

Chapter 3: Gaseous and Liquid State

Review Questions

1. A gas occupies a volume of 3.86 L at 0.750 atm. At what pressure will the volume be 4.86 L?

Solution

Applying $p_1V_1 = p_2V_2$ at constant temperature T .

Given that $p_1 = 0.750$ atm, $V_1 = 3.86$ L, $V_2 = 4.86$ L. Now, p_2 can be found as

$$p_2 = \frac{p_1V_1}{V_2} = \frac{0.75 \times 3.86}{4.86} = 0.6 \text{ atm}$$

2. What is the volume of the gas in a balloon at -195°C if the balloon has been filled to a volume of 5.0 L at 25°C ?

Solution

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

So, $V_2 = \frac{V_1T_2}{T_1} = \frac{5 \times 273}{298} = 4.57 \text{ L}$

3. A highly viscous liquid was heated from 10°C to 14°C . What will be the percent decrease in viscosity?

Solution

It has been observed that the decrease in viscosity is about 2% per degree rise of temperature. So, for 4 degree rise of temperature, decrease in viscosity will be $2\% \times 4 = 8\%$

4. Decide which law predicts the behavior of gas in each of the following conditions:

- A balloon in the winter being moved from indoors to outdoors.
- A car tire pressure fluctuating over the course of a year.
- Dry ice being used in a fog machine to cover a stage with mist.
- Piston movement in an internal combustion engine.

Solution

- Volume is affected by temperature: Charles's law.
- Tyre pressure is affected by temperature: Gay-Lussac's law.
- Volume is determined by the number of moles at constant T and p : Avogadro's law.
- The piston moves from an increase in temperature and internal pressure: combined gas law.

5. Which of the following substances can be liquefied just by compression at room temperature? Give the condition necessary for liquefaction for the other gases.

Substance	Critical Temperature (K)	Critical Pressure (atm)
Nitrogen	126	33.5
Ethanol	516	63
Butane	272.5	38
Sulphur dioxide	431	78

Solution

Ethanol and sulphur dioxide as their temperature is well above the room temperature.

6. Between H_2 and O_2 , which will move with a higher speed? Calculate the temperature at which the speed of oxygen equals that of hydrogen at 40 K.

Solution

H_2 being lighter will move with higher speed at 40 K.

7. NaCl is soluble in H_2O but is not soluble in CCl_4 . Explain why on the basis of ion-dipole interactions.

Solution

When NaCl is dissolved in water, the polar water molecules are attracted toward Na^+ ions as well as toward Cl^- ions, a process called hydration of ions. Hence, NaCl is soluble in water. CCl_4 , being non-polar, cannot interact with Na^+ and Cl^- ions. Hence, NaCl is insoluble in CCl_4 .

8. Give two practical applications indicating the useful property of incompressibility in liquids.

Solution

When you “step on the brakes” of a car, for example, you rely on the incompressibility of the brake fluid to transmit the pressure you apply with your foot to the brake shoes on the wheels. The incompressibility of liquids is also the foundation of the engineering science of *hydraulics*, which uses fluids to transmit forces that lift or move heavy objects.

9. Differentiate between a barometer and a manometer?

Solution

Barometer is used for the measurement of atmospheric pressure, whereas manometer is used for the measurement of pressure of the gas.

10. What volume of “wet” methane would you have to collect at 20.0 °C and 742 mm Hg to be sure that the sample contains 244 mL of dry methane (also at 742 mm Hg)?

Solution

The vapor pressure of water at 20°C is 17.54 mm Hg. Thus, only $(742 - 17.54) = 724$ mm Hg is due to “dry” methane. In other words, the fraction of the wet methane sample, that is, pure methane is $724/742 = 0.976$.

Volume “wet” methane $\times 0.976 = 244$ mL

Volume “wet” methane = $244 \text{ mL} / 0.976 = 250$ mL

In other words, one must collect 250 total mL of “wet methane” gas in order to have collected the equivalent of 244 mL of pure methane.

11. Using Boyle’s law and Charles’ law, derive combined gas law.

Solution

Let us assume a gas whose volume changes from V_1 to V_2 , pressure changes from p_1 to p_2 , and temperature changes from T_1 to T_2 . Now, let us suppose that the volume of a given mass of a gas changes from V_1 to V when the pressure changes from p_1 to p_2 at constant temperature T_1 (Fig. 1).

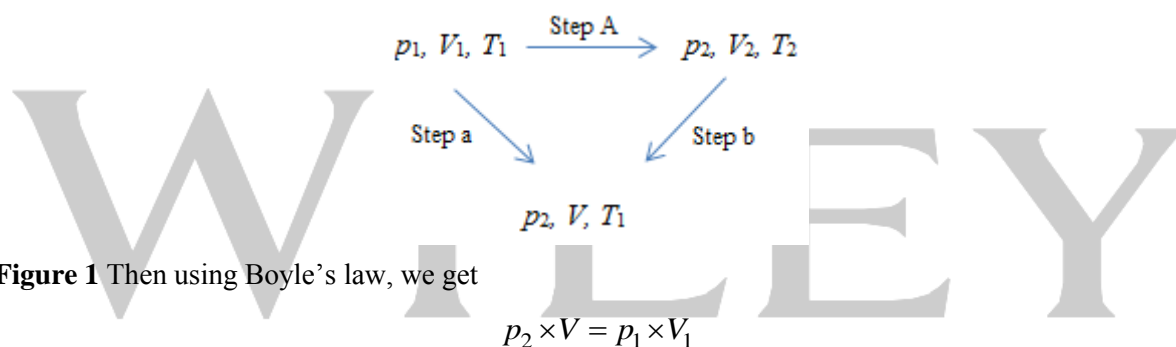


Figure 1 Then using Boyle’s law, we get

or
$$V = \frac{p_1 \times V_1}{p_2} \tag{1}$$

Assuming that volume changes from V to V_2 when the temperature changes from T_1 to T_2 at constant pressure p_2 , we get

$$\frac{V}{T_1} = \frac{V_2}{T_2} \Rightarrow V_2 = V \left(\frac{T_2}{T_1} \right)$$

Putting the value of V from Eq. (1), we have

$$V_2 = \frac{p_1 V_1}{p_2} \times \left(\frac{T_2}{T_1} \right)$$

$$\frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2}$$

This equation is known as combined gas law.

12. Why do N_2O and CO_2 have the same rate of diffusion under same conditions of temperature and pressure?

Solution

Both N_2O and CO_2 have the same molar mass ($= 44 \text{ g mol}^{-1}$). According to Graham's law of diffusion, rates of diffusion of different gases are inversely proportional to the square root of their molar masses under the same conditions of temperature and pressure.

13. What would happen to a balloon if the collisions between gas molecules were not perfectly elastic? What would happen to a balloon if the gas molecules were in a state of constant motion but the motion was not random?

Solution

If the collisions between gas molecules were not perfectly elastic, the gas particles would "stick" together causing the result of a lesser effective pressure. Accordingly, the balloon would have to diminish in size, all other factors being equal. If the gas molecules in a balloon were in a state of constant motion and the motion was not random, the balloon would not appear smoothly rounded. It would be elongated in the direction of the predominating motion and contracted in the other directions.

14. Compare the rates of diffusion of ${}^{235}_{6}\text{UF}$ and ${}^{238}_{6}\text{UF}$.

Solution

Molecular mass of ${}^{235}_{6}\text{UF} = 235 + 6 \times 19 = 349$

Molecular mass of ${}^{238}_{6}\text{UF} = 238 + 6 \times 19 = 352$

According to Graham's law of diffusion,

$$\frac{r_1({}^{235}_{6}\text{UF})}{r_2({}^{238}_{6}\text{UF})} = \left(\frac{M_2}{M_1}\right)^{1/2} = \left(\frac{352}{349}\right)^{1/2} = \frac{1.004}{1}$$

15. CO_2 is heavier than O_2 and N_2 gases present in the air, but it does not form the lower layer of the atmosphere. Why?

Solution

Gases possess the property of diffusion that is independent of the force of gravitation. Due to diffusion, the gases mix into each other and remain almost uniformly distributed in the atmosphere.

16. The molecular speeds of gaseous molecules are analogous to those of rifle bullets. Then why is the odor of a gas not detected so fast?

Solution

Although the molecules of a gas travel at high speeds, they do not travel in straight lines in one direction like bullets. As they travel, they collide with the molecules of the gases present in the air. As result, they are deflected. Thus, they follow a zig-zag path, that is, the net distance travelled in a particular direction is quite small in a given time. That is why the odor is not detected so fast.

17. What is the ratio of average kinetic energy of oxygen molecules to that of ozone molecules at 27°C?

Solution

Average kinetic energy of any gas depends only on temperature and not on the nature of the gas. Hence, both the gases will have same average kinetic energy at 27°C, that is, the ratio will be 1:1.

18. Differentiate between total kinetic energy and translational kinetic energy? For what type of molecules, are the two equal?

Solution

Total kinetic energy is the sum of translational, vibrational, and rotational kinetic energies. The total kinetic energy is equal to the translational kinetic energy for monoatomic gases as they do not possess vibrational and rotational motion but only have translational motion.

19. Out of N₂ and NH₃, which one will have greater value for van der Waals constant “*a*” and which one will have greater value for van der Waals constant “*b*”?

Solution

As NH₃ is more easily liquefiable (due to hydrogen bonding), intermolecular forces of attraction are stronger than in N₂. Hence, NH₃ will have greater value of “*a*”. The value of *b* depends on the molecular size. As NH₃ molecule is larger in size than N₂, hence, NH₃ will have greater value for “*b*”.

20. The critical temperature (*T_C*) and critical pressure (*p_C*) of CO₂ are 30.98°C and 73 atm, respectively. Can CO₂(g) be liquefied at 32°C and 80 atm pressure?

Solution

No, CO₂ cannot be liquefied at 32°C because this temperature is above its critical temperature.

21. Why are falling liquid drops spherical?

Solution

This is due to property of surface tension possessed by the liquids. This makes the surface area minimum. For a given volume, sphere has the minimum surface area.

22. What happens if a liquid is heated to the critical temperature of its vapors?

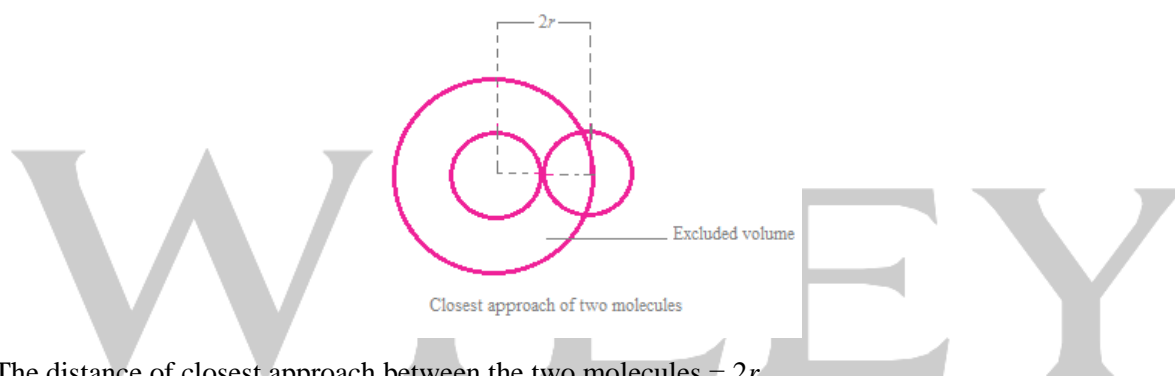
Solution

When a liquid is heated to the critical temperature of its vapor, then the surface tension of the liquid becomes zero and the meniscus between the liquid and the vapor disappears.

23. Prove that the excluded volume “ b ” is four times the actual volume of the gas molecules.

Solution

Assume molecules to be spheres with radius r . The volume of molecule = $4\pi r^3/3$.



The distance of closest approach between the two molecules = $2r$.

Since two molecules cannot come closer than distance $2r$, thus,

Excluded volume per pair of molecules in binary collision = Volume of sphere of radius $2r$

The volume of sphere of radius $2r$ is

$$\frac{4}{3}\pi(2r)^3 = 8 \times \frac{4\pi r^3}{3}$$

So,

$$\text{Excluded volume per molecule } (b) = \frac{1}{2} \left[8 \times \frac{4\pi r^3}{3} \right] = 4 \times \frac{4\pi r^3}{3} = 4 \times \text{volume of one molecule}$$

Numerical Problems

1. How many number of moles and molecules of O_2 are there in 64 g O_2 ? What is the mass of one molecule of O_2 ?

Solution

Let x be the number of molecules.

Number of moles $n = \text{Mass}/\text{Molar mass} = 64/32 = 2$

Now, $n = \text{Number of molecules}/\text{Avogadro's number}$

Substituting values, we get

$$2 = \frac{x}{6.023 \times 10^{23}}$$

or $x = 12.04 \times 10^{23}$

Therefore, there are 12.04×10^{23} molecules in 64 g O_2 . Again,

$$\frac{\text{Number of molecules}}{\text{Avogadro's number}} = \frac{\text{Mass}}{\text{Molar mass}}$$

$$\frac{1}{6.023 \times 10^{23}} = \frac{\text{Mass}}{32}$$

Mass of one molecule of $\text{O}_2 = 5.313 \times 10^{-23}$

2. Two moles of ammonia occupied a volume of 5 L at 27°C . Calculate the pressure of the gas if it obeys van der Waals equation given $a = 4.17 \text{ atm L}^2 \text{ mol}^{-1}$ and $b = 0.037 \text{ L mol}^{-1}$.

Solution

Using van der Waals equation, we get

$$\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT$$
$$\left(p + \frac{4.17 \times 4}{5 \times 5}\right)(5 - 2 \times 0.037) = 2 \times 0.0821 \times 300$$

Solving, we get $p = 9.33 \text{ atm}$

3. A gaseous system has a volume of 580 cm^3 at a certain pressure. If its pressure is increased by 0.96 atm, its volume becomes 100 cm^3 . Determine the pressure of the system.

Solution

Using Boyle's law, we get

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

Let $P_1 = x$, then $P_2 = x + 0.96$

$$\frac{x}{x + 0.96} = \frac{580}{100}$$

or $x = 1.16$. Hence, $p_{\text{sys}} = 1.16 - 0.96 = 0.2 \text{ atm}$

4. A balloon filled with helium raises to a certain height at which it gets fully inflated to a volume of 1×10^5 L. If at this altitude temperature and atmospheric pressure is 268 K and 2×10^{-3} atm, respectively, what weight of helium is required to fully inflate the balloon?

Solution

Using ideal gas equation, we get

$$pV = nRT$$

or
$$n = \frac{PV}{RT} = \frac{2 \times 10^{-3} \times 10^5}{0.0821 \times 268} = 9.09$$

Now, $n = \text{Mass/Molar mass}$. Substituting values, we get

$$9.09 = \frac{x}{4} \Rightarrow x = 36.36 \text{ g}$$

5. Time taken to diffuse 40 mL of oxygen gas is 20 s. Calculate the time required to diffuse 120 mL of CH_4 ?

Solution

or
$$\frac{V_{\text{O}_2}}{V_{\text{CH}_4}} \times \frac{t_{\text{CH}_4}}{t_{\text{O}_2}} = \left(\frac{M_{\text{CH}_4}}{M_{\text{O}_2}} \right)^{1/2}$$

$$\frac{40}{120} \times \frac{20}{t} = \left(\frac{16}{32} \right)^{1/2}$$

$t = 9.43 \text{ s.}$

6. Compressibility factor (Z) for N_2 at -50°C and 800 atm pressure is 1.95. Calculate the number of moles of N_2 gas required to fill a gas cylinder of 100 mL capacity under the given conditions.

Solution

We know that

$$Z = \frac{pV}{nRT}$$

Substituting values, we get
$$1.95 = \frac{800 \times \frac{100}{1000}}{n \times 0.0821 \times 223}$$

or $n = 2.24$.

