CHAPTER 5

States of Matter

Section-A JEE Advanced/ IIT-JEE

A Fill in the Blanks

1. The total energy of one mole of an ideal monatomic gas at 27°C is .... calories. *(1984 - 1 Mark)*
2. $C_p - C_v$ for an ideal gas is .... *(1984 - 1 Mark)*
3. The rate of diffusion of gas is .... proportional to both .... and square root of molecular mass. *(1986 - 1 Mark)*
4. The value of PV for 5.6 litres of an ideal gas is .... RT, at N.T.P. *(1987 - 1 Mark)*
5. Eight gram each of oxygen and hydrogen at 27°C will have the total kinetic energy in the ratio of .... *(1989 - 1 Mark)*

B True / False

1. Kinetic energy of a molecule is zero at 0°C. *(1985 - ½ Mark)*
2. A gas in a closed container will exert much higher pressure due to gravity at the bottom than at the top. *(1985 - ½ Mark)*
3. In the van der Waal's equation $\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$ the constant 'a' reflects the actual volume of the gas molecules. *(1993 - 1 Mark)*
4. A mixture of ideal gases is cooled upto liquid helium temperature (4.22 K) to form an ideal solution. *(1996 - 1 Mark)*

C MCQs with One Correct Answer

1. Equal weights of methane and oxygen are mixed in an empty container at 25°C. The fraction of the total pressure exerted by oxygen is *(1981 - 1 Mark)*
   (a) $\frac{1}{3}$ (b) $\frac{1}{2}$
   (c) $\frac{2}{3}$ (d) $\frac{1}{3} \times \frac{273}{298}$
2. The temperature at which a real gas obeys the ideal gas laws over a wide range of pressure is *(1981 - 1 Mark)*
   (a) Critical temperature (b) Boyle temperature
   (c) Inversion temperature (d) Reduced temperature
3. The ratio of root mean square velocity to average velocity of a gas molecule at a particular temperature is *(1981 - 1 Mark)*
   (a) 1.086 : 1 (b) 1 : 1.086
   (c) 2 : 1.086 (d) 1.086 : 2
4. Helium atom is two times heavier than a hydrogen molecule. At 298 K, the average kinetic energy of a helium atom is *(1982 - 1 Mark)*
   (a) two times that of a hydrogen molecule.
   (b) same as that of a hydrogen molecule.
   (c) four times that of a hydrogen molecule.
   (d) half that of a hydrogen molecule.
5. Equal weights of methane and hydrogen are mixed in an empty container at 25°C. The fraction of the total pressure exerted by hydrogen is : *(1984 - 1 Mark)*
   (a) $\frac{1}{2}$ (b) $\frac{8}{9}$
   (c) $\frac{1}{9}$ (d) $\frac{16}{17}$
6. Rate of diffusion of a gas is : *(1985 - 1 Mark)*
   (a) directly proportional to its density.
   (b) directly proportional to its molecular weight.
   (c) directly proportional to the square root of its molecular weight.
   (d) inversely proportional to the square root of its molecular weight.
7. The average velocity of an ideal gas molecule at 27°C is 0.3 m/sec. The average velocity at 927°C will be: *(1986 - 1 Mark)*
   (a) 0.6 m/sec (b) 0.3 m/sec
   (c) 0.9 m/sec (d) 3.0 m/sec
8. In van der Waals equation of state for a non-ideal gas, the term that accounts for intermolecular forces is *(1988 - 1 Mark)*
   (a) $(V - b)$ (b) RT
   (c) $\left(P + \frac{a}{V^2}\right)$ (d) $(RT)^{-1}$

9. A bottle of dry ammonia and a bottle of dry hydrogen chloride connected through a long tube are opened simultaneously at both ends the white ammonium chloride ring first formed will be *(1988 - 1 Mark)*

(a) at the centre of the tube.

(b) near the hydrogen chloride bottle.

(c) near the ammonia bottle.

(d) throughout the length of the tube.

10. The values of van der Waals constant '*a*' for the gases O_2, N_2, NH_3 and CH_4 are 1.360, 1.390, 4.170 and 2.253 L^2 atm mol^{-2} respectively. The gas which can most easily be liquified is : *(1989 - 1 Mark)*

(a) O_2 (b) N_2

(c) NH_3 (d) CH_4

11. The density of neon will be highest at *(1990 - 1 Mark)*

(a) S.T.P. (b) 0ºC, 2 atm

(c) 273ºC, 1 atm. (d) 273ºC, 2 atm.

12. The rate of diffusion of methane at a given temperature is twice that of a gas *X*. The molecular weight of *X* is *(1990 - 1 Mark)*

(a) 64.0 (b) 32.0

(c) 4.0 (d) 8.0

13. According to kinetic theory of gases, for a diatomic molecule *(1991 - 1 Mark)*

(a) the pressure exerted by the gas is proportional to mean velocity of the molecule

(b) the pressure exerted by the gas is proportional to the root mean velocity of the molecule

(c) the root mean square velocity of the molecule is inversely proportional to the temperature

(d) the mean translational kinetic energy of the molecule is proportional to the absolute temperature.

14. At constant volume, for a fixed number of moles of a gas the pressure of the gas increases with rise in temperature due to *(1992 - 1 Mark)*

(a) Increase in average molecular speed

(b) Increased rate of collisions amongst molecules

(c) Increase in molecular attraction

(d) Decrease in mean free path

15. Longest mean free path stands for : *(1995S)*

(a) H_2 (b) N_2

(c) O_2 (d) Cl_2

16. Arrange the van der Waals constant for the gases : *(1995S)*

I	$C_6H_{6(g)}$	A.	0.217
II	$C_6H_5.CH_{3(g)}$	B.	5.464
III	$Ne_{(g)}$	C.	18.000
IV.	$H_2O_{(g)}$	D.	24.060

(a) I-A, II-D, III-C, IV-B (b) I-D, II-A, III-B, IV-C

(c) I-C, II-D, III-A, IV-B (d) I-B, II-C, III-A, IV-D

17. The ratio between the root mean square speed of H_2 at 50 K and that of O_2 at 800 K is, *(1996 - 1 Mark)*

(a) 4 (b) 2

(c) 1 (d) 1/4

18. X mL of H_2 gas effuses through a hole in a container in 5 seconds. The time taken for the effusion of the same volume of the gas specified below under identical conditions is : *(1996 - 1 Mark)*

(a) 10 seconds : He (b) 20 seconds : O_2

(c) 25 seconds : CO (d) 55 seconds : CO_2

19. One mole of N_2O_4(g) at 300 K is kept in a closed container under one atmosphere. It is heated to 600 K when 20% by mass of N_2O_4 (g) decomposes to NO_2(g).The resultant pressure is : *(1996 - 1 Mark)*

(a) 1.2 atm (b) 2.4 atm

(c) 2.0 atm (d) 1.0 atm

20. The compressibility factor for an ideal gas is *(1997 - 1 Mark)*

(a) 1.5 (b) 1.0

(c) 2.0 (d) ∞

21.. A gas will approach ideal behaviour at *(1999 - 2 Marks)*

(a) low temperature and low pressure.

(b) low temperature and high pressure.

(c) high temperature and low pressure.

(d) high temperature and high pressure.

22. The rms velocity of hydrogen is $\sqrt{7}$ times the rms velocity of nitrogen. If *T* is the temperature of the gas, then *(2000S)*

(a) $T(H_2) = T(N_2)$ (b) $T(H_2) > T(N_2)$

(c) $T(H_2) < T(N_2)$ (d) $T(H_2) = \sqrt{7}\, T(N_2)$

23. The compressibility of a gas is less than unity at STP. Therefore, *(2000S)*

(a) $V_m > 22.4$ litres (b) $V_m < 22.4$ litres

(c) $V_m = 22.4$ litres (d) $V_m = 44.8$ litres

24. At 100°C and 1 atm, if the density of liquid water is 1.0 g cm^{-3} and that of water vapour is 0.0006 g cm^{-3}, then the volume occupied by water molecules in 1 litre of steam at that temperature is *(2000S)*

(a) 6 cm^3 (b) 60 cm^3

(c) 0.6 cm^3 (d) 0.06 cm^3

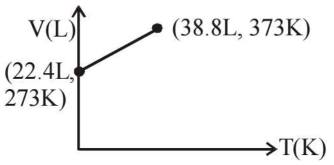
25. The root mean square velocity of an ideal gas at constant pressure varies with density (d) as *(2001S)*

(a) d^2 (b) d

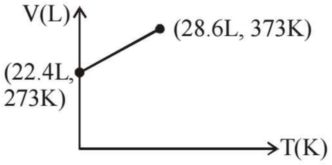
(c) $\sqrt{d}$ (d) $1/\sqrt{d}$

26. Which of the following volume (*V*) - temperature (*T*) plots represents the behaviour of one mole of an ideal gas at one atmospheric pressure ? *(2002S)*

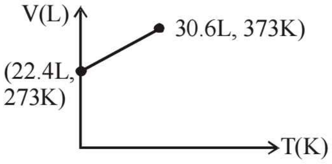
(a)



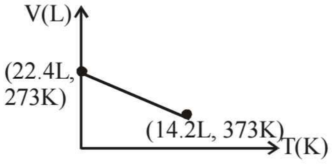
(b)



(c)



(d)



27. When the temperature is increased, surface tension of water ***(2002S)***

(a) increases
(b) decreases
(c) remains constant
(d) shows irregular behaviour

28. Positive deviation from ideal behaviour takes place because of ***(2003S)***

(a) Molecular interaction between atoms and $PV/nRT > 1$
(b) Molecular interaction between atoms and $PV/nRT < 1$
(c) Finite size of atoms and $PV/nRT > 1$
(d) Finite size of atoms and $PV/nRT < 1$

29. The root mean square velocity of one mole of a monoatomic gas having molar mass M is $u_{r.m.s.}$. The relation between the average kinetic energy (E) of the gas and $u_{r.m.s.}$ is ***(2004S)***

(a) $u_{r.m.s.} = \sqrt{\frac{3E}{2M}}$ (b) $u_{r.m.s.} = \sqrt{\frac{2E}{3M}}$

(c) $u_{r.m.s.} = \sqrt{\frac{2E}{M}}$ (d) $u_{r.m.s.} = \sqrt{\frac{E}{3M}}$

30. The ratio of the rate of diffusion of helium and methane under identical condition of pressure and temperature will be ***(2005S)***

(a) 4 (b) 2
(c) 1 (d) 0.5

31. When one mole of monoatomic ideal gas at T K undergoes adiabatic change under a constant external pressure of 1 atm volume changes from 1 litre to 2 litre. The final temperature in Kelvin would be ***(2005S)***

(a) $\frac{T}{2^{(2/3)}}$ (b) $T + \frac{2}{3} \times 0.0821$

(c) T (d) $T - \frac{2}{3} \times 0.0821$

32. A mono-atomic ideal gas undergoes a process in which the ratio of P to V at any instant is constant and equals to 1. What is the molar heat capacity of the gas

