

Answer Key

| | | | | |
|--|----------------------------------|-------------|----------------|---------|
| 1. (C) | 2. (B) | 3. (C) | 4. (C) | 5. (B) |
| 6. (C) | 7. (C) | 8. (C) | 9. (ABD) | 10. (A) |
| 11. (C) | 12. (C) | 13. (A) | 14. (B) | 15. (A) |
| 16. (C) | 17. (46.6) | 18. (3.77L) | 19. (13 times) | 20. |
| (421.9K) | | | | |
| 21. (0.825L) | 22. (16.07g, 12dm ³) | | 23. (1088g) | 24. (4) |
| 25. (10,000K) | 26. (2) | 27. (A) | | |
| 28. (i) $n = \frac{-T}{100} + 5$, (ii) $V = \frac{-RT^2}{100} + 5RT$, (iii) 51.3125 L | | | | |
| 29. ($V_c = \frac{6B}{A}$, $T_c = \frac{A^2}{6RB}P_c = \frac{A^3}{108B^2}$, compressibility factor = $\frac{P_c V_c}{RT_c} = \frac{1}{3}$) | | | | |
| 30. (4 : 7 : 5) | | | | |

Solution

- On comparing virial equation with the van der waal's equation,

$$B = b - \frac{a}{RT}$$
 Thus, the coefficient is temperature dependent.
 - A real gas behaves as ideal gas for a long range of pressure at the Boyle's temperature.

$$Z = \frac{PV_m}{RT} = 1 \text{ and } B = 0.$$
 - Using dimensional analysis, it can be concluded that the units of B and V_m are the same.
- Due to intermolecular force of attraction between the gas molecules the pressure of real gas is generally less than the pressure of the gas if it were ideal.
- $$\frac{r_x}{r_{O_2}} = \sqrt{\frac{M_{O_2}}{M_x}} \Rightarrow \left(\frac{4}{5}\right)^2 = \frac{32}{M_x} \Rightarrow M_x = 50$$

$$D_x = 0.80 \text{ kg/m}^3$$

$$V_m = \frac{1000}{800} \times 50 = 62.4 \text{ L}$$

$$Z = \frac{PV_m}{RT} = \frac{1 \times 62.5}{0.0821 \times 500} = 1.52$$

4. Suppose initial ratio is represented by n^0 .

$$\frac{r_1}{r_2} \propto \frac{n_1^0}{n_2^0} \sqrt{\frac{M_2}{M_1}}$$

$$\frac{n_1^1}{n_2^1} \propto \frac{n_1^0}{n_2^0} \sqrt{\frac{M_2}{M_1}}$$

n^{th} step ratio of moles

$$\frac{n_1^n}{n_2^n} = \frac{n_1^0}{n_2^0} \left(\sqrt{\frac{M_2}{M_1}} \right)^n$$

$$\frac{3072/2}{20/32} = \frac{240/2}{160/32} \left(\sqrt{\frac{32}{2}} \right)^n$$

$$\Rightarrow 1024 = 4^n$$

$$N = 5$$

5. $p = \frac{ZRT}{V}$

Thus, if $Z > 1$, $p > p_{\text{ideal}}$, i.e., $p > 1 \text{ atm}$



Initial moles 11 12 0

at equilibrium 9 6 4

Moles of N_2 and H_2 present at equilibrium = 15

After addition of water, $\text{NH}_3(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{NH}_4\text{OH}(\text{l})$

Volume of vessel available for gaseous mixture of N_2 and $\text{H}_2 = 20 - 3.58 \Rightarrow 16.42 \text{ L}$

Pressure exerted by gaseous mixture at 300 K = $\frac{15 \times 0.0821 \times 300}{16.42} \Rightarrow 22.5 \text{ atm}$