7. A balloon blown up has a volume of 500 mL at 5°C . The volume is decreased to seven-eighth of its maximum stretching capacity.

(a) Will it burst at 30°C

(b) Calculate the minimum temperature above which it will burst.

Solution

(a) No, the balloon would not burst.

(b) Applying Charles' law, we get

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$
$$\frac{500}{278} = \frac{500 - (7/8)500}{T_2}$$

or $T_2 = 243.75$.

Therefore, the temperature above which the balloon will burst is $278 - 243.75 = 34.75$ K.

8. 1.0 L of a mixture of CO and CO₂ is taken. The mixture is passed through the tube containing red hot charcoal. The volume now becomes 1.6 L measured under the same conditions. Find the composition of the mixture by volume.

Solution

The reaction involved is the reduction of CO₂(g) with C(s)



The CO(g) already present in the mixture remains as such.

Let the volume of CO in the mixture be V liter, so the amount of CO₂ = $1 - V$ liters

From the above reaction, we have that 1 L of CO₂ produces 2 L of CO.

So $(1 - V)$ liters of CO₂ would produce $2(1 - V)$ liters of CO.

Hence, the total volume after the reaction = volume of CO initially present + the volume of CO formed from CO₂

$$V_t = V + 2(1 - V)$$

Given that $V + 2(1 - V) = 1.6 \Rightarrow V + 2 - 2V = 1.6 \Rightarrow V = 0.4$ L.

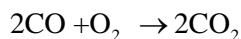
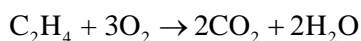
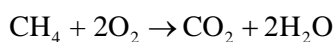
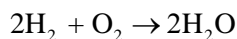
Therefore, the volume of CO₂ in the original mixture was $1 - 0.4 = 0.6$ L.

Hence, the percentage composition of CO = 40% and of CO₂ = 60%

9. A sample of coal gas contains 50% hydrogen, 30% marsh gas (CH₄), 14% carbon monoxide, and 6% ethylene. 100 mL of this coal gas is mixed with 150 mL of oxygen and mixture is exploded. What will be the volume and composition of the resulting gas when cooled to the original temperature?

Solution

The reactions of the gases in the coal gas with oxygen are as follows:



In the 100 mL of coal gas, the volume of each gas is:

$\text{H}_2 = 50 \text{ mL}$, $\text{CH}_4 = 30 \text{ mL}$, $\text{C}_2\text{H}_4 = 6 \text{ mL}$ and $\text{CO} = 14 \text{ mL}$

From the reactions we have:

2 mol of H_2 react with 1 mol of O_2 or $2 \times 22.4 \text{ mL}$ of H_2 reacts with 22.4 mL of O_2 . Therefore, oxygen used up in this reaction is

$$\frac{22.4}{44.8} \times 50 = 25 \text{ mL}$$

1 mol of CH_4 reacts with 2 mol of O_2 or 22.4 mL of CH_4 reacts with $2 \times 22.4 \text{ mL}$ of O_2 . Therefore, oxygen used up in this reaction is

$$\frac{44.8}{22.4} \times 30 = 60 \text{ mL}$$

Also, 1 mol of CH_4 generates 1 mol of CO_2 or 22.4 mL of CH_4 produces 22.4 mL of CO_2 . Therefore the volume of CO_2 formed is

$$\frac{22.4}{22.4} \times 30 = 30 \text{ mL}$$

1 mol of C_2H_4 reacts with 3 mol of O_2 or 22.4 mL of C_2H_4 reacts with $3 \times 22.4 \text{ mL}$ of O_2 . Therefore, oxygen used up in this reaction is

$$\frac{22.4 \times 3}{22.4} \times 6 = 18 \text{ mL}$$

Also, 1 mol of C_2H_4 generates 2 mol of CO_2 or 22.4 mL of C_2H_4 produces $2 \times 22.4 \text{ mL}$ of CO_2 . Therefore the volume of CO_2 formed is

$$\frac{22.4 \times 2}{22.4} \times 6 = 12 \text{ mL}$$

2 mol of CO react with 1 mol of O_2 or $2 \times 22.4 \text{ mL}$ of CO reacts with 22.4 mL of O_2 . Therefore, oxygen used up in this reaction is

$$\frac{22.4}{22.4 \times 2} \times 14 = 7 \text{ mL}$$

Also, 2 mol of CO generate 2 mol of CO₂ or 2 × 22.4 mL of CO produces 2 × 22.4 mL of CO₂.

Therefore the volume of CO₂ formed is

$$\frac{22.4 \times 2}{22.4 \times 2} \times 14 = 14 \text{ mL}$$

Therefore, the volume of CO₂ formed in the resulting mixture is 56 mL. The amount of oxygen used up is 10 mL, so amount remaining in reaction mixture is 50 mL. The volume of resulting mixture is 106 mL and composition is 47.16 % O₂ and 52.83 % CO₂.

%O₂ = 41.67% and %CO₂ = 58.33%

10. Two moles of ammonia gas are enclosed in a vessel of 5 L capacity at 27°C. Calculate the pressure exerted by the gas assuming that:

(a) the gas behaves as an ideal gas.

(b) the gas behaves as a real gas ($a = 4.17 \text{ L}^2 \text{ atm mol}^{-1}$, $b = 0.37 \text{ L mol}^{-1}$)

Solution

(a) Using ideal gas equation, we get

$$pV = nRT$$
$$p = \frac{2 \times 0.0821 \times 300}{5} = 9.85$$

(b) Using real gas equation, we get

$$\left(\frac{p + an^2}{V_2} \right) (V - nb) = nRT$$
$$\frac{p + (4.17 \times 2 \times 2)}{5 \times 5} \times (5 - (2 \times 0.37)) = 2 \times 0.0821 \times 300 = 9.32 \text{ atm}$$

11. The density of the vapor of a substance at 1 atm pressure and 500 K is 0.36 kg m⁻³. The vapor effuses through a small hole at a rate of 1.33 times faster than oxygen under the same conditions.

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

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

Solution

(a) (i) Given that $\rho = 0.36 \text{ kg m}^{-3}$. Applying Graham's law of diffusion, we get

$$\frac{r_{\text{vap}}}{r_{\text{O}_2}} = \sqrt{\frac{M_{\text{O}_2}}{M_{\text{vap}}}} \Rightarrow 1.33 = \sqrt{\frac{32}{M_{\text{vap}}}} \Rightarrow M_{\text{vap}} = 18.09 \text{ g mol}^{-1}$$

(ii) 18.09 g of vapor will have volume = $\frac{1}{0.36 \times 18.09} = 50.25 \text{ L}$

(iii) $Z = \frac{pV}{nRT} = \frac{1 \times 50.25}{1 \times 0.0821 \times 500} = 1.224$

(iv) As $Z > 1$, the repulsive forces will dominate.

(b) Translational kinetic energy = $\frac{3}{2}kt = \frac{3}{2} \times 1.38 \times 10^{-23} \times 1000 = 2.07 \times 10^{-20} \text{ J molecule}^{-1}$

12. Calculate the compressibility factor for CO_2 if 1 mol of it occupies 0.4 L at 300 K and 40 atm. Comment on the result.

Solution

$$Z = \frac{pV}{nRT} = \frac{40 \times 0.4}{1 \times 0.0821 \times 300} = 0.6496$$

13. Two gases A and B having molecular weights 60 and 45, respectively, are enclosed in a vessel. The weight of A is 0.50 g and that of B is 0.2 g. The total pressure of the mixture is 750 mm Hg. Calculate the partial pressure of the two gases.

Solution

Using Dalton's law, we get

$$p_1 = x_1 p_{\text{total}}$$

Now,

$$x_1 = \frac{0.50 / 60}{(0.50 / 60) + (0.2 / 45)} = 0.654$$

as $x_1 + x_2 = 1$, we have $x_2 = 0.346$.

So, $p_1 = 0.651 \times 750 = 490.5 \text{ mm Hg}$

$$p_2 = x_2 p_{\text{total}} = 0.3485 \times 750 = 259.5 \text{ mm Hg}$$

14. A container has SO_2 gas at 2 atm pressure in a vessel of V L capacity. If the number of moles of SO_2 is doubled in the same container at the same temperature and volume, calculate the new pressure in the container.

Solution

Given that $p_1 = 2 \text{ atm}$; $V_1 = V$; $n_1 = n$; $n_2 = 2n$; $V_2 = V$. Using combined law, we get

$$\frac{p_1 V_1}{n_1} = \frac{p_2 V}{n_2}$$

$$2 \times \frac{V}{n} = p \times \frac{V}{2n}$$

or $p = 4$ atm.

15. A tank is filled with gas to a pressure of 5 atm at 10°C. The safety valve on the tank is set for 10 atm pressure. To what temperature must the tank be heated in order for the gas to be below the safety valve?

Solution

Given that $p_1 = 5$ atm; $T_1 = 283$ K; $p_2 = 10$ atm. $T_2 = ?$

Using Gay-Lussac's law, we get

$$\frac{p_1}{T_1} = \frac{p_2}{T_2}$$

$$\frac{5}{283} = \frac{10}{T_2}$$

or $T_2 = 566$ K.

16. The compressibility factor for CO₂ gas at 273 K and 100 atm pressure is 0.2005. Calculate the volume occupied by 0.2 mol of CO₂ at 100 atm and 273 assuming (a) ideal gas nature and (b) real gas nature.

Solution

(a) Using ideal gas equation, we get

$$pV = nRT$$

$$V = \frac{nRT}{p} = \frac{0.2 \times 0.0821 \times 273}{100} = 44.82 \text{ mL}$$

(b) Real gas nature

$$Z = \frac{pV}{nRT}$$

$$0.2005 = \frac{100 \times V}{0.2 \times 0.0821 \times 273}$$

$$V = 8.98 \text{ mL}$$

17. The density of the mixture of nitrogen and oxygen is 1.15 g L⁻¹ at 750 mm Hg at 27°C. Calculate the percentage composition of these gases in the mixture. Assume the gases behave ideally.

Solution

The mass of nitrogen and oxygen is

$$m = \frac{dRT}{p} = \frac{1.15 \times 0.0821 \times 300}{\frac{750}{760}} = 28.72 \text{ g}$$

Let the percentage of N_2 be x . Then percentage of $O_2 = 100 - x$.

Therefore,

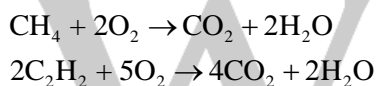
$$28.72 = \frac{x \times 28 + (100 - x) \times 32}{100}$$

Solving, we get $x(N_2) = 82.44\%$ and $\%O_2 = 17.5\%$.

18. 100 mL of mixture of methane and acetylene was exploded with excess of oxygen. After explosion and cooling the mixture was treated with KOH, when the reduction 135 mL was observed. Find the volumetric composition of the mixture. All the volumes are measured at the same temperature and pressure.

Solution

The reactions of the methane and acetylene with oxygen are:



Let the volume of methane in the mixture be x , then the volume of acetylene is $100 - x$.

From the reactions, we have

1 mol of CH_4 generates 1 mol of CO_2 or 22.4 mL of CH_4 produces 22.4 mL of CO_2 . Therefore the volume of CO_2 formed is

$$\frac{22.4}{22.4} \times x = x \text{ mL}$$

Also, 2 mol of C_2H_2 generates 4 mol of CO_2 or 2×22.4 mL of CH_4 produces 4×22.4 mL of CO_2 .

Therefore the volume of CO_2 formed is

$$\frac{4 \times 22.4}{2 \times 22.4} \times (100 - x) = 2(100 - x) \text{ mL}$$

The amount of CO_2 formed reacts with KOH and corresponds to the reduction in volume of the mixture. Therefore,

$$x + 2(100 - x) = 135 \text{ mL}$$

$$\Rightarrow x = 65 \text{ mL}$$

Thus the percentage composition of the mixture is

$$\% \text{CH}_4 = 65\% \text{ and } \% \text{C}_2\text{H}_2 = 35\%$$

19. Calculate the volume occupied by 4.0245×10^{23} molecules of O_2 at $27^\circ C$ having pressure of 700 torr.

Solution

Using ideal gas equation, we get

$$pV = nRT$$

$$n = \frac{4.0245 \times 10^{23}}{6.023 \times 10^{23}}$$

$$V = \frac{nRT}{p} = \frac{4.0245 \times 10^{23} \times 0.0821 \times 300}{6.023 \times 10^{23} \times \frac{700}{760}} = 17.87 \text{ dm}^3$$

20. Calculate the moles, molecules, and weight of hydrogen gas contained in a 10 L flask at a pressure of 75 cm Hg and at temperature $25^\circ C$.

Solution

Using ideal gas equation, we get

$$pV = nRT$$

$$n = \frac{pV}{RT} = \frac{10 \times \frac{750}{760}}{0.0821 \times 298} = 0.4$$

But $n = \frac{\text{Number of molecules}}{\text{Avogadro's number}}$

Now, Number of molecules = $0.4 \times 6.023 \times 10^{23} = 2.4 \times 10^{23}$

As $n = \frac{\text{Mass}}{\text{Molar mass}}$, we have $0.4 = \frac{\text{Mass}}{2} \Rightarrow \text{Mass} = 0.8 \text{ g}$

21. The compressibility factor for a given real gas is 0.927 at 273 K and 100 atm. Calculate the amount of O_2 required to fill a gas cylinder of 100 L capacity under given conditions (molecular weight of gas = 30).

Solution

$$Z = \frac{pV}{nRT} \Rightarrow 0.927 = \frac{100 \times 100}{n \times 0.0821 \times 273}$$

Given that $n = 481.298$, so

$$n = \frac{\text{Mass}}{\text{Molar mass}} \Rightarrow \text{Mass} = 481.298 \times 30 = 14.439 \text{ kg}$$

22. The density of oxygen at STP is $0.00143 \text{ g mL}^{-1}$. Find the rms velocity, average velocity, and most probable velocity.

Solution

We know that:

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3p}{d}} \quad (\text{using } pV = RT \text{ for 1mol of gas and } M = d \times V)$$

$$u_{\text{avg}} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8p}{\pi d}}$$

$$u_{\text{mp}} = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2p}{d}}$$

At STP, pressure is 1 atm and given that $d = 0.00143 \text{ g/mL}$, we have

$$u_{\text{rms}} = \left(\frac{3p}{d}\right)^{1/2} = \left(\frac{3 \times 1}{0.00143}\right)^{1/2} = 45.80$$

$$u_{\text{most probable}} = \left(\frac{2p}{d}\right)^{1/2} = \left(\frac{2 \times 1}{0.00143}\right)^{1/2} = 37.39$$

$$u_{\text{avg}} = \left(\frac{8p}{\pi \times d}\right)^{1/2} = \left(\frac{8 \times 1}{3.14 \times 0.00143}\right)^{1/2} = 42.16$$

Therefore, $u_{\text{rms}} = 45.80 \text{ m s}^{-1}$; $u_{\text{avg}} = 42.16 \text{ m s}^{-1}$; $u_{\text{mp}} = 37.39 \text{ m s}^{-1}$

23. Calculate the volume correction and pressure correction for 4.4 g CO_2 kept in 1 L flask. Given $a = 3.6 \text{ atm L}^2 \text{ mol}^{-2}$ and $b = 0.04 \text{ L mol}^{-1}$ for CO_2 .

Solution

We have $n = 4.4/44 = 0.1$. So,

$$\text{Volume correction} = nb = 0.1 \times 0.04 = 0.004 \text{ L}$$

$$\text{Pressure correction} = \frac{an^2}{V^2} = \frac{3.6 \times 0.1 \times 0.1}{1 \times 1} = 0.036 \text{ atm}$$

24. Two bulbs A and B of equal capacity are filled with He and SO_2 , respectively, at the same temperature.

(a) If the pressure in the two bulbs is same, what will be the ratio of the velocities of the molecules of two gases?