(a) $\frac{3R}{2}$ (b) $2R$ ***(2006 - 3M; –1)***

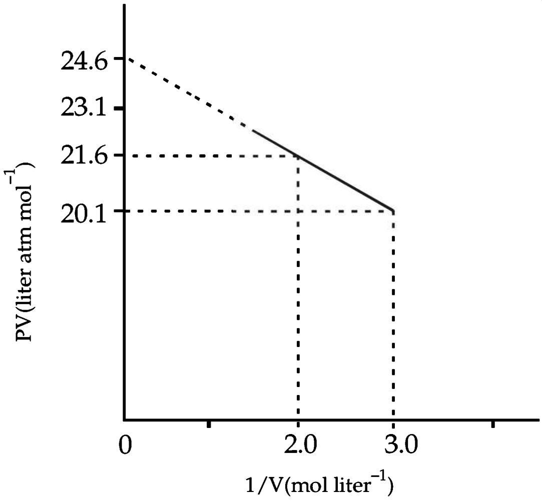
(c) 0 (d) $\frac{5R}{2}$

33. The term that corrects for the attractive forces present in a real gas in the van der Waals equation is

(a) nb (b) $\frac{an^2}{V^2}$ ***(2009 - 3M; –1)***

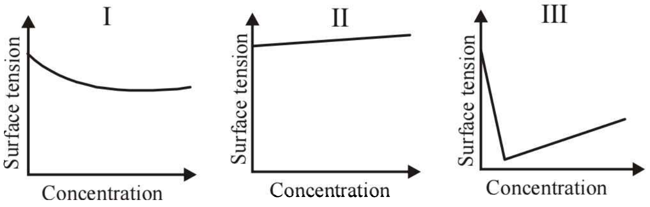
(c) $-\frac{an^2}{V^2}$ (d) $-nb$

34. For one mole of a van der Waal's gas when $b = 0$ and $T = 300$ K, the PV vs, 1/V plot is shown below. The value of the van der Waal's constant a (atm. liter^2 mol^{-2}) is : ***(2012)***



(a) 1.0 (c) 4.5
(b) 1.5 (d) 3.0

35. The qualitative sketches I, II and III given below show the variation of surface tension with molar concentration of three different aqueous solutions of KCl, CH_3OH and $CH_3(CH_2)_{11}OSO_3^- Na^+$ at room temperature. The correct assignment of the sketches is ***(JEE Adv. 2016)***



(a) I : KCl II : CH_3OH III : $CH_3(CH_2)_{11}OSO_3^- Na^+$
(b) I : $CH_3(CH_2)_{11}OSO_3^- Na^+$ II : CH_3OH III : KCl
(c) I : KCl II : $CH_3(CH_2)_{11}OSO_3^- Na^+$ III : CH_3OH
(d) I : CH_3OH II : KCl III : $CH_3(CH_2)_{11}OSO_3^- Na^+$

D MCQs with One or More Than One Correct

1. When an ideal gas undergoes unrestrained expansion, no cooling occurs because the molecules : ***(1984 - 1 Mark)***

(a) are above the inversion temperature

(b) exert no attractive forces on each other

(c) do work equal to loss in kinetic energy

(d) collide without loss of energy

2. If a gas is expanded at constant temperature :

(a) the pressure decreases ***(1986 - 1 Mark)***

(b) the kinetic energy of the molecules remains the same

(c) the kinetic energy of the molecules decreases

(d) the number of molecules of the gas increases

3. Equal weights of ethane and hydrogen are mixed in an empty container at 25°C. The fraction of the total pressure exerted by hydrogen is ***(1993 - 1 Mark)***

(a) 1 : 2 (b) 1 : 1

(c) 1 : 16 (d) 15 : 16

4. 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 ***(1998 - 2 Marks)***

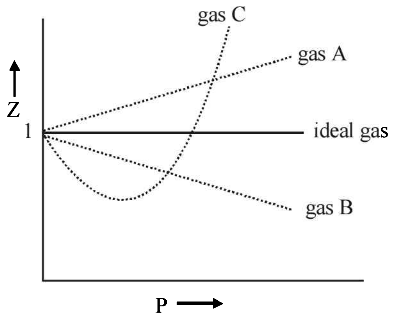
(a) $(P_A/P_B)(M_A/M_B)^{1/2}$ (b) $(M_A/M_B)(P_A/P_B)^{1/2}$

(c) $(P_A/P_B)(M_B/M_A)^{1/2}$ (d) $(M_A/M_B)(P_B/P_A)^{1/2}$

(Where P and M are pressures and molecular weights of gases A and B respectively.)

5. Refer to the figure given : ***(2006 - 5M; –1)***

Which of the following statements is wrong?



(a) For gas A, $a = 0$ and Z will linearly depend on pressure

(b) For gas B, $b = 0$ and Z will linearly depend on pressure

(c) Gas C is a real gas and we can find '*a*' and '*b*' if intersection data is given

(d) All van der Waal gases will behave like gas C and give positive slope at high pressure

6. A gas described by van der Waals equation – ***(2008- 1 Mark)***

(a) behave similar to an ideal gas in the limit of large molar volumes

(b) behaves similar to an ideal gas is in limit of large pressures

(c) is characterised by van der Waals coefficients that are dependent on the identity of the gas but are independent of the temperature.

(d) has the pressure that is lower than the pressure exerted by the same gas behaving ideally

7. According to kinetic theory of gases ***(2011)***

(a) collisions are always elastic

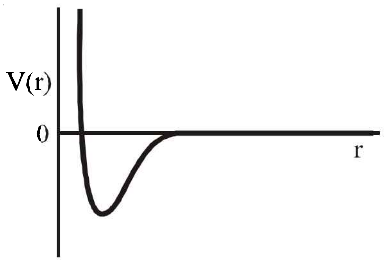
(b) heavier molecules transfer more momentum to the wall of the container

(c) only a small number of molecules have very high velocity

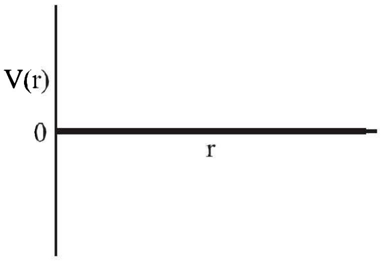
(d) between collisions, the molecules move in straight lines with constant velocities

8. One mole of a monoatomic real gas satisfies the equation $p(V - b) = RT$ where b is a constant. The relationship of interatomic potential V(r) and interatomic distance r for the gas is given by ***(JEE Adv. 2015)***

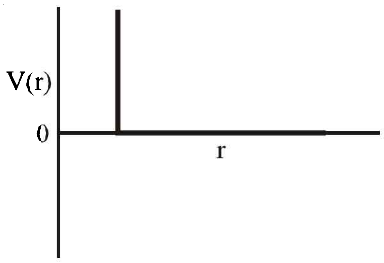
(a)



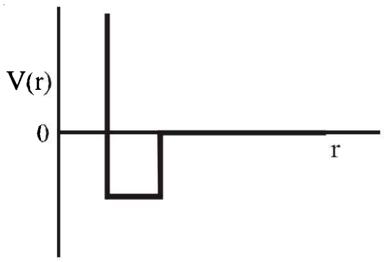
(b)



(c)



(d)



E Subjective Problems

1. Calculate density of NH_3 at 30°C and 5 atm pressure. ***(1978)***
2. 3.7 g of a gas at 25°C occupied the same volume as 0.184g of hydrogen at 17°C and at the same pressure. What is the molecular weight of the gas? ***(1979)***
3. A straight glass tube has two inlets X and Y at two ends. The length of tube is 200 cm. HCl gas through inlets X and NH_3 gas through inlet Y are allowed to enter the tube at the same time. What fumes appear at point P inside the tube. Find distance of P from X. ***(1980)***
4. 1 litre of mixture of CO and CO_2 is taken. The mixture is passed through a tube containing red hot charcoal. The volume now becomes 1.6 litre. The volumes are measured under the same conditions. Find the composition of mixture by volume. ***(1980)***
5. At room temperature, ammonia gas at 1 atm pressure and hydrogen chloride gas at P atm pressure are allowed to effuse through identical pin holes from opposite ends of a glass tube of one metre length and of uniform cross-section. Ammonium chloride 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? ***(1982 - 4 Marks)***
6. Calculate the average of kinetic energy, in Joules of the molecules in 8.0 g of methane at 27°C. ***(1982 - 2 Marks)***
7. Oxygen is present in 1 litre flask at a pressure of 7.6×10^{-10} mm of Hg. Calculate the number of oxygen molecules in the flask at 0°C. ***(1983 - 2 Marks)***
8. When 2 gm of a gas A is introduced into an evaluated flask kept at 25°C, the pressure is found to be one atmosphere. If 3 gm of another gas B is then added to the same flask, the total pressure becomes 1.5 atm. Assuming ideal gas behaviour, calculate the ratio of the molecular weights $M_A : M_B$. ***(1983 - 2 Marks)***
9. Calculate the root mean square velocity of ozone kept in a closed vessel at 20°C and 82 cm mercury pressure. ***(1985 - 2 Marks)***
10. A spherical balloon of 21 cm diameter is to be filled up with hydrogen at N.T.P. from a cylinder containing the gas at 20 atmospheres at 27°C. If the cylinder can hold 2.82 litres of water, calculate the number of balloons that can be filled up. ***(1987 - 5 Marks)***
11. The average velocity at $T_1 K$, and the most probable velocity at $T_2 K$ of CO_2 gas is 9.0×10^4 cm sec^{-1}. Calculate the value of T_1 and T_2. ***(1990 - 4 Marks)***
12. Calculate the volume occupied by 5.0 g of acetylene gas at 50°C and 740 mm pressure. ***(1991 - 2 Marks)***
13. At 27°C, hydrogen is leaked through a tiny hole into a vessel for 20 minutes. Another unknown gas at the same temperature and pressure as that of H_2 is leaked through the same hole for 20 minutes. 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 litres, what is the molecular weight of the unknown gas? ***(1992 - 3 Marks)***
14. At room temperature the following reactions proceed nearly to completion : ***(1992 - 4 Marks)***

$$2NO + O_2 \rightarrow 2NO_2 \rightarrow N_2O_4$$

The dimer, N_2O_4, solidifies at 262 K. A 250 ml flask and a 100 ml. flask are separated by a stop-cock. At 300 K, the nitric oxide in the larger flask exerts a pressure of 1.053 atm. and the smaller one contains oxygen at 0.789 atm. The gases are mixed by opening the stopcock and after the end of the reaction the flasks are cooled at 220K. Neglecting the vapour pressure of the dimer, find out the pressure and composition of the gas remaining at 220 K. (Assume the gases to behave ideally).

