\circ}\text{C}$  (d)  $+0.372^{\circ}\text{C}$
117. Equal volumes of  $M/20$  urea solution and  $M/20$  glucose solution are mixed. The mixture will have osmotic pressure:  
 (a) equal to either of the solution  
 (b) less than either of the solution  
 (c) higher than either of the solution  
 (d) zero
118. Assuming the salts to be unionised in solution, which of the following has highest osmotic pressure?  
 (a)  $1\%$   $\text{CsCl}$  (b)  $1\%$   $\text{RbCl}$  (c)  $1\%$   $\text{KCl}$  (d)  $1\%$   $\text{NaCl}$
119. Pure benzene freezes at  $5.3^{\circ}\text{C}$ . A solution of  $0.223\text{ g}$  of phenyl acetic acid ( $\text{C}_6\text{H}_5\text{CH}_2\text{COOH}$ ) in  $4.4\text{ g}$  of benzene ( $K_f = 5.12\text{ K kg mol}^{-1}$ ) freezes at  $4.47^{\circ}\text{C}$ . From the observation one can conclude that: (AFMC 2010)  
 (a) phenyl acetic acid exists as such in benzene  
 (b) phenyl acetic acid undergoes partial ionization in benzene  
 (c) phenyl acetic acid undergoes complete ionization in benzene  
 (d) phenyl acetic acid dimerizes in benzene
120. The movement of solvent molecules from higher concentration to lower concentration through semipermeable membrane under pressure is termed:  
 (a) osmosis (b) reverse osmosis  
 (c) dialysis (d) diffusion
121. During depression of freezing point experiment, an equilibrium is established between the molecules of: (EAMCET 2009)  
 (a) liquid solvent and solid solvent  
 (b) liquid solute and solid solvent  
 (c) liquid solute and solid solute  
 (d) liquid solvent and solid solute
122. The molecular weight of benzoic acid in benzene as determined by depression in freezing point method corresponds to: (IIT 1996)  
 (a) ionisation of benzoic acid  
 (b) dimerization of benzoic acid  
 (c) trimerization of benzoic acid  
 (d) solvation of benzoic acid
123. If  $0.15\text{ g}$  of a solute, dissolved in  $15\text{ g}$  of solvent, increases the boiling point by  $0.216^{\circ}\text{C}$  over that of the pure solvent, the molecular mass of the substance is (Molal elevation constant for the solvent is  $2.16$ ): (CBSE 1999)

- (a) 1.01 (b) 10  
(c) 10.1 (d) 100
124. The vapour pressure of benzene at a certain temperature is 640 mm of Hg. A non-volatile and non-electrolytic solid, weighing 2.175 g, is added to 39.08 g of benzene. The vapour pressure of the solution is 600 mm of Hg. What is the molecular mass of the solid substance? (CBSE 1999)
- (a) 49.50 (b) 59.6  
(c) 69.5 (d) 79.8
125. A 5% solution of cane sugar (mol. mass = 342) is isotonic with 1% solution of a substance  $X$ . The molecular mass of  $X$  is: (CBSE 1998)
- (a) 34.2 (b) 171.2  
(c) 68.4 (d) 136.8
126. The vapour pressure of a solvent decreased by 10 mm of mercury when a non-volatile solute was added to the solvent. The mole fraction of the solute in the solution is 0.2. What should be the mole fraction of the solvent, if the decrease in the vapour pressure is to be 20 mm of mercury? (CBSE 1998)
- (a) 0.8 (b) 0.6  
(c) 0.4 (d) 0.2
- [Hint: Mole fraction of solute =  $\frac{\text{lowering in vapour pressure}}{\text{vapour pressure of solvent}}$
- Comparing under the two conditions,
- $$\frac{0.2}{\text{mole fraction of solute}} = \frac{10}{20}$$
- or mole fraction of solute = 0.4
- mole fraction of solvent =  $(1 - 0.4) = 0.6$ ]
127. Which of the following 0.10 m aqueous solution will have the lowest freezing point? (CBSE 1997)
- (a)  $\text{Al}_2(\text{SO}_4)_3$  (b) KI  
(c)  $\text{C}_6\text{H}_{12}\text{O}_6$  (d)  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$
128. A binary liquid solution is prepared by mixing *n*-heptane and ethanol. Which one of the following statements is correct regarding the behaviour of the solution? (AIEEE 2009)
- (a) The solution formed is an ideal solution  
(b) The solution is non-ideal, showing positive deviation from Raoult's law  
(c) The solution is non-ideal, showing negative deviation from Raoult's law  
(d) *n*-heptane shows positive deviation, while ethanol shows negative deviation from Raoult's law
129.  $X$  is a non-volatile solute and  $Y$  is volatile solvent. The following vapour pressures are obtained by dissolving  $X$  in  $Y$ .
- | $X/\text{mol L}^{-1}$ | $Y/\text{mm Hg}$ |
|-----------------------|------------------|
| 0.1                   | $P_1$            |
| 0.25                  | $P_2$            |
| 0.01                  | $P_3$            |
- The correct order of vapour pressure is :
- [JAMCET (Engg.) 2010]
- (a)  $P_1 < P_2 < P_3$  (b)  $P_3 < P_2 < P_1$   
(c)  $P_3 < P_1 < P_2$  (d)  $P_2 < P_1 < P_3$
130. 12.2 g of benzoic acid ( $M = 122$ ) in 100 g water has elevation in boiling point of 0.27.  $K_b = 0.54 \text{ K kg mol}^{-1}$ . If there is 100% polymerisation, the number of molecules of benzoic acid in associated state is:
- (a) 1 (b) 2  
(c) 3 (d) 4
131. For  $[\text{CrCl}_3 \cdot x\text{NH}_3]$ , elevation in boiling point of one molal solution is double of one molal solution of glucose; hence  $x$  is, if complex is 100% ionised:
- (a) 4 (b) 5  
(c) 6 (d) 3
132. If glycerol and methanol were sold at the same price in the market, which would be cheaper for preparing an antifreeze solution for the radiator of an automobile?
- (a) Glycerol (b) Methanol  
(c) Both are equal (d) None of these
133. Two liquids  $A$  and  $B$  have  $P_A^0 : P_B^0 = 1:3$  at a certain temperature. If the mole fraction ratio of  $x_A : x_B = 1:3$ , the mole fraction of  $A$  in vapour in equilibrium with the solution at a given temperature is:
- (a) 0.1 (b) 0.2  
(c) 0.5 (d) 1.0
134. Relationship between osmotic pressure at 273 K when 1% glucose ( $\pi_1$ ), 1% urea ( $\pi_2$ ), 81% sucrose ( $\pi_3$ ) are dissolved in 1 litre of water:
- (a)  $\pi_1 > \pi_2 > \pi_3$  (b)  $\pi_2 > \pi_1 > \pi_3$   
(c)  $\pi_3 > \pi_1 > \pi_2$  (d)  $\pi_1 = \pi_2 = \pi_3$
135. Which of the following property indicates weak intermolecular forces of attraction in liquid?
- (a) High heat of vaporization (b) High vapour pressure  
(c) High critical temperature (d) High boiling point
136. One mole of sugar is dissolved in two moles of water. The vapour pressure of the solution relative to that of pure water is:
- (a) 2/3 (b) 1/3  
(c) 3/2 (d) 1/2
137. The highest temperature at which vapour pressure of a liquid can be measured is:
- (a) critical temperature (b) inversion temperature  
(c) critical solu. temperature (d) b.pt. of liquid
138. The expression relating molality ( $m$ ) and mole fraction ( $x_2$ ) of solute in a solution is:
- (a)  $x_2 = \frac{mM_1}{1 + mM_1}$  (b)  $x_2 = \frac{mM_1}{1 - mM_1}$   
(c)  $x_2 = \frac{1 + mM_1}{mM_1}$  (d)  $x_2 = \frac{1 - mM_1}{mM_1}$
139. The diagram given below is a vapour pressure composition diagram for a binary solution of  $A$  and  $B$ .
-

- In the solution,  $A - B$  interactions are:
- similar to  $A - A$  and  $B - B$  interactions
  - greater than  $A - A$  and  $B - B$  interactions
  - smaller than  $A - A$  and  $B - B$  interactions
  - unpredictable
140. The best and accurate method for determining osmotic pressure is: (AFMC 1995)
- negative pressure method
  - Berkeley and Hartely method
  - Morse and Frazer method
  - Prefter's method
141. If all the following four compounds were sold at the same price, which would be cheapest for preparing an antifreeze solution for a car radiator? (AMU 1997)
- |   |   |
|---|---|
| (a) $\text{CH}_3\text{OH}$              | (b) $\text{C}_2\text{H}_5\text{OH}$     |
| (c) $\text{C}_2\text{H}_4(\text{OH})_2$ | (d) $\text{C}_3\text{H}_5(\text{OH})_3$ |
142. What is the osmotic pressure of the solution obtained by mixing  $300 \text{ cm}^3$  of 2% (mass-volume) solution of urea with  $300 \text{ cm}^3$  of 3.42% solution of sucrose of  $20^\circ\text{C}$ ? ( $R = 0.082 \text{ L atm K}^{-1} \text{ mol}^{-1}$ ) (SCRA 2009)
- 5 atm
  - 5.2 atm
  - 2.6 atm
  - 4.5 atm
- [Hint :  $\pi V = \left[ \left( \frac{w_B}{m_B} \right)_{\text{urea}} + \left( \frac{w_B}{m_B} \right)_{\text{sucrose}} \right] RT$
- $$\pi \times \frac{600}{1000} = \left[ \frac{6}{60} + \frac{3 \times 3.42}{342} \right] 0.082 \times 293$$
- $$\pi \times 0.6 = (0.1 + 0.03) \times 0.082 \times 293$$
- $$\pi = 5.2 \text{ atm}]$$
143. A solution of 1 molal concentration of a solute will have maximum boiling point elevation when the solvent is: [PMT (MP) 2000]
- ethyl alcohol
  - acetone
  - benzene
  - chloroform
144. Isotonic solutions have: (DPMT 2000)
- same boiling point
  - same vapour pressure
  - same melting point
  - same osmotic pressure
145. The depressions in freezing point for  $1 \text{ M}$  urea,  $1 \text{ M}$  glucose and  $1 \text{ M}$  NaCl are in the ratio: [CET (Haryana) 2000]
- $1 : 2 : 3$
  - $3 : 2 : 2$
  - $1 : 1 : 2$
  - none of these
146. An aqueous solution of 6.3 g oxalic acid dihydrate is made up to 250 mL. The volume of  $0.1 \text{ N}$  NaOH required to completely neutralize 10 mL of this solution is: (IIT 2001)
- 40 mL
  - 20 mL
  - 10 mL
  - 4 mL
147. The vapour pressure of a solvent  $A$  is 0.80 atm. When a non-volatile substance  $B$  is added to this solvent, its vapour pressure drops to 0.6 atm. The mole fraction of  $B$  in the solution is: [PMT (MP) 2000]
- 0.25
  - 0.50
  - 0.75
  - 0.90
148. An aqueous solution of sucrose,  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ , containing 34.2 g/L has an osmotic pressure of 2.38 atmospheres at  $17^\circ\text{C}$ . For an aqueous solution of glucose,  $\text{C}_6\text{H}_{12}\text{O}_6$ , to be isotonic with this solution, it would have: (AMU 1997)
- 34.2 g/L
  - 17.1 g/L
  - 18.0 g/L
  - 36.0 g/L of glucose
149. The molal b.pt. constant for water is  $0.513^\circ\text{C kg mol}^{-1}$ . When 0.1 mole of sugar is dissolved in 200 g of water, the solution boils under a pressure of 1 atm at: (AIIMS 1991)
- 100.513°C
  - 100.0513°C
  - 100.256°C
  - 101.025°C
150. The correct expression relating molality ( $m$ ), molarity ( $M$ ), density ( $d$ ) and molar mass ( $M_2$ ) of a solute is:
- $$(a) m = \frac{M}{d + MM_2} \quad (b) m = \frac{M}{d - MM_2}$$
- $$(c) m = \frac{d + MM_2}{M} \quad (d) m = \frac{d - MM_2}{M}$$
151. The expression relating mole fraction of solute ( $x_2$ ) and molarity ( $M$ ) of the solution is:
- $$(a) x_2 = \frac{MM_1}{M(M_1 - M_2) + \rho} \quad (b) x_2 = \frac{MM_1}{M(M_1 - M_2) - \rho}$$
- $$(c) x_2 = \frac{M(M_1 - M_2) + \rho}{MM_1} \quad (d) x_2 = \frac{M(M_1 - M_2) - \rho}{MM_1}$$
- (where  $\rho$  is the density of solution and  $M_1$  and  $M_2$  are the molar masses of solvent and solute, respectively.)
152. The boiling point of a solution of 0.11 g of a substance in 15 g of ether was found to be  $0.1^\circ\text{C}$  higher than that of pure ether. The molecular weight of the substance will be ( $K_b = 2.16$ ): [PET (MP) 2002]
- 148
  - 158
  - 168
  - 178
153. 2.5 litre of  $1 \text{ M}$  NaOH solution are mixed with another 3 litre of  $0.5 \text{ M}$  NaOH solution. Then the molarity of the resulting solution is: [CBSE (PMT) 2002]
- 0.80 M
  - 1.0 M
  - 0.73 M
  - 0.50 M
154. In a mixture, 'A' and 'B' components show the negative deviations as: (AIEEE 2002)
- $\Delta V_{\text{mix}} > 0$
  - $\Delta V_{\text{mix}} < 0$
  - $A - B$  interaction is weaker than  $A - A$  and  $B - B$  interactions
  - none of the above reasons is correct
155. A solution contains non-volatile solute of molecular mass  $M_2$ . Which of the following can be used to calculate the molecular mass of solute in terms of osmotic pressure? [CBSE (PMT) 2002]
- $$(a) M_2 = \frac{m_2}{\pi} VRT \quad (b) M_2 = \left( \frac{m_2}{V} \right) \frac{RT}{\pi}$$
- $$(c) M_2 = \left( \frac{m_2}{V} \right) \pi RT \quad (d) M_2 = \left( \frac{m_2}{V} \right) \frac{\pi}{RT}$$
- ( $m_2$  = mass of solute;  $V$  = volume of solution;  $\pi$  = osmotic pressure)
156. 0.6 g of an organic compound when dissolved in 21.7 g water freezes at  $272.187 \text{ K}$ . The molar mass of the organic compound is close to: ( $K_f$  of water is  $1.86 \text{ deg/molality}$ ; freezing point is  $273 \text{ K}$ ) (SCRA 2009)
- 61 g  $\text{mol}^{-1}$
  - 63 g  $\text{mol}^{-1}$
  - 65 g  $\text{mol}^{-1}$
  - 67 g  $\text{mol}^{-1}$

157. Osmotic pressure of urea solution at 10°C is 500 mm. Osmotic pressure of the solution becomes 105.3 mm, when it is diluted and temperature raised to 25°C. The extent dilution is:  
 [PMT (MP) 2004]  
 (a) 8 times (b) 5 times (c) 4 times (d) 7 times
158. The average osmotic pressure of human blood is 7.8 bar at 37°C. What is the concentration of an aqueous NaCl solution that could be used in blood stream? [AIIMS 2004]  
 (a) 0.15 mol/L (b) 0.30 mol/L  
 (c) 0.45 mol/L (d) 0.60 mol/L
159. Camphor is often used in molecular mass determination because:  
 [CBSE-PMT (Pre.) 2004]  
 (a) it is readily available  
 (b) it has very high cryoscopic constant  
 (c) it is volatile  
 (d) it is a solvent for organic substances
160. A 0.004 M solution of  $\text{Na}_2\text{SO}_4$  is isotonic with a 0.010 M solution of glucose at same temperature. The apparent degree of dissociation of  $\text{Na}_2\text{SO}_4$  is:  
 [IIT (S) 2004]  
 (a) 25% (b) 50% (c) 75% (d) 85%
161. Which of the following liquid pairs shows a positive deviation from Raoult's law? [AIEEE 2004; AMU (Med) 2007]  
 (a) Water-hydrochloric acid (b) Benzene-methanol  
 (c) Water-nitric acid (d) Acetone-chloroform
162. Which one of the following statements is false?  
 [AIEEE 2004]  
 (a) Raoult's law states that vapour pressure of a component over a solution is proportional to mole fraction  
 (b) The osmotic pressure ( $\pi$ ) of a solution is given by the relation  $\pi = MRT$  where  $M$  is molarity of the solution  
 (c) The correct order of osmotic pressure for 0.01 M aqueous solution of each component is:  

$$\text{BaCl}_2 > \text{KCl} > \text{CH}_3\text{COOH} > \text{Sucrose}$$
  
 (d) Two sucrose solutions of same molality prepared in different solvents will have the same freezing point depression
163. A solution of sucrose (molar mass = 342 g mol<sup>-1</sup>) has been prepared by dissolving 68.5 g of sucrose in 1000 g of water. The freezing point of the solution obtained will be:  
 $(K_f \text{ for water} = 1.86 \text{ K kg mol}^{-1})$  [CBSE (PMT) 2010]  
 (a) -0.372°C (b) -0.520°C  
 (c) +0.372°C (d) -0.570°C
- [Hint :  $\Delta T = K_f \times \frac{w_B \times 1000}{m_B \times w_A}$   
 $= 1.86 \times \frac{68.5 \times 1000}{342 \times 1000}$   
 $= 0.372$
- Freezing point of solution = 0 - 0.372°C  
 = -0.372°C]
164. Which of the following is incorrect? [CET (J&K) 2005]  
 (a) Relative lowering of vapour pressure is independent of the nature of the solute and the solvent  
 (b) The vapour pressure is a colligative property  
 (c) Vapour pressure of a solution is lower than that of the solvent
- (d) The relative lowering of vapour pressure is directly proportional to the original pressure
165. Calculate the molal depression constant of a solvent which has freezing point 16.6°C and latent heat of fusion 180.75 J g<sup>-1</sup>.  
 [JEE (Orissa) 2005]  
 (a) 2.68 (b) 3.86 (c) 4.68 (d) 2.86
166. If for a sucrose solution, elevation in boiling point is 0.1°C then what will be the boiling point of NaCl solution for same molal concentration?  
 [BHU (Pre.) 2005]  
 (a) 0.1°C (b) 0.2°C (c) 0.08°C (d) 0.01°C
167. Which has minimum osmotic pressure?  
 (a) 200 mL of 2 M NaCl solution  
 (b) 200 mL of 1 M glucose solution  
 (c) 200 mL of 2 M urea solution  
 (d) All have same
168. Solution A contains 7 g/L of  $\text{MgCl}_2$  and solution B contains 7 g/L of NaCl. At room temperature, the osmotic pressure of:  
 [DCE 2005]  
 (a) solution A is greater than B  
 (b) both have same osmotic pressure  
 (c) solution B is greater than A  
 (d) can't determine
169. The van't Hoff factor for  $\text{BaCl}_2$  at 0.01 M concentration is 1.98. The percentage dissociation of  $\text{BaCl}_2$  at this concentration is:  
 [PET (Kerala) 2005]  
 (a) 49 (b) 69 (c) 89 (d) 98  
 (e) 100
170. Equimolar solutions in the same solvent have: [AIEEE 2005]  
 (a) same boiling point but different freezing points  
 (b) same freezing point but different boiling points  
 (c) same freezing and boiling points  
 (d) different freezing and boiling points
171. A solution of urea (mol. mass 56 g mol<sup>-1</sup>) boils at 100.18°C at the atmospheric pressure. If  $K_f$  and  $K_b$  for water are 1.86 and 0.512 K kg mol<sup>-1</sup> respectively, the above solution will freeze at:  
 [CBSE-PMT (Pre.) 2005]  
 (a) 0.654°C (b) -0.654°C  
 (c) 6.54°C (d) -6.54°C
172. If 0.5 g of a solute (molar mass 100 g mol<sup>-1</sup>) in 25 g of solvent elevates the boiling point by 1 K, the molar boiling point constant of the solvent is:  
 [PMT (Kerala) 2006]  
 (a) 2 (b) 8 (c) 5 (d) 0.5  
 (e) 10
173. Osmotic pressure observed when benzoic acid is dissolved in benzene, is less than that expected from theoretical considerations. This is because:  
 [KCET 2006]  
 (a) benzoic acid is an organic solute  
 (b) benzoic acid has higher molar mass than benzene  
 (c) benzoic acid gets associated in benzene  
 (d) benzoic acid gets dissociated in benzene
174. A 5% solution by mass of cane sugar in water has freezing point of 271 K and freezing point of pure water is 273.15 K. The freezing point of a 5% solution (by mass) of glucose in water is:  
 [AIIMS 2006]  
 (a) 271 K (b) 273.15 K (c) 269.07 K (d) 277.23 K

