

Properties of Gases

Ideal gas Eqn.

A gas at equilibrium has definite value of Pressure (P), volume (V), temperature (T) and composition (n). These are called state variables and are determined experimentally. The state of a gas can be defined by these variables.

Boyle's Law (1662) : $V \propto \frac{1}{P}$, when n and T are fixed for the gas

Charles's Law (1787) : $V \propto T$, when n and P " " " "

Avogadro's Law (1811) : $V \propto n$, when P and T " " " "

When all variables are taken into account

$$V \propto \frac{1}{P} \times T \times n \quad \text{or} \quad PV = nRT$$

— Ideal gas equation of state.

This eqn. is found to hold good most satisfactorily when $P \rightarrow 0$. At ordinary T and P , this eqn. is found to deviate about 5%.

$R \rightarrow$ universal gas constant and its value is calculated from the statement that "at STP, one mole gas occupies 22.4 L".

$$\text{Thus } R = \frac{PV}{nT} = \frac{1 \text{ atm} \times 22.4 \text{ L}}{1 \text{ mol} \times 273 \text{ K}} = 0.082 \text{ L} \cdot \text{atm} \cdot \text{mol}^{-1} \text{K}^{-1}$$

$$\text{Also, } R = \frac{PV}{nT} = \frac{76 \times 13.5 \times 981 \text{ dyne cm}^{-1} \times 22.4 \times 10^3 \text{ cm}^3}{1 \text{ mol} \times 273 \text{ K}}$$

$$= 8.314 \times 10^7 \text{ erg mol}^{-1} \text{K}^{-1}$$

$$= 8.314 \text{ J mol}^{-1} \text{K}^{-1} \quad (\text{since } 1 \text{ Joule} = 10^7 \text{ ergs})$$

$$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \quad ; \quad 1 \text{ calorie} = 4.184 \times 10^7 \text{ ergs}$$

$$= 1.987 \approx 2 \text{ cal mol}^{-1} \text{ K}^{-1}$$

Also ; $PV = \left(\frac{W}{M} \right) \times RT$; $W = \text{wt. of the gas in gm}$
 $M = \text{Molar mass of the gas}$

$$\Rightarrow P = \left(\frac{W}{V} \right) \times \frac{RT}{M}$$

$$= \left(\frac{d}{M} \right) RT \quad ; \quad \text{density, } d = \frac{W}{V}$$

If the gas contains N number of molecules and N_A is the Avogadro number, then $n = \frac{N}{N_A}$

$$\therefore PV = \left(\frac{N}{N_A} \right) \times RT$$

$$\Rightarrow P = \left(\frac{N}{V} \right) \left(\frac{R}{N_A} \right) \times T$$

$$= N' RT \quad ; \quad N' = \text{no. of molecules per unit vol. of the gas.}$$

$R = \text{Boltzmann const.}$

$$= \frac{R}{N_A} = \frac{8.314 \times 10^7}{6.02 \times 10^{23}}$$

$$= 1.38 \times 10^{-16} \text{ erg. molecule}^{-1} \text{ K}^{-1}$$

Unit of P is dyne cm^{-2} (CGS)

$\text{Nm}^{-2} = \text{Pa}$ (SI)

$$1 \text{ torr} = 1 \text{ mm of Hg} \quad \left| \quad 1 \text{ bar} = 10^5 \text{ Pa} = 750 \text{ torr} \right.$$

$$\text{So, } 1 \text{ atm} = 760 \text{ torr} \quad \left| \quad 1 \text{ Pa} = 10 \text{ dyne cm}^{-2} \right.$$

The moderate pressure is measured by manometer.

P and T are intensive properties (independent of amount of the gas present in the container)

V is extensive property \rightarrow dependent of the amount of the gas present in the container)

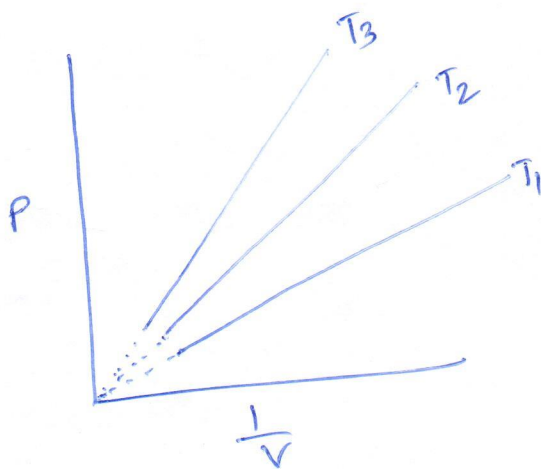
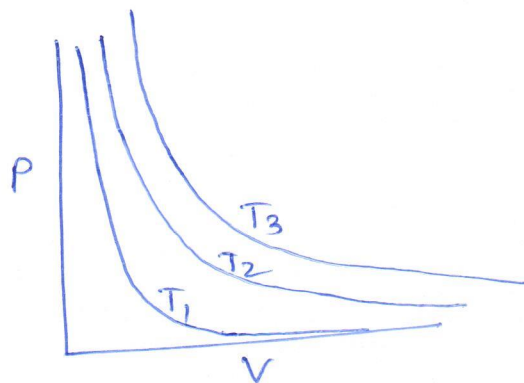
Boyle's Law : $V \propto \frac{1}{P}$