15. A gas bulb of 1 litre capacity contains 2.0×10^{21} molecules of nitrogen exerting a pressure of 7.57×10^3 Nm^{-2}. Calculate the root mean square (r.m.s) speed and the temperature of the gas molecules. If the ratio of the most probable speed to the root mean square speed is 0.82, calculate the most probable speed for these molecules at this temperature. ***(1993 - 4 Marks)***
16. A 4 : 1 molar mixture of He and CH_4 is contained in a vessel at 20 bar pressure . Due to a hole in the vessel, the gas mixture leaks out. What is the composition of the mixture effusing out initially? ***(1994 - 2 Marks)***
17. An LPG (liquefied petroleum gas) cylinder weighs 14.8 kg when empty. When full, it weighs 29.0 kg and shows a pressure of 2.5 atm. In the course of use at 27° C, the weight of the full cylinder reduces to 23.2 kg. Find out the volume of the gas in cubic meters used up at the normal usage conditions, find the final pressure inside the cylinder. Assume LPG to be n-butane with normal boiling point of 0°C. ***(1994 - 3 Marks)***
18. A mixture of ethane (C_2H_6) and ethene (C_2H_4) occupies 40 litres at 1.00 atm and at 400 K. The mixture reacts completely with 130 g of O_2 to produce CO_2 and H_2O. Assuming ideal gas behaviour, calculate the mole fractions of C_2H_4 and C_2H_6 in the mixture. ***(1995 - 4 Marks)***
19. The composition of the equilibrium mixture ($Cl_2 \rightleftharpoons 2Cl$), which is attained at 1200°C, is determined by measuring the rate of effusion through a pin–hole. It is observed that at 1.80 mmHg pressure, the mixture effuses 1.16 times as fast as krypton effuses under the same conditions. Calculate the fraction of the chlorine molecules dissociated into atoms. (Relative atomic mass of Kr = 84.) ***(1995 - 4 Marks)***
20. A 20.0 cm^3 mixture of CO, CH_4 and He gases is exploded by an electric discharge at room temperature with excess of oxygen. The volume contraction is found to be 13.0 cm^3. A further contraction of 14.0 cm^3 occurs when the residual gas is treated with KOH solution. Find out the composition of the gaseous mixture in terms of volume percentage. ***(1995 - 4 Marks)***
21. An evacuated glass vessel weighs 50.0 g when empty, 148.0 g when filled with a liquid of density 0.98 g mL^{-1} and 50.5 g

when filled with an ideal gas at 760 mmHg at 300K. Determine the molar mass of the gas. *(1998 - 3 Marks)*

22. The degree of dissociation is 0.4 at 400 K and 1.0 atm for the gaseous reaction $PCl_5 \rightleftharpoons PCl_3 + Cl_2$. Assuming ideal behaviour of all gases, calculate the density of equilibrium mixture at 400 K and 1.0 atmosphere. (Relative atomic mass of P = 31.0 and Cl = 35.5) *(1998 - 3 Marks)*

23. Using van der waal's equation, calculate the constant, '*a*' when two moles of a gas confined in a four litre flask exerts a pressure of 11.0 atmospheres at a temperature of 300 K. The value of '*b*' is 0.05 L mol^{-1}. *(1998 - 4 Marks)*

24. For the reaction, $N_2O_5(g) \rightarrow 2NO_2(g) + 0.5\,O_2(g)$, calculate the mole fraction of $N_2O_5(g)$ decomposed at a constant volume and temperature, if the initial pressure is 600 mm Hg and the pressure at any time is 960 mm Hg. Assume ideal gas behaviour. *(1998 - 3 Marks)*

25. One mole of nitrogen gas at 0.8 atm takes 38 s to diffuse through a pinhole, whereas one mole of an unknown compound of xenon with flourine at 1.6 atm takes 57 s to diffuse through the same hole. Calculate the molecular formula of the compound. *(1999 - 5 Marks)*

26. The pressure exerted by 12 g of an ideal gas at temperature *t*°C in a vessel of volume *V* litre is one atm. When the temperature is increased by 10 degrees at the same volume, the pressure increases by 10%. Calculate the temperature *t* and volume *V*. (Molecular weight of the gas = 120.) *(1999 - 5 Marks)*

27. Calculate the pressure exerted by one mole of CO_2 gas at 273 K if the van der Waal's constant $a = 3.592$ dm^6 atm mol^{-2}. Assume that the volume occupied by CO_2 molecules is negligible. *(2000 - 2 Marks)*

28. The compression factor (compressibility factor) for one mole of a van der Waals gas at 0°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*. *(2001 - 5 Marks)*

29. The density of the vapour of a substance at 1 atm pressure and 500 K is 0.36 kg m^{-3}. The vapour effuses through a small hole at a rate of 1.33 times faster than oxygen under the same condition. *(2002 - 5 Marks)*

(a) Determine
   (i) molecular weight,
   (ii) molar volume,
   (iii) compression factor (Z) of the vapour and
   (iv) which forces among the gas molecules are dominating, the attractive or the repulsive?

(b) If the vapour behaves ideally at 1000 K, determine the average translational kinetic energy of a molecule.

30. The average velocity of gas molecules is 400 m/sec. Calculate its rms velocity at the same temperature. *(2003 - 2 Marks)*

31. A graph is plotted between PV_m along *Y*-axis and *P* along *X*-axis, where V_m is the molar volume of a real gas. Find the intercept along *Y*-axis. *(2004 - 2 Marks)*

F Match The Following

Each question contains statements given in two columns, which have to be matched. The statements in Column-I are labelled A, B, C and D, while the statements in Column-II are labelled p, q, r, s and t. Any given statement in Column-I can have correct matching with ONE OR MORE statement(s) in Column-II. The appropriate bubbles corresponding to the answers to these questions have to be darkened as illustrated in the following example :

If the correct matches are A-p, s and t; B-q and r; C-p and q; and D-s then the correct darkening of bubbles will look like the given.

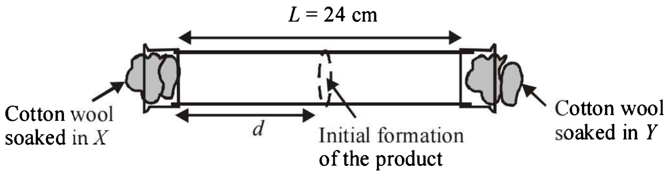
	p	q	r	s	t
A	●	○	○	●	●
B	○	●	●	○	○
C	●	●	○	○	○
D	○	○	○	●	○

1. Match gases under specified conditions listed in **Column I** with their properties/laws in **Column II**. Indicate your answer by darkening the appropriate bubbles of the 4 × 4 matrix given in the ORS. *(2007)*

	Column I		***Column II***
(A)	Hydrogen gas ($P = 200$ atm, $T = 273$ K)	(p)	Compressibility factor $\neq 1$
(B)	Hydrogen gas ($P \sim 0$, $T = 273$ K)	(q)	Attractive forces are dominant
(C)	CO_2 ($P = 1$ atm, $T = 273$ K)	(r)	$PV = nRT$
(D)	Real gas with very large molar volume	(s)	$P(V - nb) = nRT$

G Comprehension Based Questions

X and *Y* are two volatile liquids with molar weights of 10 g mol^{-1} and 40 g mol^{-1} respectively. Two cotton plugs, one soaked in *X* and the other soaked in *Y*, are simultaneously placed at the ends of a tube of length $L = 24$ cm, as shown in the figure. The tube is filled with an inert gas at 1 atmosphere pressure and a temperature of 300 K. Vapours of *X* and *Y* react to form a product which is first observed at a distance *d* cm from the plug soaked in *X*. Take *X* and *Y* to have equal molecular diameters and assume ideal behaviour for the inert gas and the two vapours.



1. The value of d in cm (shown in the figure), as estimated from Graham's law, is *(JEE Adv. 2014)*
   (a) 8 (b) 12
   (c) 16 (d) 20
2. The experimental value of d is found to be smaller than the estimate obtained using Graham's law. This is due to *(JEE Adv. 2014)*
   (a) Larger mean free path for X as compared to that of Y
   (b) Larger mean free path for Y as compared to that of X
   (c) Increased collision frequency of Y with the inert gas as compared to that of X with the inert gas
   (d) Increased collision frequency of X with the inert gas as compared to that of Y with the inert gas

H Assertion & Reason Type Questions

1. Read the following statement and explanation and answer as per the options given below :
   Assertion : The value of van der Waals' constant 'a' is larger for ammonia than for nitrogen.
   Reason : Hydrogen bonding is present in ammonia. *(1998 - 2 Marks)*
   (a) If both *assertion* and *reason* are correct, and *reason* is the correct explanation of the *assertion*.
   (b) If both *assertion* and *reason* are correct, but *reason* is not the correct explanation of the *assertion*.
   (c) If *assertion* is correct but *reason* is incorrect.
   (d) If *assertion* is incorrect but *reason* is correct.
2. Read the following statement and explanation and answer as per the options given below :
   Assertion : The pressure of a fixed amount of an ideal gas is proportional to its temperature
   Reason : Frequency of collisions and their impact both increase in proportion to the square root of temperature. *(2000S)*
   (a) If both assertion and reason are CORRECT, and reason is the CORRECT explanation of the assertion.
   (b) If both assertion and reason are CORRECT, but reason is NOT the CORRECT explanation of the assertion.
   (c) If assertion is CORRECT, but reason is INCORRECT.
   (d) If assertion is INCORRECT, but reason is CORRECT.

I Integer Value Correct Type

1. At 400 K, the root mean square (rms) speed of a gas **X** (molecular weight = 40) is equal to the most probable speed of gas **Y** at 60 K. The molecular weight of the gas **Y** is *(2009)*
2. To an evacuated vessel with movable piston under external pressure of 1 atm, 0.1 mol of He and 1.0 mol of an unknown compound (vapour pressure 0.68 atm. at 0°C) are introduced. Considering the ideal gas behaviour, the total volume (in litre) of the gases at 0°C is close to *(2011)*
3. The diffusion coefficient of an ideal gas is proportional to its mean free path and mean speed. The absolute temperature of an ideal gas is increased 4 times and its pressure is increased 2 times. As a result, the diffusion coefficient of this gas increases x times. The value of x is *(JEE Adv. 2016)*

Section-B JEE Main / AIEEE

1. For an ideal gas, number of moles per litre in terms of its pressure P, gas constant R and temperature T is
   (a) PT/R (b) PRT **[2002]**
   (c) P/RT (d) RT/P.
2. Value of gas constant R is **[2002]**
   (a) 0.082 litre atm (b) 0.987 cal mol^{-1} K^{-1}
   (c) 8.3 J mol^{-1} K^{-1} (d) 83 erg mol^{-1} K^{-1}.
3. Kinetic theory of gases proves **[2002]**
   (a) only Boyle's law
   (b) only Charles' law
   (c) only Avogadro's law
   (d) All of these.
4. According to the kinetic theory of gases, in an ideal gas, between two successive collisions a gas molecule travels
   (a) in a wavy path **[2003]**
   (b) in a straight line path
   (c) with an accelerated velocity
   (d) in a circular path
5. As the temperature is raised from 20°C to 40°C, the average kinetic energy of neon atoms changes by a factor of which of the following ? **[2004]**
   (a) $\frac{313}{293}$ (b) $\sqrt{(313/293)}$
   (c) $\frac{1}{2}$ (d) 2
6. In van der Waals equation of state of the gas law, the constant 'b' is a measure of **[2004]**
   (a) volume occupied by the molecules
   (b) intermolecular attraction
   (c) intermolecular repulsions
   (d) intermolecular collisions per unit volume
7. 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? **[2005]**
   (a) The area under the distribution curve remains the same as under the lower temperature
   (b) The distribution becomes broader
   (c) The fraction of the molecules with the most probable speed increases
   (d) The most probable speed increases
8. If 10^{-4} dm^3 of water is introduced into a 1.0 dm^3 flask at 300 K, how many moles of water are in the vapour phase when equilibrium is established ? **[2010]**

(Given : Vapour pressure of H_2O at 300 K is 3170 Pa; $R = 8.314\ J\ K^{-1}\ mol^{-1}$)

(a) 5.56×10^{-3} mol (b) 1.53×10^{-2} mol

(c) 4.46×10^{-2} mol (d) 1.27×10^{-3} mol

9. 'a' and 'b' are van der Waals' constants for gases. Chlorine is more easily liquefied than ethane because **[2011]**