[Hint:  $\Delta T = K_f \times \frac{w_B \times 1000}{m_B \times w_A}$

$$2.15 = K_f \times \frac{5 \times 1000}{342 \times 95} \quad \dots \text{(i) (for sucrose)}$$

$$\Delta T = K_f \times \frac{5 \times 1000}{180 \times 95} \quad \dots \text{(ii) (for glucose)}$$

Dividing eq. (i) by eq. (ii), we get,

$$\begin{aligned} \Delta T &= 4.18 \text{ K} \\ T &= T_0 - 4.18 \\ &= 273.15 - 4.18 = 269.07 \text{ K} \end{aligned}$$

175. 18 g glucose ( $C_6H_{12}O_6$ ) is added to 178.2 g of water. The vapour pressure of water for this aqueous solution at 100°C is: (AIEEE 2006)

(a) 759 torr (b) 7.60 torr (c) 76 torr (d) 752.4 torr

176. Depression in freezing point is 6 K for NaCl solution. If  $K_f$  for water is 1.86 K/kg·mol, amount of NaCl dissolved in 1 kg water is: (DCE 2006)

(a) 3.42 (b) 1.62 (c) 3.24 (d) 1.71

177. Observe the following observations:

$\pi_{\text{obs}}$  = observed colligative property

$\pi_{\text{cal}}$  = theoretical colligative property assuming normal behaviour of solute

van't Hoff factor ( $i$ ) is given by: [CET (J&K) 2006]

- |  |   |
|--|---|
| (a) $i = \pi_{\text{obs}} \times \pi_{\text{cal}}$ | (b) $i = \pi_{\text{obs}} + \pi_{\text{cal}}$       |
| (c) $i = \pi_{\text{obs}} - \pi_{\text{cal}}$      | (d) $i = \frac{\pi_{\text{obs}}}{\pi_{\text{cal}}}$ |

178. A 5.25% solution of a substance is isotonic with a 1.5% solution of urea (molar mass = 60 g mol<sup>-1</sup>) in the same solvent. If the densities of both the solutions are assumed to be equal to 1 g cm<sup>-3</sup>, molar mass of the substance will be: (AIEEE 2007)

- |                               |                               |
|-------------------------------|-------------------------------|
| (a) 210.0 g mol <sup>-1</sup> | (b) 90.0 g mol <sup>-1</sup>  |
| (c) 115.0 g mol <sup>-1</sup> | (d) 105.0 g mol <sup>-1</sup> |

[Hint: For isotonic solutions:

$$\pi_1 = \pi_2 \quad \therefore \quad \pi = CRT$$

$$C_1 = C_2$$

$$\frac{1.5/60}{V} = \frac{5.25/m}{V}$$

$$m = 210$$

179. Concentrated aqueous sulphuric acid 98% H<sub>2</sub>SO<sub>4</sub> by mass has a density of 1.80 g mL<sup>-1</sup>. Volume of acid required to make one litre of 0.1M H<sub>2</sub>SO<sub>4</sub> solution is: [CBSE (Med) 2007]

- |              |              |
|--------------|--------------|
| (a) 16.65 mL | (b) 22.20 mL |
| (c) 5.55 mL  | (d) 11.10 mL |

[Hint:  $M = \frac{x \times d \times 10}{m_B} = \frac{98 \times 1.80 \times 10}{98} = 18$

$$M_1 V_1 = M_2 V_2$$

$$18 \times V_1 = 0.1 \times 1000$$

$$V_1 = \frac{100}{18} = 5.55 \text{ mL}$$

180. If the vapour pressures of pure  $A$  and pure  $B$  at 298 K are 60 and 15 torr respectively, what would be the mole fraction of  $A$  in vapour phase (at this temperature) in a solution that

contains 20 mole per cent of  $A$  in the ( $A + B$ ) binary mixture in the liquid phase? (SCRA 2007)

- |         |         |
|---------|---------|
| (a) 0.2 | (b) 0.3 |
| (c) 0.5 | (d) 0.7 |

[Hint:  $x_A = \frac{20}{100} = 0.2, \therefore x_B = 0.8$

$$\begin{aligned} p &= p_A + p_B = p_A^0 x_A + p_B^0 x_B \\ &= 60 \times 0.2 + 15 \times 0.8 = 12 + 12 = 24 \end{aligned}$$

Mole fraction of  $A$  in the vapour phase, i.e.,  $y_A$  may be calculated as:

$$\begin{aligned} p_A &= y_A \times p \\ 12 &= y_A \times 24 \\ y_A &= \frac{12}{24} = 0.5 \end{aligned}$$

181. When 20 g of naphthoic acid ( $C_{11}H_8O_2$ ) is dissolved in 50 g of benzene ( $K_f = 1.72 \text{ kg mol}^{-1}$ ), a freezing point depression of 2 K is observed. The van't Hoff factor ( $i$ ) is: (IIT 2007)

- |         |       |
|---------|-------|
| (a) 0.5 | (b) 1 |
| (c) 2   | (d) 3 |

[Hint:  $\Delta T = i \times K_f \times \frac{w_B \times 1000}{m_B \times w_A}$

$$2 = i \times 1.72 \times \frac{20 \times 1000}{172 \times 50}$$

$$i = 0.5$$

182. At 80°C, the vapour pressure of pure liquid  $A$  is 520 mm of Hg and that of pure liquid  $B$  is 1000 mm of Hg. If a mixture of solution  $A$  and  $B$  boils at 80°C and 1 atm pressure, the amount of  $A$  in the mixture is: (1 atm = 760 mm of Hg) (AIEEE 2008)

- |                     |                     |
|---------------------|---------------------|
| (a) 50 mol per cent | (b) 52 mol per cent |
| (c) 34 mol per cent | (d) 48 mol per cent |

[Hint:  $p = p_A^0 x_A + p_B^0 x_B$

$$760 = 520 \times x_A + 1000 (1 - x_A)$$

$$x_A = 0.50, \text{ i.e., } 50 \text{ mol per cent.}$$

183. The vapour pressure of water at 20°C is 17.5 mm Hg. If 18 g of glucose ( $C_6H_{12}O_6$ ) is added to 178.2 g of water at 20°C, the vapour pressure of resulting solution will be: (AIEEE 2008)

- |                  |                  |
|------------------|------------------|
| (a) 17.325 mm Hg | (b) 17.675 mm Hg |
| (c) 15.75 mm Hg  | (d) 16.5 mm Hg   |

[Hint:  $p = p_A^0 x_A$

$$= 17.5 \times \frac{178.2/18}{178.2/18 + \frac{18}{180}}$$

$$= 17.325 \text{ mm Hg}$$

184. Which of the following can be measured by the Ostwald-Walker dynamic method? (KCET 2008)

- |  |  |
|--|--|
| (a) Vapour pressure of the solvent       |  |
| (b) Relative lowering of vapour pressure |  |
| (c) Lowering of vapour pressure          |  |
| (d) All of the above                     |  |

185. Cryoscopic constant is the depression in freezing point produced by:

- |                      |                      |
|----------------------|----------------------|
| (a) 1% solution      | (b) 1 molar solution |
| (c) 1 molal solution | (d) 1 N solution     |

186. Which among the following gas will greatly deviate from Henry's law in water? [PMT (Kerala) 2008]

(a)  $H_2$                                   (b)  $N_2$   
 (c)  $CH_4$                                   (d)  $CO_2$   
 (e) Ar

187. Vapour pressure increases with increase in :

[JEE (Orissa) 2008]

(a) concentration of solution containing non-volatile solute  
 (b) temperature upto boiling point  
 (c) temperature upto triple point  
 (d) altitude of the concerned place of boiling

188. When mercuric iodide is added to the aqueous solution of potassium iodide: [BHU (Mains) 2008]

(a) freezing point is raised  
 (b) freezing point is lowered  
 (c) freezing point does not change  
 (d) boiling point is raised

[Hint :  $2KI + HgI_2 \rightarrow K_2[HgI_4]$ ]

Number of particles decreases due to above reaction hence freezing point is raised.]

189. The Henry's law constant for the solubility of  $N_2$  gas in water at 298 K is  $1 \times 10^5$  atm. The mole fraction of  $N_2$  in air is 0.8. The number of moles of  $N_2$  from dissolved in 10 moles of water at 298 K and 5 atm pressure is: [IIT 2009]

(a)  $4 \times 10^{-4}$                                   (b)  $4 \times 10^{-5}$   
 (c)  $5 \times 10^{-4}$                                       (d)  $4 \times 10^{-6}$

[Hint :  $P_{N_2} = x_{N_2} \times P_{total}$   
 $= 0.8 \times 5 = 4$  atm]

According to Henry's law :

$$\begin{aligned} P_{N_2} &= K_H \times x_{N_2} \\ 4 &= 1 \times 10^5 \times \frac{n_{N_2}}{n_{N_2} \times n_{H_2O}} \\ \frac{n_{N_2} + n_{H_2O}}{n_{N_2}} &= \frac{1 \times 10^5}{4} \\ \frac{n_{N_2} + 10}{n_{N_2}} &= 0.25 \times 10^5 \\ n_{N_2} &= 4 \times 10^{-4} \end{aligned}$$

190. A 0.002 m aqueous solution of an ionic compound  $Co(NH_3)_5(NO_2)_Cl$  freezes at  $-0.00732^\circ C$ . Number of moles of ions which 1 mol of ionic compound produces on being dissolved in water will be : ( $K_f = -1.86^\circ C/m$ )

[CBSE (Med) 2009]

(a) 1    (b) 2    (c) 3    (d) 4

[Hint :  $\Delta T = i \times K_f \times m$

$$0.00732 = i \times 1.86 \times 0.002$$

$$i = 1.967 \approx 2$$

191. A solution is separated from pure solvent by a semipermeable membrane at 298 K. The difference in the height of the solution and the solvent is 0.9 m. If  $K_f$  and freezing point of the solvent are  $30\text{ K kg mol}^{-1}$  and  $250.3\text{ K}$ , respectively, the temperature at which the solution freezes is: [ISAT 2010]

(a)  $250.10\text{ K}$                                   (b)  $250.25\text{ K}$   
 (c)  $250.20\text{ K}$                                       (d)  $250.05\text{ K}$

(Assume density of solution to be 1 g/cc)

[Hint :  $\pi \times 13.6 \times g \times 76 = 90 \times g \times 1$

$$\pi = 0.087 \text{ atm}$$

$$\pi = CRT$$

$$0.087 = C \times 0.082 \times 298$$

$$C = 3.56 \times 10^{-3} M$$

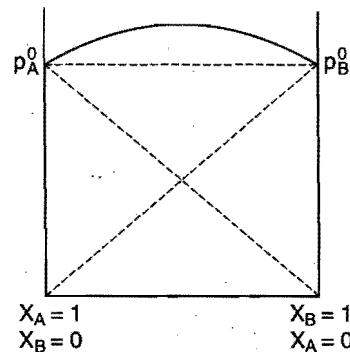
$$\Delta T = K_f \times m$$

$$= 30 \times 3.56 \times 10^{-3} \approx 0.1$$

$\therefore$  Freezing point of solution will be :  $250.3 - 0.1$   
 $= 250.2\text{ K}$

**Set-2: The questions given below may have more than one correct answers**

1. The given graph indicates:



- (a) (+) deviation                                  (b) (-) deviation  
 (c) no deviation                                      (d) none of these

2. Which is the correct statement?

- (a) Minimum boiling azeotropic mixture boils at temperature lower than either of the two pure components  
 (b) Maximum boiling azeotropic mixture boils at temperature higher than either of the two pure components  
 (c) Minimum boiling azeotropic mixture shows (+)ve deviation  
 (d) Maximum boiling azeotropic mixture shows (-)ve deviation

3. A certain non-volatile substance (non-electrolyte) contains 40% C, 6.7% H, 53.3% O. An aqueous solution containing 5% by mass of the solute boils at  $100.15^\circ C$ . Molecular formula of the compound is:

- (a)  $CH_2O$     (b)  $C_2H_4O_2$   
 (c)  $C_6H_{12}O_6$     (d)  $C_{12}H_{22}O_{11}$

4. Difference between diffusion and osmosis is:

- (a) a semipermeable membrane is required for osmosis while diffusion requires no semipermeable membrane  
 (b) in osmosis the movement of molecules is only in one direction whereas in diffusion movement is on both sides  
 (c) in osmosis only the solvent moves while in diffusion solute and solvent both move  
 (d) none of the above

5. For a non-volatile solute:

- (a) vapour pressure of solute is zero  
 (b) vapour pressure of solution = vapour pressure of pure solvent  
 (c) vapour pressure of solution = vapour pressure of solvent in solution  
 (d) all of the above

6. In which of the following cases does osmosis take place if the solutions are separated by a semipermeable membrane?

(a) 0.1 M NaCl and 0.2 M glucose  
 (b) 0.1 M sucrose and 0.1 M fructose  
 (c) 0.05 M  $\text{K}_4[\text{Fe}(\text{CN})_6]$  and 0.1 M  $\text{CaCl}_2$   
 (d)  $10^{-3}$  M  $\text{CaCl}_2$  and  $1.5 \times 10^{-3}$  M NaCl

7. Match the following:

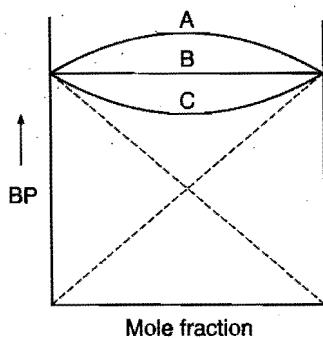
**Solute (equimolar)**

- (i) Urea, glucose, fructose  
 (ii)  $\text{NaCl}$ ,  $\text{MgCl}_2$ ,  $\text{K}_2\text{SO}_4$   
 (iii)  $\text{Al}_2(\text{SO}_4)_3$ ,  $\text{Na}_3\text{PO}_4$ ,  $\text{K}_4\text{Fe}(\text{CN})_6$   
 (iv) Glucose,  $\text{NaCl}$ ,  $\text{CaCl}_2$

**$\pi$  (OP) ratio**

- |                 |               |               |               |
|-----------------|---------------|---------------|---------------|
| (A) 1 : 0.8 : 1 | (B) 1 : 2 : 3 | (C) 1 : 1 : 1 | (D) 2 : 3 : 3 |
| (i)             | (ii)          | (iii)         | (iv)          |
| (a) A           | B             | C             | D             |
| (b) B           | D             | C             | A             |
| (c) D           | B             | A             | C             |
| (d) C           | D             | A             | B             |

8. Match the following graph:



A (i) (+) deviation

B (ii) Ideal

C (iii) (-) deviation

(a) (A) (i), (B) (ii), (C) (iii)

(b) (A) (iii), (B) (ii), (C) (i)

(c) (A) (ii), (B) (iii), (C) (i)

(d) none of these

9. Vapour pressure of methyl alcohol and ethyl alcohol solutions is represented by  $P = 115x_A + 140$  where  $x_A$  is the mole fraction of methyl alcohol. The value of  $\lim_{x_A \rightarrow 0} \frac{P_B^0}{x_B}$  is:

- (a) 255 (b) 115  
 (c) 140 (d) 135

10. To 10 mL of 1 M  $\text{BaCl}_2$  solution 5 mL of 0.5 M  $\text{K}_2\text{SO}_4$  is added,  $\text{BaSO}_4$  is precipitated out. What will happen?

- (a) F.pt. is increased (b) B.pt. is increased  
 (c) F.pt. is lowered (d) B.pt. is lowered

11. Which is a dimensionless quantity?

(a) Mole fraction (b) Molality  
 (c) % by wt. of solvent (d) % by wt. of solution

12. Which of the following concentration terms is/are independent of temperature? [PET (Kerala) 2006; CET (Gujarat) 2006; DCE 2007]

(a) Molarity  
 (b) Molarity and mole fraction  
 (c) Mole fraction and molality  
 (d) Molality and normality  
 (e) Only molality

13. In the depression of freezing point experiment, it is found that: [IIT 1999]

(a) the vapour pressure of the solution is less than that of pure solvent  
 (b) the vapour pressure of solution is more than that of pure solvent  
 (c) only solute molecules solidify at the freezing point  
 (d) only solvent molecules solidify at the freezing point

14. Which of the following is/are correct for a solution of a particular concentration?

(a) Molarity is always less than molality  
 (b) Formality is equivalent to molarity  
 (c) Mole fraction is equivalent to mass fraction  
 (d) Normality of  $\text{H}_2\text{SO}_4$  solution is double than its molarity

15. Effect of adding a non-volatile solute to a solvent is:

(a) to lower the vapour pressure  
 (b) to increase its freezing point  
 (c) to increase its boiling point  
 (d) to decrease its osmotic pressure

16. Which of the following form/s an ideal solution?

(a) Ethyl bromide + ethyl iodide  
 (b) Ethyl alcohol + water  
 (c) Chloroform + benzene  
 (d) Benzene + toluene

17. Osmotic pressure of a solution is:

(a) directly proportional to the molar concentration of the solution  
 (b) inversely proportional to the molecular weight of the solute  
 (c) inversely proportional to the temperature  
 (d) directly proportional to the volume of the solution

18. Which of the following is/are true?

(a) For the same solution, elevation in boiling point = depression in freezing point  
 (b) van't Hoff factor for a dilute solution of  $\text{BaCl}_2$  is 3  
 (c) Elevation in boiling point is due to increase in vapour pressure  
 (d) Depression in freezing point is due to decrease in vapour pressure

19. In the following question, more than one of the answers given may be correct. Select correct answer and mark it according to the code: [BHU (Mains) 2008]

A solution containing components *A* and *B* exhibits positive deviation from Raoult's law only when

- (1)  $\Delta V_{\text{mixing}} = + \text{ve}$
- (2)  $\Delta H_{\text{mixing}} = - \text{ve}$
- (3)  $A - B$  attraction forces <  $A - A$  and  $B - B$  attraction forces
- (4)  $A - B$  attraction forces >  $A - A$  and  $B - B$  attraction forces

**Codes:**

- (a) 1, 2 and 3 are correct
  - (b) 1 and 2 are correct
  - (c) 2 and 4 are correct
  - (d) 1 and 3 are correct
20. Consider the following statements in respect of an ideal solution:
- 1. Raoult's law is valid for an ideal solution over the whole concentration range
  - 2. Enthalpy of mixing is zero, i.e.,  $\Delta H_{\text{mix}} = 0$
  - 3. Volume of mixing is not zero, i.e.,  $\Delta V_{\text{mix}} \neq 0$
  - 4. The components of ideal solution cannot be separated by fractional distillation.

Which of the statements given above is/are correct?