(b) At what temperature will the velocity of SO_2 molecules become half of the velocity of the He molecules at 27°C ?

(c) How will the velocities be affected if the volume of B becomes four times that of A?

(d) How will the velocities be affected if half of the molecules of SO_2 are removed from B?

Solution

$$(a) \frac{v_1}{v_2} = \left(\frac{M_2}{M_1}\right)^{1/2} = \left(\frac{64}{4}\right)^{1/2} = 4$$

(b) Let $v_1 = x$, then $v_2 = x/2$

$$\text{Therefore, } \frac{v_1}{v_2} = \left(\frac{T_1 M_2}{T_2 M_1}\right)^{1/2} \Rightarrow 2 = \left(\frac{300 \times 64}{T \times 4}\right)^{1/2} \Rightarrow T = 1200 \text{ K.}$$

(c) There is no effect on volume as it does not depend on volume.

(d) There is no effect as it does not depend on number of molecules.

25. Total pressure exerted by a mixture of two gases in a container is 500 mm Hg. The pressure of the first gas is 200 mm Hg. Then calculate mole fraction of each gas and partial pressure of gas.

Solution

Using Dalton's law, we get

$$p_1 = x_1 p_{\text{total}}$$

where $x_1 = 200/500 = 0.4$. As $x_1 + x_2 = 1$, we have

$$x_2 = 1 - 0.4 = 0.6$$

So, $p_2 = x_2 p_{\text{total}} = 0.6 \times 500 = 300 \text{ mm Hg}$

26. Calculate the temperature of gas if it obeys van der Waals equation from the following data. A flask of 25 L contains 10 mol of a gas under 50 atm. Given $a = 5.46 \text{ atm L}^2 \text{ mol}^{-2}$ and $b = 0.031 \text{ L mol}^{-1}$.

Solution

Using van der Waals equation, we get

$$\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

$$\left(50 + \frac{5.46 \times 10 \times 10}{25 \times 25}\right)(25 - 10 \times 0.031) = 10 \times 0.0821 \times T$$

$$T = 1529.93 \text{ K} = 1256.93^\circ \text{C}$$

27. 10 mL of gaseous hydrocarbon are exploded with 100 mL of oxygen. The residual gas, on cooling, is found to measure 95 mL of which 20 mL are absorbed by KOH solution and the remaining by pyrogallol solution. Determine the molecular formula of hydrocarbon.

Solution

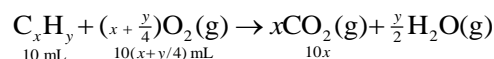
The volume of the residual gas on cooling = 95 mL = CO₂ formed + Unreacted O₂

Volume of the gas after treatment with KOH solution = Volume of CO₂ gas = 20 mL

Hence, volume of unreacted O₂ = volume of gas absorbed by pyragallol = 90 – 20 = 75 mL

or the volume of O₂ reacting = 100 – 75 = 25 mL

The reaction can be represented as



Now, $10x = 20 \Rightarrow x = 2$ and $10(x + y/4) = 25 \Rightarrow y = 2$.

Therefore, the hydrocarbon is C₂H₂.

28. A gas is contained in a closed container volume of 20 L at 300 K. If the temperature is increased by 50%, then calculate % change in volume assuming pressure is constant.

Solution

There will be a 50% increase, as T is directly proportional to V (Charles' law).

29. Pressure as low as 10^{-9} torr (1 torr = 1/760 atm) is obtained in high vacuum systems at 30°C. How many gaseous molecules per mL are present in such a vacuum?

Solution

Using ideal gas equation, we get

$$pV = nRT \Rightarrow p = n/VRT \Rightarrow n/V = p/RT$$

Therefore, the number of gaseous molecules per mL present is

$$\frac{N}{V} = \frac{10^{-9} \times 6.023 \times 10^{23}}{760 \times 0.0821 \times 10^{-3} \times 303} = 3.18 \times 10^{13}$$

30. Temperature at the foot of a mountain is 30°C and pressure is 760 mm Hg whereas at the top of the mountain these are 0°C and 710 mm Hg. Compare the densities of the air at the foot and at the top of the mountain.

Solution

The densities at the foot and the top are as follows:

$$d_{\text{foot}} = \frac{p_{\text{foot}} M}{RT_{\text{foot}}} \quad \text{and} \quad d_{\text{top}} = \frac{p_{\text{top}} M}{RT_{\text{top}}}$$

Taking their ratios, we get

$$\frac{d_{\text{foot}}}{d_{\text{top}}} = \frac{p_{\text{foot}} M}{RT_{\text{foot}}} \times \frac{RT_{\text{top}}}{p_{\text{top}} M} = \frac{760 \times 273}{303 \times 710} = \frac{0.964}{1}$$

31. The volume of 0.0227 mol of gas is 550 mL at a pressure of 1.25 atm and a temperature of 22°C.

- (a) What is the volume at 1.25 atm and 44°C?
- (b) What is the volume if 0.0115 mol of gas is added at the same T and p ?
- (c) What is the pressure at 122°C if the volume remains 550 mL?
- (d) What is the pressure at 22°C if the volume expands to 825 mL?
- (e) What is the volume when you convert to STP conditions?

Solution

(a) Using combined gas law, we get

$$\frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2}$$
$$\frac{1.25 \times 550}{295} = \frac{1.25 \times V_2}{317}$$
$$V_2 = 591.01 \text{ mL}$$

(b)

$$\frac{p_1 V_1}{n_1 T_1} = \frac{p_2 V_2}{n_2 T_2}$$
$$\frac{V_1}{0.0115} = \frac{550}{0.0227}$$
$$V_1 = 278.63 \text{ mL}$$

(c)

$$\frac{p_1}{T_1} = \frac{p_2}{T_2}$$
$$\frac{p_1}{395} = \frac{1.25}{295}$$
$$p_1 = 1.67 \text{ atm}$$

(d) $p_1 \times \frac{825}{295} = 1.25 \times \frac{550}{295}$

$$p_1 = 0.833 \text{ atm}$$

(e) $pV = nRT$

$$V = \frac{1 \times 0.0821 \times 273}{1} = 22.4 \text{ L}$$

32. Calculate the average volume available to a molecule in a sample of nitrogen gas at STP. What is the average distance between neighboring molecules if a nitrogen molecule is assumed to be spherical?

Solution

At STP, 1 mol of N₂ gas occupies 22.4 L or 22400 cm³ of volume. This means that 6.023 × 10²³ molecules of N₂ gas will occupy 22400 cm³ of volume.

So, one molecule of N₂ will occupy $\frac{22400 \text{ cm}^3}{6.023 \times 10^{23} \text{ molecules}} = 3.72 \times 10^{-20} \text{ cm}^3 \text{ molecule}^{-1}$

But, volume of a spherical object = $\frac{4}{3}\pi r^3$

and the volume available per molecule is 3.72 × 10⁻²⁰ cm³. Equating both of them, we get

$$3.72 \times 10^{-20} = \frac{4}{3}\pi r^3$$

Therefore, $r^3 = 8.88 \times 10^{-21} \text{ cm}^3 \Rightarrow r = 20.7 \times 10^{-8} \text{ cm}$

So, the average distance between the neighboring molecules = 2r = 41.4 × 10⁻⁸ cm

Additional Objective Questions

Single Correct Choice Type

1. The compressibility of a gas is less than unity at STP. Therefore, (IIT-JEE 2000)

- (A) $V_m > 22.4 \text{ L}$ (B) $V_m < 22.4 \text{ L}$ (C) $V_m = 22.4 \text{ L}$ (D) $V_m > 44.8 \text{ L}$

Solution

(B) It is given that $Z < 1$, so

$$\frac{pV}{RT} < 1 \Rightarrow pV < RT \Rightarrow V < \frac{RT}{p} \Rightarrow V < 0.0821 \times 273 \Rightarrow V < 22.4 \text{ mL}$$

2. A gaseous compound X contained 44.4% C, 51.9% N, and 3.7% H. Under the same conditions, 30 cm³ of X diffused through a pinhole in 25 s and the same volume of H₂ diffused in 4.81 s. The molecular formula of X is

- (A) C₂H₂N (B) C₂H₄N₂ (C) C₂H₂N₂ (D) C₄H₂N₂

Solution

(C) From the given data, we have

Element	Mass %	Mole %	Relative molar ratio
C	44.4	3.7	1
N	51.9	3.7	1

H	3.7	3.7	1
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So, empirical formula of X = CNH

Therefore, empirical mass = 12 + 1 + 14 = 27 g

Ratio of rate of diffusion of X and that of H₂ is given by

$$\frac{r_x}{r_{H_2}} = \sqrt{\frac{M_{H_2}}{M_x}} \Rightarrow \sqrt{\frac{2}{M_x}} = \frac{30 \times 4.81}{25 \times 30} \Rightarrow M_x = 2 \times \left(\frac{25}{4.81}\right)^2 = 54 \text{ g mol}^{-1}$$

Therefore, Molecular formula of X is C₂H₂N₂.

3. Four particles have velocities 1, 0, 2, and 3 m s⁻¹. The root mean square of the particles is (in m s⁻¹)

- (A) 3.5 (B) $\sqrt{3.5}$ (C) 1.5 (D) $\sqrt{14/3}$

Solution

$$(B) v_{\text{rms}} = \sqrt{\frac{1^2 + 0^2 + 2^2 + 3^2}{4}} = \sqrt{3.5}$$

4. A mixture of methane and ethene in the molar ratio of x:y has a mean molar mass of 20. What would be the mean molar mass if the gases are mixed in the molar ratio of y:x?

- (A) 22 g mol⁻¹ (B) 24 g mol⁻¹ (C) 20.8 g mol⁻¹ (D) 19 g mol⁻¹

Solution

$$(B) \text{ Case I: Mean molar mass} = \frac{16x + 28y}{x + y} = 20 \text{ (given)}$$

$$16x + 28y = 20x + 20y \Rightarrow y = 0.5x$$

Case II: Mean molar mass

$$\frac{16x + 28y}{x + y} = \frac{8x + 28x}{x + 0.5x} = \frac{36}{1.5} = 24$$

5. A flask of capacity 1 L contains NH₃ at 1 atm and 25°C. A spark is passed through until all the NH₃ is decomposed into N₂ and H₂. Calculate the pressure of gases left at 25°C.

- (A) 2 atm (B) 0.5 atm (C) 1.5 atm (D) 1 atm

Solution

(A) Ammonia decomposes into N₂ and H₂ completely when a spark is passed through it.

	$\text{NH}_3(\text{g}) \rightarrow \frac{1}{2}\text{N}_2(\text{g}) + \frac{3}{2}\text{H}_2(\text{g})$		
Initial pressure in atm	1	0	0
Final pressure	0	$\frac{1}{2}$	$\frac{3}{2}$

The total pressure of N_2 and H_2 after complete decomposition is given by

$$p_T = p_{\text{N}_2} + p_{\text{H}_2} = 0.5 + 1.5 = 2 \text{ atm}$$

6. The rms speed of the gas molecule at temperature 27 K and pressure 1.5 bar is $1 \times 10^4 \text{ cm s}^{-1}$. If both temperature and pressure are raised three times, the rms speed of the gas molecules will be

- (A) $9 \times 10^4 \text{ cm s}^{-1}$ (B) $3 \times 10^4 \text{ cm s}^{-1}$ (C) $\sqrt{3} \times 10^4 \text{ cm s}^{-1}$ (D) $1 \times 10^4 \text{ cm s}^{-1}$

Solution

(C) Do remember that rms speed does not depend on the pressure.

$$\bar{C}_2 = \sqrt{\frac{3R \times 27}{M}} \Rightarrow \frac{\bar{C}_2}{\bar{C}_1} = \sqrt{3}$$

$$\bar{C}_1 = \sqrt{\frac{3R \times 27}{M}} \quad \text{or} \quad \bar{C}_2 = \sqrt{3} \bar{C}_1 = \sqrt{3} \times 10^4 \text{ cm s}^{-1}$$

7. Since the atomic weights of C, N and O are 12, 14 and 16 u, respectively, among the following pair, the pair that will diffuse at the same rate is

- (A) carbon dioxide and nitrous oxide. (B) carbon dioxide and nitrogen peroxide.
 (C) carbon dioxide and carbon monoxide. (D) nitrous oxide and nitrogen peroxide.

Solution

(A) Molecular weight of CO = 28; Molecular weight of CO_2 = 44

Molecular weight of N_2O = 28 + 16 = 44

Molecular weight of CO_2 = 12 + 32 = 44

Since CO_2 and N_2O have the same molecular weight, therefore, the rate of diffusion for both the gases is the same.

8. $\text{SO}_3(\text{g})$ decomposes according to the equation $2\text{SO}_3(\text{g}) \rightarrow 2\text{SO}_2(\text{g}) + \text{O}_2(\text{g})$. A sealed container contains 0.5 mol of SO_3 gas at 100°C and 2 atm pressure. What would be the pressure in the container if the SO_3 gas is decomposed completely according to the above equation and the temperature were maintained at 100°C ?

- (A) 0.5 atm (B) 1.0 atm (C) 2.0 atm (D) 3.0 atm

Solution

(D) $\frac{n_f}{n_i} = \frac{p_f}{p_i} \Rightarrow p_f = p_i \frac{n_f}{n_i}$ or $2 \times \frac{3}{2} = 3 \text{ atm}$

9. If the pressure of a given mass of gas is reduced to half and temperature is doubled simultaneously, the volume will be

- (A) same as before. (B) twice as before.
 (C) four times as before. (D) one-fourth as before.

Solution

(C) As per equation of state,

$$\frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2}$$

Given that $p_2 = \frac{p_1}{2}$, $T_2 = 2T_1$

So,
$$V_2 = \frac{T_2}{T_1} \times \frac{p_1}{p_2} = \frac{2T_1}{T_1} \times \frac{p_1}{p_1/2} \times V_1 = 4V_1$$

10. A general form of equation of state for gases is $pV = RT \left[A + \frac{B}{V} + \frac{C}{V^2} + \dots \right]$ where V is the molar volume of the gas and A, B, C, \dots are constants for the gas. If the gas obeys van der Waals equation, the values of A and B are, respectively,

- (A) $\frac{a}{RT}, b$ (B) $\frac{2a}{RT}, b$ (C) $1, b - \frac{a}{RT}$ (D) $1, \frac{a}{27b}$

Solution

(C) In the expression, $pV = RT \left[A + \frac{B}{V} + \frac{C}{V^2} + \dots \right]$ the first term, that is, A within the brackets is the main term and the rest are correction term for non-ideality. Therefore, A should be 1, since $PV = RT$ per mole of an ideal gas. The van der Waals' equation for 1 mol is

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

Expanding the above equation, we get

$$\begin{aligned} pV &= RT + bp - \frac{a}{V} + \frac{ab}{V^2} \approx RT + bp - \frac{a}{V} \\ &= RT \left[1 + \frac{bp}{RT} - \frac{a}{RTV} \right] \end{aligned}$$

Applying the ideal gas equation in the correction term, we get

$$pV = RT \left[1 + \frac{b}{V} - \frac{a}{RTV} \right] = RT \left[1 + \frac{1}{V} \left(b - \frac{a}{RT} \right) \right]$$

Thus,

$$A = 1; B = \left(b - \frac{a}{RT} \right)$$

11. I, II, and III are three isotherms, respectively, at T_1 , T_2 , and T_3 as shown in Fig. 2. The temperatures will be in the order:

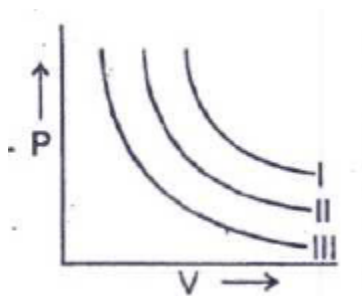


Figure 2

(A) $T_1 = T_2 = T_3$ (B) $T_1 < T_2 < T_3$ (C) $T_1 > T_2 > T_3$ (D) $T_1 > T_2 = T_3$

Solution

(C) As $pV = nRT$, therefore, $p \propto 1/V$ at constant T .