(a) a and b for Cl_2 > a and b for C_2H_6

(b) a and b for Cl_2 < a and b for C_2H_6

(c) a for Cl_2 < a for C_2H_6 but b for Cl_2 > b for C_2H_6

(d) a for Cl_2 > a for C_2H_6 but b for Cl_2 < b for C_2H_6

10. The compressibility factor for a real gas at high pressure is : **[2012]**

(a) $1 + \frac{RT}{pb}$ (b) 1

(c) $1 + \frac{pb}{RT}$ (d) $1 - \frac{pb}{RT}$

11. For gaseous state, if most probable speed is denoted by C*, average speed by $\overline{C}$ and mean square speed by C, then for a large number of molecules the ratios of these speeds are : **[JEE M 2013]**

(a) $C^* : \overline{C} : C = 1.225 : 1.128 : 1$

(b) $C^* : \overline{C} : C = 1.128 : 1.225 : 1$

(c) $C^* : \overline{C} : C = 1 : 1.128 : 1.225$

(d) $C^* : \overline{C} : C = 1 : 1.225 : 1.128$

12. If Z is a compressibility factor, van der Waals equation at low pressure can be written as: **[JEE M 2014]**

(a) $Z = 1 + \frac{RT}{Pb}$ (b) $Z = 1 - \frac{a}{VRT}$

(c) $Z = 1 - \frac{Pb}{RT}$ (d) $Z = 1 + \frac{Pb}{RT}$

13. The ratio of masses of oxygen and nitrogen in a particular gaseous mixture is 1 : 4. The ratio of number of their molecule is: **[JEE M 2014]**

(a) 1 : 4 (b) 7 : 32

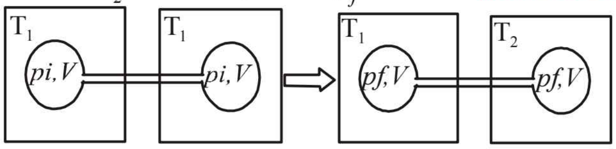
(c) 1 : 8 (d) 3 : 16

14. The intermolecular interaction that is dependent on the inverse cube of distance between the molecules is : **[JEE M 2015]**

(a) London force (b) hydrogen bond

(c) ion - ion interaction (d) ion - dipole interaction

15. Two closed bulbs of equal volume (V) containing an ideal gas initially at pressure p_i and temperature T_1 are connected through a narrow tube of negligible volume as shown in the figure below. The temperature of one of the bulbs is then raised to T_2. The final pressure p_f is : **[JEE M 2016]**



(a) $2p_i\left(\frac{T_2}{T_1+T_2}\right)$ (b) $2p_i\left(\frac{T_1T_2}{T_1+T_2}\right)$

(c) $p_i\left(\frac{T_1T_2}{T_1+T_2}\right)$ (d) $2p_i\left(\frac{T_1}{T_1+T_2}\right)$

5

States of Matter

Section-A : JEE Advanced/ IIT-JEE

A **1.** 900 **2.** R **3.** inversely, time **4.** 0.25 **5.** 1 : 16

B **1.** F **2.** F **3.** F **4.** F

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

D **1.** (b) **2.** (a, b) **3.** (d) **4.** (c) **5.** (b) **6.** (a, c) **7.** (a, b, c, d) **8.** (c)

E **1.** 3.42 g/litre **2.** 39.13 **3.** 85.2 cm **4.** 3 : 2
5. 2.197 atm **6.** 6.21×10^{-21} joules/molecule **7.** 2.7×10^{10} molecules **8.** 1 : 3
9. 3.9×10^{4} cm sec^{-1} **10.** 10 **11.** 1682.5 K, 2143.4 K **12.** 5.23 L
13. 1033 **14.** 0.0043, 0.221 atm **15.** 494.16 m/s, 274.13K, 405.2 m/sec **16.** 8 : 1
17. 2.463 m^3, 1.478 atm **18.** 33.75% and 66.25% **19.** 13.7%
20. CH_4-20%, CO-50%, He-30% **21.** 123 **22.** 4.53 g/litre **23.** 6.46 atm litre^2 mol^{-2}
24. 0.4 **25.** XeF_6 **26.** 100 K, 0.82 litre **27.** 0.9922 atm **28.** 1.253 atm L^2 mol^{-2}
29. (a) (i) 18.09, (ii) 41.025L, (iii) 1.224, (b) 2.07×10^{-20} **30.** 434 ms^{-1} **31.** RT

F **1.** (A) - (p, s); (B) - (r); (C) - (p, q); (D) - (r);

G **1.** (c) **2.** (d)
H **1.** (a) **2.** (a)
I **1.** 4 **2.** 7 **3.** 4

Section-B : JEE Main/ AIEEE

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

Section-A JEE Advanced/ IIT-JEE

A. Fill in the Blanks

1. **900;** Energy of one mole of an ideal monoatomic gas $= \frac{3}{2}$ RT

$$R = 8.314 \text{ J K}^{-1} \text{ mole}^{-1} = 1.99 \text{ cal K}^{-1} \text{ mole}^{-1}$$
$$T = 27°C = 273 + 27 = 300 \text{ K}$$

$$\Rightarrow \quad E = \frac{3}{2} \times 1.99 \times 300 = 900 \text{ cal}$$

2. **R.** $[\because C_p - C_v = R]$

3. **Inversely, time;** $\left[\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}} = \frac{t_2}{t_1} = \sqrt{\frac{M_2}{M_1}}\right]$.

4. **0.25;** $\left(\because 5.6 l \equiv \frac{1}{4} \text{ mole of an ideal gas}\right)$

Using ideal gas equation

$$PV = nRT = \frac{1}{4}RT = 0.25 \text{ RT}$$

5. **1 : 16;** $\frac{K.E._{O_2}}{K.E._{H_2}} = \frac{(3/2)n_{O_2}RT}{(3/2)n_{H_2}RT} = \frac{n_{O_2}}{n_{H_2}} = \frac{8/32}{8/2} = \frac{1}{16}$

B. True / False

1. **False :** K.E. = $\frac{3}{2}$ KT, and cannot be zero at 0°C or 273 K.
2. **False :** The pressure exerted by the gas is the result of collisions of the molecules on the walls of the container.
3. **False :** The constant '*a*' reflects the intermolecular attraction between gaseous molecules. The constant '*b*' reflects the actual volume of one mole of gaseous molecules.
4. **False :** An ideal gas cannot be liquefied as there exists no intermolecular attraction between molecules.

C. MCQs with One Correct Answer

1. **(a) TIPS/Formulae :**

$$\text{Mole fraction of } O_2 = \frac{\text{Moles of } O_2}{\text{Total moles}}$$

Partial pressure of O_2 = Mole fraction of O_2

$$\text{Mole fraction of } O_2 = \frac{\frac{W}{32}}{\frac{W}{16}+\frac{W}{32}} = \frac{1}{3}$$

2. **(b)** The temperature at which a real gas behaves like an ideal gas is called Boyle's temperature or Boyle's point.

3. **(a)** $U_{rms} : U_{av} = \sqrt{\frac{3RT}{M}} : \sqrt{\frac{8RT}{\pi M}}$ *or* $\sqrt{3} : \sqrt{\frac{8}{\pi}} = 1.086 : 1$

4. **(b)** Average kinetic energy depends only on temperature and does not depend upon the nature of the gas. ($\because$ K.E. = 3/2 KT)

5. **(b)** Pressure exerted by hydrogen will be proportional to its mole fraction.

$$\text{Mole fraction of } H_2 = \frac{\frac{w}{2}}{\frac{w}{16}+\frac{w}{2}} = \frac{8}{9}$$

6. **(d)** $\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}}$

7. **(a)** $U_{av} = \sqrt{\frac{8RT}{\pi M}}$; $\begin{Bmatrix} T_1 = 27+273 = 300\text{ K} \\ T_2 = 927+273 = 1200\text{ K} \end{Bmatrix}$

$$\frac{U_{av_1}}{U_{av_2}} = \sqrt{\frac{T_1}{T_2}} \text{ or } \frac{0.3}{U_{av_2}} = \sqrt{\frac{300}{1200}} \text{ or } \frac{0.3}{U_{av_2}} = \sqrt{\frac{1}{4}}$$

or U_{av_2} = **0.6 m/sec.**

8. **(c)** $\left(P+\frac{a}{V^2}\right)(V-b) = RT$; Here $\left(P+\frac{a}{V^2}\right)$ represents the intermolecular forces.

9. **(b) TIPS/Formulae :**

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

$\because$ Molecular mass of HCl > molecular mass of NH_3

$\therefore$ HCl diffuses at slower rate and white ammonium chloride is first formed near HCl bottle.

10. **(c)** '*a*' is directly related to forces of attraction. Hence greater the value of '*a*', more easily the gas is liquified.

11. **(b) TIPS/Formulae :**

$$d = \frac{PM}{RT}$$

It means density of gas is directly proportional to pressure and inversely proportional to temperature. Density of neon will be maximum at highest pressure and lowest temperature.

$\therefore$ (b) is correct answer.

12. **(a)** $\frac{r_{CH_4}}{r_x} = 2 = \sqrt{\frac{M_x}{M_{CH_4}}} = \sqrt{\frac{M_x}{16}}$, or $M_x = 64$

13. **(d)** Pressure exerted by the gas, $P = \frac{1}{3}\frac{mnu^2}{V}$ ...(1)

Here, u = root mean square velocity

m = mass of a molecule, n = No. of molecules of the gas

Hence (a) & (b) are clearly wrong.

Again $u^2 = \frac{3RT}{M}$ [explained from (1)]

Here, M = Molecular wt. of the gas;

Hence (c) is wrong

Further, Average K.E. = $\frac{3}{2}$ KT; Hence (d) is true.

14. **(a)** Due to increase in the temperature, the kinetic energy of the gas molecules increases resulting in an increase in average molecular speed. The molecules are bombarded to the walls of the container with a greater velocity resulting in an increase in pressure.

15. **(a)** The mean free path, $\lambda = \frac{1}{\sqrt{2}\,\pi a^2 N}$

or $\lambda \propto \frac{1}{a^2}$, where a = molecular diameter

$\therefore$ Smaller the molecular diameter, longer the mean free path. Hence H_2 is the answer.

16. **(c) NOTE :** The value of '*a*' indicates the magnitude of attractive forces between gas molecules.

Value of '*a*' $\propto$ size of molecule.