(SCRA 2009)

- (a) 3 and 4
  - (b) 1 and 4
  - (c) 1 and 2
  - (d) 2 and 3
21. Consider the following:  
At constant pressure, boiling point of a solution is greater than the boiling point of its pure liquid solvent because
- 1. Solute is non-electrolyte
  - 2. Solute is involatile
  - 3. Chemical potential of solvent in solution is less than the chemical potential of solvent in its pure state at constant pressure
- Which of the above are correct? (SCRA 2009)
- (a) 1, 2 and 3
  - (b) 1 and 2 only
  - (c) 1 and 3 only
  - (d) 2 and 3 only
22. Which values can be obtained from the information represented by the vapour pressure curve of a liquid?
- 1. Normal boiling point
  - 2. Normal freezing point
  - 3. Enthalpy of vaporisation
- (DUMET 2010)
- (a) 1 only
  - (b) 1 and 2 only
  - (c) 1 and 3 only
  - (d) 1, 2 and 3

## **Assertion-Reason TYPE QUESTIONS**

The questions given below consist of two statements each printed as 'Assertion' (A) and 'Reason' (R). While answering these questions you are required to choose any one of the following four options:

- (a) If both (A) and (R) are correct and (R) is the correct explanation for (A).
  - (b) If both (A) and (R) are correct but (R) is not the correct explanation for (A).
  - (c) If (A) is correct but (R) is incorrect.
  - (d) If (A) is incorrect but (R) is correct.
1. (A) The dissolution of gases in water is always an endothermic process.  
(R) Dissolution of gases in water proceed with negative value of  $\Delta S$ .
2. (A) Water boiling at  $100^{\circ}\text{C}$  at 1 atmospheric pressure in a beaker is not at equilibrium.  
(R) It refers to an open system.
3. (A) A solution which contains one gram equivalent of solute per litre of the solution is called a normal solution.  
(R) A normal solution means a solution in which the solute does not associate or dissociate.
4. (A) The sum of mole fractions of all the components of a solution is unity.  
(R) Mole fraction is a temperature dependent quantity.
5. (A) Iodine is more soluble in  $\text{CCl}_4$  than in water.  
(R) Non-polar solutes are more soluble in non-polar solvents.
6. (A) Vapour pressure of  $0.5\text{ M}$  sugar solution is more than  $0.5\text{ M}$   $\text{KCl}$  solution.  
(R) Lowering of vapour pressure is directly proportional to the number of species present in the solution.
7. (A) Non-ideal solutions form azeotropic mixture.  
(R) Boiling point of azeotropic mixture is higher than boiling points of its both components.
8. (A) One molar solution is always more concentrated than one molal solution.  
(R) The amount of solvent in  $1\text{ M}$  and  $1\text{ m}$  aqueous solution is not equal.
9. (A) Camphor is used as solvent in the determination of molecular mass of naphthalene and anthracene etc.  
(R) Camphor has high molal elevation constant.
10. (A)  $0.1\text{ M}$  solution of glucose has same increment in freezing point than  $0.1\text{ M}$  solution of urea.  
(R)  $K_f$  for both has different values. (AIIMS 1997)
11. (A) Molarity of  $0.02\text{ N}$  solution of  $\text{HNO}_3$  is  $0.02\text{ M}$ .  
(R) Molarity and normality of a solution are never equal.
12. (A) Larger the value of cryoscopic constant of the solvent, lesser will be the freezing point of the solution.  
(R) Depression in the freezing point depends on the nature of the solvent.
13. (A)  $0.1\text{ M}$  solution of  $\text{NaCl}$  has greater osmotic pressure than  $0.1\text{ M}$  solution of glucose at same temperature.  
(R) In solution,  $\text{NaCl}$  dissociates to produce more number of particles.
14. (A) Henry's law and Raoult's law are not independent, i.e., one can be derived from the other.  
(R) The partial pressure is directly proportional to the mole fraction of the concerned species for ideal solutions.
15. (A) The water pouch of instant cold pack for treating athletic injuries breaks when squeezed and  $\text{NH}_4\text{NO}_3$  dissolves thus lowering the temperature.  
(R) Addition of non-volatile solute into solvent results into depression of freezing point of solvent. (AIIMS 2006)
16. (A) In a pressure cooker, the water is brought to boil. The cooker is then removed from the stove. Now on removing the lid of pressure cooker, the water starts boiling again.  
(R) The impurities in water bring down its boiling point.  
[Hint: In pressure cooker, water boils above  $100^{\circ}\text{C}$ . When the lid of cooker is opened, pressure is lowered so that boiling point decreases and water boils again.]
17. (A) An increase in surface area increases the rate of evaporation.  
(R) Stronger the inter-molecular attractive forces, faster is the rate of evaporation at a given temperature.
18. (A) An ideal solution obeys Raoult's law.  
(R) In an ideal solution, solute-solute as well as solvent-solvent interactions are similar to solute-solvent interaction.

**Answers : OBJECTIVE QUESTIONS****• Set-1**

- |          |          |          |          |          |          |          |          |
|----------|----------|----------|----------|----------|----------|----------|----------|
| 1. (a)   | 2. (c)   | 3. (b)   | 4. (d)   | 5. (b)   | 6. (d)   | 7. (c)   | 8. (b)   |
| 9. (c)   | 10. (d)  | 11. (a)  | 12. (a)  | 13. (d)  | 14. (c)  | 15. (a)  | 16. (d)  |
| 17. (a)  | 18. (b)  | 19. (c)  | 20. (b)  | 21. (d)  | 22. (c)  | 23. (a)  | 24. (b)  |
| 25. (c)  | 26. (d)  | 27. (b)  | 28. (a)  | 29. (c)  | 30. (b)  | 31. (d)  | 32. (d)  |
| 33. (b)  | 34. (a)  | 35. (d)  | 36. (c)  | 37. (b)  | 38. (c)  | 39. (b)  | 40. (d)  |
| 41. (a)  | 42. (a)  | 43. (b)  | 44. (c)  | 45. (d)  | 46. (b)  | 47. (b)  | 48. (d)  |
| 49. (c)  | 50. (c)  | 51. (b)  | 52. (a)  | 53. (b)  | 54. (d)  | 55. (d)  | 56. (a)  |
| 57. (c)  | 58. (b)  | 59. (b)  | 60. (c)  | 61. (a)  | 62. (d)  | 63. (c)  | 64. (d)  |
| 65. (a)  | 66. (d)  | 67. (a)  | 68. (c)  | 69. (b)  | 70. (c)  | 71. (a)  | 72. (b)  |
| 73. (d)  | 74. (b)  | 75. (a)  | 76. (c)  | 77. (d)  | 78. (d)  | 79. (a)  | 80. (d)  |
| 81. (b)  | 82. (a)  | 83. (a)  | 84. (d)  | 85. (d)  | 86. (b)  | 87. (c)  | 88. (b)  |
| 89. (b)  | 90. (c)  | 91. (a)  | 92. (d)  | 93. (d)  | 94. (d)  | 95. (b)  | 96. (b)  |
| 97. (c)  | 98. (b)  | 99. (a)  | 100. (c) | 101. (d) | 102. (b) | 103. (b) | 104. (b) |
| 105. (c) | 106. (c) | 107. (c) | 108. (a) | 109. (a) | 110. (d) | 111. (b) | 112. (d) |
| 113. (a) | 114. (d) | 115. (a) | 116. (c) | 117. (a) | 118. (d) | 119. (d) | 120. (b) |
| 121. (a) | 122. (b) | 123. (d) | 124. (c) | 125. (c) | 126. (b) | 127. (a) | 128. (b) |
| 129. (d) | 130. (b) | 131. (a) | 132. (b) | 133. (a) | 134. (b) | 135. (b) | 136. (a) |
| 137. (d) | 138. (c) | 139. (c) | 140. (b) | 141. (a) | 142. (b) | 143. (c) | 144. (d) |
| 145. (c) | 146. (a) | 147. (a) | 148. (c) | 149. (c) | 150. (b) | 151. (a) | 152. (b) |
| 153. (c) | 154. (b) | 155. (b) | 156. (b) | 157. (b) | 158. (b) | 159. (b) | 160. (c) |
| 161. (b) | 162. (d) | 163. (a) | 164. (d) | 165. (b) | 166. (b) | 167. (b) | 168. (a) |
| 169. (a) | 170. (d) | 171. (b) | 172. (c) | 173. (c) | 174. (c) | 175. (d) | 176. (b) |
| 177. (d) | 178. (a) | 179. (c) | 180. (c) | 181. (a) | 182. (a) | 183. (a) | 184. (b) |
| 185. (c) | 186. (d) | 187. (b) | 188. (a) | 189. (a) | 190. (b) | 191. (c) |          |

**• Set-2**

- |            |                 |               |              |            |            |            |            |
|------------|-----------------|---------------|--------------|------------|------------|------------|------------|
| 1. (a)     | 2. (a, b, c, d) | 3. (c)        | 4. (a, b, c) | 5. (a, c)  | 6. (c)     | 7. (d)     | 8. (b)     |
| 9. (c)     | 10. (b, c)      | 11. (a, c, d) | 12. (c)      | 13. (a, d) | 14. (b, d) | 15. (a, c) | 16. (a, d) |
| 17. (a, d) | 18. (b, d)      | 19. (d)       | 20. (c)      | 21. (d)    | 22. (b)    |            |            |

**Answers : ASSERTION-REASON TYPE QUESTIONS**

- |         |         |         |         |         |         |         |         |
|---------|---------|---------|---------|---------|---------|---------|---------|
| 1. (d)  | 2. (a)  | 3. (c)  | 4. (c)  | 5. (a)  | 6. (a)  | 7. (c)  | 8. (d)  |
| 9. (a)  | 10. (c) | 11. (c) | 12. (a) | 13. (a) | 14. (b) | 15. (a) | 16. (c) |
| 17. (c) | 18. (a) |         |         |         |         |         |         |

## BRAIN STORMING PROBLEMS

### OBJECTIVE QUESTIONS for IIT ASPIRANTS

The following questions contain single correct option:

1. Three solutions of HCl having normality 12 N, 6 N and 2 N are mixed to obtain a solution of 4 N normality. Which among the following volume ratio is correct for the above three components?

(a) 1:1:5    (b) 1:2:6    (c) 2:1:9    (d) 1:2:4

[Hint:  $N_1V_1 + N_2V_2 + N_3V_3 = N_R(V_1 + V_2 + V_3)$

$$12 \times 1 + 6 \times 2 + 2 \times 6 = N_R(9)$$

$$N_R = 4]$$

2. 6.8 g H<sub>2</sub>O<sub>2</sub> is dissolved in 224 mL solution. This solution will be labelled as:

(a) 0.224 V    (b) 20 V    (c) 5 V    (d) 10 V

[Hint:  $M = \frac{w_B \times 1000}{m_B \times V} = \frac{6.8}{34} \times \frac{1000}{224}$

$$= \frac{200}{224}$$

Volume strength  $V = M \times 11.2$

$$= \frac{200}{224} \times 11.2 = 10]$$

3. A solution weighing  $a$  g has molality  $b$ . The molecular mass of solute if the mass of solute is  $c$  g, will be:

(a)  $\frac{c}{b} \times \frac{1000}{(a-c)}$     (b)  $\frac{b}{a} \times \frac{1000}{(a-b)}$

(c)  $\frac{b}{c} \times \frac{1000}{(a-c)}$     (d)  $\frac{c}{a} \times \frac{1000}{(b-a)}$

[Hint: Molality,  $m = \frac{w_B \times 1000}{m_B \times w_A}$

$$b = \frac{c}{m_B} \times \frac{1000}{(a-c)}$$

$$m_B = \frac{c}{b} \times \frac{1000}{(a-c)}$$

4. Two solutions of H<sub>2</sub>SO<sub>4</sub> of molarities  $x$  and  $y$  are mixed in the ratio of  $V_1$  mL :  $V_2$  mL to form a solution of molarity  $M_1$ . If they are mixed in the ratio of  $V_2$  mL :  $V_1$  mL, they form a solution of molarity  $M_2$ . Given  $V_1/V_2 = \frac{x}{y} > 1$  and  $\frac{M_1}{M_2} = \frac{5}{4}$ , then  $x:y$  is:

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

[Hint: Molarity of the mixture can be calculated as:

$$M_1V_1 + M_2V_2 = M_R(V_1 + V_2)$$

where,  $M_R$  = resultant solution

$$V_1 \times x + V_2 \times y = M_1(V_1 + V_2) \quad \dots (i)$$

$$V_2 \times x + V_1 \times y = M_2(V_1 + V_2) \quad \dots (ii)$$

Dividing eq. (i) by eq. (ii), we get

$$\frac{V_1x + V_2y}{V_2x + V_1y} = \frac{M_1}{M_2}$$

Substituting  $\frac{M_1}{M_2} = \frac{5}{4}$  and  $\frac{V_1}{V_2} = \frac{x}{y}$  we can calculate  $x:y$ ]

5. You are given 500 mL of 2 N HCl and 500 mL of 5 N HCl. What will be the maximum volume of 3 M HCl that you can make from these two solutions?

(a) 250 mL    (b) 750 mL    (c) 500 mL    (d) 1000 mL

6. The mole fraction of a given sample of I<sub>2</sub> in C<sub>6</sub>H<sub>6</sub> is 0.2. The molality of I<sub>2</sub> in C<sub>6</sub>H<sub>6</sub> is:

(a) 0.32    (b) 3.2    (c) 0.032    (d) 0.48

[Hint:  $m = \frac{x_B \times 1000}{(1-x_B)m_A}$      $m$  = molality  
 $x_B$  = mole fraction of solute  
 $m = \frac{0.2 \times 1000}{0.8 \times 78}$      $m_A$  = molar mass of solvent ]

7. A 15-volume sample of an H<sub>2</sub>O<sub>2</sub> solution is equivalent to:

(a) 5.30 N    (b) 1.77 N    (c) 2.68 N    (d) 7.50 N

[Hint:  $V = 5.6 N$

$$15 = 5.6 N$$

$$N = 2.68]$$

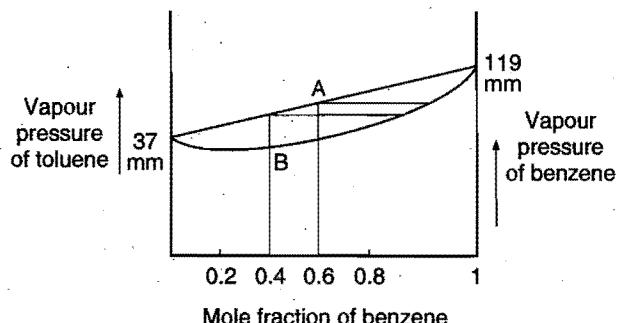
8. If  $P_A$  is the vapour pressure of a pure liquid  $A$  and the mole fraction of  $A$  in the mixture of two liquids  $A$  and  $B$  is  $x$ , the partial vapour pressure of  $A$  is:

(a)  $(1-x)P_A$     (b)  $xP_A$     (c)  $\frac{x}{(1-x)} P_A$     (d)  $\frac{1-x}{x} P_A$

9. Difference between diffusion and osmosis is:

(a) a semipermeable membrane is required for osmosis while diffusion requires no semipermeable membrane  
(b) in osmosis, movement of molecules is in one direction whereas in diffusion, the movement is on both sides  
(c) in osmosis only the solvent moves while in diffusion solute and solvent both move  
(d) all of the above

10.



Choose the correct option:

- (a) 'A' represents vapour composition and 'B' the liquid composition  
(b) 'A' as well as 'B' represent liquid composition  
(c) Both 'A' and 'B' represent vapour composition  
(d) 'A' represents liquid composition and 'B' the vapour composition

11. Insulin ( $C_2H_{10}O_5$ )<sub>n</sub> is dissolved in a suitable solvent and the osmotic pressure ( $\pi$ ) of solutions of various concentrations (g/cc)  $C$  is measured at 20°C. The slope of the plot of  $\pi$  against ' $C$ ' is found to be  $4.65 \times 10^{-3}$ . The molecular weight of insulin is:

(a)  $4.8 \times 10^5$  (b)  $9 \times 10^5$  (c)  $3 \times 10^5$  (d)  $5.17 \times 10^6$

[Hint:  $\pi V = \frac{w_B}{m_B} \times RT$

$$\pi = \left( \frac{w_B}{V} \right) \frac{RT}{m_B}$$

$$\pi = C \times \frac{RT}{m_B} \times 1000 \quad \dots (i)$$

where  $C$  = concentration in g/cc,

$$y = x \times m \quad \dots (ii)$$

Comparing eqs. (i) and (ii),

$$\text{Slope} = \frac{RT}{m_B} \times 1000$$

$$m_B = \frac{RT}{\text{Slope}} \times 1000$$

$$= \frac{0.0821 \times 293 \times 1000}{4.65 \times 10^{-3}}$$

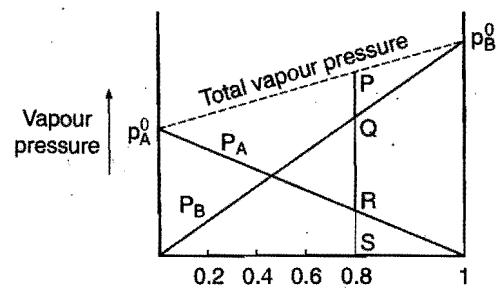
$$= 5.17 \times 10^6]$$

12. Solubility of deliquescent substances in water is generally:

(a) high (b) low  
(c) moderate (d) cannot be predicted

[Hint: A deliquescent substance absorbs large amount of water, hence solubility is very high.]

13. Consider the following vapour pressure-composition graph,  $SP$  is equal to:



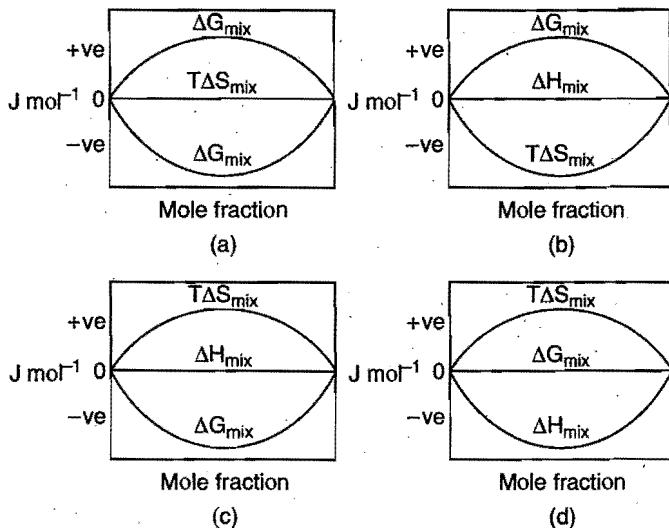
- (a)  $PQ + RS$  (b)  $PQ + QR + RS$   
(c)  $SR + SQ$  (d)  $PQ + QR$

14.  $y$  g of a non-volatile organic substance of molecular mass  $M$  is dissolved in 250 g benzene. Molal elevation constant of benzene is  $K_b$ . Elevation in its boiling point is given by:

- (a)  $\frac{M}{K_b y}$  (b)  $\frac{4K_b y}{M}$  (c)  $\frac{K_b y}{4M}$  (d)  $\frac{K_b y}{M}$

[Hint:  $\Delta T = K_b \times \frac{w_B \times 1000}{m_B \times w_A}$   
 $= K_b \times \frac{y \times 1000}{M \times 250} = \frac{4K_b y}{M}$ ]

15. Which of the following represents correctly the changes in thermodynamic properties during the formation of 1 mole of an ideal binary solution?



16. A solute forms a pentamer when dissolved in a solvent. The van't Hoff factor ' $i$ ' for the solute will be:

- (a) 0.2 (b) 0.8 (c) 0.5 (d) 0.6

17. What is the molarity of HCl in a solution prepared by dissolving 5.5 g HCl in 200 g ethanol if the density of the solution is  $0.79 \text{ g mL}^{-1}$ ?

- (a)  $21 M$  (b)  $0.93 M$  (c)  $6 \times 10^{-4} M$  (d)  $1.7 M$   
(e)  $0.58 M$

[Hint:  $V = \frac{W \text{ (mass)}}{d} = \frac{205.5}{0.79} = 260.13 \text{ mL}$   
 $M = \frac{w_B \times 1000}{m_B \times V}$   
 $= \frac{5.5 \times 1000}{36.5 \times 260.13} = 0.58 M$ ]

18. Which statement about the composition of vapour over an ideal 1:1 molar mixture of benzene and toluene is correct? Assume the temperature is constant at 25°C.