12. A certain gas diffuses from two different vessels A and B. The vessel A has a circular orifice, while vessel B has a square orifice of length equal to the radius of the orifice of vessel A. Calculate the ratio of the rates of diffusion of the gas from vessel A to vessel B, assuming same temperature and pressure.

(A) π (B) $1:\pi$ (C) 1:1 (D) 2:1

Solution

(A) $r \propto$ area of orifice

$r_1 \propto \pi r^2$ (circle)

$r_2 \propto r^2$ (square)

Therefore, $r_1/r_2 = \pi$.

13. What would happen to the volume of a balloon filled with 0.357 L of H_2 gas collected at 741.3 mm Hg if the atmospheric pressure increased to 758.1 mm Hg?

(A) 0.45 L (B) 0.35 L (C) 0.25 L (D) 0.15 L

Solution

(B) Using Boyle's law, $p_1V_1 = p_2V_2$ where $T =$ constant, $p_1 = 741.3$ mm Hg and $V_1 = 0.357$ L, $p_2 = 758.1$ mm Hg and $V_2 = ?$

$$V_2 = \frac{p_1 V_1}{p_2} = \frac{741.3 \text{ mm Hg} \times 0.357 \text{ L}}{758.1 \text{ mm Hg}} = 0.349 \text{ L}$$

The volume of the balloon will decrease.

14. A gas bulb containing air is connected to an open limb manometer at 27°C and at 750 mm Hg. Assuming that initially the level of Hg in the both limbs were same, the bulb was heated to 77°C. What will be the difference in the levels of Hg in the two limbs? (Assume that the volume difference of the gas produced is negligible at higher temperature).

- (a) 7.5 cm Hg (b) 8 cm Hg (c) 6 cm Hg (d) 12.5 cm Hg

Solution

(D) As $\frac{p_1}{T_1} = \frac{p_2}{T_2}$, we have

$$\frac{750}{300} = \frac{p_2}{350} \Rightarrow p_2 = 875 \text{ mm Hg}$$

So, the difference in height = 875 – 750 = 125 mm Hg = 12.5 cm of Hg.

15. The critical temperature and critical pressure of a gas obeying van der Waals equation are 30°C and 73 atm, respectively. Its van der Waals constant, b (in L s mol⁻¹) is, therefore,

- (A) 0.500 (B) 0.060 (C) 0.265 (D) 0.128

Solution

(D) The van der Waals constant T_c , p_c , and V_c are related by the expression

$$V_c = 3b; \quad T_c = a \frac{8a}{27Rb}; \quad \text{and } p_c = \frac{a}{27b^2}$$

16. The van der Waals constants for HCl are $a = 371.843 \text{ kPa}$ and $b = 40.8 \text{ cm}^3 \text{ mol}^{-1}$. The critical temperature is

- (A) 324.8 K (B) 424.8 K (C) 350.9 K (D) 450.9 K

Solution

$$(A) T_c = \frac{8a}{27Rb} = \frac{8 \times 371.843 \times 1000 \times 101325}{27 \times 0.0821 \times 40.8} = 324.8 \text{ K}$$

17. A certain volume of argon gas (molar weight = 40 g mol⁻¹) requires 45 s to effuse through a hole at a certain pressure and temperature. The same volume of another gas of unknown molecular weight

requires 60 s to pass through the same hole under the same conditions of temperature and pressure.

The molecular weight of the gas is

- (A) 53 g mol⁻¹ (B) 35 g mol⁻¹ (C) 71 g mol⁻¹ (D) 120 g mol⁻¹

Solution

(C) This is based on Graham's law of diffusion.

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

Substituting values, we get

$$\frac{45}{60} = \sqrt{\frac{40}{M_2}} \Rightarrow M_2 = \frac{40 \times 60 \times 60}{45 \times 45} = 71.1 \text{ g mol}^{-1}$$

18. 400 cm³ of oxygen at 27°C were cooled -3°C without change in pressure. The contraction in volume will be:

- (A) 40 cm³ (B) 30 cm³ (C) 44.4 cm³ (D) 60 cm³

Solution

(A) $V_1/T_1 = V_2/T_2$

19. Consider the following statements: The mean free path of gas molecules

- (I) decreases with increase in concentration.
(II) increases with decrease in pressure at constant temperature.
(III) decrease with increase in molecular size.
(A) I, II (B) I, III (C) II, III (D) I, II, III

Solution

(D) Check for yourself that all are correct.

- Decrease with increase in concentration—means increase in the number of molecules.
- Increase with decrease in pressure at constant temperature—means increase in the volume available for gas molecules.
- Decreases with increase in molecular size—means decrease in the volume of available for gas molecules.

20. At 47°C and 16.0 atm, the molar volume of NH₃ gas is about 10% less than the molar volume of an ideal gas. Which of the following is the true reason?

- (A) NH_3 decomposes to N_2 and H_2 at 47°C .
 (B) The force of attraction between NH_3 molecules is significant at this temperature and pressure.
 (C) The volume occupied by NH_3 molecules themselves is a significant fraction of the volume of the container at this temperature and pressure.
 (D) At 16 atm, NH_3 molecules no longer move randomly.

Solution

$$(B) Z = \frac{V_{m, \text{real}}}{V_{m, \text{ideal}}} = 0.9$$

Therefore, there will be attractive molecular forces as $Z < 1$.

21. How much time would it take to distribute one Avogadro's number of wheat grains if 10^{10} grains are distributed in each second?

- (A) 4×10^2 years (B) 9×10^6 years (C) 6×10^4 years (D) 2×10^6 years

Solution

(D) Since the time taken to distribute 10^{10} wheat grains = 1 s, so

$$\begin{aligned} \text{Time taken to distribute } 6.023 \times 10^{23} \text{ wheat grains} &= \frac{1 \times 6.022 \times 10^{23}}{10^{10}} = 6.022 \times 10^{13} \text{ s} \\ &= \frac{6.022 \times 10^{13}}{60 \times 60 \times 24 \times 365} = 1.90956 \times 10^6 \text{ years} \end{aligned}$$

22. At what temperature will the rate of effusion of N_2 be 1.625 times the rate of effusion of SO_2 at 500°C ?

- (A) 273 K (B) 830 K (C) 110 K (D) 173 K

Solution

(B)

$$\begin{aligned} \frac{r_{\text{SO}_2}}{r_{\text{N}_2}} &= \sqrt{\frac{M_{\text{N}_2}}{M_{\text{SO}_2}}} \times \frac{T_{\text{SO}_2}}{T_{\text{N}_2}} \quad \text{or} \quad \frac{x}{1.625x} = \sqrt{\frac{28}{64}} \times \frac{773}{T_{\text{N}_2}} \\ T_{\text{N}_2} &= \sqrt{\frac{28}{64}} \times 773 \times 1.625 = \sqrt{7} \times \frac{773 \times 1.625}{4} = 830 \text{ K} \end{aligned}$$

as Rate \propto Temperature

23. 2.9 g of gas at 95°C occupied the same volume as 0.184 g of dihydrogen at 17°C , at the same pressure. What is the molar mass of the gas?

- (A) 120 g mol^{-1} (B) 20 g mol^{-1} (C) 80 g mol^{-1} (D) 40 g mol^{-1}

Solution

(D) For gas:

$$V_{\text{gas}} = \frac{nRT}{p} \quad (1)$$

For H_2 ,

$$V_{\text{H}_2} = \frac{n_{\text{H}_2}RT_{\text{H}_2}}{p_{\text{H}_2}} \quad (2)$$

Now, $n = W / M$. From Eqs. (1) and (2), we have

$$\frac{2.9 \times 368}{M_{\text{gas}}} = \frac{0.184 \times 290}{2} \Rightarrow M_{\text{gas}} = 40 \text{ g mol}^{-1}$$

Since volume and pressure of both the gases are the same.

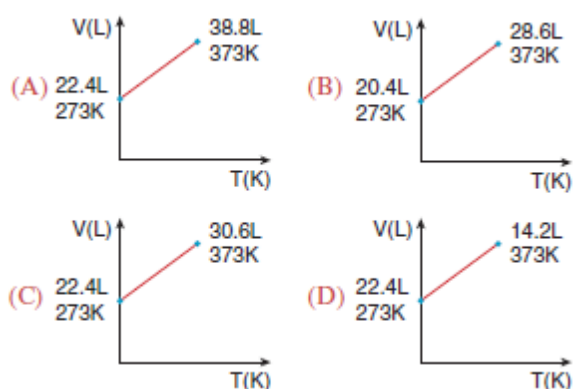
24. The compressibility of a gas is less than unity at STP. Therefore,

(A) $V_m > 22.4 \text{ L}$ (B) $V_m < 22.4 \text{ L}$ (C) $V_m = 22.4 \text{ L}$ (D) $V_m = 44.8 \text{ L}$

Solution

(B) $Z < 1$ or $V = \frac{ZRT}{p}$; $Z = \frac{V_m}{V_{\text{ideal}}}$ $Z < 1$, attractive forces dominate.

25. Which of the following V, T plots represents the behavior of 1 mol of an ideal gas at one atmosphere?



(IIT-JEE 2002)

Solution

(C) Ideal gas will obey all gas laws. So, as per Charles' law,

$$V_2 = \left(\frac{T_2}{T_1} \right) \times V_1 = \left(\frac{373}{273} \right) \times 22.4 = 30.6 \text{ L}$$

26. 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

- (A) $\frac{1}{3}$ (B) $\frac{1}{2}$ (C) $\frac{2}{3}$ (D) $\frac{1}{3} \times \frac{273}{298}$

Solution

$$(A) \frac{n_{\text{methane}}}{n_{\text{O}_2}} = \frac{w_{\text{CH}_4}}{w_{\text{O}_2}} \times \frac{M_{\text{O}_2}}{M_{\text{CH}_4}} = \frac{32}{16} = 2$$

According to Dalton's law of partial pressure $p_{\text{CH}_4} = x_{\text{CH}_4} \times P_{\text{total}}$

$$\text{As } x_{\text{CH}_4} = \frac{2}{3} \text{ and } x_{\text{O}_2} = \frac{1}{3}, \text{ so } p_{\text{O}_2} = x_{\text{O}_2} \times P_{\text{total}} = \frac{1}{3} \text{ part}$$

27. The root mean square velocity of 1 mol of a monoatomic gas having molar mass M is u_{rms} . The relation between the average kinetic energy (E) of the gas and u_{rms} is

(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) $u_{\text{rms}} = \sqrt{\frac{E}{3M}}$

Solution

(C) Since $\text{KE} = \frac{1}{2} M u_{\text{rms}}^2$, therefore,

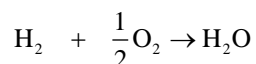
$$u_{\text{rms}} = \sqrt{\frac{2E}{M}} \quad \left(\text{using } u_{\text{rms}} = \left(\frac{3RT}{M} \right)^{1/2} \text{ and } pV = \frac{1}{3} m n u^2 \right)$$

28. 40 mL of mixture of H_2 and O_2 was placed in a gas burette at 18°C and 1 atm. A spark was produced so that the formation of water was complete. The remaining pure gas had a volume of 10 mL at 18°C and 1 atm. If the remaining gas was H_2 , what was initial mole % of H_2 in mixture?

- (A) 75% (B) 25% (C) 60% (D) 45%

Solution

(A) Let the volume of O_2 in the mixture be x mL; therefore, $\text{H}_2 = 40 - x$



Initial volume in mL $(40 - x)$ x

Final volume in mL $(40 - 3x)$ 0

Final volume of $\text{H}_2 = 10$ mL

$$40 - 3x = 10$$

$$x = 10 \text{ mL}$$

Therefore, initial volume of $H_2 = 30$ mL; initial mole % of $H_2 = \frac{30}{40} \times 100 = 75\%$

29. 80 mL of oxygen is added to 50 mL of a mixture of H_2 , C_2H_2 and CO , after which the total mixture is burnt. The volume of the cooled mixture after combustion measures 65 mL. This is reduced to 15 mL by treatment with aqueous KOH solution. Calculate the volume of each gas in the original mixture.

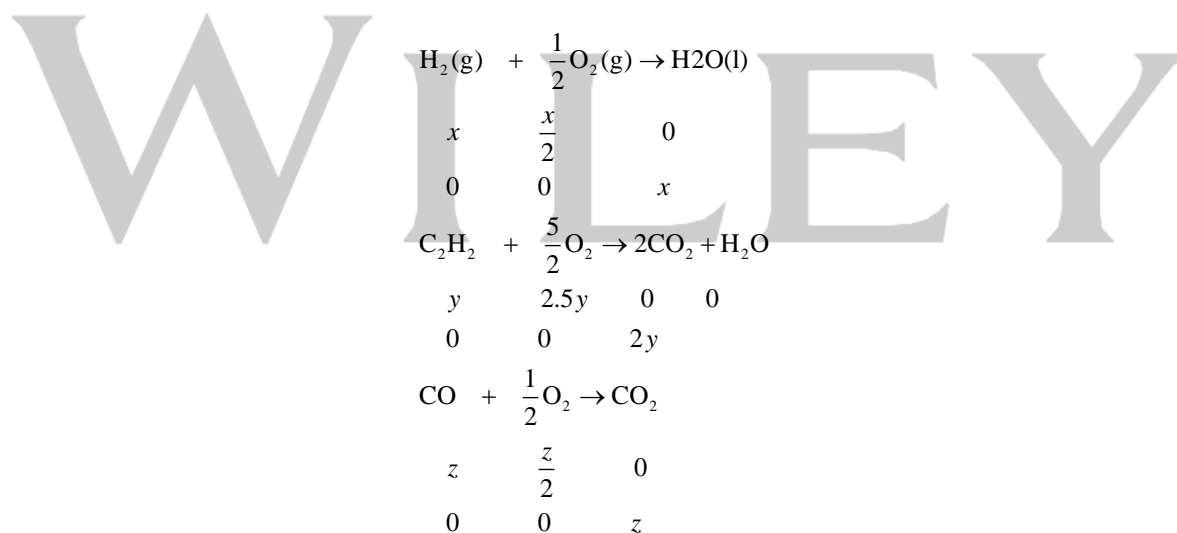
- (A) 20 mL of H_2 , 20 mL of C_2H_2 , 10 mL of CO .
 (B) 10 mL of H_2 , 20 mL of C_2H_2 , 20 mL of CO .
 (C) 15 mL of H_2 15 mL of C_2H_2 , 20 mL of CO .
 (D) 10 mL of H_2 15 mL of C_2H_2 , 25 mL of CO .

Solution

(A) Let $H_2 = x$, $C_2H_2 = y$, $CO = z$; therefore,

$$x + y + z = 50 \quad (1)$$

The reactions can be expressed as



Therefore, $1.5x + 1.5y + 0.5z = 65 \quad (2)$

$$2y + z = 50 \quad (3)$$

Solving, we get $x = 10$, $y = 20$, and $z = 10$.

30. The kinetic energy (in kcal) of 80 g of methane gas at $227^\circ C$ is

- (A) 15 (B) 2.5 (C) 25 (D) 7.5

Solution

(D) The kinetic energy is given by

$$KE = \frac{3}{2} \times n \times RT = \frac{3}{2} \times \frac{80}{16} \times 2 \times 500 = 7.5 \text{ kcal}$$

31. If a certain mass of gas is expanded at constant temperature,

- (A) the pressure of the gas decreases.
- (B) the kinetic energy of the gas molecules increases.
- (C) the kinetic energy of the molecules decreases.
- (D) the number of molecules of the gas increases.

Solution

(A) Concept based.

32. The rate of effusion of helium gas at a pressure of 1000 torr is 10 torr min^{-1} . What will be the rate of effusion of hydrogen gas at a pressure of 2000 torr at the same temperature?