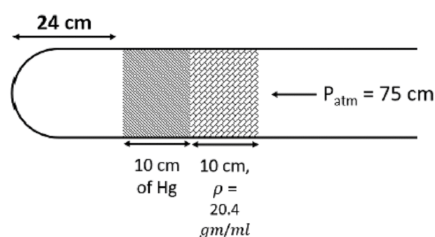
7. $K \propto d, p = kd$ and $k = \frac{1 \text{ atm}}{1 \text{ metre}}$

$$PV = nRT, kd \left(\frac{1}{6} \pi d^3 \right) = nRT$$

$$\frac{d_1^4}{d_2^4} = \frac{n_1}{n_2}, \frac{1}{4^4} = n_1 / n_2, n_2 = 256$$

No. of moles added = $256 - 1 = 255$

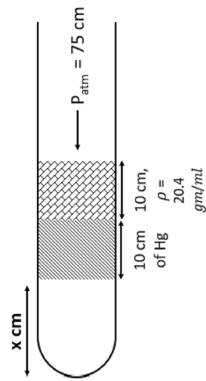
8. Initial condition:



$$P_{\text{initial}} = 75 \text{ cm Hg}$$

$$V_{\text{initial}} = 24A$$

Final condition:



$$P_{\text{final}} = 75 + \frac{10 \times 20.4}{13.6} + 10$$

$$= 100 \text{ cm Hg}$$

$$V_{\text{final}} = Ax$$

Applying Boyle's law,

$$75 \times 24 A = 100 \times Ax$$

$$\Rightarrow x = \frac{75 \times 24}{100} = 18 \text{ cm}$$

9. $PT = (1 + 3\infty) = 1 + 3 \times 0.1 = 1.3 \text{ atm.}$

$$\Delta P = 0.2 \text{ atm or } 76 \times 0.3 \text{ cm of Hg or } 760 \times 0.3 \text{ mm of Hg}$$

10. $\frac{dp}{dt} = \frac{KT}{V} \times \frac{-pA_0}{(2\pi mKT)^{\frac{1}{2}}}$

$$\int \frac{dp}{p} = -\frac{(KT)^{\frac{1}{2}}}{V} \frac{A_0}{(2\pi m)^{\frac{1}{2}}} \int dt$$

$$[\ln p]_{p_0}^{p_0/e} = \sqrt{\frac{KT}{2\pi m}} \frac{A_0}{V} [dt]_0^t$$

$$\left(\ln \frac{p_0}{e} - \ln p_0 \right) = -\sqrt{\frac{KT}{2\pi m}} \frac{A_0}{V} \times t$$

$$\ln e^{-1} = -\sqrt{\frac{KT}{2\pi m}} \frac{A_0}{V} \cdot t \quad \Rightarrow \quad t = \sqrt{\frac{2\pi m}{KT}} \frac{V}{A_0}$$

11. From the equation in previous problem,

$$t \propto \sqrt{\frac{m}{T}} \times \frac{1}{A_0}$$

$$\frac{t_1}{t_2} = \sqrt{\frac{m_1}{m_2}} \times \sqrt{\frac{T_2}{T_1}} \times \frac{(A_0)_2}{(A_0)_1}$$

$$\frac{t}{t_2} = \sqrt{\frac{1}{9}} \times \sqrt{\frac{4}{1}} \times \frac{2}{1}$$

$$\frac{t}{t_2} = \frac{1}{3} \times 2 \times 2 \quad \Rightarrow \quad t_2 = \frac{3}{4} t \quad \Rightarrow \quad t_2 = 0.75t$$

12. The equation can be written as,

$$\ln \frac{P}{P_0} = -\sqrt{\frac{KT}{2\pi m}} \frac{A_0}{V} \times t$$

$$P = P_0 e^{-\sqrt{\frac{KT}{2\pi m}} \frac{A_0}{V} \times t}$$

- After infinite time, $P = P_{\text{ext}}$.
- For pressure to become half, $P = \frac{P_0}{2}$

$$-\ln 2 = -\sqrt{\frac{KT}{2\pi m}} \times \frac{A_0}{V} \times t$$

$$t = \frac{\ln 2 \times V}{A_0} \times \sqrt{\frac{2\pi m}{KT}}$$

Thus, it is independent of initial pressure.