Vapour pressure data (25°C):

Benzene	75 mm Hg
Toluene	22 mm Hg

- (a) The vapour will contain higher percentage of benzene  
(b) The vapour will contain higher percentage of toluene  
(c) The vapour will contain equal amount of benzene and toluene  
(d) Not enough information is given to make a prediction

[Hint: A : Benzene B : Toluene

$$\begin{aligned} p &= p_A + p_B \\ p &= p_A^0 x_A + p_B^0 x_B \\ &= 75 \times \frac{1}{2} + 22 \times \frac{1}{2} \\ &= 37.5 + 11 = 48.5 \end{aligned}$$

$$\text{Mole fraction of benzene in vapour, } y_A = \frac{p_A}{p} = \frac{37.5}{48} = 0.78$$

Similarly, mole fraction of toluene in vapour,  $y_B = 0.22$

∴ The vapour will contain higher percentage of benzene.]

19. When 1.2 g of sulphur is melted with 15 g of naphthalene, the solution freezes at 77.2°C. What is the molar mass of this form of sulphur?

**Data for naphthalene:**

Melting point (m.pt.)	80°C
Freezing point depression constant $K_f$	6.80 K m <sup>-1</sup>

- (a) 180 g mol<sup>-1</sup>      (b) 190 g mol<sup>-1</sup>  
 (c) 260 g mol<sup>-1</sup>      (d) 450 g mol<sup>-1</sup>

$$[\text{Hint: } \Delta T = K_f \times \frac{w_B \times 1000}{m_B \times w_A}]$$

$$m_B = \frac{K_f}{\Delta T} \times \frac{w_B \times 1000}{w_A}$$

$$= \frac{6.8}{2.8} \times \frac{1.2 \times 1000}{15} \approx 190]$$

20. Which concentrations can be calculated if the mole fraction and density of an aqueous solution of HCl are known?

1. Molality    2. Molarity    3. Percentage by mass  
 (a) 1 only                         (b) 3 only  
 (c) 1 and 2 only                 (d) 1, 2 and 3

21. The vapour pressure of a liquid in a closed container depends on:

- (1) temperature of liquid    (2) quantity of liquid  
 (3) surface area of the liquid  
 (a) 1 only                         (b) 2 only  
 (c) 1 and 3 only                 (d) 1, 2 and 3

22. A solution is prepared by dissolving a 2.5 g sample of an unknown compound in 34 g of benzene (C<sub>6</sub>H<sub>6</sub>) boils at 1.38°C higher than pure benzene. Which expression gives the molar mass of the unknown compound?

Compound	$K_b$
C <sub>6</sub> H <sub>6</sub>	2.53°C m <sup>-1</sup>
(a) $2.53 \times \frac{2.50}{1.38}$	(b) $1.38 \times \frac{34}{2.53} \times 2.50$
(c) $2.5 \times 10^3 \times \frac{2.53}{34} \times \frac{1}{1.38}$	(d) $2.50 \times 10^3 \times \frac{1.38}{34} \times 2.53$

23. If liquids A and B form an ideal solution:

- (a) the free energy of mixing is zero  
 (b) the free energy as well as entropy of mixing are zero  
 (c) enthalpy of mixing is zero  
 (d) the entropy of mixing is zero

24. Solute A is a ternary electrolyte and solute B is a non-electrolyte. If 0.1 M solution of B produces an osmotic pressure of 2P at temperature 3T K then 0.05 M solution of A at T K will produce an osmotic pressure of:

- (a) P                                 (b) 1.5P                         (c) 2P                                 (d) 10P

25. Which of the following plots represents the behaviour of an ideal binary liquid solution?

- (a) Plot of  $P_{\text{total}}$  vs  $y_A$  (mole fraction of A in vapour) is linear  
 (b) Plot of  $P_{\text{total}}$  vs  $y_B$  is linear  
 (c) Plot of  $1/P_{\text{total}}$  vs  $y_A$  is linear  
 (d) Plot of  $1/P_{\text{total}}$  vs  $y_B$  is non-linear

26. Total vapour pressure of mixture of 1 mol A ( $p_A^0 = 150$  torr) and 2 mol B ( $p_B^0 = 240$  torr) is 200 torr. In this case:

- (a) there is positive deviation from Raoult's law  
 (b) there is negative deviation from Raoult's law  
 (c) there is no deviation from Raoult's law  
 (d) molecular masses of A and B are also required for calculating the deviation

$$[\text{Hint: } x_A = \frac{1}{3}, x_B = \frac{2}{3}$$

$$p = p_A^0 x_A + p_B^0 x_B$$

$$= 150 \times \frac{1}{3} + 240 \times \frac{2}{3} = 50 + 160 = 210 \text{ mm}$$

$$p_{\text{exp.}} < p_{\text{calculated}}$$

∴ There is negative deviation from Raoult's law.]

27. A compound MX<sub>2</sub> has observed and normal molar masses 65.6 and 164 respectively. Calculate the apparent degree of ionization of MX<sub>2</sub>:

- (a) 75%                             (b) 85%                             (c) 65%                             (d) 25%

$$[\text{Hint: } i = \frac{\text{Normal molar mass}}{\text{Observed molar mass}}$$

$$= \frac{164}{65.6} = 2.5$$

$$\alpha = \frac{i-1}{n-1}, \quad n = 3 \text{ (number of ions)}$$

$$= \frac{2.5-1}{3-1} = \frac{1.5}{2} = 0.75$$

∴ Percentage ionization of MX<sub>2</sub> will be 75%.]

28. Compound PdCl<sub>4</sub> · 6H<sub>2</sub>O is a hydrated complex; 1 molal aqueous solution of it has freezing point 269.28 K. Assuming 100% ionization of complex, calculate the molecular formula of the complex ( $K_f$  for water = 1.86 K kg mol<sup>-1</sup>):

- (a) [Pd(H<sub>2</sub>O)<sub>6</sub>]Cl<sub>4</sub>                     (b) [Pd(H<sub>2</sub>O)<sub>4</sub>Cl<sub>2</sub>]Cl<sub>2</sub> · 2H<sub>2</sub>O  
 (c) [Pd(H<sub>2</sub>O)<sub>3</sub>Cl<sub>3</sub>]Cl · 3H<sub>2</sub>O    (d) [Pd(H<sub>2</sub>O)<sub>2</sub>Cl<sub>4</sub>] · 4H<sub>2</sub>O

$$[\text{Hint: } \Delta T = i \times K_f \times m]$$

$$(273 - 269.28) = i \times 1.86 \times 1$$

$$3.72 = i \times 1.86$$

$$i = 2$$

$$\alpha = \frac{i-1}{n-1}$$

$$1 = \frac{2-1}{n-1} \text{ or } n = 2$$

Thus, the complex should give two ions in the solution, i.e., the complex will be [Pd(H<sub>2</sub>O)<sub>3</sub>Cl<sub>3</sub>]Cl · 3H<sub>2</sub>O]

29. Inulin is dissolved in suitable solvent and the osmotic pressure ( $\pi$ ) of solutions of various concentrations (g/cm<sup>3</sup>) C is measured at 27°C. The slope of plot of  $\pi$  against C is found to be  $4.1 \times 10^{-3}$ . The molecular mass of inulin is:

- (a)  $6 \times 10^6$                      (b)  $3 \times 10^6$                      (c)  $6 \times 10^3$                      (d)  $3 \times 10^3$

$$[\text{Hint: } \pi V = nRT]$$

$$\pi V = \frac{w}{m} RT$$

$$\pi = \left( \frac{w}{V} \right) \times \frac{1}{m} RT$$

$$\pi = C \left( \frac{RT}{m} \right)$$

$$y = MX$$

... (i)  
... (ii)

Slope of the line will be  $\frac{RT}{m}$ ,

$$\text{i.e., } \frac{RT}{m} = 4.1 \times 10^{-3}$$

$$m = \frac{RT}{4.1 \times 10^{-3}} = \frac{0.0821 \times 1000 \times 300}{4.1 \times 10^{-3}} \\ = 6 \times 10^6 ]$$

30. pH of a 0.1 M monobasic acid is measured to be 2. Its osmotic pressure at a given temperature  $T$  K is:

(a)  $0.1RT$     (b)  $0.11RT$     (c)  $1.1RT$     (d)  $0.01RT$

[Hint:  $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$

$$t = 0 \quad C \quad 0 \quad 0$$

$$t_{\text{eq.}} \quad C - C\alpha \quad C\alpha \quad C\alpha$$

$$[\text{H}^+] = C\alpha; [\text{H}^+] = 10^{-\text{pH}}$$

$$\therefore C\alpha = 10^{-2}$$

$$0.1\alpha = 10^{-2}$$

$$\alpha = 0.1$$

$$\alpha = \frac{i-1}{n-1}; 0.1 = \frac{i-1}{2-1}$$

$$i = 1.1$$

$$\pi = iCRT$$

$$= 1.1 \times 0.1 \times RT = 0.11RT ]$$

31. The amount of ice that will separate on cooling a solution containing 50 g of ethylene glycol in 200 g water at  $-9.3^\circ\text{C}$ ,  $K_f = 1.86 \text{ K kg mol}^{-1}$ :

(a) 38.71 g    (b) 38.71 mg    (c) 42 g    (d) 42 mg

[Hint:  $\Delta T = K_f \times \frac{w_B \times 1000}{m_B \times w_A}$

$$9.3 = 1.86 \times \frac{50 \times 1000}{62 \times w_A}$$

$$w_A = 161.29 \text{ g (amount of water present at } -9.3^\circ\text{C)}$$

$$\therefore \text{Amount of ice separated} = 200 - 161.29 \\ = 38.71 \text{ g}]$$

32. 2 moles each of liquids  $A$  and  $B$  are dissolved to form an ideal solution. What will be the mole fraction of  $B$  in the vapour phase?

$$p_A^0 = 120 \text{ torr}; p_B^0 = 80 \text{ torr.}$$

(a) 1/4    (b) 1/2    (c) 3/5    (d) 2/5

[Hint:  $p = p_A + p_B$

$$p = p_A^0 x_A + p_B^0 x_B \\ = 120 \times \frac{2}{4} + 80 \times \frac{2}{4} \\ = 60 + 40 = 100 \text{ torr}$$

$y_B$  = mole fraction of  $B$  in the vapour phase

$$= \frac{p_B}{p_{\text{total}}} = \frac{40}{100} = \frac{2}{5} ]$$

33. Lowering of vapour pressure in 1 molal aqueous solution at  $100^\circ\text{C}$  is:

(a) 13.44 mm Hg    (b) 14.12 mm Hg  
(c) 31.2 mm Hg    (d) 35.2 mm Hg

[Hint: Molality and mole fraction are related as follows:

$$m = \frac{x_B \times 1000}{(1-x_B)m_A}$$

$$m = 1$$

$x_B$  = mole fraction of solute

$$1 = \frac{x_B \times 1000}{(1-x_B) \times 18}$$

$m_A$  = molar mass of solvent

$$x_B = 0.0176, \quad x_A = 0.9824$$

$$p = p_0 x_A$$

$$p = 760 \times 0.9824$$

$$= 746.624$$

$$\Delta p = p_0 - p = 760 - 746.624$$

$$\approx 13.4 \text{ mm Hg}]$$

34. The temperature at which the molarity of pure water is equal to its molality is:

(a) 273 K    (b) 298 K  
(c) 277 K    (d) none of these

35. Isopiestic solutions have:

(a) same vapour pressure    (b) same osmotic pressure  
(c) same freezing point    (d) same boiling point

36. Molarity and molality of a solution of caustic soda are respectively 11.12 M and 94.12 m. The density of the solution is:

(a) 0.556 g mL<sup>-1</sup>    (b) 5.56 g mL<sup>-1</sup>  
(c) 55.6 g mL<sup>-1</sup>    (d) none of these

[Hint:  $d = M \left( \frac{1}{m} + \frac{\text{molar mass of solute}}{1000} \right)$

$$d = 11.12 \left( \frac{1}{94.12} + \frac{40}{1000} \right)$$

$$= 0.556 \text{ g mL}^{-1}]$$

37. Which of the following solutions has osmotic pressure nearer to that of equimolar solution of  $\text{K}_4[\text{Fe}(\text{CN})_6]$ ?

(a)  $\text{Na}_2\text{SO}_4$     (b)  $\text{BaCl}_2$   
(c)  $\text{Al}_2(\text{SO}_4)_3$     (d)  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$

38. Equal amounts of a solute are dissolved in equal amounts of two solvents  $A$  and  $B$ . The lowering of vapour pressure for the solution  $A$  is twice the lowering of vapour pressure for the solution  $B$ . If  $M_A$  and  $M_B$  are the molecular weights of solvents  $A$  and  $B$  respectively, then:

(a)  $M_A = M_B$     (b)  $M_A = M_B / 2$   
(c)  $M_A = 4M_B$     (d)  $M_A = 2M_B$

Following questions may have more than one correct options:

1. Consider the following solutions:

I. 1 M sucrose    II. 1 M  $\text{KCl}$   
III. 1 M benzoic acid in benzene IV. 1 M  $(\text{NH}_3)_3\text{PO}_4$

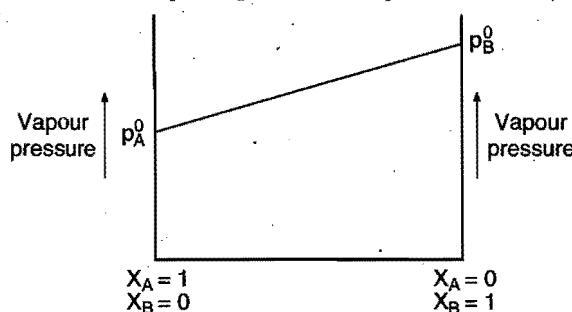
Which of the following is/are true?

- (a) All solutions are isotonic  
(b) III is hypotonic of I, II and IV  
(c) I, II and III are hypertonic of IV  
(d) IV is hypertonic of I, II and III

2. Osmotic pressure of the solution depends on:

- (a) nature of solute  
(b) nature of solvent  
(c) temperature  
(d) molar concentration of solute

3. The following is a graph plotted between the vapour pressures of two volatile liquids against their respective mole fractions.



Which of the following statements are correct?

- (a) When  $x_A = 1$  and  $x_B = 0$ , then  $p = p_A^0$
  - (b) When  $x_B = 1$  and  $x_A = 0$ , then  $p = p_B^0$
  - (c) When  $x_A = 1$  and  $x_B = 0$ , then  $p < p_B^0$
  - (d) When  $x_B = 1$  and  $x_A = 0$ , then  $p > p_A^0$
4. Which of the following combinations are correct for a binary solution, in which the solute as well as solvent are liquid?
- (a)  $C_6H_6$  and  $C_6H_5CH_3$ ;  $\Delta H_{\text{Sol}} > 0$ ;  $\Delta V_{\text{Sol}} = 0$
  - (b)  $CH_3 - \overset{\underset{\parallel}{O}}{C} - CH_3$  and  $CHCl_3$ ;  $\Delta H_{\text{Sol}} < 0$ ;  $\Delta V_{\text{Sol}} < 0$
  - (c)  $H_2O$  and  $HCl$ ;  $\Delta H_{\text{Sol}} > 0$ ;  $\Delta V_{\text{Sol}} < 0$
  - (d)  $H_2O$  and  $C_2H_5OH$ ;  $\Delta H_{\text{Sol}} > 0$ ;  $\Delta V_{\text{Sol}} > 0$
5. A solution containing 0.1 g of a non-volatile organic substance  $P$  (molecular mass 100) in 100 g of benzene raises the boiling point of benzene by  $0.2^\circ C$ , while a solution containing 0.1 g of another non-volatile substance  $Q$  in the same amount of benzene raises the boiling point of benzene by  $0.4^\circ C$ . What is the ratio of molecular masses of  $P$  and  $Q$ ? (SCRA 2007)
- (a) 1:2      (b) 2:1      (c) 1:4      (d) 4:1
- [Hint : 
$$\frac{(\Delta T)_P}{(\Delta T)_Q} = \frac{K_b \times \left( \frac{w_B \times 1000}{m_B \times w_A} \right)_P}{K_b \times \left( \frac{w_B \times 1000}{m_B \times w_A} \right)_Q}$$
- $$\frac{0.2}{0.4} = \frac{\left( \frac{0.1 \times 1000}{100 \times 100} \right)_P}{\left( \frac{0.1 \times 1000}{100 \times m_B} \right)_Q}$$
- $$\frac{1}{2} = \frac{(m_B)_Q}{100}$$
- $$m_B = 50$$
- $$\therefore (m_B)_P : (m_B)_Q = 100 : 50 = 2 : 1$$
6. Consider 0.1 M solution of two solutes  $X$  and  $Y$ . The solute  $X$  behaves as uni-univalent electrolyte while the solute  $Y$  dimerises in solution. Which of the following statements are correct regarding these solutions?
1. The boiling point of solution of  $X$  will be higher than that of  $Y$

2. The osmotic pressure of solution of  $Y$  will be lower than that of  $X$

3. The freezing point of the solution of  $X$  will be lower than that of  $Y$

4. The relative lowering of vapour pressure of both the solutions will be the same

Select the correct answer from the codes given below:

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

7. For a given value of degree of dissociation, which of the following have correct van't Hoff factor?

- (a)  $NaCl$        $i = 2 + \alpha$

- (b)  $Ca(NO_3)_2$        $i = 1 + 2\alpha$

- (c)  $K_4[Fe(CN)_6]$        $i = 1 + 4\alpha$

- (d)  $(NH_3)_3PO_4$        $i = 3 + \alpha$

8. 1 mole benzene ( $p_{\text{benzene}}^0 = 42$  mm) and 2 mole toluene ( $p_{\text{toluene}}^0 = 36$  mm) will have:

- (a) total vapour pressure 38 mm

- (b) mole fraction of vapours of benzene above liquid mixture is  $7/19$

- (c) positive deviation from Raoult's law

- (d) negative deviation from Raoult's law

[Hint: 
$$p = p_A^0 x_A + p_B^0 x_B$$
       $A \rightarrow \text{Benzene}, B \rightarrow \text{Toluene}$

$$= 42 \times \frac{1}{3} + 36 \times \frac{2}{3}$$

$$= \frac{114}{3} = 38 \text{ mm}$$

Mole fraction of benzene in vapour  $= \frac{p_{\text{benzene}}}{p_{\text{total}}} = \frac{42/3}{38} = 7/19$

9. The decrease in freezing point of an aqueous solution of a substance is  $1.395$  K and that in the freezing point of a benzene solution of the same substance is  $1.28$  K. The substance:

- (a) dissociates in aqueous solution as well as in the benzene solution
- (b) forms complexes in the solution
- (c) associates in the benzene solution
- (d) dissociates in the aqueous solution and not in the benzene solution

10. The vapour pressure of water at  $T$  (K) is 20 mm Hg. The following solutions are prepared at  $T$  (K):

- I. 6 g of urea (mol. wt. = 60) is dissolved in 178.2 g of water.
- II. 0.01 mole of glucose is dissolved in 179.82 g of water.
- III. 5.3 g of  $Na_2CO_3$  (mol. wt. = 106) is dissolved in 179.1 g of water.

Identify the correct order in which the vapour pressures of solutions increase: [EAMCET (Medical) 2006]

- (a) III, I, II      (b) II, III, I      (c) I, II, III      (d) I, III, II

[Hint:

$$\text{I. } x_B = \frac{n_B}{n_A + n_B} = \frac{6/60}{178.2/18} + \frac{6}{60} = 0.01$$

$$\frac{\Delta p}{p_0} = x_B = 0.01$$

$$\text{II. } x_B = \frac{n_B}{n_A + n_B} = \frac{0.01}{\frac{179.82}{18} + 0.01} \\ = 0.001$$

$$\frac{\Delta p}{p_0} = 0.001$$

$$\text{III. } x_B = \frac{n_B}{n_A + n_B} = \frac{5.3/106}{\frac{179.1}{18} + \frac{5.3}{106}} = 0.005 \\ \frac{\Delta p}{p_0} = ix_B \\ = 3 \times 0.005 \\ = 0.015$$

- ∴ Vapour pressures of solutions will increase in the following sequence:  
 (III) < (I) < (II).]