- (A) 20 torr min^{-1}
- (B) 40 torr min^{-1}
- (C) $20\sqrt{2} \text{ torr min}^{-1}$
- (D) 10 torr min^{-1}

Solution

(C) At a given temperature,

$$\text{Rate of effusion} \propto p \text{ and Rate of effusion} \propto \frac{1}{\sqrt{M}}$$

$$\text{Rate of effusion of hydrogen gas} = 10 \text{ torr min}^{-1} \times \frac{2000}{1000} \sqrt{\frac{4}{2}} = 20\sqrt{2} \text{ torr min}^{-1}$$

33. A closed vessel contains equal number of oxygen and hydrogen molecules. Consider the following statements:

- (I) The average speed of hydrogen molecules is greater.
- (II) The two gases have different average energies.
- (III) Hydrogen molecules strike the walls more often.
- (IV) Weight of hydrogen is one-eighth of the weight of oxygen.

The incorrect statements are

- (A) 1 and 2
- (B) 2 and 3
- (C) 1 and 3
- (D) 2 and 4

Solution

(D) At the same temperature, oxygen and hydrogen molecules will have the same average energy; weight of H_2 molecules is $(1/16)$ of O_2 molecules. So, the statements 2 and 4 are wrong.

34. The molecules of mass m , moving with velocity v are absorbed after colliding with walls of a container. If the number of molecules per unit volume of the gas is N , then the pressure exerted by the gas will be

- (A) $\frac{mNv^2}{2}$ (B) $2mNv^2$ (C) $\frac{mNv^2}{3}$ (D) mNv^2

Solution

(D)

35. For a real gas, pV is a constant over a small range of pressures at

- (A) Boyle's temperature. (B) critical temperature.
(C) inversion temperature. (D) ordinary temperature.

Solution

(A) This is referred as Boyle's temperature.

36. The average, rms, and most probable velocities of gas molecules at STP increase in the order

- (A) rms < Average velocity < Most probable velocity
(B) Most probable velocity < Average velocity < rms
(C) Average velocity < rms < Most probable velocity
(D) rms < Most probable velocity < Average velocity

Solution

(B) Molecular speed of gases are as follows:

(1) The rms (root mean square) velocity

$$C = \sqrt{\frac{3RT}{M}}$$

(2) Average velocity = $\sqrt{\frac{8RT}{\pi M}}$

$$v_{\text{rms}} = 1.085 \times v_{\text{avg}}$$

(3) Most probable velocity = $\sqrt{\frac{2RT}{M}}$

The ratio is

Most probable velocity: Average velocity : rms

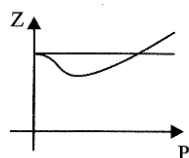
$$\sqrt{2} : \sqrt{\frac{8}{\pi}} : \sqrt{3} = 1 : 1.128 : 1.224$$

37. Which of the following statement is correct?

- (A) The slope of Z vs. p at constant temperature for all real gases, is b/RT .
 (B) The slope of Z vs. p at constant temperature for both He and H_2 is b/RT .
 (C) The slope of Z vs. p at low pressure for all real gases, at constant temperature is b/RT .
 (D) The slope of Z vs. p at high pressure and at constant temperature for real gas is $-b/RT$.

Solution

- (B) Slope = $\frac{b}{RT}$ only in the high-pressure region.



For H_2 and He, $a = 0 \Rightarrow$ Slope = $\frac{b}{RT}$

38. The density of the gaseous mixture (He and N_2) is $10/22.4 \text{ g L}^{-1}$ at NTP. What is the percentage composition of He and N_2 by volume in this mixture, respectively?

- (A) 75%, 25% (B) 25%, 75% (C) 30%, 70% (D) 40%, 60%

Solution

(A) $M_{\text{mix}} = \frac{10}{22.4} \times 22.4 = 10$

Now, $M_{\text{mix}} = \sum M_i X_i$

Let the volume of He = V_1 mL

Let the volume of N_2 = V_2 mL

$$V_1 + V_2 = 100 \text{ mL}$$

$$10 = \left(\frac{V_1}{100}\right) \times 4 + \frac{V_2}{100} \times 28$$

Solving the above equations, we get $V_1 = 75\%$ (as mole fraction \propto volume fraction).

39. Which of the following statements is (are) correct for a gas X having molar mass 5 g and density 0.3 g L^{-1} at 0.5 atm pressure at 300 K?

- (A) The gas X will behave ideally.
 (B) The force of attraction will dominate over the force of repulsion among the gas molecules.
 (C) The force of repulsion will dominate over the force of attraction among the gas molecules.
 (D) None of these.

Solution

$$(B) Z = \frac{pV_m}{RT} = \frac{pV}{nRT} = \frac{pV \times M_0}{g \times RT} = \frac{pM_0}{\rho RT}$$

Substituting values, we get

$$Z = \frac{0.5 \times 5}{0.3 \times 0.082 \times 300} = 0.34 < 1.$$

Therefore, attractive forces dominate and gas is more liquefiable.

40. At STP, a container has 1 mol of Ar, 2 mol of CO₂, 3 mol of O₂, and 4 mol of N₂. Without changing the total pressure if 1 mol of O₂ is removed, the partial pressure of O₂

(A) is changed by about 26%. (B) is halved.

(C) is unchanged.

(D) changed by 33%.

Solution

(A)

$$p_i = p_f \Rightarrow \frac{10RT}{V_i} = \frac{9RT}{V_f}$$

$$V_f = \frac{9V_i}{10}$$

$$p_{O_2,i} = \frac{3RT}{V_i} \quad \text{and} \quad p_{O_2,f} = \frac{2RT}{V_f}$$

$$\frac{p_{O_2,i} - p_{O_2,f}}{p_{O_2,i}} = \frac{3 - \frac{20}{9}}{3} = 26\%$$

41. When 100 mL sample of methane and ethane along with excess of O₂ is subjected to electric spark, the contraction in volume was observed to be 212 mL. When the resulting gases were passed through KOH solution, further contraction in volume was

(A) 60 mL

(B) 96 mL

(C) 100 mL

(D) 112 mL

Solution

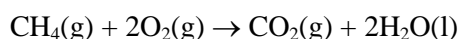
(D) CH₄ + C₂H₆

x mL y mL

Therefore,

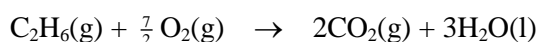
$$x + y = 100$$

(1)



$$x \qquad 2x \qquad 0 \qquad 0$$

$$0 \qquad 0 \qquad x$$



$$\begin{array}{cccc} y & 7/2 y & 0 & 0 \\ 0 & 0 & 2y & \end{array}$$

$$2x + 2.5y = 212 \quad (2)$$

$$\text{KOH(contraction)} = x + 2y$$

42. Under the same conditions of temperature and pressure, a hydrocarbon of molecular formula C_nH_{2n-2} was found to diffuse $3\sqrt{3}$ times slower than hydrogen. Find the value of n ?

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

Solution

(B)

$$\frac{r_{H_2}}{r_{C_nH_{2n-2}}} = \left(\frac{M_{C_nH_{2n-2}}}{M_{H_2}} \right)^{1/2}$$

$$\frac{3\sqrt{3}}{1} = \left(\frac{M_{C_nH_{2n-2}}}{M_{H_2}} \right)^{1/2}$$

$$\left(\frac{3\sqrt{3}}{1} \right)^2 = \frac{M_{C_nH_{2n-2}}}{M_{H_2}}$$

$$27 = \frac{M_{C_nH_{2n-2}}}{M_{H_2}}$$

$$54 = M_{C_nH_{2n-2}}$$

$$54 = n \times 12 + (2n - 2) \times 1$$

$$56 = 14n$$

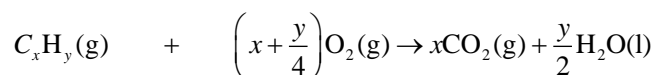
$$n = 4$$

43. 5 mL of a gaseous hydrocarbon was exposed to 30 mL of O_2 . The resultant gas, on cooling, is found to measure 25 mL, of which 10 mL was absorbed by NaOH and the remainder by pyrogallol. All measurements are made at constant pressure and temperature. The molecular formula of the hydrocarbon is

- (A) C_2H_2 (B) C_3H_8 (C) C_2H_4 (D) C_2H_6

Solution

(C) Let the formula of hydrocarbon be C_xH_y . Its combustion reaction is given as



Initial volume in mL	5		30		
Final volume			$30 - \left(x + \frac{y}{4}\right)5$	5x	

Out of 25 mL of resultant gas 10 mL was CO₂ (absorbed by NaOH) and the remaining 15 mL was oxygen (absorbed by pyrogallol). Therefore,

$$5x = 10 \Rightarrow x = 2$$

$$30 - \left(x + \frac{y}{4}\right)5 = 15$$

On solving the above equation, we get $y = 4$.

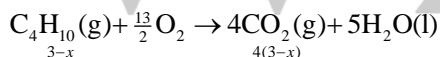
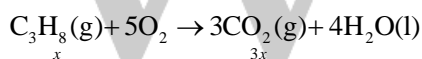
Therefore, the formula of gaseous hydrocarbon is C₂H₄.

44. A gas mixture of 3 L of propane (C₃H₈) and butane (C₄H₁₀) on complete combustion at 25°C produced 10 L CO₂. What is the composition of gas mixture, that is, volume of C₃H₈ and C₄H₁₀, respectively?

- (A) 1.5 L, 1.5 L (B) 1 L, 2 L (C) 2 L, 1.0 L (D) 1.75 L, 1.25 L

Solution

(C) The reactions involved are



The total amount of CO₂ formed is 10 L, therefore,

$$3x + 4(3 - x) = 10$$

Solving, we get $x = 2$. Therefore, volume of C₃H₈ = 2 L and of C₄H₁₀ = 1 L.

45. A vessel of volume 0.02 m³ contains a mixture of hydrogen and helium at 20°C and 2 atm pressure. The mass of mixture is 5 g. Find the ratio of mass of hydrogen to that of helium in the mixture (atomic weight of He = 4 u.)

- (A) 1:2 (B) 1:3 (C) 2:3 (D) 3:2

Solution

$$(A) n = \frac{2 \times 20}{293 \times 0.0821} = 1.67 = \frac{5}{3}$$

$$\Rightarrow \frac{x}{2} + \frac{5-x}{4} = \frac{5}{3} \Rightarrow 15 + 3x = 20$$

$$\text{So, } x = \frac{5}{3}$$

$$\text{Required ratio } \frac{x}{5-x} = \frac{\frac{5}{3}}{5-\frac{5}{3}} = \frac{1}{2}$$

46. The average speed of an ideal gas molecule at 27°C is 0.3 m s^{-1} . Calculate average speed at 927°C ?

- (A) 0.6 m s^{-1} (B) 6 m s^{-1} (C) 60 m s^{-1} (D) 8 m s^{-1}

Solution

(A) Given that

$$(u_{\text{avg}})_i = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8R \times 300}{\pi M}} = 0.3 \text{ m s}^{-1} \quad (1)$$

$$\text{Also, } (u_{\text{avg}})_f = \sqrt{\frac{8R \times 1200}{\pi M}} \quad (2)$$

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

$$\frac{(u_{\text{avg}})_f}{(u_{\text{avg}})_i} = \sqrt{\frac{1200}{300}} \Rightarrow (u_{\text{avg}})_f = 2 \times 0.3 = 0.6 \text{ m s}^{-1}$$

47. The pressure–volume plot for an ideal gas at a given temperature has the form of a

- (A) straight line. (B) exponential curve.
(C) rectangular hyperbola. (D) U-shaped curve.

Solution

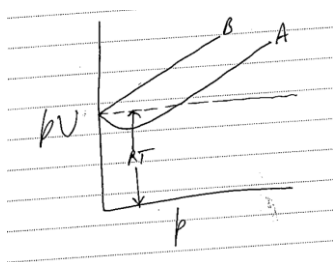
(C) The variation of the volume of a given mass of gas with pressure at constant temperature has the shape of rectangular hyperbola. This curve is called as isotherm.

48. If a graph is drawn for 1 mol of real gas in such a way that pV is drawn in y -axis and p in x -axis, then which of the following will be the value for the intercept of the graph in y -axis.

- (A) $RT + \frac{ab}{V^2} - aV$ (B) $RT + pb + a$ (C) $RT + pb + ab$ (D) RT

Solution

(D)



For a real gas, the plot of pV vs p can be of the type A or B but at the point of intercept, $p = 0$ and at any low pressure, van der Waals equation reduces to ideal gas equation

$$pV = nRT$$

$$\text{or } pV = RT$$

Hence, y intercept of graph will be $= RT$

Therefore, intercept is given by option (D).

49. Joule–Thomson expansion of an ideal gas is an

(A) isothermal process.

(B) isobaric process.

(C) isenthalpic process.

(D) ideal process.

Solution

(C) Joule–Thomson effect occurs at constant enthalpy.

50. There are 201 equidistant rows of spectators sitting in a hall. A magician releases laughing gas N_2O from the front and the tear gas ($M_o = 176$) from the rear of the hall simultaneously. Which row of spectators will have a tendency to smile and weep simultaneously?

(A) 130

(B) 134

(C) 120

(D) 100

Solution

(B) We know that

$$\frac{r_{\text{laughing gas}}}{r_{\text{tear gas}}} = \left(\frac{M_{\text{tear gas}}}{M_{\text{laughing gas}}} \right)^{1/2} \Rightarrow \frac{r_{\text{laughing gas}}}{r_{\text{tear gas}}} = \left(\frac{176}{44} \right)^{1/2} = 2$$

Now, time taken to reach a row by laughing gas should be equal to time taken by tear gas to reach the same row. So,

$$\frac{l_{\text{laughing gas}}}{r_{\text{laughing gas}}} = \frac{l_{\text{tear gas}}}{r_{\text{tear gas}}} \Rightarrow \frac{r_{\text{laughing gas}}}{r_{\text{tear gas}}} = \frac{l_{\text{laughing gas}}}{l_{\text{tear gas}}}$$

Now, given that $l_{\text{laughing gas}} + l_{\text{tear gas}} = 201$, therefore,

$$2 = \frac{l_{\text{laughing gas}}}{201 - l_{\text{laughing gas}}} \Rightarrow l_{\text{laughing gas}} = 201 \times \frac{2}{3} = 134$$

Therefore, bench = 134

51. The average kinetic energy of 2 mol of CO_2 at a certain temperature is 1800 cal. The temperature of the gas is

- (A) 300 K (B) 150 K (C) 200 K (D) 400 K

Solution

(A) The average kinetic energy of molecule is given by $\frac{3}{2} \frac{RT}{N}$ where $\frac{R}{N}$ is Boltzmann constant. The

Boltzmann constant is $1.9872 \text{ cal mol}^{-1} \text{ K}^{-1}$. Substituting, we get

$$1800 = 2 \times \frac{3}{2} \times 1.98 \times T \Rightarrow T = 300 \text{ K}$$

52. Equal volumes of SO_2 and He at a temperature T and pressure p are allowed to effuse through a hole. The rate of effusion of helium is

- (A) equal to the rate of effusion of SO_2 . (B) four times the rate of effusion of SO_2 .
(C) half of the rate of effusion of SO_2 . (D) twice the rate of effusion of SO_2 .

Solution

(B) The relative rates of diffusion of gases with respect to molecular weights is given by the expression.

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}; \quad M_2 = 64 \text{ and } M_1 = 4$$

53. At point A the gas is at Boyle's temperature and it is brought to B as shown in Fig. 3. Then at point B, the gas will have compressibility factor

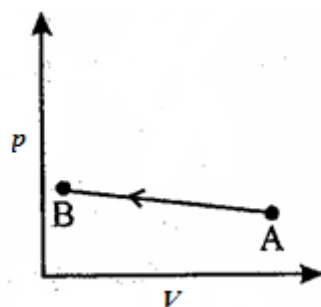


Figure 3

- (A) 1 (B) $Z > 1$ (C) $Z < 1$ (D) $Z = 3/8$

Solution

(C)

The compressibility factor is given by $Z = \frac{pV_{\text{real}}}{RT}$

At Boyle's temperature, point A, the rate of change of pV is constant. As the gas is brought to point B, the pressure is found to increase, this implies that gas is more compressible and attractive forces dominate so $Z < 1$.