13. $\therefore Z = 1 + \frac{Pb}{RT}$

At 1000 atm,

$$2 = 1 + \frac{1000b}{RT} \quad \dots(i)$$

$$2 \cdot 2 = 1 + \frac{1200b}{RT} \quad \dots(ii)$$

$$\text{Eq. (2)} - \text{eq. (1)} \Rightarrow \frac{200b}{RT} = 0.2$$

$$\frac{b}{RT} = \frac{0.2}{200} = 10^{-3} \text{ atm}$$

14. For high-pressure region,

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

Thus, slope for Z vs. P,

$$m = \frac{b}{RT}$$

Slope will decrease with increase in temperature.

15. • The graph shown by A is same as the one shown by a gas above its critical temperature.
Thus, $T > T_A$.

- The graph shown by B is the same as the one shown by a gas below its critical temperature.
Thus, $T < T_B$.

16. • Since the gas B is below its critical temperature, significant intermolecular forces operate in the gas. Thus, pressure correction term will be more significant (or less negligible for gas B).
- Above critical temperature, gases generally follow the isotherm obtained from Boyle's law (the curve shown by gas A).
 - Gas A is already showing the graph for the condition $T > T_A$.

17. For mixture of O_2 and other gas of molecular mass M ,

$$M_{\text{mix}} = \frac{80 \times 32 + 20M}{100}$$

$$M_{\text{mix}} = 25.6 + 0.2 M$$

$$\text{Now, } r \propto \frac{1}{\sqrt{M}}$$

$$\frac{r_{O_2}}{r_{\text{mix}}} = \sqrt{\frac{M_{\text{mix}}}{32}}$$

$$\Rightarrow \frac{\frac{1}{234}}{\frac{1}{224}} = \sqrt{\frac{M_{\text{mix}}}{32}}$$

$$\Rightarrow \left(\frac{234}{224}\right)^2 = \frac{M_{\text{mix}}}{32}$$

$$\Rightarrow M_{\text{mix}} = 32 \times \left(\frac{234}{224}\right)^2$$

$$\Rightarrow M_{\text{mix}} = 34.92$$

$$\Rightarrow 25.6 + 0.2 M = 34.92$$

$$\Rightarrow 0.2 M = 9.32$$

$$\Rightarrow M = \frac{9.32}{0.2} = 46.6$$

18. $Z = \frac{PV_{\text{real}}}{RT}$

$$\Rightarrow \frac{Z_1}{Z_2} = \frac{P_1}{P_2} \times \frac{T_2}{T_1} \times \frac{V_1}{V_2}$$

$$\Rightarrow \frac{1.95}{1.1} = \frac{800}{200} \times \frac{373}{223} \times \frac{1}{V}$$

$$\Rightarrow V = 4 \times \frac{373}{223} \times \frac{1.1}{1.95}$$

$$\Rightarrow V = 3.77422 \text{ L}$$

19. Let's assume there were total 100 moles of all gases combined initially in the cave. After each sucking, the total moles of all gases are reduced to half (i.e., carbon monoxide moles will also reduce to half every time) and after effusion of fresh air the total moles will again becomes 100. Thus, after each sucking, percentage of carbon monoxide is getting reduced to half of the initial value. For the percentage to decrease from 5% to 0.001%,

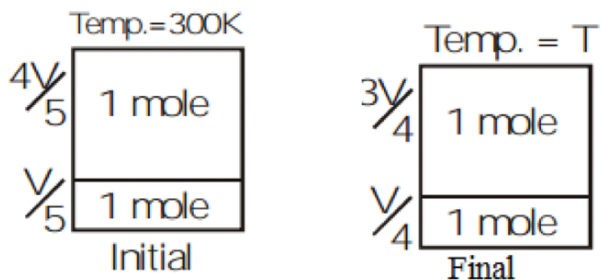
$$\frac{5}{2^n} = 0.001$$

$$5000 = 2^n$$

$$n = 12.28$$

Thus, he must suck the air 13 times in-order to reach safe levels.

20.



The Volume and Temperature are as shown in the above figure.