11. Consider lowering of vapour pressure ( $\Delta p$ ), elevation in boiling point ( $\Delta T_b$ ) and depression in freezing point ( $\Delta T_f$ ) of a solvent for the same molar concentration of each of the following three solutes :

1.  $\text{BaCl}_2$  2.  $\text{NaCl}$  3.  $\text{MgCl}_2$

Which of the following is/are the correct sequence?

(SCRA 2009)

- (a)  $\Delta p : 3 < 2 < 1$  (b)  $\Delta T_b : 1 > 2 > 3$   
 (c)  $\Delta T_f : 3 < 2 < 1$  (d) None of these

[Hint : van't Hoff factor of both  $\text{BaCl}_2$  and  $\text{MgCl}_2$  are same, i.e., 3, hence none of the given sequence are correct.]

## Answers

### ● Single correct option

1. (b)	2. (d)	3. (a)	4. (a)	5. (b)	6. (b)	7. (c)	8. (b)
9. (d)	10. (c)	11. (d)	12. (a)	13. (c)	14. (b)	15. (c)	16. (a)
17. (e)	18. (b)	19. (b)	20. (d)	21. (a)	22. (c)	23. (c)	24. (a)
25. (c)	26. (b)	27. (a)	28. (c)	29. (a)	30. (b)	31. (a)	32. (d)
33. (a)	34. (c)	35. (a)	36. (a)	37. (c)	38. (b)		

### ● One or more than one correct options

1. (b, c, d)	2. (c, d)	3. (a, b)	4. (b, d)	5. (b)	6. (a)	7. (b, c)	8. (a, b)
9. (c, d)	10. (a)	11. (d)					

## LINKED COMPREHENSION TYPE QUESTIONS

### ● Passage 1

A 1.24 M aqueous solution of KI has density of 1.15 g/cm<sup>3</sup>.

Answer the following questions about this solution:

1. Percentage composition of solute in the solution is:  
(a) 17.89    (b) 27.89    (c) 37.89    (d) 47.89
2. Molality of this solution will be:  
(a) 2.61    (b) 1.31    (c) 4.12    (d) 3.12
3. What is the freezing point of the solution if the KI is completely dissociated in the solution?  
(a) -4.87°C    (b) -3.22°C  
(c) -1.22°C    (d) None of these
4. Experimental freezing point of the solution is -4.46°C. What % of KI is dissociated?  
(a) 82%    (b) 90%    (c) 83%    (d) None
5. Normality of this solution is:  
(a) 0.62    (b) 1.24    (c) 2.48    (d) 3.72

### ● Passage 2

The colligative properties of electrolytes require a slightly different approach than the one used for the colligative properties of non-electrolytes. The electrolytes dissociate into ions in a solution. It is the number of solute particles that determines the colligative properties of a solution. The electrolyte solutions, therefore, show abnormal colligative properties. To account for this effect we define a quantity called the van't Hoff factor, given by:

$$i = \frac{\text{Actual number of particles in solution after dissociation}}{\text{Number of formula units initially dissolved in solution}}$$

$i = 1$  (for non-electrolytes);

$i > 1$  (for electrolytes, undergoing dissociation)

$i < 1$  (for solutes, undergoing association).

Answer the following questions:

1. Benzoic acid undergoes dimerisation in benzene solution. The van't Hoff factor ' $i$ ' is related to the degree of association ' $\alpha$ ' of the acid as:  
(a)  $i = 1 - \alpha$     (b)  $i = 1 + \alpha$   
(c)  $i = 1 - \frac{\alpha}{2}$     (d)  $i = 1 + \frac{\alpha}{2}$
2. A substance trimerises when dissolved in a solvent  $A$ . The van't Hoff factor ' $i$ ' for the solution is:  
(a) 1    (b) 1/3  
(c) 3    (d) unpredictable
3. For a solution of a non-electrolyte in water, the van't Hoff factor is:  
(a) always equal to 0    (b)  $\leq 1$   
(c) always equal to 2    (d)  $> 1$  but  $< 2$
4. 0.1 M  $K_4[Fe(CN)_6]$  is 60% ionized. What will be its van't Hoff factor?  
(a) 1.4    (b) 2.4    (c) 3.4    (d) 4.4

[Hint:  $\alpha = \frac{i-1}{n-1}$ ,  $n = 5$  since,  $K_4[Fe(CN)_6]$  gives 5 ions in the solution

$$0.6 = \frac{i-1}{5-1}$$

$$i = 3.4$$

5. A solution of benzoic acid dissolved in benzene such that it undergoes molecular association and its molar mass approaches 244. Benzoic acid molecules will exist as:  
(a) dimer    (b) monomer  
(c) tetramer    (d) trimer
6. The molar mass of the solute sodium hydroxide obtained from the measurement of the osmotic pressure of its aqueous solution at 27°C is 25 g mol<sup>-1</sup>. Therefore, its dissociation percentage in this solution is: [CET (J&K) 2009]

- (a) 75    (b) 60  
(c) 80    (d) 70

[Hint:  $i = \frac{\text{Normal molar mass}}{\text{Abnormal molar mass}}$  ... (i)

$$\alpha = \frac{i-1}{n-1}$$

$i = 1 + \alpha$  for binary electrolyte

$$1 + \alpha = \frac{40}{25}; \alpha = 0.6$$

$$\% \text{ ionisation} = 60$$

### ● Passage 3

Many chemical and biological processes depend on osmosis which is, the selective passage of solvent molecules through a porous membrane from a dilute solution to a more concentrated one. The osmotic pressure  $\pi$  depends on molar concentration of the solution ( $\pi = CRT$ ). If two solutions are of equal solute concentration and, hence, have the same osmotic pressure, they are said to be isotonic. If two solutions are of unequal osmotic pressures, the more concentrated solution is said to be hypertonic and the more diluted solution is described as hypotonic.

Osmosis is the major mechanism for transporting water upward in the plants. Transpiration in the leaves supports the transport mechanism of water. The osmotic pressure of seawater is about 30 atm; this is the pressure that must be applied to the seawater (separated from pure water using a semipermeable membrane) to get drinking water.

Answer the following questions:

1. A plant cell shrinks when it is kept in:  
(a) hypotonic solution    (b) hypertonic solution  
(c) isotonic solution    (d) pure water
2. 4.5% solution of glucose would be isotonic with respect to ..... solution of urea.  
(a) 4.5%    (b) 13.5%  
(c) 1.5%    (d) 9%
3. Glucose solution to be injected into the bloodstream must have same ..... as that of the bloodstream.  
(a) molarity    (b) vapour pressure  
(c) osmotic pressure    (d) viscosity

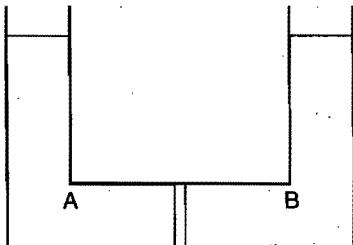
4. Isotonic solutions have same:

- |               |                   |
|---------------|-------------------|
| (a) density   | (b) molarity      |
| (c) molality  | (d) mole fraction |
| (e) normality |                   |

5. Osmotic rise of a solution depends on:

- |                       |                   |
|-----------------------|-------------------|
| (a) density           | (b) temperature   |
| (c) nature of solvent | (d) none of these |

### ● Passage 4



Compartments 'A' and 'B' have the following combinations of solutions:

*A*                            *B*

1. 0.1 M $KCl$	0.2 M $KCl$
2. 0.1% ( $m/V$ ) $NaCl$	10% ( $m/V$ ) $NaCl$
3. 18 g/L glucose	34.2 g/L sucrose
4. 20% ( $m/V$ ) glucose	10% ( $m/V$ ) glucose

Answer the following questions:

1. Indicate the solutions which is/are isotonic:

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

2. The solutions in which the compartment 'B' is hypertonic:

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

3. Indicate the solution(s) in which the compartment 'A' will show the increase in volume:

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

4. Indicate the solution(s) in which the compartment 'B' will show the increase in volume:

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

5. The solution in which there will be no change in the level of the solution in the compartments 'A' and 'B' is:

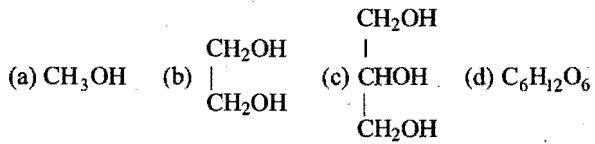
- (a) 1      (b) 2      (c) 3      (d) 4

### ● Passage 5

The boiling point elevation and the freezing point depression of solutions have a number of practical applications. Ethylene glycol ( $CH_2OH \cdot CH_2OH$ ) is used in automobile radiators as an antifreeze because it lowers the freezing point of the coolant. The same substance also helps to prevent the radiator coolant from boiling away by elevating the boiling point. Ethylene glycol has low vapour pressure. We can also use glycerol as antifreeze. For boiling point elevation to occur, the solute must be non-volatile, but no such restriction applies to freezing point depression. For example, methanol ( $CH_3OH$ ), a fairly volatile liquid that boils only at  $65^\circ C$  is sometimes used as antifreeze in automobile radiators.

Answer the following questions:

1. Which of the following is a better reagent for depression in freezing point but not for elevation in boiling point?



2. 124 g each of the two reagents glycol and glycerol are added in 5 kg water of the radiators in the two cars. Which of the following statements is wrong?

- (a) Both will act as antifreeze
- (b) Glycol will be better
- (c) Glycerol is better because its molar mass is greater than glycol
- (d) Glycol is more volatile than glycerol

3. 620 g glycol is added to 4 kg water in the radiator of a car. What amount of ice will separate out at  $-6^\circ C$ ?  $K_f = 1.86 \text{ K kg mol}^{-1}$ :

- (a) 800 g      (b) 900 g      (c) 600 g      (d) 1000 g

4. If cost of glycerol, glycol and methanol are same, then the sequence of economy to use these compounds as antifreeze will be:

- (a) glycerol > glycol > methanol
- (b) methanol > glycol > glycerol
- (c) methanol = glycol = glycerol
- (d) methanol > glycol < glycerol

5. Which among the following is the most volatile and the best antifreeze?

- (a)  $CH_3OH$       (b)  $C_2H_5OH$       (c) Glycerol      (d) Glycerol

### ● Passage 6

The solutions which boil at constant temperature like a pure liquid and possess same composition in liquid as well as vapour state are called azeotropes. The components of azeotropes cannot be separated by fractional distillation. Only non-ideal solutions form azeotropes. Solutions with negative deviation form maximum boiling azeotrope and the solutions with positive deviation form minimum boiling azeotrope. Boiling point of an azeotrope is never equal to the boiling points of any of the components of the azeotrope.

Answer the following questions:

1. The azeotropic solutions of two miscible liquids:

- (a) can be separated by simple distillation
- (b) may show positive or negative deviation from Raoult's law
- (c) are supersaturated
- (d) behave like single pure component and boil at a fixed temperature

2. Solutions which distill without any change in composition or temperature are called:

- (a) saturated      (b) supersaturated
- (c) ideal      (d) azeotrope

3. The azeotropic mixture of water and HCl boils at  $108.5^\circ C$ . This solution is:

- (a) ideal
- (b) non-ideal with positive deviation
- (c) non-ideal with negative deviation
- (d) cannot be predicted

4. 100 mL liquid A and 50 mL liquid B are mixed to form 138 mL solution. It is:  
 (a) ideal solution                          (b) high boiling azeotrope  
 (c) low boiling azeotrope                (d) none of these
5. Which among the following combinations is maximum boiling azeotrope?  
 (a)  $\text{H}_2\text{O} + \text{CH}_3\text{OH}$                           (b)  $\text{CCl}_4 + \text{CHCl}_3$   
 (c)  $(\text{CH}_3)_2\text{CO} + \text{C}_2\text{H}_5\text{OH}$                   (d)  $\text{H}_2\text{O} + \text{HNO}_3$

### ● Passage 7

The properties such as boiling point, freezing point and vapour pressure of a pure solvent change when solute molecules are added to get homogeneous solution. These are called colligative properties. Applications of colligative properties are very useful in day-to-day life. One of its examples is the use of ethylene glycol and water mixture as anti-freezing liquid in the radiator of automobiles.

A solution M is prepared by mixing ethanol and water.

The mole fraction of ethanol in the mixture is 0.9.

Given : Freezing point depression constant of water ( $K_f$  for water) =  $1.86 \text{ K kg mol}^{-1}$

Freezing point depression constant of ethanol ( $K_f$  for ethanol) =  $2.0 \text{ K kg mol}^{-1}$

Boiling point elevation constant of water ( $K_b$  for water) =  $0.52 \text{ K kg mol}^{-1}$

Boiling point elevation constant of ethanol ( $K_b$  for ethanol) =  $1.2 \text{ K kg mol}^{-1}$

Standard freezing point of water =  $273 \text{ K}$

Standard freezing point of ethanol =  $155.7 \text{ K}$

Standard boiling point of water =  $373 \text{ K}$

Standard boiling point of ethanol =  $351.5 \text{ K}$

Vapour pressure of pure water =  $32.8 \text{ mm Hg}$

Vapour pressure of pure ethanol =  $40 \text{ mm Hg}$

Molecular weight of water =  $18 \text{ g mol}^{-1}$

Molecular weight of ethanol =  $46 \text{ g mol}^{-1}$

In answering the following questions, consider the solutions to be ideal dilute solutions and solutes to be non-volatile and non-dissociative.

Answer the following questions:

- The freezing point of the solution M is:  
 (a)  $268.7 \text{ K}$                           (b)  $268.5 \text{ K}$                           (c)  $234.2 \text{ K}$                           (d)  $150.9 \text{ K}$
- The vapour pressure of the solution M is:  
 (a)  $39.3 \text{ mm Hg}$                           (b)  $36.0 \text{ mm Hg}$   
 (c)  $29.5 \text{ mm Hg}$                                   (d)  $28.8 \text{ mm Hg}$
- Water is added to the solution M such that the mole fraction of water in the solution becomes 0.9. The boiling point of this solution is:  
 (a)  $380.4 \text{ K}$                           (b)  $376.2 \text{ K}$                           (c)  $375.5 \text{ K}$                           (d)  $354.7 \text{ K}$

(IIT 2008)

[Hint:

$$1. \text{ Molality } m = \frac{x_B \times 1000}{(1 - x_B) m_A} = \frac{0.1 \times 1000}{0.9 \times 46} \\ = 2.415$$

$$\Delta T = K_f \times m \\ = 2 \times 2.415 = 4.83$$

Freezing point of solution =  $155.7 - 4.83 = 150.9 \text{ K}$

$$2. \quad p = p_A^0 x_A \\ = 40 \times 0.9 = 36 \text{ mm Hg}$$

3. When water becomes solvent, the molality of solution will be :

$$m = \frac{x_B \times 1000}{x_A \times m_A} = \frac{0.1 \times 1000}{0.9 \times 18} = 6.172$$

$$\Delta T = K_b \times m = 0.52 \times 6.172 = 3.209$$

Boiling point of solution =  $373 + 3.209 \\ = 376.2 \text{ K}]$

## Answers

Passage 1.	1. (a)	2. (b)	3. (a)	4. (c)	5. (b)	
Passage 2.	1. (c)	2. (b)	3. (b)	4. (c)	5. (a)	6. (b)
Passage 3.	1. (b)	2. (c)	3. (c)	4. (b)	5. (a, b)	
Passage 4.	1. (b)	2. (a)	3. (d)	4. (b)	5. (c)	
Passage 5.	1. (a)	2. (c)	3. (b)	4. (b)	5. (a)	
Passage 6.	1. (b, d)	2. (d)	3. (c)	4. (b)	5. (d)	
Passage 7.	1. (d)	2. (b)	3. (b)			

# SELF ASSESSMENT

## ASSIGNMENT NO. 5

### SECTION-I

#### Straight Objective Type Questions

This section contains 12 multiple choice questions. Each question has 4 choices (a), (b), (c) and (d), out of which only one is correct.

1. The relative lowering of vapour pressure of a dilute aqueous solution containing non-volatile solute is 0.0125. The molality of solution is about: [PET (Kerala) 2007]  
 (a) 0.70      (b) 0.50      (c) 0.90      (d) 0.80  
 (e) 0.60
2. If the elevation in boiling point of a solution of 10 gm of solute (mol. mass = 100) in 100 g of water is  $\Delta T_b$ , the ebullioscopic constant of water is: [PET (Kerala) 2007]  
 (a) 10      (b)  $100 T_b$       (c)  $\Delta T_b$       (d)  $\frac{\Delta T_b}{10}$   
 (e)  $10 T_b$
3. Which one of the following aqueous solutions will exhibit highest boiling point? [DPMT 2009]  
 (a) 0.1 M KNO<sub>3</sub>      (b) 0.1 M Na<sub>3</sub>PO<sub>4</sub>  
 (c) 0.1 M BaCl<sub>2</sub>      (d) 0.1 M K<sub>2</sub>SO<sub>4</sub>
4. A solution containing 10 g per dm<sup>3</sup> of urea (molecular mass = 60 g mol<sup>-1</sup>) is isotonic with a 5% solution of a non-volatile solute. The molecular mass of this non-volatile solute is: [AIIMS 2007]  
 (a) 300 g mol<sup>-1</sup>      (b) 350 g mol<sup>-1</sup>  
 (c) 200 g mol<sup>-1</sup>      (d) 250 g mol<sup>-1</sup>
5. The molarity of 5 molal aqueous solution of NaOH having density 1.2 g / cc is:  
 (a) 5 M      (b) 4.1 M      (c) 6 M      (d) 8 M
6. The value of osmotic pressure does not depend on:  
 (a) concentration of solution  
 (b) van't Hoff factor  
 (c) temperature  
 (d) structure of solute particles
7. Henry's law constants for O<sub>2</sub> and N<sub>2</sub> are:  
 $k_{O_2} = 3.3 \times 10^7$ ,  $k_{N_2} = 6.51 \times 10^7$   
 Calculate the ratio of  $\frac{x_{O_2}}{x_{N_2}}$ , i.e., the ratio of mole fractions of O<sub>2</sub> and N<sub>2</sub> dissolved in water at 25°C from air:  
 (a) 0.62      (b) 0.92      (c) 0.42      (d) 0.52
8. The molal lowering of vapour pressure of water at 100°C is:  
 (a) 13.68 mm      (b) 46 mm  
 (c) 65 mm      (d) 13.68 cm
9. USP ethanol in aqueous solution containing 95% ethanol by volume. At 20°C, pure ethanol has a density of 0.789 g/mL and USP ethanol density 0.813 g/mL. What is the mass percentage of ethanol in USP ethanol?  
 (a) 46%      (b) 90%      (c) 86%      (d) 92.3%

10. A solution of 7.45 g KCl in 1000 mL shows osmotic pressure of 4.68 atm at 300K. Calculate the percentage dissociation of KCl:  
 (a) 70%      (b) 80%      (c) 90%      (d) 10%
11. The mass of glucose that should be dissolved in 50g of water in order to produce same lowering of vapour pressure as is produced by dissolving 1 g of urea in the same quantity of water is : [MGIMS (Wardha) 2008]  
 (a) 1 g      (b) 3 g      (c) 6 g      (d) 18 g
12. Consider the following aqueous solutions and assume 100% ionisation in electrolytes :  
 I. 0.1 m urea      II. 0.04 m Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>  
 III. 0.05 m CaCl<sub>2</sub>      IV. 0.005 m NaCl  
 The correct statement regarding the above solutions is : [BHU (Mains) 2008]  
 (a) freezing point will be lowest for solution I  
 (b) freezing point will be highest for solution IV  
 (c) boiling point will be highest for solution IV  
 (d) Vapour pressure will be highest for solution II

### SECTION-II

#### Multiple Answers Type Objective Questions

13. K<sub>2</sub>HgI<sub>4</sub> is 50% ionised in aqueous solution. Which of the following are correct?  
 (a)  $n = 7$       (b)  $n = 3$       (c)  $i = 2$       (d)  $i = 4$
14. Henry's law is invalid for gases like.....  
 (a) CO<sub>2</sub>      (b) SO<sub>2</sub>      (c) HCl      (d) N<sub>2</sub>
15. The azeotropic mixture of two liquids:  
 (a) boils at constant temperature  
 (b) can be separated by simple distillation  
 (c) is super saturated  
 (d) deviates from Raoult's law
16. Cryoscopic constant of a liquid depends on:  
 (a) the latent heat of fusion of solvent  
 (b) the freezing point of solvent  
 (c) the concentration of solution  
 (d) the melting point of solute
17. Which of the following is/are influenced by the temperature?  
 (a) Freezing point      (b) Boiling point  
 (c) Vapour pressure      (d) Osmotic pressure

### SECTION-III

#### Assertion-Reason Type Questions

This section contains 5 questions. Each question contains Statement-1 (Assertion) and Statement-2 (Reason). Each question has following 4 choices (a), (b), (c) and (d), out of which only one is correct.