54. The van der Waals constants for a gas are: $a = 4 \text{ L}^2 \text{ atm mol}^{-2}$, $b = 0.04 \text{ L mol}^{-1}$. Its Boyle's temperature is roughly

- (A) 100°C (B) 1220 K (C) 1220°C (D) 1600 K

Solution

(B) Boyle's temperature,

$$T_B = \frac{a}{Rb} = \frac{4 \text{ L}^2 \text{ atm. mol}^{-2}}{0.082 \text{ L atm. K}^{-2} \times 0.04 \text{ L}^2 \text{ mol}^{-1}} = 1219.5 \text{ K} = 1220 \text{ K}$$

55. Oxygen is present in 1 L flask at a pressure of 7.6×10^{-10} mm Hg. Calculate the number of oxygen molecules in the flask at 0°C .

- (A) 2.686×10^{10} (B) 26.86×10^{10} (C) 0.626×10^{12} (D) 4.123×10^8

Solution

(A) Using the expression $pV = nRT$, we have

$$n = \frac{pV}{RT} = \frac{\left\{ \left(\frac{7.6 \times 10^{-10}}{760} \right) \text{ atm} \right\} (1 \text{ L})}{(0.0821 \text{ atm L K}^{-1} \text{ mol}^{-2})(273.15 \text{ K})} = 4.459 \times 10^{-14} \text{ mol}$$

$$N = nN_A = (4.459 \times 10^{-14} \text{ mol}^{-1}) = 2.686 \times 10^{10}$$

56. Pressure remaining the same, the volume of given mass of an ideal gas increases for every degree centigrade rise in temperature by definite fraction of its volume at

- (A) 0°C . (B) its critical temperature.
(C) absolute zero. (D) its Boyle temperature.

Solution

$$(A) (V_2 - V_1) = V_0 a(t_2 - t_1) \Rightarrow \Delta V = aV_0$$

For every 1°C increase in temperature, the volume of a given mass of an ideal gas increases by a definite fraction $1/273.15$ of V_0 .

57. 4.0 g of argon has pressure p atm at temperature T K in a vessel. On keeping the sample at 50° higher temperature, 0.8 g gas was given out to maintain the pressure p . The original temperature was
 (A) 73 K (B) 100 K (C) 200 K (D) 510 K

Solution

(C) At constant p and V , $n_1T_1 = n_2T_2$; as $pV = nRT$

$$4 \times T_1 = 3.2 \times (T_1 + 50)$$

On solving, we get $T_1 = 200$ K

58. X mL of H_2 gas is effused through a hole in a container in 5 s. The time taken for the effusion of the same volume of the gas specified below under identical conditions is:

- (A) 10 s:He (B) 20 s: O_2 (C) 25 s:CO (D) 55 s: CO_2

Solution

(B) We know that
$$\frac{r_{H_2}}{r_{gas}} = \left(\frac{M_{gas}}{M_{H_2}} \right)^{1/2} \quad (1)$$

Now,
$$r_{H_2} = \frac{V_{H_2}}{\text{Time interval}} = \frac{X}{5}$$

$$\frac{r_{H_2}}{r_{gas}} = \frac{X/5}{X/t} = \frac{t}{5} \quad (2)$$

Working with the options one by one using Eq. (1), we find that the best fit is O_2 .

$$\frac{r_{H_2}}{r_{O_2}} = \left(\frac{M_{O_2}}{M_{H_2}} \right)^{1/2} = 4$$

Substituting in Eq. (2), we get

$$4 = \frac{t}{5} \Rightarrow t = 20 \text{ s}$$

59. The rms velocity of hydrogen is $\sqrt{7}$ times the rms velocity of nitrogen. If T is temperature of the gas, then

- (A) $T(H_2) = T(N_2)$ (B) $T(H_2) > T(N_2)$ (C) $T(H_2) < T(N_2)$ (D) $T(H_2) = \sqrt{7} T(N_2)$

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Solution

(C) The rms velocity is given by

$$u_{\text{rms}} = \left(\frac{3RT}{M} \right)^{1/2}$$

Given that

$$\frac{(u_{\text{rms}})_{\text{H}_2}}{(u_{\text{rms}})_{\text{N}_2}} = \sqrt{7}$$

So,

$$\frac{(u_{\text{rms}})_{\text{H}_2}}{(u_{\text{rms}})_{\text{N}_2}} = \sqrt{7} \Rightarrow \frac{(3RT_{\text{H}_2} / 2)^{1/2}}{(3RT_{\text{N}_2} / 28)^{1/2}} = \sqrt{7} \Rightarrow 4T_{\text{H}_2} = T_{\text{N}_2}$$

60. Flask X is filled with 20 g of CH_4 gas at 100°C and another identical flask Y with 40 g O_2 gas at the same temperature. Which one of the following statements is correct? [Molar masses in g mol^{-1} of $\text{CH}_4 = 16.0$ and $\text{O}_2 = 32.0$]

- (A) The pressure of the gases in the two flasks are identical.
- (B) The pressure of CH_4 in flask X is higher than that of O_2 in flask Y.
- (C) The pressure of CH_4 in flask X is lower than that of O_2 in flask Y.
- (D) The pressure of CH_4 in flask X is half that of O_2 in flask Y.

Solution

$$(A) n_{\text{CH}_4} = \frac{20}{16} = \frac{5}{4} \text{ and } n_{\text{O}_2} = \frac{40}{32} = \frac{5}{4}$$

Hence, pressure is equal.

61. What would be the SI unit for the quantity pV^2T^2/n ?

- (A) $\text{dm}^5 \text{Pa K}^2 \text{mol}^{-1}$
- (B) $\text{dm}^3 \text{Pa K}^2 \text{mol}^{-1}$
- (C) $\text{dm}^2 \text{Pa}^2 \text{K}^2 \text{mol}^{-1}$
- (D) $\text{dm}^6 \text{Pa K mol}^{-1}$

Solution

$$(A) \text{Unit} = \frac{\text{Pa} \times (\text{dm}^3)^2 \times \text{K}^2}{\text{mol}}$$

62. At 0°C , the density of a certain gaseous oxide at 2 bar is same as that of dinitrogen at 5 bar. What is the molecular mass of the oxide?

- (A) 70 g mol^{-1}
- (B) 35 g mol^{-1}
- (C) 140 g mol^{-1}
- (D) None of these

Solution

(A) Using $pM = dRT$ and substituting $p = 2\text{bar}$ and $T = 273 \text{ K}$. Given that $d_{\text{N}_2} = d_{\text{oxide}}$

$$d_{\text{N}_2} = \frac{5 \times 0.98 \text{ atm} \times 28}{0.0821 \times 273} = 6.12 \text{ g L}^{-1}$$

For the gaseous oxide,

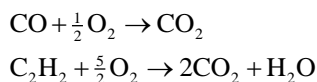
$$M = \frac{dRT}{p} = \frac{6.12 \times 0.0821 \times 273}{2 \times 0.98} = 70 \text{ g mol}^{-1}$$

63. 40.0 mL of a gaseous mixture of CO and C₂H₂ is mixed with 100.0 mL of O₂ and burnt. The volume of the gas after the combustion is 105 mL. Calculate the composition of the original mixture.

- (A) 25 mL of CO and 15 mL of C₂H₂ (B) 15 mL of CO and 25 mL of C₂H₂
 (C) 10 mL of CO and 30 mL of C₂H₂ (D) 20 mL of CO and 20 mL of C₂H₂

Solution

(A) The reactions are



$$x + y = 40$$

$$0.5x + 1.5y = 35$$

Solving, we get $x = 25$ and $y = 15$.

64. 380 mL of a gas at 27°C, 800 mm Hg weighs 0.455 g. The molecular weight of gas in g mol⁻¹ is

- (A) 27 (B) 28 (C) 29 (D) 30

Solution

(B)

$$pV = \frac{w}{M}RT = \frac{800}{760} \times \frac{380}{1000} = \frac{0.455}{M} \times 0.0821 \times 300$$

$$M = \frac{0.455 \times 0.0821 \times 300 \times 5}{2} = 28.016 \text{ g mol}^{-1}$$

65. The rate of diffusion of O₂ and H₂ at same p and T are in the ratio

- (A) 1:4 (B) 1:8 (C) 1:16 (D) 4:1

Solution

$$(A) \frac{u_{\text{O}_2}}{u_{\text{H}_2}} = \sqrt{\frac{M_{\text{H}_2}}{M_{\text{O}_2}}} = \sqrt{\frac{2}{32}} = \frac{1}{4} \text{ as } p_1 = p_2$$

66. What will be the pressure exerted by a mixture of 3.2 g of methane and 4.4 g of carbon dioxide contained in 9 dm³ flask at 27°C?

- (A) 8.314 Pa (B) 8.314 × 10² Pa (C) 2 × 10² Pa (D) 8.314 × 10⁴ Pa

Solution

$$(D) n_{\text{total}} = n_{\text{CH}_4} + n_{\text{CO}_2} = \frac{3.2}{16} + \frac{4.4}{44}, V = 9 \text{ L}, T = 300 \text{ K}, R = 0.0821 \text{ L atm}^{-1} \text{ mol}^{-1}$$

Substituting the above values in $p_{\text{total}} \times V_{\text{T}} = n_{\text{total}}RT$, we get $p = 8.314 \times 10^4 \text{ Pa}$

67. The average velocity of an ideal gas molecule at 27°C is 0.3 m s⁻¹. The average velocity at 927°C will be

- (A) 0.6 m s⁻¹ (B) 0.3 m s⁻¹ (C) 0.9 m s⁻¹ (D) 3.0 m s⁻¹

Solution

$$(A) \quad u_{\text{avg}} \propto \sqrt{T} \Rightarrow \frac{u_1}{u_2} = \sqrt{\frac{T_1}{T_2}} = \sqrt{\frac{300}{1200}} = \frac{1}{2}$$

$$u_2 = 2 \times 0.3 = 0.6 \text{ m s}^{-1}$$

68. The root mean square velocity of an ideal gas at constant pressure varies with density as

- (A) ρ^2 (B) ρ (C) $\rho^{1/2}$ (D) $1/\rho^{1/2}$ (IIT-JEE 2001)

Solution

(D) For an ideal gas, $pV = nRT$, therefore,

$$u_{\text{rms}} = \left(\frac{3RT}{M} \right)^{1/2} = \left(\frac{3pV/n}{M} \right)^{1/2} = \left(\frac{3pV \times M/w}{M/V} \right)^{1/2} = \left(\frac{3p}{\rho} \right)^{1/2}$$

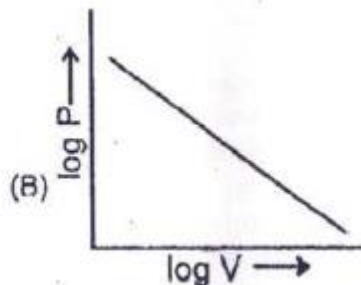
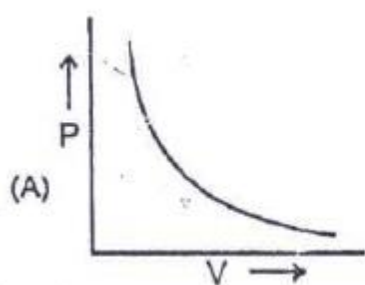
69. The values of van der Waals constant a for the gases O₂, N₂, NH₃, and CH₄ are 1.360, 1.390, 4.170, and 2.253 L² atm mol⁻², respectively. The gas that can most easily be liquefied is

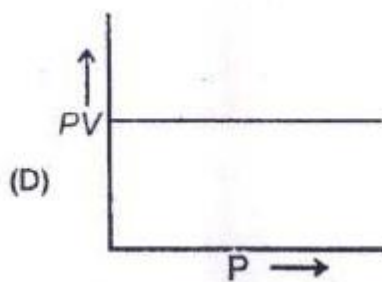
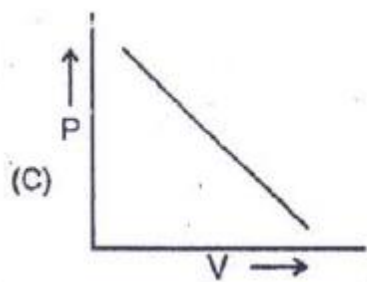
- (A) O₂ (B) N₂ (C) NH₃ (D) CH₄

Solution

(C) The more the value of a , more is its compressibility as it represents attractive forces.

70. Which curve does not represent Boyle's law?





Solution

(C) Graphs (A), (B), and (D) represent Boyle's law, that is, $pV = K$ (constant). Graph (C) does not represent Boyle's law since $pV \neq \text{Constant}$.

71. The circulation of blood in human body supplies O_2 and releases CO_2 . The concentration of O_2 and CO_2 is variable but on the average, 100 mL blood contains 0.02 g of O_2 and 0.08 g of CO_2 . The volume of O_2 and CO_2 at 1 atm and at body temperature of $37^\circ C$, assuming 10 L blood in human body, would be

- (A) 2 L, 4 L (B) 1.5 L, 4.5 L (C) 1.59 L, 4.62 L (D) 3.82 L, 4.62 L

Solution

(C) Number of moles of O_2 in 10 L blood = $\frac{0.02 \times 10}{0.1 \times 32} = \frac{1}{16}$

Number of moles of CO_2 in 10 L blood = $\frac{0.08 \times 10}{0.1 \times 44} = \frac{2}{11}$

Volume of O_2 at 1 atm and $37^\circ C = \frac{0.0821 \times 310}{16 \times 1} = 1.59 \text{ L}$

Volume of CO_2 at 1 atm and $37^\circ C = \frac{2 \times 0.0821 \times 310}{11 \times 1} = 4.63 \text{ L}$

72. In the graph shown in Fig. 4 of Maxwell–Boltzmann distribution of molecular velocities

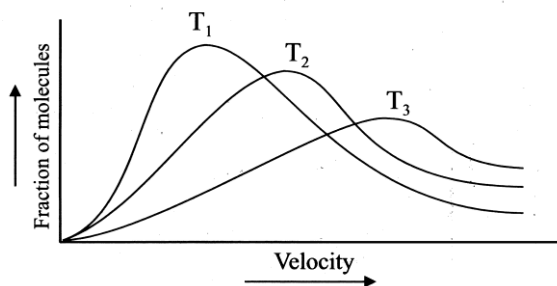


Figure 4

Which of the following is the correct order of temperature?

- (A) $T_1 < T_2 < T_3$ (B) $T_3 < T_2 < T_1$ (C) $T_2 < T_1 < T_3$ (D) None of these

Solution

(A) As the peak of the curve decreases, temperature increases.

73. The vapor density of gas is 11.2. The volume occupied by 11.2 g of this gas at STP is

- (A) 22.4 L (B) 11.2 L (C) 1 L (D) 2.24 L

Solution

(B) $2 \times \text{Vapor density} = \text{Molecular weight}$

$pV = (w/M)RT$ at STP, that is, $p = 1$ atm and $T = 273$ K

Substituting, we get
$$V = \frac{1}{p} \times \frac{w}{M} \times RT = \frac{1}{1} \times \frac{11.2}{2 \times 11.2} \times 0.0821 \times 273 = 11.2 \text{ L}$$

74. NH_3 gas is liquefied more easily than N_2 ; thus,

- (A) van der Waals constants a and b of NH_3 is higher than that of N_2 .
 (B) van der Waals constant a and b of NH_3 is less than that of N_2 .
 (C) a of $\text{NH}_3 > a$ of N_2 , but b of $\text{NH}_3 < b$ of N_2 .
 (D) a of $\text{NH}_3 < a$ of N_2 , but b of $\text{NH}_3 > b$ of N_2 .