Initially,

$$P_{\text{lower}} = P_{\text{upper}} + P_{\text{piston}}$$

$$5 \times \frac{R \times 300}{V} = 5 \times \frac{R \times 300}{4V} + P_{\text{piston}}$$

$$P_{\text{piston}} = \left(\frac{5R \times 300}{V} \right) \times \frac{3}{4} \dots\dots(1)$$

Finally,

$$P_{\text{lower}} = P_{\text{upper}} + P_{\text{piston}}$$

$$\frac{4RT}{V} = \frac{4RT}{3V} + P_{\text{piston}}$$

$$\frac{8RT}{3V} = P_{\text{piston}} \dots\dots(2)$$

From equation (1) and (2)

$$\frac{15}{4} \times \frac{R \times 300}{V} = \frac{8RT}{3V} \Rightarrow T = 421.9K$$

21.

14g N \rightarrow 0.5mole

T = 200 K, P = 8.21 atm

$$\frac{P_c V_c}{RT_c} = \frac{3}{8}, \frac{P_r V_r}{T_r} = 2.2$$

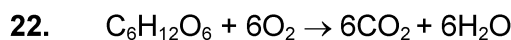
$$P_r = \frac{P}{P_c}, V_r = \frac{V}{V_c}, T_r = T/T_c$$

$$\text{So, } \frac{(P_c P_r)(V_c V_r)}{R(T_c T_r)} = \frac{3}{8} \times 2.2$$

$$\Rightarrow \frac{PV}{RT} = \frac{3}{8} \times 2.2$$

$$V = \frac{3}{8} \times \frac{2.2 \times 0.0821 \times 200}{8.21} = 1.65L$$

so, volume of 0.5 mole N₂ = 1.65 \times 0.5 = 0.825 L



$$n_{\text{O}_2} = 60 \times \frac{0.2}{22.4} = 0.5357$$

$$n_{\text{glucose}} = \frac{0.5357}{6} = 0.08928 \text{ moles}$$

$$W_{\text{glucose}} = 180 \times 0.08928 = 16.07 \text{ gm}$$

$$n_{\text{CO}_2} = n_{\text{O}_2} = 0.5357 \text{ moles}$$

$$V_{\text{CO}_2} = 22.4 \times 0.5357 = 12 \text{ dm}^3$$

23. $PV = nRT$

$$\text{or } 6 \times 3 = n \times 0.0821 \times 300$$

$$\text{or } n = 0.7308$$

$$n_{\text{H}_2} = 0.7 \text{ (given)}$$

$$n_{\text{gas}} = 0.7308 - 0.7 = 0.0308$$

Applying Graham's law of diffusion, we get

$$\frac{r_{\text{H}_2}}{r_{\text{gas}}} = \sqrt{\frac{M_{\text{gas}}}{M_{\text{H}_2}}}$$

$$\text{or } \frac{n_{\text{H}_2}}{n_{\text{gas}}} = \sqrt{\frac{M_{\text{gas}}}{M_{\text{H}_2}}}$$

(because the time of diffusion is the same)

$$\text{or } \frac{0.7}{0.0308} = \sqrt{\frac{M_{\text{gas}}}{2}}$$

$$\text{or } M_{\text{gas}} = 1088.05 \approx 1088 \text{ g}$$

24. $\frac{W_{\text{D}_2}}{W_{\text{H}_2}} = \frac{1}{4}$

Total moles

$$PV = nRT$$

$$n = \frac{24.6 \times 3}{0.0821 \times 300} = 3$$

Total moles

$$n_{\text{H}_2} + 1 = 3 \text{ moles}$$

$$n_{\text{H}_2} = 3 - 1 = 2 \text{ moles}$$

$$\text{Required } \frac{W_{\text{D}_2}}{W_{\text{H}_2}} = \frac{1}{4} \Rightarrow \frac{\text{Mole} \times \text{MW}}{\text{Mole} \times \text{MW}} = \frac{1}{4} \Rightarrow \frac{n_{\text{D}_2}}{n_{\text{H}_2}} \times \frac{2}{1} = \frac{1}{4}$$

$$\text{Thus, final } \frac{n_{\text{D}_2}}{n_{\text{H}_2}} \times \frac{1}{8}$$

$$\frac{n_{\text{H}_2}}{n_{\text{D}_2}} = \frac{P_{\text{H}_2}}{P_{\text{D}_2}} \left(\sqrt{\frac{\text{MW}_{\text{D}_2}}{\text{MW}_{\text{H}_2}}} \right)^n \Rightarrow \frac{8}{1} = \frac{2}{1} \left(\sqrt{\frac{4}{2}} \right)^n \Rightarrow n = 4.$$