- (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.
- 18. Statement-1:** Solubility of ionic compounds in water depends on both the lattice energy and the hydration energy.

**Because**

**Statement-2:** Ionic compounds dissolve in water when their hydration energy exceeds the lattice energy.

- 19. Statement-1:** Isotonic solutions have same molar concentration.

**Because**

**Statement-2:** Solutions which have same osmotic pressure at same temperature are known as isotonic solutions.

[Hint: It is not necessary that solutions at same molar concentration have same osmotic pressure, e.g.,

$\pi(0.1M \text{ NaCl}) > \pi(0.1M \text{ glucose})$  because NaCl is ionised]

- 20. Statement-1:** The vapour pressure of  $0.1M \text{ Hg}_2\text{Cl}_2$  is equal to  $0.1M \text{ AlCl}_3$  solution.

**Because**

**Statement-2:**  $0.1M \text{ AlCl}_3$  and  $0.1M \text{ Hg}_2\text{Cl}_2$  give different numbers of ions in a solution.

- 21. Statement-1:** Elevation in boiling point will be high if the molal elevation constant of solvent is high.

**Because**

**Statement-2:** Elevation in boiling point is a colligative property.

- 22. Statement-1:** Ethylene glycol is used as antifreeze for the radiator of a car.

**Because**

**Statement-2:** Ethylene glycol dissolves in water with the help of hydrogen bond and it lowers the freezing point.

## SECTION-IV

### Matrix-Matching Type Questions

This section contains 3 questions. Each question contains statements given in two columns which have to be matched.

Statements (a, b, c and d) in Column-I have to be matched with statements (p, q, r and s) in Column-II. The answers to these questions have to be appropriately bubbled as illustrated in the following examples:

If the correct matches are (a-p,s), (b-q,r), (c-p,q) and (d-s), then correct bubbled  $4 \times 4$  matrix should be as follows:

	p	q	r	s
a	<input checked="" type="radio"/> p	<input type="radio"/> q	<input type="radio"/> r	<input type="radio"/> s
b	<input type="radio"/> p	<input checked="" type="radio"/> q	<input type="radio"/> r	<input type="radio"/> s
c	<input checked="" type="radio"/> p	<input type="radio"/> q	<input type="radio"/> r	<input type="radio"/> s
d	<input type="radio"/> p	<input checked="" type="radio"/> q	<input type="radio"/> r	<input checked="" type="radio"/> s

- 23. Match the Column-I with Column II:**

**Column-I**                    **Column-II**

- |   |  |
|---|--|
| (a) $\text{CCl}_4 + \text{CHCl}_3$              | (p) Raoult's law                         |
| (b) $\text{C}_6\text{H}_6 + \text{H}_2\text{O}$ | (q) Nearly ideal solution                |
| (c) $p_A \propto x_A$                           | (r) Negative deviation from Raoult's law |
| (d) $p_A < p_A^0 x_A$                           | (s) Positive deviation from Raoult's law |

- 24. Match the Column-I with Column II:**

**Column-I**                    **Column-II**

- |  |                     |
|--|---------------------|
| (Species completely ionised)             | (van't Hoff factor) |
| (a) $\text{Hg}_2\text{Cl}_2$             | (p) 5               |
| (b) $\text{K}_3[\text{Fe}(\text{CN})_6]$ | (q) 4               |
| (c) $\text{Ca}_3(\text{PO}_4)_2$         | (r) 1               |
| (d) glucose                              | (s) 3               |

- 25. Match the Column-I with Column II:**

**Column-I**                    **Column-II**

- |                   |                                |
|-------------------|--------------------------------|
| (a) Mole fraction | (p) $\text{mol kg}^{-1}$       |
| (b) Molality      | (q) Depends on temperature     |
| (c) Molarity      | (r) Unitless                   |
| (d) Normality     | (s) Independent of temperature |

## Answers

- |                             |                                 |         |         |            |               |                                |            |
|-----------------------------|---------------------------------|---------|---------|------------|---------------|--------------------------------|------------|
| 1. (a)                      | 2. (c)                          | 3. (b)  | 4. (a)  | 5. (a)     | 6. (d)        | 7. (d)                         | 8. (a)     |
| 9. (d)                      | 10. (c)                         | 11. (b) | 12. (b) | 13. (b, c) | 14. (a, b, c) | 15. (a, d)                     | 16. (a, b) |
| 17. (c, d)                  | 18. (a)                         | 19. (d) | 20. (d) | 21. (b)    | 22. (a)       | 23. (a-q) (b-s) (c-p, q) (d-r) |            |
| 24. (a-s) (b-q) (c-p) (d-r) | 25. (a-r,s) (b-p,s) (c-q) (d-q) |         |         |            |               |                                |            |

# CHAPTER 6

## THE COLLOIDAL STATE

### 6.1 INTRODUCTION

The foundation of colloid chemistry was laid down by an English scientist, **Thomas Graham**, in 1861. The credit for the various advances in this field goes to eminent scientists like **Tyndall, Hardy, Zsigmondy, N.R. Dhar, S.S. Bhatnagar and others.**

Thomas Graham classified the soluble substances into two categories depending upon the rate of their diffusion through animal and vegetable membranes or parchment paper. He observed that certain substances diffuse freely through the membrane, whereas others do not diffuse. The former type of substances on account of their crystalline nature like common salt, sugar, urea, etc., were named **crystalloids** while the second type of substances were termed as **colloids** (Greek word, *Kolla*, meaning glue-like). All inorganic acids, bases and salts and organic compounds such as sugar, urea, etc., were included in crystalloids while substances such as starch, gelatin, gums, silicic acid, etc., belonged to the colloidal group.

It was soon realised that the above classification was not perfect since many crystalline substances can be converted into colloidal form by suitable means. The colloidal form of sodium chloride, a crystalloid, can be obtained in benzene. Silver, copper, gold, etc., which are completely insoluble in water, can be transformed into colloidal state by suitable methods. X-ray examination of certain colloids like glue and gelatin revealed that these were crystalline in nature. Thus, the above classification was discarded, i.e., the term **colloid** does not apply to a particular class of substances but is a state of matter like solid, liquid and gas. Any substance can be brought into colloidal state by suitable means.

### 6.2 PARTICLE SIZE AND COLLOIDAL STATE

The colloidal state depends on the particle size. It is regarded as intermediate state between true solution and suspension. In

Table 6.1 Comparison of Suspensions, Colloids and True Solutions

S.No.	Property	Suspension	Colloid	True solution
1.	Particle size	$> 10^{-5}$ cm or $10^3 \text{ \AA}$ or $100 \text{ m}\mu$	$10^{-7}$ cm to $10^{-5}$ cm or $10 \text{ \AA}$ to $10^3 \text{ \AA}$ or $1 \text{ m}\mu$ to $100 \text{ m}\mu$	$< 10^{-7}$ cm or $10 \text{ \AA}$ or $1 \text{ m}\mu$
2.	Visibility	Visible with naked eye	Visible with ultramicroscope	Not visible with any of the optical means
3.	Separation			
	(a) with filter paper	Possible	Not possible	Not possible
	(b) with membranes	Possible	Possible	Not possible
4.	Diffusion	Does not diffuse	Diffuses very slowly	Diffuses rapidly
5.	Settling	Settles under gravity	Does not settle but it may settle under centrifuge	Does not settle
6.	Nature	Heterogeneous	Heterogeneous	Homogeneous
7.	Appearance	Opaque	Generally clear	Clear

true solutions, the size of the particles of solute is very small and, thus, these cannot be detected by any optical means and freely diffuse through membranes while in suspensions the size of the particles is large enough and, thus, can be seen even by naked eye and do not pass through filter paper.

True solutions are homogeneous systems while suspensions are heterogeneous. These are two extreme systems and the colloidal state is an intermediate between the two. If we start with particles of large size (suspension) and go on subdividing them till we reach the size of particles found in solution, there is continuous change in the characteristics. During transition, the mixture passes through an intermediate state which shares the characteristics of both. This has been shown in Fig. 6.1.

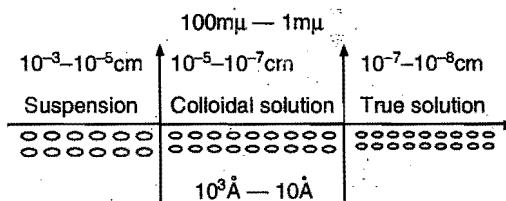


Fig. 6.1

A system is said to be in colloidal state if particles of one or more components have the size range\*  $10 \text{ \AA}$  to  $10^3 \text{ \AA}$ . However, it is not possible to draw a sharp line of demarcation between colloidal state and suspension. The properties of one gradually appear into those of the other. Roughly speaking, the colloidal state is a heterogeneous dispersion of solute particles of size ranging between  $10 \text{ \AA}$  to  $10^3 \text{ \AA}$  into a solvent.

Some properties of the three systems (suspension colloids and true solutions) are summarized in table 6.1.

### 6.3 TYPES OF COLLOIDAL SOLUTIONS

The colloidal solutions consist of two-phases, one of which is dispersed in the other. This is called **dispersed phase**, the **internal phase** or the **discontinuous phase**. The phase in which the dispersion is done is termed **dispersion phase**, the **external**

phase or the **continuous phase**. This phase forms the larger part of the colloidal solution. Depending upon the physical state of dispersed and dispersion phases, the types of colloidal solutions given in table 6.2 are possible.

A colloidal solution of gas in gas is not possible as gases are completely miscible and always form true solutions.

#### Lyophobic and Lyophilic Colloids

Colloidal solutions in which the dispersed phase has very little affinity for the dispersion phase are termed as **lyophobic** (solvent hating) colloids. These are also termed **suspensoids**. Colloidal solutions of metals which have negligible affinity for solvents are examples of this type. Generally, lyophobic sols are less stable. On evaporation of solvent, the residue cannot be easily transformed back into colloidal state by ordinary means. Lyophobic colloids are, therefore, also called **irreversible colloids**.

Table 6.2

S. No.	Dispersed phase (Colloidal particles)	Dispersion phase (Solvent)	Name	Examples
1.	Gas	Liquid	Foam	Froths of air
2.	Gas	Solid	Solid foam	Pumice stone, dried sea foam
3.	Liquid	Gas	Liquid aerosol	Cloud, mist
4.	Liquid	Liquid	Emulsion	Milk; cream
5.	Liquid	Solid	Gel	Jellies, curd, cheese
6.	Solid	Gas	Aerosol	Smoke, haze
7.	Solid	Liquid	Sol	Goldsol, sulphursol
8.	Solid	Solid	Solid-sol	Ruby glass, minerals, gems

Colloidal solutions in which the dispersed phase has considerable affinity for the dispersion phase, i.e., colloidal solution, can be prepared by bringing them together, are called **lyophilic** (solvent loving) colloids. These are also known as

Table 6.3 Comparison of Lyophobic and Lyophilic Sols

S. No.	Property	Lyophobic sols (Suspensoid)	Lyophilic sols (Emulsoid)
1.	Preparation	Cannot be easily prepared. Special methods are required for preparation.	Can easily be prepared by shaking or warming the substance with solvent.
2.	Stability	Are less stable.	Are more stable.
3.	Reversibility	Are irreversible.	Are reversible.
4.	Viscosity	Viscosity is nearly the same as that of solvent.	Viscosity is much higher than that of solvent.
5.	Surface tension	Surface tension is almost the same as that of the solvent.	Surface tension is usually low.
6.	Hydration or solvation	These are less solvated as the particles have less affinity for solvent.	These are highly solvated as the particles have great affinity for solvent.
7.	Charge	The particles carry a characteristic charge either positive or negative.	The particles have little or no charge at all.
8.	Visibility	Particles can be seen under microscope.	Particles cannot be seen under microscope.
9.	Coagulation	Easily coagulated by addition of electrolytes.	Cannot be easily coagulated.

\*  $1 \text{ \AA}$  (Angstrom unit) =  $10^{-8} \text{ cm} = 10^{-7} \text{ mm} = 0.1 \text{ m}\mu$  (millimicron)

**emulsoids.** Gelatin, proteins, starch, etc., are the examples of this type. Colloidal solutions of this type are more stable and are also known as **reversible colloids** since the residue left on evaporation can be readily transformed back into colloidal state simply by adding solvent. When the dispersion medium is water, the above colloidal solutions are termed as **hydrophobic** and **hydrophilic**. (For comparison, see table 6.3)

The colloidal solutions are also named according to the dispersion phase or medium used. The colloidal solutions in alcohol and benzene are known as **alcosols** and **benzosols** respectively. The colloidal solutions where water is used as the dispersion medium are called **hydrosols** or **aquasols**.

Note: Colloidal solutions of solids in liquids are abbreviated as sols.

## 6.4 PREPARATION OF COLLOIDAL SOLUTIONS

**1. Preparation of lyophilic sols:** The colloidal solutions of lyophilic colloids like starch, glue, gelatin, etc., can be readily prepared by dissolving these substances in water either in cold or on warming. Solutions of colloidal electrolytes such as soaps and dye stuffs can also be prepared similarly.

**2. Preparation of lyophobic sols:** To get a substance in colloidal form either the substance in bulk is broken down into fine particles of colloidal dimension ( $1 \text{ \AA}$  to  $10^3 \text{ \AA}$ ) or increasing the size of molecular particles as to form larger aggregates. In some cases, a third substance is usually added to increase the stability of the sol. These substances are called **stabilizers**. Thus, there are two ways by which the lyophobic sols can be prepared:

(i) **Dispersion methods:** By splitting coarse aggregates of a substance into colloidal size.

(ii) **Condensation methods:** By aggregating very small particles (atoms, ions or molecules) into colloidal size.

Table 6.4

S. No.	Dispersion methods	Condensation methods
1.	Mechanical dispersion	Exchange of solvents
2.	Electro-dispersion	Change of physical state
3.	Ultrasonic dispersion	Chemical methods:
4.	Peptization	(i) Double decomposition (ii) Oxidation (iii) Reduction (iv) Hydrolysis

### Dispersion Methods

**1. Mechanical dispersion:** Solid material is first finely ground by usual methods. It is then mixed with dispersion medium which gives a coarse suspension. The suspension is now introduced into the **colloid mill**. The simplest form of colloid mill consists of two metal discs held at a small distance apart from one another and capable of revolving at a very high speed (about 7000 revolutions per minute) in opposite directions. The particles are ground down to colloidal size and are then dispersed in the liquid. A stabilizer is often added to stabilize the colloidal solution. Colloidal graphite (a lubricant) and printing ink are made by this method. Tannin is used as a stabilizer in the preparation of

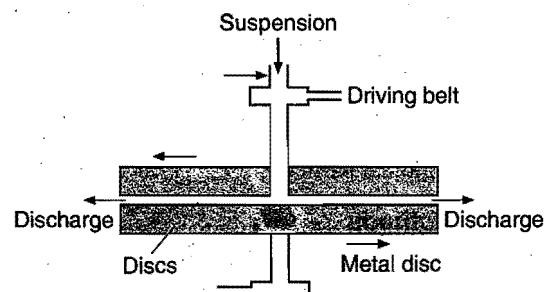


Fig. 6.2

colloidal graphite and gum arabic in lampblack colloidal solution (Indian ink).

**2. Electro-dispersion (Bredig's arc method):** This method is suitable for the preparation of colloidal solutions of metals like gold, silver, platinum, etc. An arc is struck between the metal electrodes under the surface of water containing some stabilizing

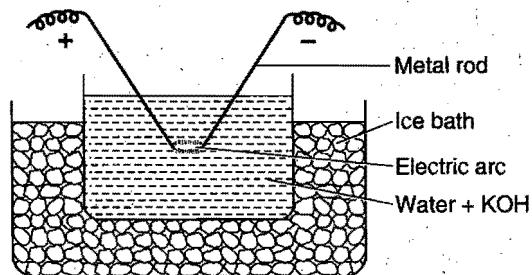


Fig. 6.3

agents such as a trace of KOH. The water is cooled by immersing the container in an ice bath. The intense heat of the arc vaporises some of the metal which condenses under cold water.

Note: 1. This method is not suitable when the dispersion medium is an organic liquid as considerable charring occurs.  
2. This method comprises both dispersion and condensation.

**3. Ultrasonic dispersion:** The sound waves of high frequency are usually called ultrasonic waves. These waves can be produced when quartz crystal discs are connected with a high frequency generator. The application of ultrasonic waves for the preparation of colloidal solutions was first introduced by Wood and Loomis, in 1927. Various substances like oils, mercury, sulphur, sulphides and oxides of metals can be dispersed into colloidal state very easily with the help of ultrasonic waves.

**4. Peptization:** The dispersion of a freshly precipitated material into colloidal solution by the action of an electrolyte in solution is termed peptization. The electrolyte used is called a **peptizing agent**.

A few examples of sols obtained by peptization are:

(i) Freshly prepared ferric hydroxide on treatment with a small amount of ferric chloride solution at once forms a dark reddish brown solution. Ferric chloride acts as a peptizing agent.

(ii) Freshly prepared stannic oxide on treatment with a small amount of dilute hydrochloric acid forms a stable colloidal solution of stannic oxide.

(iii) Freshly precipitated silver chloride can be converted into a colloidal solution by adding a small amount of hydrochloric acid.

(iv) Cadmium sulphide can be peptized with the help of hydrogen sulphide.

The process of peptization thus involves the adsorption of suitable ions (supplied by the electrolyte added—particularly a common ion) and electrically charged particles then split from the precipitate as colloidal particles.

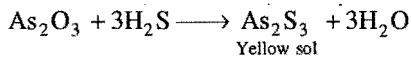
### Condensation Methods

**1. By exchange of solvents:** If a solution of sulphur or phosphorus prepared in alcohol is poured into water, a colloidal solution of sulphur or phosphorus is obtained due to low solubility in water. Thus, there are a number of substances whose colloidal solutions can be prepared by taking a solution of the substance in one solvent and pouring it into another solvent in which the substance is relatively less soluble.

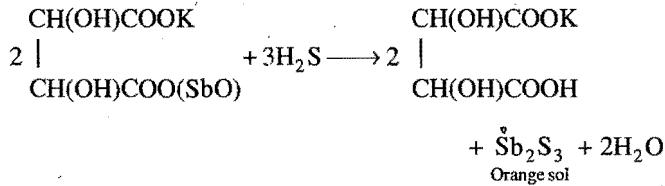
**2. By change of physical state:** Colloidal solutions of certain elements such as mercury and sulphur are obtained by passing their vapour through cold water containing a stabilizer (an ammonium salt or a citrate).