Solution

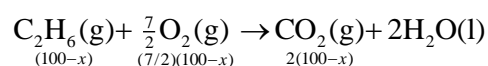
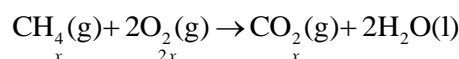
(C) Greater the value of a , easier the liquefaction.

75. When 100 mL sample of methane and ethane along with excess of O_2 is subjected to electric spark, the contraction in volume was observed to be 212 mL. When the resulting gases were passed through KOH solution, further contraction in volume was:

- (A) 60 mL (B) 96 mL (C) 108 mL (D) None of these

Solution

(D) The reactions involved are



From the given data, we have the total contraction in volume as

$$2x + 2.5(100 - x) = 212 \Rightarrow 0.5x = 38 \Rightarrow 76 \text{ mL}$$

Hence, the on passing KOH, the further contraction observed = volume of CO_2 evolved

which can be obtained from the reactions as $x + 2(100 - x) = 76 + 200 - 2(76) = 124 \text{ mL}$.

76. At STP, a container has 1 mol of Ar, 2 mol of CO₂, 3 mol of O₂, and 4 mol of N₂. Without changing the total pressure if 1 mol of O₂ is removed, the partial pressure of O₂:

- (A) is changed by about 26%. (B) is halved.
(C) is unchanged. (D) changed by 33%.

Solution

(A) Given that $p_i = p_f$, or

$$\frac{10RT}{V_i} = \frac{9RT}{V_f} \Rightarrow V_f = \frac{9V_i}{RT}$$

Now,

$$p_{O_{2i}} = \frac{3RT}{V_i} \quad \text{and} \quad p_{O_{2f}} = \frac{2RT}{V_f}$$

Therefore,

$$\frac{p_{O_{2i}} - p_{O_{2f}}}{p_{O_{2i}}} = \frac{3 - (20/9)}{3} = 26\%$$

77. The ratio, rms velocity of SO₂ to that of He at 30°C is equal to

- (A) 4 (B) 0.25 (C) 0.10 (D) 8

Solution

(A) The rms velocity is given by $u_{\text{rms}} = \sqrt{\frac{3RT}{M}}$.

78. Predict which of the following statements are true and which are false.

- (I) For constant volume if temperature is increased pressure increases due to the increase in the number of collisions among the molecules.
(II) For a real gas at NTP if $Z > 1$ then $V_m < 22.4$ L.
(III) Gases can be solidified just below their critical temperature.
(A) T T T (B) T T F (C) T F F (D) F F F

Solution

(C)

79. Choose the correct statement for viscosity (η) variation with T and p for an ideal gas.

- (A) η of a gas increases with increase in temperature (T), but it is independent of pressure.
(B) η of a gas decreases with increase in T and increases with increase in p .
(C) η of a gas is independent of temperature and pressure.
(D) η of a gas increases with increase in both T and p .

Solution

(A) In the case of gases, the viscous resistance arises from the transport of molecules from one layer to another, with transfer of momenta, so that the fast-moving molecules in one layer are slowed down, while the slow moving molecules in the other are accelerated. This momentum transfer increases with increases in temperature.

A simple expression for the viscosity of a gas is

$$\eta = \frac{1}{3} c d \ell \quad \text{where } d \text{ is the density and } \ell \text{ is the mean free path.}$$

$d \propto \text{pressure}$ and $\ell \propto \frac{1}{\text{Pressure}}$, so η is independent of pressure.

80. What is the ratio of $u_{\text{rms}}/u_{\text{mp}}$ for methane gas at 300 K?

- (A) 1.22 (B) 2.22 (C) 2.08 (D) 1.08

Solution

$$(A) \frac{u_{\text{rms}}}{u_{\text{mp}}} = \frac{(3RT/M)^{1/2}}{(2RT/M)^{1/2}} = \left(\frac{3}{2}\right)^{1/2} = 1.22$$

81. For a sample of gas X shown in Fig. 5, the rms velocity at temperature T will be

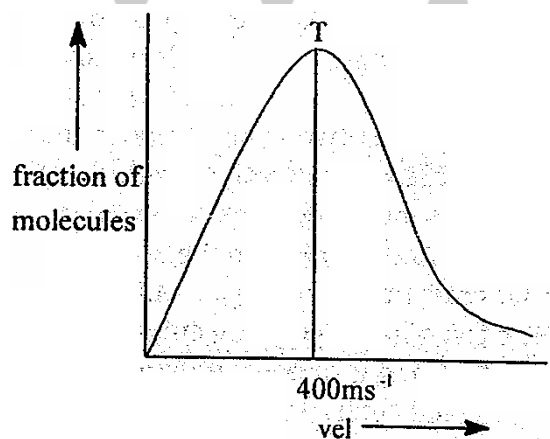


Figure 5

- (A) 328 m s^{-1} (B) $\sqrt{\frac{3\pi}{8}} \times 400 \text{ m s}^{-1}$ (C) 490 m s^{-1} (D) 400 m s^{-1}

Solution

(C) Given that $u_{\text{mp}} = 400 \text{ m s}^{-1}$, therefore, $u_{\text{rms}} = 1.22 \times 400 = 488 \text{ m s}^{-1}$

Multiple Correct Choice Type

1. Which of the following statements are correct?

- (A) He diffuses at a rate of 8.65 times as much as CO does.
- (B) He escapes at a rate of 2.65 times as much as CO does.
- (C) He escapes at a rate of 4 times of as CO₂.
- (D) He escapes at a rate of 4 times as fast as SO₂ does.

Solution

$$(B, D) \frac{r_{\text{He}}}{r_{\text{CO}}} = \left(\frac{M_{\text{CO}}}{M_{\text{He}}} \right)^{1/2} = \left(\frac{28}{4} \right)^{1/2} = 2.645 \quad \text{and} \quad \frac{r_{\text{He}}}{r_{\text{SO}_2}} = \left(\frac{M_{\text{SO}_2}}{M_{\text{He}}} \right)^{1/2} = \left(\frac{64}{4} \right)^{1/2} = 4$$

2. Select correct statements:

- (A) Gases tend to behave non-ideally at low temperatures and high pressures.
- (B) Gases tend to behave ideally at high temperature and low pressures.
- (C) The extent to which Z deviates from 1 is a measure of the non-ideality of a gas.
- (D) Z = 1 under critical states.

Solution

(A, B, C) Concept based.

3. Which of the following statements is/are wrong?

- (A) At a given temperature the transitional kinetic energy of 1 mol of every gas is same which is equal to $(3/2)RT$.
- (B) Kinetic energy of a gas depends on its mass.
- (C) Kinetic energy depends on the volume.
- (D) Kinetic energy depends on the pressure.

Solution

(C, D) Concept based.

4. What is the conclusion you would draw from the following graphs shown in Fig. 6?

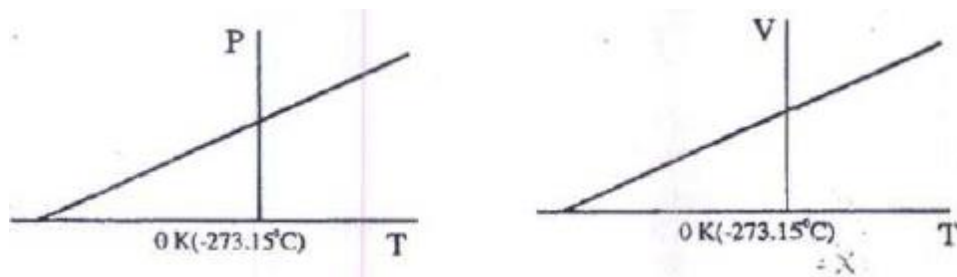


Figure 6

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

Solution

(C, D) $p \propto T$ and $V \propto T$.

5. Which of the following statements is wrong for gases?

- (A) Gases do not have a definite shape and volume.
- (B) Volume of the gas is equal to volume of container confining the gas.
- (C) Confined gas exerts uniform pressure on the walls of its container in all directions.
- (D) Mass of gas cannot be determined by weighing a container in which it is enclosed.

Solution

(A, C)

6. A gas described by van der Waals equation:

- (A) behaves similar to an ideal gas in the limit of larger molar volumes.
- (B) behaves similar to an ideal gas in the limit of large pressures.
- (C) is characterized 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.

Solution

(A, C, D)

When V_m approaches large value, p approaches zero $\Rightarrow Z = 1$.

When p approaches large value $\Rightarrow Z > 1$ and increases.

van der Waals gas constant does not depend on the temperature and pressure and depends on the identity of the gas. A real gas exerts pressure less than an ideal gas due to the presence of the attractive force.

7. According to kinetic theory of gases.

- (A) Pressure of the gas molecule is proportional to most probable speed of the gas molecules.
- (B) The pressure exerted by the gas molecule is proportional to root mean square speed of the gas molecules.

- (C) The root mean square speed is directly proportional to square root of the Kelvin temperature.
 (D) Kinetic energy of the gas molecules does not depend on, p , V , and molar mass of the gas molecules.

Solution

(B, C, D) According to kinetic gas equation; $pV = \frac{1}{3} mNu^2$ based on kinetic gas postulates.

8. Consider a sample of equimolar mixture of He gas and NO gas both at 300 K and 1 atm. Assuming ideal gas behavior which of the following quantities are equal for two samples?

- (A) Root mean square speed of molecules
 (B) Mean translational kinetic energy of molecules
 (C) Number density of molecules
 (D) Kinetic energy of molecules

Solution

(B, C, D)

9. Consider the following statements. Which of the following are true?

- (A) Atmospheric pressure is less at the top of a mountain than at sea level.
 (B) Gases are much more compressible than solids or liquids.
 (C) When the atmospheric pressure increases, the height of the mercury column rises.
 (D) Both c and d.

Solution

(A, B)

10. For an ideal gas, under isobaric condition, a graph between $\log V$ vs. $\log T$:

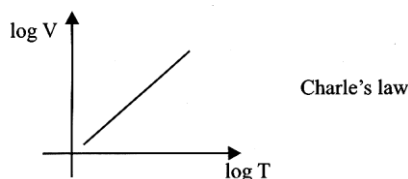
- (A) is linear with unit slope. (B) represents Boyle's law.
 (C) represents Charles' law. (D) represents Gay-Lussac's law.

Solution

(A, C) $V = (\text{const.})T = kT$

$$\log V = \log T + \log k$$

The graph based on the above equation is



11. A mixture of O_2 and He kept in a container at $27^\circ C$. Which of the following statements are correct?

- (A) O_2 molecule will hit the wall of the container with smaller average speed as compared to He.
- (B) O_2 molecules will hit the wall of the container with greater average speed as compared to He.
- (C) O_2 molecule will hit the wall of the container with the greater kinetic energy as compare to He.
- (D) O_2 molecule will hit the wall the container with equal kinetic energy as compare to He.

Solution

(A, D) As per kinetic theory of gases.

12. Which of the following are correct statements?

- (A) van der Waals constant a is a measure of attractive force.
- (B) van der Waals constant b is also called co-volume or excluded volume.
- (C) b is expressed in $L mol^{-1}$.
- (D) b is one-third of critical volume.

Solution

(A, B, C, D)

13. H_2 and N_2 are contained in two separate isothermal vessels connected by a thin tube. When the valve separating the two vessels is opened, which of the following will be true for the final state? Both the vessels are at same temperature

- (A) Mass of H_2 in vessel A = Mass of H_2 in vessel B
- (B) Mass of N_2 in vessel A = Mass of N_2 in vessel B
- (C) Mass of H_2 in vessel A = Mass of N_2 in vessel A
- (D) Total pressure will be same in vessels A and B

Solution

(A, B, D)

Assertion–Reasoning Type

Choose the correct option from the following:

- (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.

1. Statement 1: One mole of helium atoms should occupy 22.4 L volume at STP.

Statement 2: Taking 31 pm as radius of helium atoms, if we pack together a mole of helium atoms, the mole of atoms should have a volume of 22.4 L.

Solution

(C) One mole of molecules of all gases occupies 22.4 L at 273 K and 760 mm Hg pressure (STP). Hence, molar volume of all gases at STP is 22.4 L.

2. Statement 1: At low pressure van der Waals equation is reduced to $\left(p + \frac{a}{V^2}\right)V = RT$

Statement 2: The compressibility factor corresponding to low pressure is given by $1 - \frac{RTV}{a}$.

Solution

(C) $pV + \frac{a}{V} = RT \Rightarrow pV = RT - \frac{a}{V}$; As at low pressure V is large; therefore, $V - b \sim V$

Therefore,
$$Z = \frac{pV}{RT} = \left[1 - \frac{a}{RTV}\right]$$

3. Statement 1: A sample of 8.00 mol of chlorine gas in 94.00 L tank at 27°C leads to a pressure of 2.096 atm according to ideal gas law.

Statement 2: The actual pressure of the sample of chlorine is nearly 20 atm less than the ideal pressure.

Solution

(B) $p = \frac{nRT}{V} = \frac{8 \times 0.082 \times 300}{94} = 2.096 \text{ atm}$

4. Statement 1: The value of the van der Waals constant a is large for NH_3 than PH_3 .

Statement 2: Hydrogen bonding is present in NH_3 .

Solution

(A) Due to H-bonding in NH_3 , the intermolecular forces are stronger; hence, large value of 'a' and hence easily liquefiable.

5. Statement 1: Absolute zero is lowest possible temperature.

Statement 2: A lower temperature than absolute zero would correspond to negative value of volume of gas which is meaningless.

Solution

(A) Much before this temperature a gas liquefies, and then solidifies.

6. Statement 1: Equal volumes of all gases under similar conditions of temperature and pressure contain equal number of molecules.

Statement 2: Volume of a gas is inversely proportional to pressure.

Solution

(A)

7. Statement 1: Compressibility factor for hydrogen varies with pressure with positive slope at all pressures.

Statement 2: Even at low pressures, repulsive forces dominate hydrogen gas.

Solution

(A) In case of H_2 , compressibility factor increases with the pressure. At 273 K, $Z > 1$, which shows that it is difficult to compress the gas as compared to ideal gas. In this case, repulsive forces dominate. The value of a is very small.

Linked Comprehension Type

Read the paragraphs and answer the questions that follow.

Paragraph I

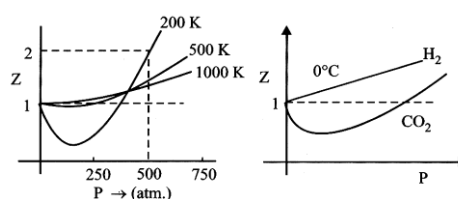
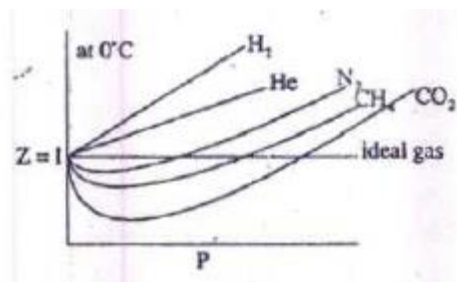
The real gases deviate from ideal behavior due to the following reasons:

- (a) The actual volume occupied by the gas molecule is negligible as compared to the total volume of the gases.
- (b) The forces of attraction and repulsion among the gas molecules are negligible.

The extent of deviation of the real gas from ideal behavior is explained by compressibility factor (Z), which is function of pressure and temperature for real gas.

For ideal gas, $Z = 1$ whereas for real gases two cases arise. When $Z > 1$, which means it is less compressible because force of repulsion dominates over force of attraction. When $Z < 1$, the force of attraction dominates over the force repulsion.

The graph of Z vs. p for different gases at one temperature is shown in Fig. 7(a), and the graph of Z vs. p for 1 mol of hypothetical gas at three distinct temperature temperatures is shown in Fig. 7(b).