$\therefore$ inert gas will have minimum value of '*a*' followed by H_2O, C_6H_6 and $C_6H_5CH_3$

17. **(c)** The expression of root mean square speed is

$$U_{rms} = \sqrt{\frac{3RT}{M}}$$

Hence,

$$\frac{U_{rms}(H_2)}{U_{rms}(O_2)} = \left[\frac{3R(50K)/(2\,g\,mol^{-1})}{3R(800K)/(32\,g\,mol^{-1})}\right]^{1/2} = 1$$

18. (b) Under identical conditions, $\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$

As rate of diffusion is also inversely proportional to time, we will have, $\frac{t_2}{t_1} = \sqrt{\frac{M_2}{M_1}}$

(a) Thus, For He, $t_2 = \sqrt{\frac{4}{2}}(5s) = 5\sqrt{2}s \neq 10s$;

(b) For O_2, $t_2 = \sqrt{\frac{32}{2}}(5s) = 20s$

(c) For CO, $t_2 = \sqrt{\frac{28}{2}}(5s) \neq 25s$;

(d) For CO_2, $t_2 = \sqrt{\frac{44}{2}}(5s) \neq 55s$

19. (b)

	$N_2O_4(g) \rightleftharpoons$	$2NO_2(g)$
At start	100/92 mol = 1.08 mol	0
At equilibrium	80/92 mol = 0.86 mol	20/46 mol =0.43 mol

According to ideal gas equation, at two conditions

At 300 K; $P_0V = n_0RT_0$

$1 \times V = 1.08 \times R \times 300$ ...(i)

At 600 K; $P_1V = n_1RT_1$

$P_1 \times V = (0.86 + 0.43) \times R \times 600$ ...(ii)

Divide (ii) by (i),

$$\frac{P_1}{1} = \frac{1.29 \times 600}{1.08 \times 300};$$

$$P_1 = \frac{1.29 \times 2}{1.08} = 2.38 \text{ atm.} \simeq 2.4 \text{ atm.}$$

20. (b) The compressibility factor of a gas is defined as

$$Z = \frac{pV_m}{RT}$$

For an ideal gas, $pV_m = RT$. Hence $Z = 1$

21. (c) For an ideal-gas behaviour, the molecules of a gas should be far apart. The factors favouring this condition are high temperature and low pressure.

22. (c) TIPS/Formulae :

$$U_{rms} = \sqrt{\frac{3RT}{M}} \Rightarrow \sqrt{\frac{3RT_{H_2}}{2}} = \sqrt{7}\sqrt{\frac{3RT_{N_2}}{28}};$$

$$\therefore\ T_{N_2} = 2T_{H_2} \text{ or } T_{N_2} > T_{H_2}$$

23. (b) $(PV)_{Observed}/(PV)_{Ideal} < 1$

$\Rightarrow V_{obs} < V_{ideal}$, $V_{obs} < 22.4$ litre.

24. (c) Mass of 1 L of vapour = volume × density

$= 1000 \times 0.0006 = 0.6$ g

V of liquid water $= \frac{\text{mass}}{\text{density}} = \frac{0.6}{1} = 0.6\ cm^3$

25. (d) $U_{RMS} = \sqrt{\frac{3RT}{M}}$ Using ideal gas equation,

$PV = nRT = \frac{w}{M}RT$; $\frac{RT}{M} = \frac{PV}{w} = \frac{p}{d}$ where d is the density of the gas

$\therefore\ U_{RMS} = \sqrt{\frac{3P}{d}}$ at constant pressure, $U_{RMS} \propto \frac{1}{\sqrt{d}}$

26. (c) TIPS/Formulae :

Find the volume by either

$V = RT/P$ ($PV = RT$) or $P_1V_1 = P_2V_2$ and and match it with the values given in graph to find correct answer.

Volume of 1 mole of an ideal gas at 273 K and 1 atm is 22.4 L and that at 373 K and 1 atm pressure is calculated as ;

$$V = \frac{RT}{P} = \frac{0.082 \times 373}{1} = 30.58L \simeq 30.6 \text{ L}$$

27. (b) Upon increase of temperature the internal energy of water or any system increases resulting in decrease in intermolecular force and hence decrease in surface tension. Surface tension decreases with increase in mobility due to increase in temperature.

28. (c) For positive deviation: $PV = nRT + nPb$

$$\Rightarrow \frac{PV}{nRT} = 1 + \frac{Pb}{RT}$$

Thus, the factor nPb is responsible for increasing the PV value, above ideal value. b is actually the effective volume of molecule. So, it is the finite size of molecules that leads to the origin of b and hence positive deviation at high pressure.

29. (c) Average KE $= E = \frac{1}{2}Mu_{rms}^2$

$$\therefore\ u_{rms}^2 = \frac{2E}{M} \text{ or } u_{rms} = \sqrt{\frac{2E}{M}}$$

30. (b) TIPS/Formulae :

Use Grahams' law of diffusion

$$\frac{r_{He}}{r_{CH_4}} = \sqrt{\frac{M_{CH_4}}{M_{He}}} = \sqrt{\frac{16}{4}} = 2$$

31. **(a)** $TV^{\gamma-1}$ = Constant (∵ change is adiabatic)

$$T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$$

For monoatomic gas $\gamma = \frac{5}{3}$

$$\therefore T_1V_1^{2/3} = T_2V_2^{2/3} \Rightarrow T(1)^{2/3} = T_2(2)^{2/3}$$

$$T_2 = \frac{T}{2^{(2/3)}}$$

32. **(b)** In general, the molar heat capacity for any process is given by

$C = C_v + \frac{R}{1-n}$, when PV^n = constant

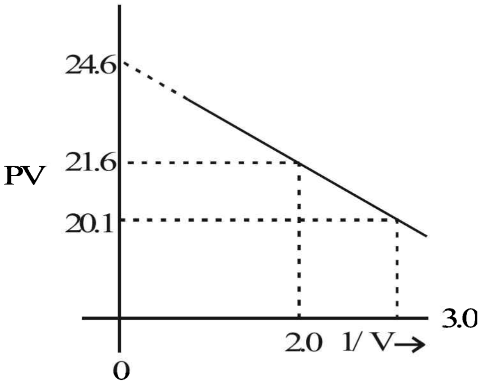
Here $\frac{P}{V} = 1$, i.e. PV^{-1} = constant

For monoatomic gas, $C_v = \frac{3}{2}R$

$$\therefore C = \frac{3}{2}R + \frac{R}{1-(-1)} = \frac{3}{2}R + \frac{R}{2} = \frac{4R}{2} = 2R.$$

33. **(b)** Correction factor for attractive force for n moles of real gas is given by the term mentioned in (b).

34. **(c)**



$$\left(P + \frac{a}{V^2}\right)(V) = RT$$

PV + a/V = RT; PV = RT – a(V)

y = RT – a(x)

So, slope = $a = \frac{21.6-20.1}{3-2} = \frac{1.5}{1} = 1.5$

35. **(d)**

- A solution of CH_3OH and water shows positive deviation from Raoult's law, it means by adding CH_3OH intermolecular force of attraction decreases and hence surface tension decreases.
- By adding KCl in water, intermolecular force of attraction bit increases, so surface tension increases by small value.
- By adding surfactant like $CH_3(CH_2)_{11}OSO_3^-Na^+$, surface tension decreases rapidly and after forming micelle it slightly increases.

D. MCQs with One or More Than One Correct

1. **(b)** No work is required to tear apart the molecules due to the absence of attractive forces in an ideal gas.

2. **(a,b)** At constant temp., when gas expands the K.E. of the molecules remains the same, but the pressure decreases. $\left(\because P \propto \frac{1}{V}\right)$

3. **(d)** Pressure exerted by H_2 is proportional to its mole fraction.

$$\text{Mole fraction of } H_2 = \frac{\frac{W}{2}}{\frac{W}{2}+\frac{W}{30}} = \frac{30}{32} = \frac{15}{16}$$

4. **(c)** According to Graham's law of diffusion for two gases undergoing diffusion at different pressures through same hole

$$\frac{r_A}{r_B} = \sqrt{\frac{M_B}{M_A}} \times \frac{P_A}{P_B}$$

$$\left(r \propto P \times \sqrt{\frac{1}{M}} \quad \text{At constant temperature}\right)$$

5. **(b)** For gas A, $a = 0, Z = 1 + \frac{Pb}{RT}$ implies Z varies linearly with pressure.

For gas B, $b = 0, Z = 1 - \frac{a}{VRT}$. Hence, Z does not vary linearly with pressure.

Given the intersection data for gas C, it is possible to find the values of 'a' and 'b'. All vander Waal gases, like gas C, give positive slope at high pressures.

6. **(a,c)** Vander Waals equation is

$$\left(P + \frac{n^2a}{V^2}\right)(V - nb) = nRT \quad \text{[For n moles of a gas)}$$

a, b are vander Waals constants

The ideal gas equation is $PV = nRT$ [For n moles of a gas]

where P is pressure excerted by ideal gas and V is volume occupied by ideal gas.

In vander Waals equation the term $\left(P + \frac{n^2a}{V^2}\right)$ represents the pressure exerted by the gas and $(V - nb)$ the volume occupied by the gas. At low pressure, when the gas occoupies large volume the intermolecular distance between gaseous moleculas is quite large and in such case there is no significant role played by intermolecular forces and thus the gas behaves like an ideal gas thus (a) is correct

NOTE : Under high pressure the intermolecular distance decreases and the intermolecular forces play a significant role and the gas shows a devation from ideal behaviour.

Thus (b) is *not* correct.

a, b i.e. the vander Waals coefficients defined on the nature of gas and are independent of temperature so (c) is correct.

The pressure $\left(P+\frac{n^2a}{V}\right)$ is not lower than P so (d) is not correct.

Hence the correct anser is (a, c).

7. **(a, b, c, d)**
8. **(c)** $P(V-b)=RT$

$$\Rightarrow \quad PV-Pb=RT$$

$$\Rightarrow \quad \frac{PV}{RT}=\frac{Pb}{RT}+1$$

$$\Rightarrow \quad Z=1+\frac{Pb}{RT}$$

Hence $Z>1$ at all pressures.

This means , repulsive tendencies will be dominant when interatomic distance are small.

This means, interatomic potential is never negative but becomes positive at small interatomic distances.

E. Subjective Problems

1. **TIPS/Formulae :**

$$PV=\frac{m}{M}RT \Rightarrow P=\frac{m}{V}\times\frac{RT}{M}=d\frac{RT}{M} \quad \therefore d=\frac{MP}{RT}$$

Substituting the value, we get

$$d=\frac{17\times5}{0.082\times303}=\mathbf{3.42\ g/litre}$$

2. Given, moles $=\frac{\text{mass}}{\text{mol.wt}}$

mass of gas = 3.7g, mass of hydrogen = 0.184g

$T_1=298\text{K}, T_2=17°\text{C}=273+17=290\text{K}$

$$\text{Moles of } H_2=n_1=\frac{\text{Mass}}{\text{M. wt.}}=\frac{0.184}{2}=0.092$$

$$\text{Moles of gas}=n_2=\frac{\text{Mass}}{\text{M. wt.}}=\frac{3.7}{\text{M}}$$

For hydrogen $P_1V_1=n_1RT_1$ ....(i)

For gas $P_1V_1=n_2RT_2$ ....(ii)

($\because$ Pressure and volume of gas are same)

$\therefore$ From equation (i) and equation (ii)

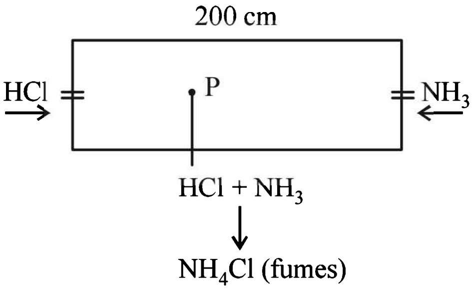
$$\frac{P_1V_1}{P_1V_1}=\frac{n_1RT_1}{n_2RT_2} \text{ or } 1=\frac{0.092\times298}{n_2\times290}$$

$$\text{or } n_2=\frac{0.092\times298}{290} \text{ or } \frac{3.7}{\text{M}}=\frac{0.092\times298}{290}$$

$$\text{or } \frac{3.7}{\text{M}}=0.0945 \therefore \text{M}=\frac{3.7}{0.0945}=\mathbf{39.15}$$