**3. Chemical methods:** The chemical methods involve chemical reactions in a medium in which the dispersed phase is sparingly soluble. A condition of supersaturation is produced but the actual precipitation is avoided. Some familiar reactions used are:

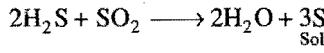
(a) *Double decomposition:* (i) Arsenious sulphide sol: A 1% solution of arsenious oxide is prepared in hot water. The solution is cooled, filtered and is then gradually added to water saturated with hydrogen sulphide, whilst a stream of  $H_2S$  is being passed through the solution. This is continued till an intense yellow-coloured solution is obtained. Excess of  $H_2S$  is removed by bubbling hydrogen through the solution.



(ii) Antimony sulphide sol: A 0.5% solution of potassium antimonyl tartarate is added drop by drop to water saturated with  $H_2S$ , whilst  $H_2S$  is being passed through the solution. Orange coloured solution of antimony sulphide is obtained.

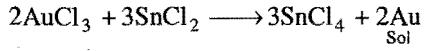


(b) *Oxidation:* A colloidal solution of sulphur is obtained by passing  $H_2S$  into a solution of sulphur dioxide.



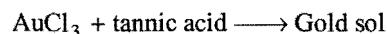
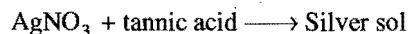
Sulphur sol can also be obtained when  $H_2S$  is bubbled through an oxidising agent (bromine water or nitric acid).

(c) *Reduction:* Colloidal solutions of metals like gold, silver, platinum, lead, etc., can be obtained when their salts solutions are acted upon by reducing agents.

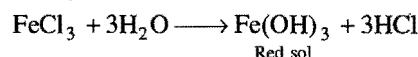


\*Blood is a colloidal solution. In case of kidney failure, blood cannot be purified. Under such condition, the blood is separated from dissolved toxic impurities by dialysis and re-introduced in the blood stream.

Organic reducing agents such as formaldehyde, phenyl hydrazine, tannic acid, etc., can also be used.



(d) *Hydrolysis:* Colloidal solutions of some salts can be prepared by hydrolysis. A colloidal solution of ferric hydroxide is obtained by boiling a dilute solution of ferric chloride.



The colloidal solution of silicic acid is also obtained by hydrolysis of dilute solution of sodium silicate with 4N hydrochloric acid which is added drop by drop with constant stirring.

### 6.5 PURIFICATION OF COLLOIDAL SOLUTIONS

Colloidal solutions prepared by above methods generally contain excessive amount of electrolytes and some other soluble impurities. The presence of traces of electrolyte is essential for the stability of the colloidal solution but larger quantities coagulate it. It is, therefore, necessary to reduce the concentration of these soluble impurities to a requisite minimum. **The process used for reducing these impurities to a requisite minimum is known as purification of colloidal solution.** The purification of colloidal solution is carried out by the following methods:

(i) **Dialysis\***: It is a process of removing a dissolved substance from a colloidal solution by means of diffusion through suitable membrane. Since, particles in true solution (ions or smaller molecules) can pass through animal membranes (bladder) or parchment paper or cellophane sheet but colloidal particles do not, the above can be used for dialysis. The apparatus used for this purpose is called **dialyser**. A bag of suitable membrane containing the colloidal solution is suspended in a vessel through which fresh water is continuously flown (Fig. 6.4). The molecules and ions diffuse through the membrane into the outer water and pure colloidal solution is left behind.

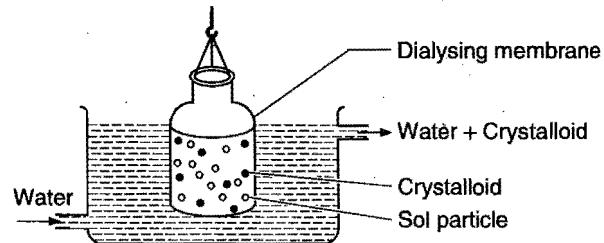


Fig. 6.4

(ii) **Electro-dialysis**: Ordinarily, the process of dialysis is quite slow. It can be made faster by applying an electric field if the dissolved substance in the impure colloidal solution is only electrolyte. The process is then named electro-dialysis. The colloidal solution is placed between two **electrodes** while pure water is taken in a compartment on each side. Electrodes are fitted in the compartment as shown in Fig. 6.5. The ions present

in the colloidal solution migrate out to the oppositely charged electrodes.

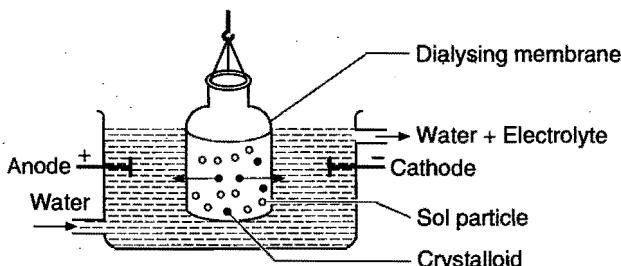


Fig. 6.5

**(iii) Ultrafiltration:** Ultrafiltration is the process of separating the colloidal particles from the solvent and soluble solutes present in the colloidal solution by especially prepared filters, which are permeable to all substances except the colloidal particles.

Colloidal particles can pass through ordinary filter paper because the pores are too large. However, the pores of filter paper can be reduced in size by impregnating with colloidion solution and subsequently hardened by soaking in formaldehyde. The usual colloidion is a 4% solution of nitro-cellulose in a mixture of alcohol and ether. An ultra-filter paper may be prepared by soaking the filter paper in a colloidion solution and hardened by formaldehyde and finally drying it. Thus, by using ultra-filter paper, the colloidal particles are separated from rest of the materials. Ultrafiltration is a slow process. To speed up the process, pressure or suction is used.

The colloidal particles left on the ultra-filter paper are then stirred with fresh dispersion medium (solvent) to get a pure colloidal solution.

## 6.6 PROPERTIES OF COLLOIDAL SOLUTION

**1. Heterogeneous character:** Colloidal solutions are heterogeneous in character as they consist of two phases: (a) dispersed phase and (b) dispersion medium.

**2. Visibility:** It is not possible to see colloidal particles with naked eye or with the help of microscope. It is a well known fact that no particle is visible if its diameter is less than half the wavelength of the light used. The shortest wavelength of the visible light is about  $4000 \text{ \AA}$  or  $400 \text{ m}\mu$ . Hence, no particle of diameter less than  $200 \text{ m}\mu$  can be seen. The size of colloidal particles is less than  $200 \text{ m}\mu$ .

Recently, three new techniques have been developed to determine the size and shape of the colloidal particles. These are:

- Scanning electron microscope (SEM).
- Transmission electron microscope (TEM).
- Scanning transmission electron microscope (STEM).

**3. Filtrability:** Colloidal particles pass through an ordinary filter paper. However, the particles do not pass through parchment and other fine membranes.

**4. Surface tension and viscosity:** The surface tension and viscosity of lyophobic sols are not very different from those of the dispersion medium. On the other hand, lyophilic sols show

higher viscosity and lower surface tension in comparison to the dispersion medium.

**5. Colligative properties:** Colloidal particles are bigger aggregates. Thus, the number of particles in the colloidal solution is comparatively small as compared to true solution and hence, the values of colligative properties (osmotic pressure, lowering in vapour pressure, depression in freezing point and elevation in boiling point) are of small order as compared to values shown by true solutions at same concentrations.

**6. Tyndall effect:** If a heterogeneous solution placed in dark is observed in the direction of light, it appears clear and if it is observed from a direction at right angles to the direction of light beam, it appears perfectly dark. Colloidal solutions show a mild to strong opalescence, when viewed at right angles to the path of light, i.e., the path of the beam is illuminated by a bluish light. This effect was first observed by Faraday and later studied in detail by Tyndall and is termed as **Tyndall effect**. The bright cone of the light is called **Tyndall cone** (Fig. 6.6). The Tyndall effect is due to the fact that colloidal particles absorb light energy and then scatter in all directions in space. This scattering of light illuminates the path of beam in the colloidal dispersion.

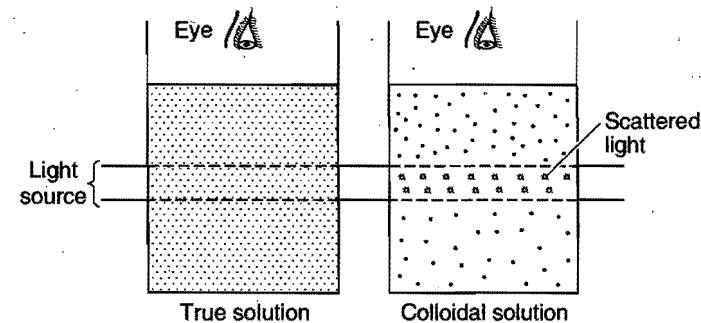


Fig. 6.6

Tyndall effect can be observed during the projection of picture in the cinema hall due to scattering of light by dust and smoke particles present there. Tyndall effect is observed only when the following two conditions are satisfied:

- The diameter of the dispersed particles is not much smaller than the wavelength of the light used; and
- The refractive indices of the dispersed phase and the dispersion medium must differ greatly in magnitude. This

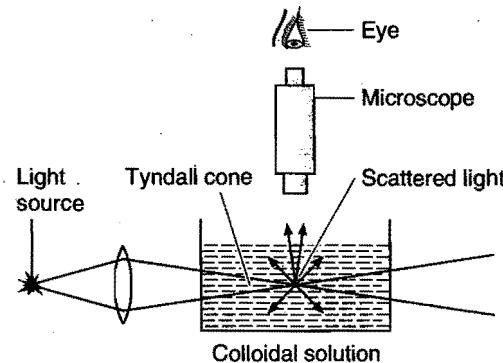


Fig. 6.7

condition is satisfied by lyophobic sols. The lyophilic sols show little or no Tyndall effect as there is very small difference in the refractive indices of the dispersed phase and the dispersion medium.

Some examples of Tyndall effects are:

- Blue colour of sky and seawater
- Visibility of tails of comets
- Twinkling of stars.

Tyndall effect is used to distinguish between a colloidal and true solution. Zsigmondy, in 1903, used Tyndall effect to set up an apparatus known as ultramicroscope. An intense beam of light is focussed on the colloidal solution contained in a glass vessel. The focus of the light is then observed with a microscope at right angles to the beam. Individual colloidal particles appear as bright stars against a dark background. Ultramicroscope does not render visible the actual colloidal particles but only the light scattered by them. Thus, ultramicroscope does not provide any information about the size and shape of colloidal particles.

**7. Colour:** The colour of colloidal solution depends on the wavelength of light scattered by the dispersed particles. The wavelength of light further depends on the size and nature of the particles. The colour of colloidal solution also changes with the way the observer receives the light. For example, milk and water mixture appears blue when viewed by the reflected light and looks red by the transmitted light. Finest gold sol is red in colour. As size of the particles increases, it becomes purple, then blue and finally golden yellow.

**8. Brownian movement:** When colloidal solutions are viewed under a powerful ultramicroscope, the colloidal particles appear to be in a state of continuous motion in zig-zag directions all over the field of view. This motion was first observed by the

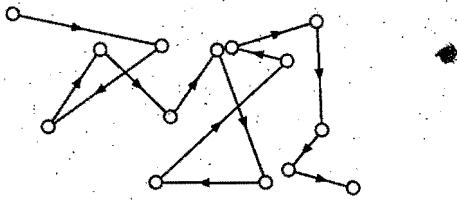


Fig. 6.8

British botanist Robert Brown and hence is known as Brownian movement (Fig. 6.8). This motion is independent of the nature of the colloid but depends on the size of the particles and the viscosity of solution. Smaller the size and lesser the viscosity, faster is the motion. The motion becomes intense at high temperature. The distance between two points decreases at elevated temperature.

The Brownian movement has been explained to be due to the unbalanced bombardment of the particles by the molecules of the dispersion medium. The Brownian movement has a stirring effect which does not permit the particles to settle and thus, is responsible for the stability of sols.

**9. Charge on colloidal particles:** Colloidal particles always carry an electric charge. This charge is of the same type on all the particles in a given colloidal solution and may be either

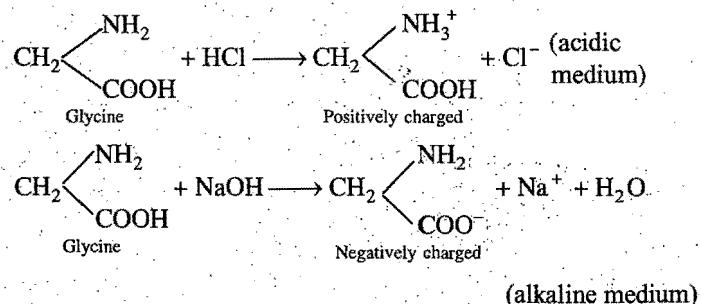
positive or negative. A list of some common sols with the type of charge on their particles is given in table 6.5.

Table 6.5

S. No.	Positively charged	Negatively charged
1.	Metallic hydroxides, e.g., $\text{Cr(OH)}_3$ , $\text{Al(OH)}_3$ and $\text{Fe(OH)}_3$ sols.	Metals, e.g., copper, silver, gold-sols.
2.	Basic dyestuffs, e.g., methylene blue sol.	Metallic sulphides, e.g., $\text{As}_2\text{S}_3$ , $\text{Sb}_2\text{S}_3$ , $\text{CdS}$ sols.
3.	Proteins in acidic medium.	Acid dyestuffs, e.g., eosin, congo red-sols.
4.	Oxides, e.g., $\text{TiO}_2$ sol.	Sols of starch, gum, gelatin, clay, charcoal, etc.

The charge on the sol particles is due to one or more of the following reasons:

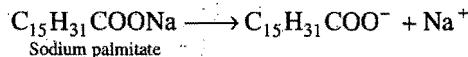
(i) Due to the presence of acidic or basic groups: A protein molecule has a carboxylic group and a basic  $\text{NH}_2$  group. The particles of proteins in sols can either have positive charge or negative charge depending upon the pH of the medium.



**Isoelectric point of a colloid:** In case of colloidal solution proteins, the nature of charge depends on the pH of the solution called isoelectric point. Above this pH, the particles are negatively charged and below this pH, they have positive charge. At isoelectric point, colloidal particles exist in the form of Zwitter ion hence they do not migrate under the influence of external electric field.

Examples:	Colloidal sol	Isoelectric pH
	Haemoglobin	4.3—5.3
	Casein from human milk	4.1—4.7
	Gelatin	4.7

(ii) Due to self-dissociation: When colloidal particles such as soaps or detergents are dissolved in water, ionised molecules associate to form a micelle. The outer surface will be thus charged depending on the charge of the ions from which it is formed. Thus, sodium palmitate solution will have negative charge on its sol particles.

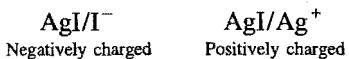


(iii) Due to electron capture by sol particles: e.g., during electro-dispersion of metals.

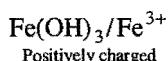
(iv) Due to preferential adsorption of ions: This is the most accepted view. The sol particles acquire positive or negative charge by preferential adsorption of +ve or -ve ions. When two

or more ions are present in the dispersion medium, preferential adsorption of the ion common to the colloidal particle usually takes place. This can be explained by taking the following examples:

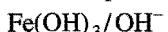
(a) If silver nitrate solution is added to potassium iodide solution, the precipitated silver iodide will adsorb iodide ions from the dispersion medium and negatively charged colloidal solution will result. However, when KI solution is added to  $\text{AgNO}_3$  solution, positively charged sol will result due to adsorption of  $\text{Ag}^+$  ions from dispersion medium.



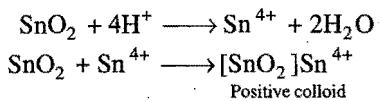
(b) If  $\text{FeCl}_3$  is added to excess of hot water, a positively charged sol of ferric hydroxide is formed due to adsorption of  $\text{Fe}^{3+}$  ions.



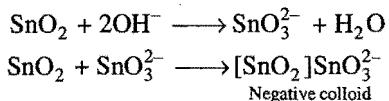
However, when ferric chloride is added to NaOH a negatively charged sol is obtained with adsorption of  $\text{OH}^-$  ions.



$\text{SnO}_2$  is positively charged colloidal sol due to adsorption of  $\text{Sn}^{4+}$  ions.



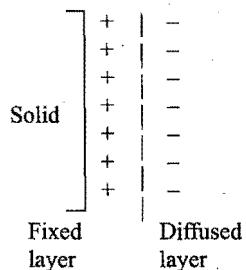
On the other hand in alkaline medium,  $\text{SnO}_2$  forms negatively charged colloidal sol due to adsorption of  $\text{SnO}_3^{2-}$  ions formed.



**Electrical double layer:** The surface of a colloidal particle acquires a positive or a negative charge by selective adsorption of ions carrying positive or negative charge respectively as stated above. This layer attracts counter ions from the medium which form a second layer.



The combination of the two layers of opposite charges around the colloidal particle is called **Helmholtz electrical double layer**. According to modern views, the first layer of ions is firmly held and is termed **fixed layer** while the second layer is mobile which is termed **diffused layer**. Since, separation of charge is a seat of potential, the charges of opposite signs on the fixed and diffused parts of the double layer results in a difference in potential between these layers. This potential difference between the fixed charged layer and the diffused layer of opposite charge is called the **electrokinetic potential** or **zeta potential**.



$$\xi = \frac{4\pi\eta u}{D}$$

where,  $\eta$  = Coefficient of viscosity

$u$  = Velocity of colloidal particles

$D$  = Dielectric constant of the medium

The presence of equal and similar charges on colloidal particles is largely responsible in providing stability to the colloidal solution because the forces of repulsion exist between same charged particles which prevent them from coalescing or aggregating when they come closer to one another.

**10. Electrophoresis:** When electric potential is applied across two platinum electrodes dipping in a colloidal solution, the colloidal particles move towards one or the other electrode. This movement of colloidal particles under an applied electric field is called **electrophoresis**. Positively charged particles move towards the cathode while negatively charged particles move towards anode. This can be demonstrated by the following experiment:

The apparatus consists of a U-tube provided with a stopcock through which it is connected to a funnel-shaped reservoir (Fig. 6.9). A small amount of water is first taken in the U-tube and then a requisite quantity of colloidal solution is placed in the

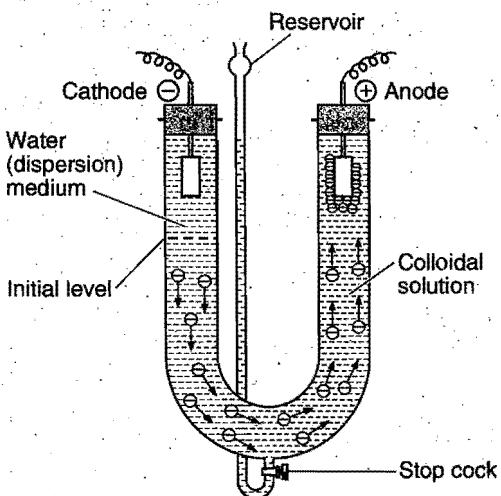


Fig. 6.9

reservoir. The stopcock is slightly opened and the reservoir is gradually raised as to introduce the colloidal solution into the U-tube. The water is displaced upwards producing a sharp boundary line in each arm. The platinum electrodes are fitted in the water layer and a voltage of 50 to 200 volts is applied. The movement of the particles can be observed towards one of the electrodes by seeing the position of boundary. When the colloidal particles are negatively charged, the boundary moves down in the cathodic arm and moves upwards in the anodic arm showing that particles move towards anode. It is, thus, possible to ascertain the charge on particles by noting the movement of boundary.

When electrophoresis, i.e., movement of particles is prevented by some suitable means, it is observed that the dispersion medium begins to move in an electric field. This phenomenon is termed **electro-osmosis**.

### Summary of Electrokinetic Phenomena

#### Motion Causing Potential :

Sedimentation Potential	Streaming Potential
Medium rests but dispersed particles move.	Medium moves but dispersed particles rest.