25. $P = \frac{V}{8.21}$

or $P = \frac{RT}{8.21P}$

or $T = \frac{8.21P^2}{R}$

Thus, temperature increases with increase in pressure. The maximum temperature will be obtained at 10 atm.

$$T = \frac{8.21(10)^2}{0.0821} = 10,000\text{K}$$

26. $Z = 1 + \frac{Pb}{RT}$ high pressure

$$\frac{dZ}{dP} = \frac{b}{RT} = \frac{1}{2.8}$$

$$b = \frac{RT}{2.8} = \frac{22.4}{2.8} = 4 \times \left(N_A \times \frac{4}{3} \pi R^3 \right)$$

$$\left(N_z \times \frac{4}{3} \pi R^3 \right) = \text{Volume of 1 mole gas}$$

$$= \frac{5.6}{2.8} = 2$$

27. For the same pressure, volume is maximum for the gas 3. Thus, density will be minimum, temperature will be maximum. Thus, (A) matches with (s).

28. (i) Let $n = mT + C$
 $2 = 300m + C$ & $3 = 200m + C$

On solving $m = -\frac{1}{100}, C = 5$

So, $n = \frac{-T}{100} + 5$

(ii) $PV = nRT$

$$\Rightarrow 1 \times V = \left(\frac{-T}{100} + 5 \right) RT$$

(iii) For max. volume

$$\frac{dV}{dT} = 0 \Rightarrow \frac{-2RT}{100} + 5R = 0, T = 250$$

$$V = \frac{-R(250)^2}{100} + 5 \times 250R = -625R + 1250R$$

$$V = 625R = 625 \times 0.0821 \text{ L} = 51.3125 \text{ L}$$

29. $PV = RT - \frac{A}{V} + \frac{2B}{V^2}$

$$V^3 - \frac{RTV^2}{P} + \frac{A}{P}V - \frac{2B}{P} = 0$$

At critical point, $(V - V_c)^3 = 0$

$$V^3 - 3V_c V^2 + 3V_c^2 V - V_c^3 = 0$$

On comparing,

$$3V_c^2 = A/P \quad \dots(i)$$

$$3V_c = RT/P \quad \dots(ii)$$

$$V_c^3 = 2B/P \quad \dots(iii)$$

$$\text{on } \frac{(3)}{(1)} \Rightarrow \frac{V_c}{3} = \frac{2B}{A}$$

$$= V_c = 6B/A$$

$$\text{from equation (i), } 3\left(\frac{6B}{A}\right)^2 = A/P_c \Rightarrow P_c = \frac{A^2}{108B^2}$$

$$\text{equation (ii), } T_c = \frac{3P_c V_c}{R} = \frac{3}{R} \left(\frac{A^3}{108B^2} \right) \left(\frac{6B}{A} \right)$$

$$T_c = \frac{A^2}{6RB} \Rightarrow Z = \frac{P_c V_c}{R} = \frac{\frac{A^3}{108B^2} \cdot \frac{6B}{A}}{R \cdot \frac{A^2}{6RB}} = \frac{1}{3}$$

30. **Left chamber Middle chamber Right Chamber**

| | Left chamber | Middle chamber | Right Chamber |
|-------------------------------|---------------------------------------|--|--|
| Initial moles | $\frac{60}{2} = 30 \text{ moles H}_2$ | $\frac{160}{32} = 5 \text{ moles O}_2$ | $\frac{140}{28} = 5 \text{ moles N}_2$ |
| Final moles (H ₂) | 10 | 10 | 10 |
| Final moles (O ₂) | 0 | 5 | 0 |
| Final moles (N ₂) | 0 | 2.5 | 2.5 |
| | ----- | ----- | ----- |
| Total final moles | 10 | 17.5 | 12.5 |
| Ratio is 4 : 7 : 5 | | | |