3. Let NH_3 diffuse through $=x$ cm

HCl diffuses through $=y$ cm



According to Graham's law of diffusion

$$\frac{x}{y}=\sqrt{\frac{\text{Mol. wt HCl}}{\text{Mol. wt of } NH_3}}=\sqrt{\frac{36.5}{17}}=\sqrt{2.14}=1.465$$

$x=1.465y$ ... (1)

$x+y=200$ cm ... (2)

From these equations; $y=85.2$ cm

Distance between P and X $=y=$ **85.2 cm.**

4. Following reaction takes places in tube

$$C+CO_2 \longrightarrow 2CO$$

Volume of mixture of CO and CO_2 = 1L

Let volume of CO_2 in mixture $=x$

$\therefore$ Volume of CO in mixture $=2x$

$\therefore$ Original volume of CO in mixture $=1-x$

Total volume of CO after reaction $=(1-x)+2x=1+x$

$1+x=1.6$ ($\because$ It is given total volume after reaction = 1.6L)

$\therefore x=0.6$ L $\quad\therefore$ Volume of $CO_2=0.6$ L

Volume of CO = 0.4 L

$CO_2 : CO=\mathbf{3:2}$

5. Since the pressures of gases are different, and the temperature is constant, the rate at which molecules of the two gases diffuse is directly proportional to the pressure. This rate of diffusion is also directly proportional to the distance travelled by the gas. Hence

r_1 (of HCl gas) at pressure $P=60=\frac{kP}{\sqrt{36.5}}$ .....(i)

and r_2 (of NH_3) at 1 atm. pressure $P=40=\frac{k\times1}{\sqrt{17}}$ .....(ii)

From (i) and (ii)

$$\frac{r_1}{r_2}=\frac{60}{40}=\frac{kP}{\sqrt{36.5}}\times\frac{\sqrt{17}}{k\times 1}$$

$$P=\frac{60}{40}\times\frac{\sqrt{36.5}}{\sqrt{17}}=\mathbf{2.197\ atm}$$

6. **TIPS/Formulae :**

Total kinetic energy = $n\,(3/2\ RT)$

where n = Number of moles of the gas
R = Gas constant
T = Absolute temperature

Molecular weight of methane,

$CH_4 = 12 + 4 \times 1 = 16$

∴ Number of moles of methane in 8.0 gm of methane

$$=\frac{8.0}{16.0}=0.5$$

R = 8.314 joules/K/mole, $T = 27 + 273 = 300$ K

∴ Total kinetic energy of the molecules in 8.0 gm of methane at 27°C $= n \times 3/2\ RT = 0.5 \times 3/2 \times 8.314 \times 300 = 1870.65$ joules

$$\therefore \text{ Average kinetic energy} = \frac{1870.65}{6.023\times10^{23}\times0.5}$$

$$= \mathbf{6.21 \times 10^{-21}\ joules/molecule}$$

7. **NOTE THIS STEP :** First we should calculate the number of moles of the gas under the given conditions by the relation $PV = nRT$

Here $P = 7.6 \times 10^{-10}$ mm Hg

$$=\frac{7.6\times10^{-10}}{760}\text{ atm.} = 1\times10^{-12}\text{ atm.}$$

V = 1 litre, $T = 273 + 0 = 273$K, R = 0.082 litre atm./K/mol

Putting the values in equation

$$n=\frac{PV}{RT}=\frac{1\times10^{-12}\times1}{0.082\times273}\text{ moles}$$

Now since 1 mole = 6.023×10^{23} molecules

$$\frac{10^{-12}}{0.082\times273}\text{ moles}=\frac{6.023\times10^{23}\times10^{-12}}{0.082\times273}\text{ molecules}$$

$$= \mathbf{2.7 \times 10^{10}\ molecules}$$

8. From ideal gas equation,

$$PV = nRT \Rightarrow PV = \left(\frac{m}{M}\right)RT \text{ or } M = m\frac{RT}{PV}$$

Let the molecular wt. of A and B be M_A and M_B respectively.

$$\text{Then } M_A = 2\frac{RT}{1\times V};\ M_B=\frac{3\times RT}{0.5\times V}$$

$$\therefore \frac{M_A}{M_B}=\frac{2RT}{V}\times\frac{0.5V}{3RT}=\frac{2\times0.5}{3}=\frac{1}{3}$$

Therefore, the ratio $M_A : M_B = \mathbf{1 : 3}$

9. $$U_{rms}=\sqrt{\frac{3RT}{M}}$$

Given $T = 20°C = 20 + 273 = 293$K
$R = 8.314 \times 10^7$ erg per degree per mol
$M(\text{of } O_3) = 48$

$$\therefore U_{rms}=\sqrt{\frac{3\times8.314\times10^7\times293}{48}}=3.9\times10^4\text{ cm sec}^{-1}$$

10. Volume of ballon = 4.851 L (as calculated above)

Let no. of balloons to be filled = n

∴ Total volume occupied by n balloons = $4.851 \times n$

Volume of H_2 present in cylinder = 2.82 L (given)

∴ Total volume of H_2 at NTP = $(4.851n + 2.82)$L

$P_1 = 1$ atm $\quad P_2 = 20$ atm
$V_1 = 4.85 \times n + 2.82$ L $\quad V_2 = 2.82$ L
$T_1 = 273$ K $\quad T_2 = 300$ K

$$\frac{P_1V_1}{T_1}=\frac{P_2V_2}{T_2}\text{ or }\frac{1\times(4.85\times n+2.82)}{273}=\frac{20\times2.82}{300}$$

$$\therefore n=\frac{48.504}{4.851}\simeq10$$

11. **TIPS/Formulae :**

$$\text{Average velocity} = \sqrt{\frac{8RT}{\pi M}}$$

$$\text{and Most probable velocity} = \sqrt{\frac{2RT}{M}}$$

Given - For CO_2

Average velocity at T_1 = Most probable velocity at T_2

$$= 9\times10^4\text{ cm/sec} = \frac{9\times10^4}{100}\text{ m/sec.}$$

$$= 9\times10^2\text{ m/sec.}$$

$$\therefore 9\times10^2=\sqrt{\frac{8\times8.314\times T_1}{3.14\times44\times10^{-3}}}\quad ...(A)$$

[Average velocity at T_1K]

$$\text{and } 9\times10^2=\sqrt{\frac{2\times8.314\times T_2}{44\times10^{-3}}}\quad ...(B)$$

[Most probable velocity at T_2K]

On solving, T_1 = **1682.5 K,** T_2 = **2143.4 K**

12. Applying the general gas equation

$$PV = nRT = \frac{m}{M}RT$$

Here, Mol. wt. of acetylene i.e., C_2H_2 (M) = 26, $P=\frac{740}{760}$ atm,

$T = 50°C = 50 + 273 = 323$ K

$$\therefore\quad V=\frac{mRT}{MP}\text{ or }V=\frac{5\times0.082\times323\times760}{26\times740}=\mathbf{5.23\ L}$$

13. Using gas equation; $PV = nRT$

Total no. of moles of gases in the mixture (n)

$$= \frac{PV}{RT} = \frac{6\times 3}{0.0821\times 300} = 0.7308 \text{ mol.}$$

Thus no. of moles of unknown gas $= 0.7308 - 0.7$
$= 0.0308$ mol.

Now we know that

$$\frac{r_1}{r_2} = \frac{\text{moles of hydrogen gas}}{\text{moles of unknown gas}} = \frac{0.7}{0.0308}$$

Also we know that $\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$

$$\therefore \quad M_2 = \left(\frac{r_1}{r_2}\right)^2 M_1 \quad \text{or} \quad M_2 = \left(\frac{0.7}{0.0308}\right)^2 \times 2 = \mathbf{1033}$$

14. $2NO + O_2 \rightarrow 2NO_2 \rightarrow N_2O_4$

Calculating the number of moles of NO and O_2 by applying the formula, $n = \frac{PV}{RT}$

$$\text{Moles of NO in the larger flask} = \frac{1.053\times 0.250}{0.082\times 300} = 0.0107$$

[250 mL = 0.250 L]

$$\text{Moles of } O_2 \text{ in the smaller flask} = \frac{0.789\times 0.100}{0.082\times 300} = 0.0032$$

[100 mL = 0.100 L]

The reaction takes place as follows.

	$2NO$ +	$O_2 \longrightarrow$	N_2O_4
Mols before reaction	0.0107	0.0032	0
Mole after reaction	(0.0107 – 2 × .0032)	0	0.0032

Hence moles of NO reacting completely with 0.0032 moles of $O_2 = 2 \times 0.0032 = 0.0064$

Moles of NO left $= 0.0107 - 0.0064 = \mathbf{0.0043}$

NOTE : Oxygen will be completely changed into NO_2 which in turn is completely converted into N_2O_4 which solidifies at 262 K. Hence at 220 K, the dimer is in the solid state and only NO present in excess will remain in the gaseous state occupying volume equal to 350 ml.

Hence pressure (P) of NO gas left

$$= \frac{nRT}{V} = \frac{0.0043\times 0.082\times 220}{0.350} = \mathbf{0.221\ atm}$$

[Total volume = 0.250 + 0.100 = 0.350 L]

15. Given $V = 1\text{L} = 10^{-3}\text{ m}^3$, $P = 7.57\times 10^{-3}\text{ Nm}^{-2}$, $R = 8.314\text{J}$, $n = 2\times 10^{21}/6.023\times 10^{23}$ moles

$$PV = nRT \quad \text{or} \quad T = \frac{PV}{nR}$$

$$= \frac{7.57\times 10^{-3}\times 10^{-3}\times 6.023\times 10^{23}}{2\times 10^{21}\times 8.31} = 274.13\text{ K}$$

$$U_{rms} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3\times 8.314\times 274.13}{28\times 10^{-3}}}\ \text{m/s} = 494.15\text{ m/s}$$

(Given U)

$$\frac{U_{mp}}{U_{rms}} = 0.82 \text{ (given)}$$

$$\therefore U_{mp} = 0.82\times U_{rms} = 0.82\times 494.15 = 405.2\text{ m/sec}$$

16. **TIPS/Formulae :**

Partial pressure = Mole fraction × Total pressure

$$\therefore p_{He} = x_{He}\times P = \frac{4}{5}\times 20 = 16\text{ bar}$$

$$\left[\text{mole fraction of He} = \frac{4}{5}\right]$$

$$\therefore \quad p_{CH_4} = 20 - 16 = 4\text{ bar}$$

Now applying the formula

$$\frac{r_{He}}{r_{CH_4}} = \frac{P^0_{He}}{P^0_{CH_4}}\sqrt{\frac{M_{CH_4}}{M_{He}}} = \frac{16}{4}\sqrt{\frac{16}{4}} = \frac{16}{4}\sqrt{4}$$

$$\therefore \quad r_{He} : r_{CH_3} = 8:1$$

∴ Composition of the mixture (He : CH_4) effusing out = **8 : 1**

17. *Calculation of volume of gas :*

Weight of cylinder with gas = 29.0 kg

Weight of empty cylinder = 14.8 kg

∴ Weight of gas in the cylinder = 14.2 kg

Pressure in cylinder = 2.5 atm

∴ No. of moles (n) in 14.2 kg (14.2×10^3 g) of butane

$$n = \frac{\text{Wt. of butane}}{\text{Mol. wt. of butane}} = \frac{14.2\times 10^3}{58} = 244.83\text{ mol}$$

Applying gas equation,

$$V = \frac{nRT}{P} = \frac{244.83\times 0.0821\times 300}{2.5} = 2412\text{ litres}$$

[27°C = 273 + 27 = 300]

Calculation of pressure in cylinder after use.