(a)

(b)

Figure 7

Boyle's temperature $T_B = a/Rb$ is the temperature at which a gas shows ideal behavior over a pressure range in the low pressure region. If a plot is obtained at temperature well below Boyle's temperature than the curve will show negative deviation, in low pressure region and positive deviation in the high pressure region. Near critical temperature the curve is more likely as CO_2 and the temperature well above critical temperature curve is more like H_2 at (0°C) as show above. At high pressure suppose all the constant temperature curve varies linearly with pressure according to the following equation:

$$Z = 1 + \frac{pb}{RT} \quad (R = \text{cal mol}^{-1}\text{K}^{-1})$$

The van der Waals equation of state for 1 mol of gas is as under:

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT \quad (1)$$

where a and b are van der Waals constants. The van der Waals constant a measures the amount of the force of attraction among the gas molecules. Higher the value of a , higher will be the ease of liquefaction.

When pressure is too high like in case of H_2 and He , the equation will reduce to $p(V - b) = RT$.

When pressure is too low like in case of N_2 , CH_4 , or CO_2 , the equation will reduce to

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

1. What is the correct increasing order of a of the gases shown as in Fig. 7(b)?

(A) $\text{H}_2 < \text{He} < \text{N}_2 < \text{CO}_2$ (B) $\text{CO}_2 < \text{N}_2 < \text{He} < \text{H}_2$

(C) $\text{N}_2 < \text{CO}_2 < \text{H}_2 < \text{He}$ (D) $\text{N}_2 < \text{H}_2 < \text{He} < \text{CO}_2$

Solution

(A) Greater the attractive forces, higher the value of a .

2. Which of the following is correct?

(A) $(a/b) < 0.4 \text{ cal mol}^{-1}$ (B) $0.4 \text{ kcal mol}^{-1} < (a/b) < 2 \text{ kcal mol}^{-1}$

(C) $(a/b) > 0.4 \text{ kcal mol}^{-1}$ (D) $(a/b) = 1 \text{ kcal mol}^{-1}$

Solution

(D) Check that 500 K is Boyle's temperature. So,

$$500 = \frac{a}{2 \times b} \Rightarrow \frac{a}{b} = 1 \text{ kcal mol}^{-1}$$

3. For 500 K, the plot the value of Z changes from 2 to 2.2. If pressure is varied from 100 atm to 1200 atm (high pressure), then the value of b/RT will be:

- (A) 10^{-3} atm^{-1} (B) $2 \times 10^{-3} \text{ atm}^{-1}$ (C) $5 \times 10^{-4} \text{ atm}^{-1}$ (D) 10^{-4} atm^{-1}

Solution

(A) Slope is high p region $= \frac{b}{RT} = \frac{2.2 - 2}{1200 - 1000} = \frac{0.2}{200} = 10^{-3} \text{ atm}^{-1}$

4. As shown in Fig. 7(b) at 200 K and 500 atm value of compressibility factor is 2 (approx.). Then volume of the gas at this point will be:

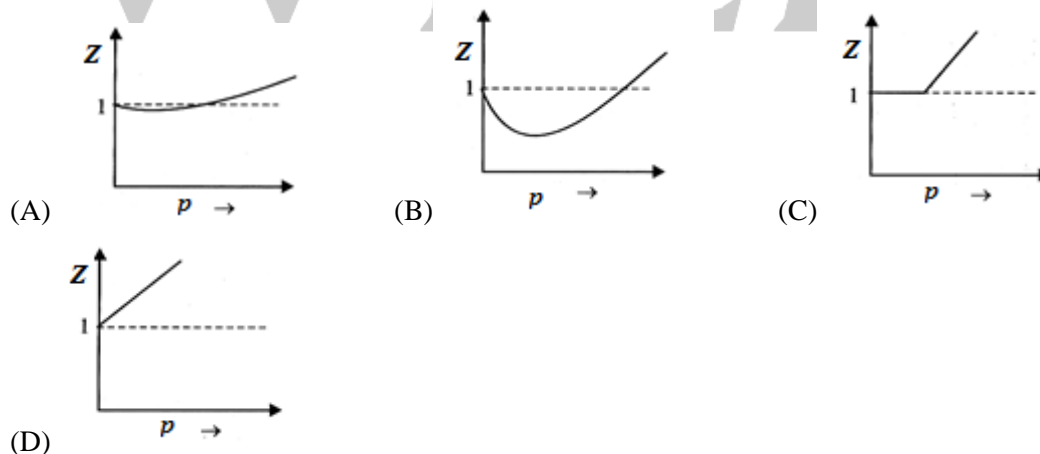
- (A) 0.01 L (B) 0.09 L (C) 0.065 L (D) 0.657 L

Solution

(C) $Z = 2 = \frac{pV_m}{RT}$

Therefore, $V_m = \frac{2RT}{p} = \frac{0.082 \times 200 \times 2 \text{ L}}{500} = 0.066 \text{ L}$

5. Plot of Boyle's temperature for the gas will be:



Solution

(A) At Boyle's temperature, Z versus p curve lies close to the curve for ideal gas at $p = 0$ and rises above the ideal gas curve only very slowly with increase in pressure.

6. Which of the following is the correct increasing order of temperature? For a given gas as shown in Fig. 7(b),

$$(A) T_1 < T_2 < T_3 < T_4$$

$$(B) T_2 < T_1 < T_3 < T_4$$

$$(C) T_3 < T_4 < T_1 < T_2$$

$$(D) T_4 < T_3 < T_2 < T_1$$

Solution

(D) At higher temperature, the gas behaves ideally.

Paragraph II

Gas molecules are in a constant state of motion, thus colliding with each other and with the wall of container. Maxwell and Boltzmann proposed that due to such collisions, the velocities of gas molecules are always variable. A fraction of molecules can be considered to have a particular molecular velocity at a time. Maxwell calculated the distribution of velocity among fraction of total number of molecules based on probability. The average, most probable, and root mean square velocities of the fraction of gas molecules are expressed as

$$u_{\text{avg}} = \sqrt{\frac{8RT}{\pi M}} \quad u_{\text{mp}} = \sqrt{\frac{2RT}{M}} \quad u_{\text{rms}} = \sqrt{\frac{3RT}{M}}$$

7. The ratio $u_{\text{rms}}:u_{\text{avg}}:u_{\text{mp}}$ is

$$(A) 1:0.921:0.816 \quad (B) 2:0.0921:1 \quad (C) 3:0.0921:8 \quad (D) 4:0.0921:0816$$

Solution

(A) From their relationship, this can be worked out.

8. Calculate rms speed of O_2 molecules having kinetic energy of 2 kcal mol^{-1} .

$$(A) 22.795 \text{ m s}^{-1} \quad (B) 30 \text{ m s}^{-1} \quad (C) 32 \text{ m s}^{-1} \quad (D) 52 \text{ m s}^{-1}$$

Solution

(A) We know that

$$\text{Kinetic energy} = \frac{3}{2} RT \Rightarrow 3RT = 4000$$

$$v_{\text{rms}} = \left(\frac{3RT}{M} \right)^{1/2} = \left(\frac{4000}{32} \right)^{1/2} = 11.18 \text{ m s}^{-1}$$

Paragraph III

For 1 mol of gas, the van der Waals equation is

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

where a signifies the force of attraction among the gas molecules and b signifies the incompressible volume, that is, the volume having no effect of compression and expansion. The compressible

volume, that is, the volume having effect of compression and expansion is $V - b$ for 1 mol real gas. Another form of van der Waals equation of states is called virial equation. The virial equation for 1 mol real gas is

$$\frac{pV_m}{RT} = 1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \dots \text{ to higher powers of } n$$

where B and C are known as first and second virial coefficients, respectively. The temperature at which real gases obey ideal gas equation, $pV = RT$, is known as Boyle's temperature, T_B .

9. If the second virial coefficient of 3 mol of He at NTP be $6.4 \times 10^{-2} \text{ (L mol}^{-1}\text{)}^3$, then what will be the real volume of He gas?

- (A) 66.0 L (B) 23.6 L (C) 25 L (D) 68.4 L

Solution

$$(D) \frac{pV_m}{RT} = 1 + \frac{B}{V_m} \Rightarrow \frac{1 \times V_m}{0.0821 \times 298} = 1 + \frac{6.4 \times 10^{-2}}{V_m}$$

Solving, we get a quadratic equation as

$$V_m^2 - (6.4 \times 10^{-2})(0.0821 \times 298) - (0.0821 \times 298)V_m = 0$$

Solving, we get $V_m = 22.8 \text{ L mol}^{-1}$. Therefore, the real volume is $3 \times 22.8 = 68.4 \text{ L}$

10. Which of the following is the correct statement about the Boyle's temperature (T_B)?

- (A) The temperature at which second virial coefficient becomes zero.
 (B) The temperature at which first virial coefficient is zero.
 (C) The value of T_B is $2a/Rb$.
 (D) None of these.

Solution

(A) At Boyle's temperature, $pV = RT$.

11. For the constant value of b , if the Boyle's temperature of the gases is increased, then what will be the effect on the ease of liquefaction ?

- (A) It will increase, on increasing the Boyle's temperature.
 (B) It will decrease, on increasing the Boyle's temperature.
 (C) First liquefaction will increase, then it will decrease.
 (D) No effect

Solution

(A)

Integer Answer Type

1. The stop cock connecting two bulbs of volume 5 and 10 L containing an ideal gas at 9 and 6 atm, respectively, is opened. The final pressure (in atmosphere) in the two bulbs if the temperature remains the same is ____.

Solution

$$(7) \frac{p_1V_1 + p_2V_2}{V_{\text{Total}}} = p_{\text{Total}} \Rightarrow p_{\text{Total}} = \frac{5 \times 9 + 10 \times 6}{15} = \frac{45 + 60}{15} = 7 \text{ atm}$$

2. A compound exists in the gaseous phase both as monomer (A) and dimer (A₂). The molecular weight of A is 48. In an experiment 96 g of compound was confined in vessel of volume 33.6 L and heated to 273°C. Calculate the pressure developed if the compound exists as dimer to the extent of 50% by weight under these conditions.

Solution

(2) Since A and A₂ are two states in gaseous phase having their weight ratio 50%, that is, 1:1.

$$\text{Moles of A} = \frac{96}{2} \times \frac{1}{48} = 1 \quad \left(n = \frac{w}{m} \right) 2A \leftrightarrow A_2$$

$$\text{Moles of A}_2 = \frac{96}{2} \times \frac{1}{96} = \frac{1}{2}$$

$$\text{So, total moles of A and A}_2 \text{ are} = 1 + \frac{1}{2} = \frac{3}{2}$$

Thus, from $pV = nRT$

$$p \times 33.6 = \frac{3}{2} \times 0.0821 \times 546 = 2 \text{ atm}$$

3. If the pressure and absolute temperature of 2 L of carbon dioxide are doubled, the volume (in liter) of carbon dioxide would become ____.

Solution

$$(2) p \propto \frac{1}{V} \text{ and } V \propto T$$

If p doubles, V becomes half, then when T doubles, V becomes its original value = 2 L.

4. 4 g of an ideal gas was introduced into a bulb of volume of 0.821 dm³ at certain pressure p and temperature T . The above bulb was placed in a thermostat mentioned at temperature $(T + 125)$ K of 0.8 g of the gas was left off to keep the original pressure. Calculate the pressure in atmosphere. [Molecular weight of the gas is 40 g mol⁻¹ and R value is 0.0821 L atm k⁻¹ kmol.

Solution

$$(5) \text{ Initial number of moles} = \frac{4}{40} = 0.1$$

$$\text{Final number of moles} = \frac{3.2}{40} = 0.08$$

Since p and V are constant, $n_1T_1 = n_2T_2$ as $pV = nRT$

Therefore, $nT = \text{Constant}$

$$0.1T_1 = 0.08(T_1 + 125) \Rightarrow T_1 = 500 \text{ K}$$

From $pV = nRT$

$$p = \frac{0.1 \times 0.082 \times 500}{0.821} = 5 \text{ atm}$$

5. One mole of an ideal monoatomic gas is mixed with 1 mol of an ideal diatomic gas. The molar specific heat (in calories) of the mixture at constant volume is ____.

Solution

(4) 1 mol of monoatomic gas, $\gamma = 1.66$

1 mol of diatomic gas, $\gamma = 1.40$

$$\gamma \text{ for the mixture} = \frac{1.66 + 1.40}{2} = 1.50$$

$$\gamma = \frac{C_p}{C_v} \Rightarrow 1.5 = \frac{C_p}{C_v} \text{ or } C_p = 1.5C_v$$

As $C_p - C_v = R$, so $1.5C_v - C_v = 2 \text{ cal mol}^{-1} \text{ K}^{-1}$

$$C_v(1.5 - 1) = 2 \Rightarrow C_v(0.5) = 2 \Rightarrow C_v = \frac{2}{0.5} \Rightarrow C_v = 4 \text{ cal}$$

6. If the slope of Z (compressibility factor) vs. p curve is constant (slope = $0/492.6 \text{ atm}^{-1}$) at a particular temperature (300 K) and very high pressure, then calculate the diameter of the molecules. (Given $N_A = 6.0 \times 10^{23}$, $R = 0.0821 \text{ atm L mol}^{-1} \text{ K}^{-1}$.)

Solution

(5) We know that

$$\left(p + \frac{a}{V_2}\right)(V - b) = RT \text{ and } Z = \frac{pV}{RT}$$

$$Z = 1 + \frac{pb}{RT} \text{ at high pressure}$$

$$\text{Slope} = \frac{b}{RT} = \frac{\pi}{492.6} \Rightarrow b = \frac{\pi}{492.6} \times 0.0821 \times 300 \quad (1)$$

But

$$b = \frac{4}{3} \pi r^3 \times 4N_A \quad (2)$$

Solving, we get $r = 2.5 \text{ \AA}$, therefore, $d = 5 \text{ \AA}$.

Matrix–Match Type

1. Match the term with its expression.

Column I	Column II
(A) RMS velocity	(p) $\sqrt{\frac{8RT}{\pi M}}$
(B) Average velocity	(q) $\frac{1}{3} \frac{mNu^2}{V}$
(C) Most probable velocity	(r) $\sqrt{\frac{3RT}{M}}$
(D) Pressure by kinetic theory of gases	(s) $\sqrt{\frac{2RT}{M}}$
	(t) $\sqrt{\frac{2p}{\rho}}$

Solution

A \rightarrow (r), B \rightarrow (p), C \rightarrow (s,t), D \rightarrow (q)

They are derived from kinetic gas equation.

2. Match the expression with the type of changes it undergoes.

Column I	Column II
(A) $p = 2V^2$	(p) If volume increases the temperature will also increase.
(B) $pV^2 = \text{constant}$	(q) If volume increases the temperature will decrease.
(C) $C = C_V + 2R$	(r) For expansion, heat will have to be supplied to the gas.
(D) $C = C_V - 2R$	(s) If temperature increases then work done by gas is positive.

Solution

A \rightarrow (p, r, s); B \rightarrow (q, r); C \rightarrow (q); D \rightarrow (p, r, s)

(A) $p = 2V^2$

If the volume increases, the pressure will also increase.

(B) $pV^2 = \text{constant}$.

If volume increases, the temperature will decrease.

(C) $C = C_V + 2R$

For expansion, heat will have to be supplied to the gas.

$$(D) \quad C = C_V - ZR$$

If volume increases, the temperature will decrease.

3. Match the compression factor under different conditions with its values

Column I	Column II
(A) Compression factor (Z) for ideal gas	(p) $3/8$
(B) Z for real gas at low P	(q) $(1 + pb)/RT$
(C) Z for real gas at high P	(r) 1
(D) Z for critical state	(s) $(1 - a/RTV)$
	(t) pV/nRT

Solution

$$A \rightarrow (r, t) \quad B \rightarrow (s, t) \quad C \rightarrow (q, r), \quad D \rightarrow (p, t)$$

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT \quad \text{and} \quad Z = \frac{V_m}{V_{\text{ideal}}}$$

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