#### Potential Causing Motion :

Electrophoresis	Electro-osmosis
Medium rests but dispersed particles move.	Medium moves but dispersed particles rest.

**11. Coagulation or precipitation:** The stability of the lyophobic sols is due to the presence of charge on colloidal particles. If, some how, the charge is removed, the particles will come nearer to each other and thus, aggregate or flocculate and settle down under the force of gravity.

The flocculation and settling down of the colloidal particles is called coagulation or precipitation of the sol.

The coagulation of the lyophobic sols can be carried out by following methods:

(i) **By electrophoresis:** In electrophoresis, the colloidal particles move towards oppositely charged electrode. When these come in contact with the electrode for long, these are discharged and precipitated.

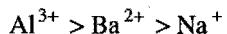
(ii) **By mixing two oppositely charged sols:** When oppositely charged sols are mixed in almost equal proportions, their charges are neutralised. Both sols may be partially or completely precipitated as the mixing of ferric hydroxide (+ve sol) and arsenious sulphide (-ve sol) bring them in precipitated form. This type of coagulation is called **mutual coagulation or metateral coagulation**.

(iii) **By boiling:** When a sol is boiled, the adsorbed layer is disturbed due to increased collisions with the molecules of dispersion medium. This reduces the charge on the particles and ultimately they settle down to form a precipitate.

(iv) **By persistent dialysis:** On prolonged dialysis, the traces of the electrolyte present in the sol are removed almost completely and the colloids become unstable.

(v) **By addition of electrolytes:** When excess of an electrolyte is added, the colloidal particles are precipitated. The reason is that colloidal particles take up ions carrying charge opposite to that present on themselves. This causes neutralisation leading to their coagulation. The ion responsible for neutralisation of charge on the particles is called the **flocculating ion**. A negative ion causes the precipitation of positively charged sol and *vice-versa*.

It has been observed that, generally, the greater the valency of the flocculating ion added, the greater is its power to cause precipitation. This is known as **Hardy-Schulze rule**. In the coagulation of a negative sol, the flocculating power of  $\text{Na}^+$ ,  $\text{Ba}^{2+}$  and  $\text{Al}^{3+}$  ions is in the order of:



Similarly, in the coagulation of a positive sol, the flocculation power of  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$  and  $[\text{Fe}(\text{CN})_6]^{4-}$  is in the order of:



The minimum concentration of an electrolyte in millimole per litre required to cause precipitation of a sol in 2 hours is called **flocculation value**. The smaller the flocculating value, the higher will be the coagulating power of an ion.

Flocculation value of an ion depends on its charge :

$$\text{Flocculation value} \propto \frac{1}{(Z)^6} \text{ where } Z = \text{charge of ion}$$

Flocculation value of  $\text{M}^\pm$ ,  $\text{M}^{2\pm}$ ,  $\text{M}^{3\pm}$ ,  $\text{M}^{4\pm}$  ions lies in following ratio.

$$\frac{1}{(1)^6} : \frac{1}{(2)^6} : \frac{1}{(3)^6} : \frac{1}{(4)^6}$$

$$1 : 0.0156 : 0.00137 : 0.00024$$

$$100 : 1.56 : 0.137 : 0.024$$

**Coagulation of lyophilic sols:** There are two factors which are responsible for the stability of lyophilic sols. These factors are the charge and solvation of the colloidal particles. When these two factors are removed, a lyophilic sol can be coagulated. This is done (i) by adding electrolyte and (ii) by adding suitable solvent. When solvents such as alcohol and acetone are added to hydrophilic sols, the dehydration of dispersed phase occurs. Under this condition, a small quantity of electrolyte can bring about coagulation.

**12. Protection of colloids:** Lyophilic sols are more stable than lyophobic sols. This is due to the fact that lyophilic colloids are extensively solvated, i.e., colloidal particles are covered by a sheath of the liquid in which they are dispersed.

Lyophilic colloids have a unique property of protecting lyophobic colloids. When a lyophilic sol is added to the lyophobic sol, the lyophilic particles form a layer around lyophobic particles and thus, protect the latter from electrolytes. Lyophilic colloids used for this purpose are called **protective colloids**.

The lyophilic colloids differ in their protective power. The protective power is measured in terms of **Gold Number**. This number was introduced by Zsigmondy and is defined as the number of milligrams of a lyophilic colloid that will just prevent the precipitation of 10 mL of a gold sol on the addition of 1 mL of 10% sodium chloride solution.

The gold numbers of some of the common protective colloids are listed below:

Table 6.6

S.No.	Protective Colloid	Gold Number
1.	Gelatin	0.005–0.01
2.	Haemoglobin	0.03
3.	Gum arabic	0.15
4.	Egg albumin	0.08–0.10
5.	Potato starch	25
6.	Sodium oleate	0.4
7.	Gum tragacanth	2
8.	Starch	25–50

Higher is the gold number, lower will be the protective power. Thus, gelatin and starch have the maximum and minimum protective powers. The use of protective colloids is widespread. Gelatin is added in the preparation of ice cream as protective agent to the colloidal particles of ice. Argyrol, used as eye drops, is a silver sol protected by organic material.

Some facts :

(i) Blood is a colloidal solution, it is not coagulated by the electrolytes ( $\text{NaCl}$ ,  $\text{Ca}_3(\text{PO}_4)_2$  etc.) present in blood itself because proteins present in blood act as protective colloid.

(ii) Milk of human mother is better protected than cow's and buffaloes milk.

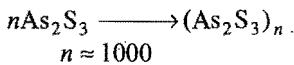
(iii) The proteins which are not coagulated at their iso-electric pH are better protective colloid.

(iv) **Ageing** : It is spontaneous destabilisation of colloidal solution. In this process, dispersed is separated from dispersion medium by itself, i.e., no artificial method is used.

### Congo Rubin Number

Ostwald proposed that it is the amount of protective colloid in mg which prevents the colour change in 100 mL of 0.01% Congo rubin dye solution to which 0.16 g equivalent of  $\text{KCl}$  are added when observed after 10–15 min.

**13. Colligative properties:** The value of colligative properties are of very small order because they have very small van't Hoff factor.



$$\text{van't Hoff factor } i = \frac{1}{1000}$$

Colligative properties are directly proportional to the van't Hoff factor.

## 6.7 EMULSIONS

These are liquid-liquid colloidal systems, i.e., the dispersion of finely divided droplets in another liquid. If a mixture of two immiscible or partially miscible liquids is shaken, a coarse dispersion of one liquid in the other is obtained which is called **emulsion**. Generally, one of the two liquids is water. There are two types of emulsions:

- (i) Oil dispersed in water (O/W type),
- (ii) Water dispersed in oil (W/O type).

In the first system, water acts as dispersion medium. Examples of this type of emulsions are milk and vanishing cream. In milk, liquid fat is dispersed in water.

In the second system, oil acts as dispersion medium. Common examples of this type are butter and cream.

Emulsions of oil and water are unstable and sometimes they separate into two layers on standing. For the stabilization of an emulsion, a third component called **emulsifying agent** is usually added. The emulsifying agents form an interfacial film between suspended particles and the medium. The principal agents for O/W emulsions are proteins, gums, natural and synthetic soaps, etc. For W/O emulsions, the principal emulsifying agents are

heavy metal salts of fatty acids, long chain alcohols, lampblack, etc.

Emulsions can be diluted with any amount of the dispersion medium. On the other hand, the dispersed liquid, when mixed, forms at once a separate layer. The droplets in emulsions are often negatively charged and can be precipitated by electrolytes. They also show Brownian movement and Tyndall effect. Emulsions can be broken into constituent liquids by heating, freezing, centrifuging, etc.

**Detection of emulsion:** Following tests can be used to detect the type of emulsion:

(i) **Dye test:** An oil soluble dye is shaken up with the emulsion and a drop is seen under microscope. If coloured drops are seen, the emulsion is water in oil type otherwise of oil in water type.

(ii) **Viscosity test:** Water in oil type emulsion has greater viscosity than oil in water type emulsion.

(iii) **Electrical conductivity test:** Electrical conductivity of oil in water type emulsion is much greater than water in oil type emulsion. If electrolyte like  $\text{NaCl}$  is added to oil in water type emulsion, its conductivity greatly increases.

(iv) **Spreading test:** Water in oil type emulsion easily spread on the surface of an oil but not on the surface of water.

(v) **Dilution test:** Oil in water type emulsion can easily be diluted with water. On the other hand water in oil type emulsion cannot be diluted with water. For example, milk—which is oil in water type emulsion can be diluted with water, but butter or milk cream which are water in oil type emulsion cannot be diluted with water.

(vi) **Coalescence:** It is the phenomena of disappearance of the boundary between two particles (generally droplets or bubbles) in contact. Coalescence leads to the reduction of the total surface area. The flocculation of an emulsion, viz., the formation of aggregates, may be followed by coalescence. In extensive condition, the coalescence leads to the formation of a macrophase and emulsion is said to break. Coalescence of solid particles is called sintering.

## 6.8 CLASSIFICATION OF COLLOIDS BASED ON THE TYPE OF PARTICLES OF DISPERSED PHASE

Depending upon the type of particles of dispersed phase, colloids are classified as:

- (i) Multimolecular,
- (ii) Macromolecular,
- (iii) Associated colloids.

(i) **Multimolecular colloids:** On dissolution, a large number of atoms or smaller molecules of a substance aggregate together to form species having size in colloidal dimension (diameter less than 1 nm). The species thus formed are called multimolecular colloids. For example: Gold sol, sulphur sol. In these colloids, the particles are held together by van der Waals' forces.

(ii) **Macromolecular colloids:** Macromolecular substances dissolve in suitable solvent to form solutions in which the size of macromolecules lie in colloidal dimension. These are called

macromolecular colloids and they are quite stable. For example: Starch, cellulose, proteins and enzymes, etc.

(iii) **Associated colloids:** Substances whose molecules aggregate spontaneously in a given solvent to form particles of colloidal dimensions are called **associated colloids**. These substances which when dissolved in a medium at low concentrations behave as normal, strong electrolytes, but at higher concentrations they exhibit colloidal properties due to the formation of aggregated particles (also called associated colloids). The molecules of soaps and detergents are usually smaller than the colloidal particles. However, in concentrated solutions, these molecules associate and form aggregates of colloidal size. These aggregates of soaps or detergent molecules are called **micelles**. The formation of micelles takes place only above a particular concentration called **critical micelle concentration (CMC)**. For soaps, the CMC is  $10^{-4}$  to  $10^{-3}$  mol L<sup>-1</sup>. These colloids have both lyophobic and lyophilic parts. Micelles may contain the aggregate of (30–100) molecules or more. Soaps and detergents are strong electrolytes and when dissolved in water they furnish ions.

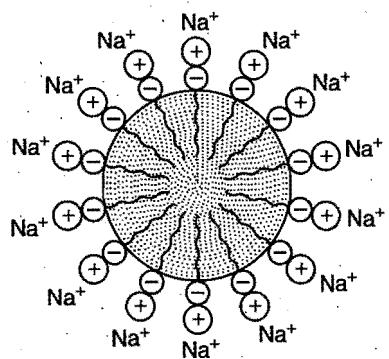
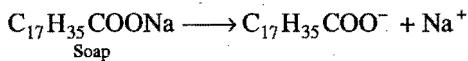


Fig. 6.10

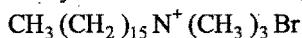
The negative ions aggregate to form a micelle of colloidal size. The negative ion has a long hydrocarbon chain and a polar group ( $-\text{COO}^-$ ) at one end. In micelle formation, the long hydrocarbon chain (tail) which is insoluble in water is directed towards the centre while the soluble polar head is on the surface in contact with water (Fig. 6.10). The charge on the micelle is responsible for the stability of this system. The cleansing action of soap is due to these micelles. The grease stain is absorbed into the interior of the micelle and gets detached from the fabric. The dust particles sticking to the stain are also removed. This action is similar to emulsification of grease.

Some other examples of micelle systems are as follows:

(i) Sodium lauryl sulphate  $\text{CH}_3-(\text{CH}_2)_{11}\text{SO}_4^- \text{Na}^+$

(ii) Sodium oleate  $\text{C}_{17}\text{H}_{35}\text{COO}^- \text{Na}^+$

(iii) Cetyltrimethyl ammonium bromide;



Micellisation with cationic terminals are also known, e.g., in cetyltrimethyl ammonium chloride. It may be diagrammatically represented as :

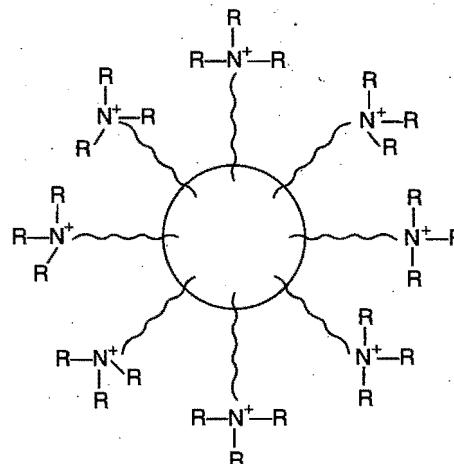


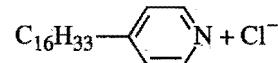
Fig. 6.11

(iv) *p*-Dodecyl benzene sulphonate;



Surfactants are those substances which are preferentially adsorbed at the interfaces like air-water, oil-water and solid-water interfaces. Thus, it is the surfactant which is responsible for **micellisation** and emulsification. Surfactants are divided into three categories:

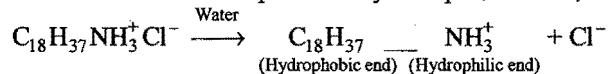
(i) **Cationic surfactants:** Such substances on ionisation give a cation having hydrophobic and hydrophilic group, e.g., cetyl pyridinium chloride,



Cetyltrimethyl ammonium chloride,  $\text{C}_{16}\text{H}_{33}(\text{CH}_3)_3\text{N}^+\text{Cl}^-$

Octadecyl ammonium chloride,  $\text{C}_{18}\text{H}_{37}\text{NH}_3^+\text{Cl}^-$

Ionisation of these compounds may be represented as,



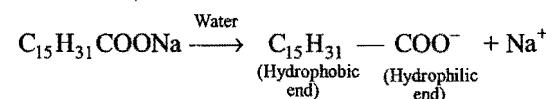
(ii) **Anionic surfactants:** Such substances give anion which act as surfactant, e.g.,

Sodium Palmitate  $\text{C}_{15}\text{H}_{31}\text{COONa}$

Sodium Oleate  $\text{C}_{17}\text{H}_{35}\text{COONa}$

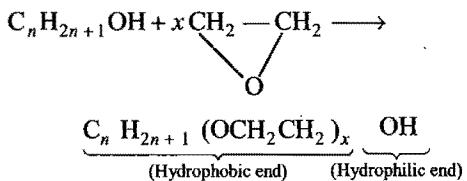
and salts of sulphonic acid having molecular formula

$\text{C}_n\text{H}_{2n+1}\text{SO}_3^- M^+$  where,  $M^+ = \text{Na}^+, \text{K}^+, \text{NH}_4^+$ , etc.



**(iii) Non-ionogenic surfactants:** These surfactants do not ionise or dissociate in aqueous medium, but these molecules also have hydrophobic and hydrophilic end.

High molecular mass alcohol adds to several molecules of ethylene oxide to form hydroxy surfactant.



**Kraft point:** The temperature above which a surfactant forms micelle is called kraft point.

### Some Important Features of Micelle

- At critical micelle concentration (CMC), surfactants begins to form spherical aggregates made of 30 to 100 ions with their hydrocarbon tails in the interior of the aggregate and their charged terminals exposed to water on the out side (see Fig. 6.12).
- Increase in temperature usually increases CMC.
- CMC also depends on chain length, greater is the chain length of hydrocarbon tail, smaller is the CMC. Increase in the hydrophobic part of the surfactant molecules, favours the formation of micelles.
- CMC of ionic micelles decreases on addition of simple electrolyte like NaCl. Screening action of added ions reduces the repulsion between charged groups at the surface of micelles.
- Below the Kraft temperature, solubility of surfactant is not enough to form micelles. Kraft temperature increases with increase in the number of carbon atoms.

Number of carbon atoms in sodium alkyl sulphates	10	12	14
Kraft temperature °C	8	16	30

- Micellisation is found to be spontaneous; it is confirmed by negative value of  $\Delta G$  in following equation :

$$\Delta G = \Delta H - T\Delta S \quad \dots(1)$$

$\Delta H = -ve$  and  $T\Delta S = +ve$  for micellisation

Standard enthalpy change of micellisation may be calculated as,

$$\Delta H^\circ = \Delta G^\circ + T\Delta S^\circ$$

$$= -2.303 RT^2 \frac{d(\log CMC)}{dT}$$

### Physical Properties of Critical Micelle Concentration

Physico-chemical properties of surfactant solution changes sharply in the region of the C.M.C. Variation of physico-chemical properties of surfactant solution with concentration is represented in following figure :

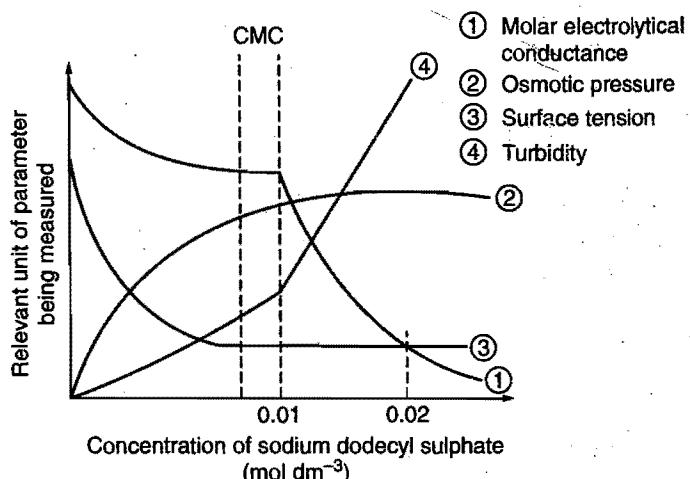


Fig. 6.12

### 6.9 GELS

When a colloidal solution is coagulated, a precipitate is usually formed which may or may not be gelatinous. Under certain set of conditions, it is possible to obtain the dispersed phase as more or less rigid mass enclosing within it all of the liquid. The product in this form is known as a gel and the process is called **gelation**. The gel is, thus, a colloidal semi-solid system rich in liquid phase. Gel usually consists of two components; one is solid, such as gelatin, silicic acid, sodium oleate, etc., and the other is a liquid such as water.

Gels may be elastic or non-elastic according to their mechanical properties. Elastic gels can be prepared by dissolving the substance in warm water and cooling it till sets. Examples are agar-agar and gelatin gels. Non-elastic gels are prepared by appropriate chemical action. The silica gel is formed by action of HCl with sodium silicate solution.

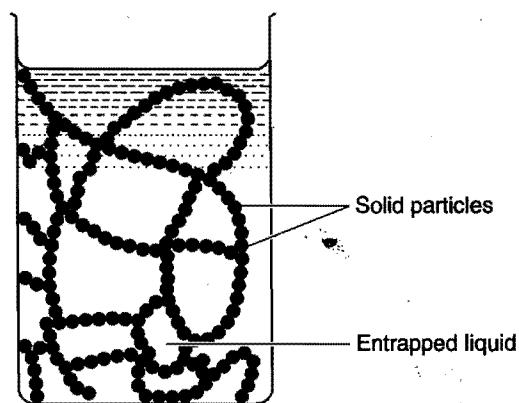


Fig. 6.13

Gel may shrink on keeping by loosing some of the liquid held by them. This is known as **syneresis** or weeping of gel. Some gels liquify on shaking and reset on being allowed to stand. This, reversible Sol-Gel transformation is known as **thixotropy**. The softening behaviour of a marshy land under trading is due to thixotropic behaviour of bentonite clay present in such soils.