Weight of cylinder after use = 23.2 kg

Weight of empty cylinder = 14.8 kg

$$\therefore \text{Wt. of unused gas} = 8.4\text{ kg} = \frac{8.4\times 10^3}{58}\text{ moles of butane}$$

$$\text{Thus } P = \frac{nRT}{V} = \frac{8.4\times 10^3\times 0.0821\times 300}{58\times 2412} = \mathbf{1.478\ atm}$$

[V = 2412 L]

Calculation of volume of used gas at 2.5 atm and 27°C.

Weight of used gas = 14.2 – 8.4 = 5.8 kg

Pressure under normal usage conditions = 1 atm

$$V=\frac{nRT}{P}=\frac{5.8\times10^3}{58}\times\frac{0.0821\times300}{1}\qquad\left[\because n=\frac{5.8}{58}\right]$$

= 2463 litres = $\mathbf{2.463\ m^3}$

18. Let the volume of ethane in mixture = x litre

$\therefore$ Volume of ethene = $(40-x)$ litre

Combustion reactions of ethane and ethene are :

(i) $C_2H_6(g)+3\frac{1}{2}O_2(g)\longrightarrow 2CO_2(g)+3H_2O(l)$

or $2C_2H_6(g)+7O_2(g)\longrightarrow 4CO_2(g)+6H_2O(l)$

(ii) $C_2H_4(g)+3O_2(g)\longrightarrow 2CO_2(g)+2H_2O(l)$

Volume of O_2 required for complete combustion of ethane

$=\frac{7x}{2}$ [For x litres]

Volume of O_2 required for complete combustion of ethene

$=(40-x)\times3$ [For $(40-x)$ L]

$\therefore$ Total volume of O_2 required $=\frac{7x}{2}+(40-x)3\ l$

Calculation of number of moles (n)

$P=1$ atm, $V=\frac{7x}{2}+(40-x)3\ l$; $R=0.082\ l$ atm K^{-1} mol^{-1}; $T=400$ K

$$\text{Since } n=\frac{PV}{RT}=\frac{1\times\left[\frac{7x}{2}+(40-x)3\right]}{0.082\times400}=\frac{7x+(40-x)6}{2\times0.082\times400}$$

$$\text{Mass of } n \text{ moles of } O_2=\left[\frac{7x+(40-x)6}{2\times0.082\times400}\right]\times32=130$$

$$\text{or } 130=\left[\frac{7x+240-6x}{65.6}\right]\times32$$

$$\Rightarrow 8528=32x+240\times32\Rightarrow 32x=848\Rightarrow \text{or } x=\frac{848}{32}=26.5$$

Hence mole fraction (%) of ethane $=\frac{26.5}{40}\times100=\mathbf{66.25\%}$

Mole fraction (%) of ethene = **33.75%**

19.

Mixture	Krypton
$r_{mix}=1.16$	$r_{Kr}=1$
$M_{mix}=?$	$M_{Kr}=84$

We know that

$$\frac{r_{mix}}{r_{Kr}}=\sqrt{\frac{M_{Kr}}{M_{min}}}\text{ or }\frac{1.16}{1}=\sqrt{\frac{84}{M_{mix}}}$$

$$\text{or } (1.16)^2=\frac{84}{M_{mix}}\Rightarrow M_{mix}=\frac{84}{(1.16)^2}=62.426$$

<u>Determination of the composition of the equilibrium mixture</u>

Let the fraction of Cl_2 molecules dissociated at equlibrium = x

	Cl_2 $\rightleftharpoons$	$2Cl$	Total
Initially	1	0	1
At equilibrium	$1-x$	$2x$	$1-x+2x=1+x$

$\therefore$ Total moles at equilibrium $=1-x+2x=1+x$

$$\because\ \frac{\text{Normal molecular mass}}{\text{Experimental molecular mass}}=1+x$$

$$\therefore\ \frac{71}{64.426}=1+\alpha$$

$\therefore \alpha=0.137=\mathbf{13.7\%}.$

20. **TIPS/Formulae :**

(i) He does not react with oxygen.

(ii) KOH absorbs only CO_2.

NOTE : When the mixture of CO, CH_4 and He gases (20 ml) are exploded by an electric discharge with excess of O_2, He gas remains as such and the other reactions involved are :

$$CO(g)+\frac{1}{2}O_2(g)\to CO_2(g)\qquad\text{...(i)}$$

$$CH_4(g)+2O_2(g)\to CO_2(g)+2H_2O(l)\qquad\text{...(ii)}$$

Let the volumes of CO and CH_4 to be 'a' ml and 'b' ml in the mixture then

Volume of He gas = $[20-(a+b)]$ ml

For the initial contraction of 13 ml,

Volume of left hand side in the above reactions – 13 = Volume of right hand side.

$$\therefore\ [20-(a+b)]+\left(a+\frac{1}{2}a\right)+(b+2b)-13$$

$=[20-(a+2b)]+a+b$ [neglect the volume of H_2O (l)]

(Since for gases, volume α no. of moles)

$$\therefore\ \frac{1}{2}a+2b=13\text{ or } a+4b=26\qquad\text{...(iv)}$$

NOTE THIS STEP : The CO_2 produced above in reactions (ii) & (iii), $(a+b)$ ml, reacts with KOH sol for a further contraction of 14 ml.

$CO_2(g)+2KOH(l)\to K_2CO_3(l)+H_2O(l)$

$(a+b)$ ml

$\therefore\ a+b=14$ ...(v)

Solving (iv) & (v) we get, $a=10$ ml & $b=4$ ml

$$\therefore CH_4=\frac{4}{20}\times100=\mathbf{20\%},\ CO=\frac{10}{20}\times100=\mathbf{50\%}$$

& He = 100 – (20 + 50) = **30%**

21. Weight of liquid = 148 – 50 = 98 g

Volume of liquid $=\frac{98}{0.98}=100$ ml = volume of vessel

It means, vessel of 100 ml contains ideal gas at 760 mm Hg at 300 K

Weight of gas = 50.5 – 50 = 0.5g

using, $PV = nRT = \frac{w}{m}RT$

$$\frac{760}{760}\times\frac{100}{1000}=\frac{0.5}{m}\times 0.082\times 300 \qquad \left[n=\frac{0.5}{m}\right]$$

∴ Molecular weight of gas (m) = **123**

22. $$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

	PCl_5	PCl_3	Cl_2
Initial moles	1	0	0
Moles at eq.	1–0.4	0.4	0.4

∴ Total moles at equilibrium = $1 - 0.4 + 0.4 + 0.4 = 1.4$

Also $\frac{\text{Normal mol. wt. of } PCl_5}{\text{Exp. mol. wt. of } PCl_5} = 1 + \alpha = 1.4$

or $\frac{208.5}{\text{Exp. mol. wt. of } PCl_5} = 1.4$

∴ Exp. mol. wt. of PCl_5 or m. wt. of mixture $= \frac{208.5}{1.4}$

Now using, $PV = \frac{w}{m}RT$ for mixture

$$d = \frac{w}{V} = \frac{Pm}{RT} = \frac{1\times 208.5}{1.4\times 0.082\times 400} = \mathbf{4.53\ g/litre}$$

23. van der Waals equation for n moles of gas is

$$\left[P+\frac{n^2a}{V^2}\right][V-nb]=nRT$$

Given $V = 4$ litre; $P = 11.0$ atm, $T = 300$ K;
$b = 0.05$ litre mole^{-1}, $n = 2$

Thus, $$\left[11+\frac{2^2 a}{4^2}\right][4-2\times 0.05]=2\times 0.082\times 300$$

∴ $a = \mathbf{6.46\ atm\ litre^2\ mol^{-2}}$

24. $$N_2O_5(g) \rightleftharpoons 2NO_2(g) + \frac{1}{2}O_2(g)$$

	$N_2O_5(g)$	$2NO_2(g)$	$\frac{1}{2}O_2(g)$
Initial pressure	600	0	0
Final pressure	600-P	2P	P/2

$P \propto$ moles when V and T are constant
(where moles equivalent to pressure P are decomposed)
Total pressure = $600 - P + 2P + P/2 = 960$ mm of Hg
∴ $P = 240$ mm Hg

Thus moles of N_2O_5 decomposed $= \frac{240}{600} = \mathbf{0.4}$

25. We know that

$$\frac{r_1}{r_2}=\sqrt{\frac{M_2}{M_1}}\times\frac{P_1}{P_2} \text{ or } \frac{n_1}{t_1}\times\frac{t_2}{n_2}=\sqrt{\frac{M_2}{M_1}}\times\frac{P_1}{P_2}$$

$$\text{or } \frac{1}{38}\times\frac{57}{1}=\sqrt{\frac{M}{28}}\times\frac{0.8}{1.6} \qquad \therefore M=252$$

$$\left[\begin{array}{l} Xe+(F)_x=252 \\ 131+19x=252\ ;\quad \therefore x=6 \end{array}\right.$$

Thus compound of xenon with fluorine is **XeF_6**

26. (I) Given $P = 1$ atm, $w = 12$ g; $T = (t + 273)$K; $V = V$ litre
(II) If $T = t + 10 + 273 = t + 283$ K ; $V = V$ litre,

$$P = 1+\frac{10}{100}=1.1 \text{ atm}$$

Using gas equation, $PV = \frac{w}{m}RT$

Case I. $1\times V = \frac{12}{m}R(t+273)$ ... (1)

Case II. $1.1\times V = \frac{12}{m}R(t+283)$ ...(2)

From (1) and (2), $t = -173$°C or $t = \mathbf{100\ K}$

Also from (1), on substituting t and m (120), $V = \mathbf{0.82\ litre}$

27. van der Waals' equation for one mole of a gas is

$$\left[P+\frac{a}{V^2}\right](V-b)=RT \qquad ...(1)$$

Given that volume occupied by CO_2 molecules, 'b' = 0

Hence, (1) becomes $\left[P+\frac{a}{V^2}\right]V = RT$ or $P = \frac{RT}{V}-\frac{a}{V^2}$

Using $R = 0.082$, $T = 273$K, $V = 22.4$ l for 1 mole of an ideal gas at 1 atm pressure.

$$\therefore P=\frac{0.082\times 273}{22.4}-\frac{3.592}{(22.4)^2}=\mathbf{0.9922\ atm.}$$

28. We know that, Compressibility factor , $Z = \frac{PV}{RT}$

$$0.5=\frac{100\times V}{0.082\times 273} \qquad \therefore V = 0.1119L$$

NOTE : Further when volume of a gas molecule is negligible, van der Waal's equation becomes

$$\left(P+\frac{a}{V^2}\right)(V-0)=RT$$

or $PV = RT - \frac{a}{V}$ or $a = RTV - PV^2$

Substituting the values
$a = (0.082 \times 0.1119 \times 273) - (100 \times 0.1119 \times 0.1119)$
= **1.253 atm L^2 mol^{-2}**

29. (a) $d = 0.36$ kg m^{-3} = 0.36 g/L

(i) From Graham's Law of diffusion

$$\frac{r_v}{r_{O_2}}=\sqrt{\frac{M_{O_2}}{M_v}};\ 1.33=\sqrt{\frac{32}{M_v}}$$

$$\therefore M_v=\frac{32}{(1.33)^2}=\mathbf{18.09};$$

where $M_v = MW$ of the vapour

(ii) Thus, $0.36\text{g} = \frac{0.36}{18.09}$ mol

$\frac{0.36}{18.09}$ mol occupies 1 L volume, so 1 mol occupies

$\frac{18.09}{0.36}$ L = 50.25L

Thus, molar volume of vapour = **50.25 L**

Assuming ideal behaviour the volume of the vapour can be calculated by

$$\frac{V_1}{T_1}=\frac{V_2}{T_2}\Rightarrow V_2=22.4\times\frac{500}{273}=\mathbf{41.025L}$$

(iii) Compressibility factor (Z)

$$=\frac{(PV)_{\text{obs}}}{(PV)_{\text{ideal}}}=\frac{1\times 50.25}{1\times 41.025}=\mathbf{1.224}$$

(iv) Z is greater than unity, hence it is the short range repulsive force that would dominate.
($\because$ actual density is less than given density)

(b) $$E = \frac{3}{2}KT = \frac{3}{2}\times\frac{8.31}{6.02\times10^{23}}\times100$$
$$= \mathbf{2.07\times10^{-20}\ J\ per\ molecule}$$
($\because$ K, Boltzmann constant = R/N)

30. TIPS/Formulae :

$$C_{rms} = \sqrt{\frac{3RT}{M}},\ C_{av} = \sqrt{\frac{8RT}{\pi M}}$$

$$\frac{C_{rms}}{C_{av}} = \sqrt{\frac{3RT}{M}}\times\sqrt{\frac{\pi M}{8RT}} = \sqrt{\frac{3\pi}{8}} = 1.085$$

$$C_{rms} = 1.085\times C_{av} = 1.085\times400 = \mathbf{434\ ms^{-1}}$$

31. The van der Waal equation (for one mole) of a real gas is

$$\left(P+\frac{a}{V_m^2}\right)(V_m-b) = RT\ ;\ PV_m - Pb + \frac{a}{V_m} - \frac{ab}{V_m^2} = RT$$

$$PV_m = RT + Pb - \frac{a}{V_m} + \frac{ab}{V_m^2} \qquad ...(i)$$

NOTE THIS STEP : To calculate the intercept $P\to0$, hence $V_m\to\infty$ due to which the last two terms on the right side of the equation (i) can be neglected.

$\therefore PV_m = RT + Pb$

When $P = 0$, intercept = $\boldsymbol{RT}$

F. Match The Following

1. **(A) : (p) and (s)** Because 200 atm pressure is very large. For H_2 gas, at very high pressure $Z > 1$.

(B) : (r) Since $P\sim0$, it means very low presure, so ideal behaviour is observed.

(C) : (p) and (q) Since P is 1 atm, Z for CO_2 would be less than 1.

(D) : (r) In real gas with very high molar volume, molecules will be very far apart from each other due to which van der Waal's forces as well as actual volume occupied by molecules will be negligible.

G. Comprehension Based Questions

1. **(c)** According to Graham's law of diffusion, if all conditions are identical,

$$r = \frac{1}{\sqrt{M}}$$

As in this question, all conditions are identical for X and Y, then

$$\frac{r_x}{r_y} = \sqrt{\frac{M_y}{M_x}}$$

$$\frac{d}{24-d} = \sqrt{\frac{40}{10}} = 2$$

$\Rightarrow d = 48 - 2d \Rightarrow 3d = 48 \Rightarrow d = 16\ cm$

2. **(d)** The general formula of mean free path (λ) is

$$\lambda = \frac{RT}{\sqrt{2}\pi d^2 N_A p}$$

(d = diameter of molecule, p = pressure inside the vessel)

Since d and p are same for both gases, ideally their λ are same. Hence it must be the higher drift speed of X due to which it is facing more collisions per second with the inert gas in comparison to gas Y. Hence X faces more resistance from inert gas than Y and hence covers lesser distance than that predicted by Graham's law.

H. Assertion & Reason Type Questions

1. **(a)** 'a' indicates the magnitude of the attractive forces among the gas molecules, which increases in NH_3 due to H-bonding.

2. **(a)** At constant volume.

$P\propto T$ (from $PV = nRT$)

$$U_{rms} = \sqrt{\frac{3RT}{M}} \quad \therefore \quad U_{rms}\propto\sqrt{T} \qquad ......(i)$$

Collision frequency is directly proportional to U_{rms}.

Thus collision frequency $\propto\sqrt{T}$

Hence, on increasing the collosion pressure, increases frequency.

I. Integer Value Correct Type

1. $$v_{rms}\text{ of X} = \sqrt{\frac{3RT_x}{M_x}}\ ;\ v_{mp}\text{ of Y} = \sqrt{\frac{2RT_y}{M_y}}$$

Given $v_{rms} = v_{mp} \Rightarrow \sqrt{\frac{3RT_x}{M_x}} = \sqrt{\frac{2RT_y}{M_y}}$

$$\Rightarrow M_y = \frac{2RT_yM_x}{3RT_x} = \frac{2\times60\times40}{3\times400} = 4$$

2. **7**

$P_{He} = 1 - 0.68 = 0.32$ atm, $n = 0.1$

$$V = \frac{nRT}{P} = \frac{0.1\times0.0821\times273}{0.32} = 7$$

3. **(4)** Diffusion coefficient $\propto\lambda\mu$

Since $\lambda\propto\frac{T}{P}$ and $\mu\propto\sqrt{T}$

$\therefore$ Diffusion coefficient $\propto\frac{T\sqrt{T}}{P}$

Thus $$\frac{D_i}{D_f} = \frac{\frac{T\sqrt{T}}{P}}{\frac{4T\sqrt{4T}}{2P}} = \frac{1}{(4\times2)/2} = \frac{1}{4} \quad\text{or}\quad \frac{D_f}{D_i} = \frac{4}{1}$$

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1. **(c)** PV = nRT (number of moles = n/V) $\therefore$ n/V = P/RT.

2. **(c)** Value of gas constant

$$(R) = 0.0821\,L\,atm\,K^{-1}\,mol^{-1}$$
$$= 8.314 \times 10^7\,ergs\,K^{-1}mol^{-1}$$
$$= 8.314\,JK^{-1}mol^{-1} = 1.987\,cal\,K^{-1}\,mol^{-1}$$

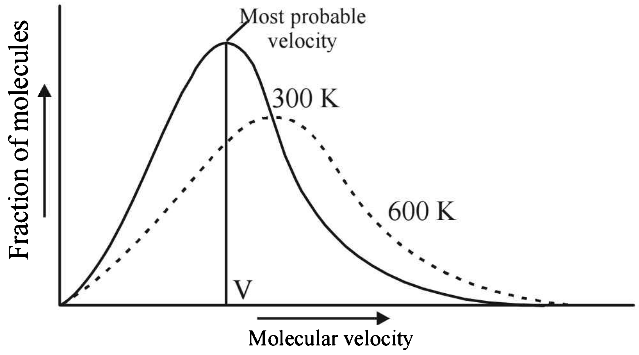
3. **(d)** Kinetic theory of gases proves all the given gas laws.

4. **(b)** According to kinetic theory the gas molecules are in a state of constant rapid motion in all possible directions colloiding in a random manner with one another and with the walls of the container and between two successive collisions molecules travel in a straight line path but show haphazard motion due to collisions.

5. **(a)**
$$\frac{\text{K.E of neon at }40°C}{\text{K.E of neon at }20°C} = \frac{\frac{3}{2}K \times 313}{\frac{3}{2}K \times 293} = \frac{313}{293}$$

6. **(a)** In van der waals equation 'b' is for volume correction

7. **(c)** Distribution of molecular velocities at two different temperature is given shown below.



NOTE : At higher temperature more molecules have higher velocities and less molecules have lower velocities.

As evident from fig. thus it is clear that With the increase in temperature the most probable velocity increase butthe fraction of such molecules decreases.

8. **(d)** From the ideal gas equation :

$$PV = nRT \text{ or } n = \frac{PV}{RT} = \frac{3170 \times 10^{-3}}{8.314 \times 300} = 1.27 \times 10^{-3}$$

9. **(d)** The value of a is a measure of the magnitude of the attractive forces between the molecules of the gas. Greater the value of 'a', larger is the attractive intermolecular force between the gas molecules.

The value of b related to the effective size of the gas molecules. It is also termed as excluded volume.

The gases with higher value of a and lower value of b are more liquefiable, hence for Cl_2 "a" should be greater than for C_2H_6 but for it b should be less than for C_2H_6.

10. **(c)** $\left(P + \frac{a}{V^2}\right)(V - b) = RT$ at high pressure $\frac{a}{V^2}$ can be neglected

$$PV - Pb = RT \quad \text{and} \quad PV = RT + Pb$$
$$\frac{PV}{RT} = 1 + \frac{Pb}{RT}$$
$$Z = 1 + \frac{Pb}{RT};\ Z > 1 \text{ at high pressure}$$

11. **(c)** Most probable speed $(C^*) = \sqrt{\frac{2RT}{M}}$

Average Speed $(\bar{C}) = \sqrt{\frac{8RT}{\pi M}}$

Root mean square velocity $(c) = \sqrt{\frac{3RT}{M}}$

$$C^* : \bar{C} : C = \sqrt{\frac{2RT}{M}} : \sqrt{\frac{8RT}{\pi M}} : \sqrt{\frac{3RT}{M}}$$
$$= 1 : \sqrt{\frac{4}{\pi}} : \sqrt{\frac{3}{2}} = 1 : 1.128 : 1.225$$

12. **(b)** Compressibility factor $(Z) = \frac{PV}{RT}$

(For one mole of real gas)
van der Waals equation

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

At low pressure, volume is very large and hence correction term b can be neglected in comparison to very large volume of V.

i.e. $V - b \approx V$

$$\left(P + \frac{a}{V^2}\right)V = RT\ ;\ PV + \frac{a}{V} = RT$$
$$PV = RT - \frac{a}{V}\ ;\ \frac{PV}{RT} = 1 - \frac{a}{VRT}$$

Hence, $\boxed{Z = 1 - \frac{a}{VRT}}$

13. **(b)** Number of moles of $O_2 = \frac{w}{32}$

Number of moles of $N_2 = \frac{4w}{28} = \frac{w}{7}$

$\therefore$ Ratio $= \frac{w}{32} : \frac{w}{7} = 7 : 32$

14. **(b)** Hydrogen bond is a type of strong electrostatic dipole-dipole interaction and dependent on the inverse cube of distance between the molecular ion-dipole interaction $\propto \frac{1}{r^3}$.

15. **(a)** For a given mass of an ideal gas, the volume and amount (moles) of the gas are directly proportional if the temperature and pressure are constant. i.e

$V \propto n$

Hence in the given case.

Initial moles and final moles are equal $(n_T)_i = (n_T)_f$

$$\frac{P_iV}{RT_1} + \frac{P_iV}{RT_1} = \frac{P_fV}{RT_1} + \frac{P_fV}{RT_2}$$
$$2\frac{P_i}{T_1} = \frac{P_f}{T_1} + \frac{P_f}{T_2} \Rightarrow P_f = \frac{2\,P_iT_2}{T_1 + T_2}$$