$$PV = K \text{ (constant)}$$

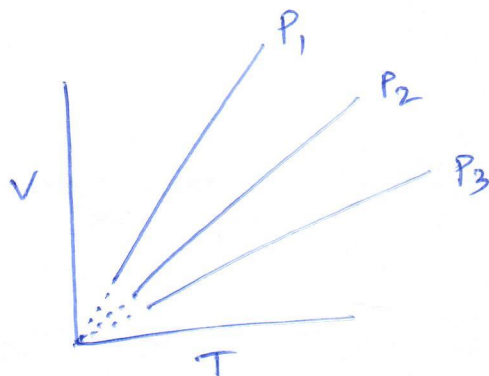
Plot : Hyperbola

Isotherm

$$T_3 > T_2 > T_1$$

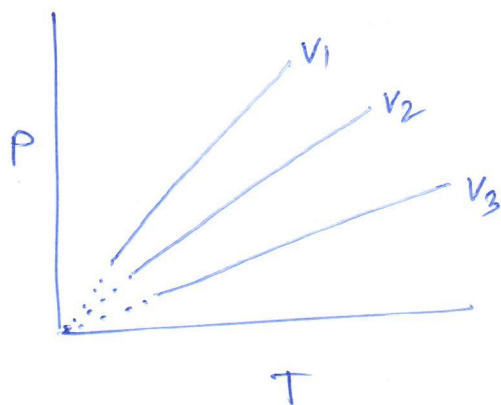


Charles's Law :



$$P_3 > P_2 > P_1$$

Isobars extrapolates to zero volume at $T=0$ or -273°C



$$V_3 > V_2 > V_1$$

Limiting Density:

$$P = \left(\frac{d}{M} \right) RT ; d = \text{density of the gas in g/cc}$$

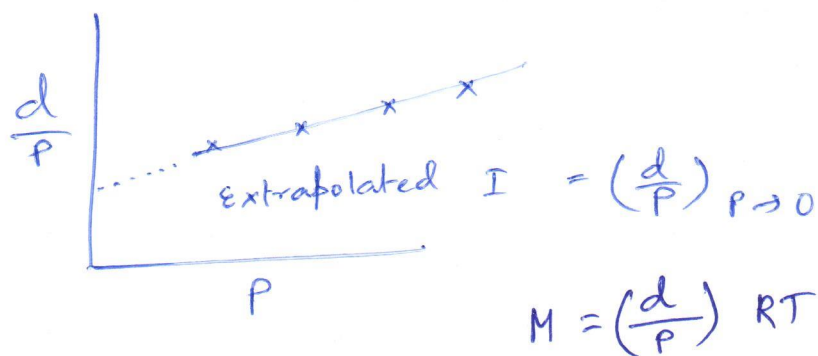
$$\Rightarrow M = \left(\frac{d}{P} \right) RT ; \frac{d}{P} = \text{normal density} \rightarrow \text{density of the gas per unit pressure}$$

This eqn. is obeyed accurately by the gas when P is very low.

$$\text{Thus, } M = \left(\frac{d}{P} \right)_{P \rightarrow 0} \times RT ; \left(\frac{d}{P} \right)_{P \rightarrow 0} = \begin{matrix} \text{Density per unit pr.} \\ \text{at } P \rightarrow 0 \end{matrix}$$

\uparrow
 Limiting density of the gas
 at temperature T

But, as $P \rightarrow 0$, $d \rightarrow 0$ and experimentally this low density cannot be measured accurately. However, this quantity is measured by graphical method. The density (d) of the gas is determined at various pressures, at low pressure and $\frac{d}{P}$ is plotted against P . This gives a st. line and the extrapolation of the curve provides the value of $\left(\frac{d}{P} \right)_{P \rightarrow 0}$.



The value of M is obtained from the product of this extrapolated intercept and RT of the gas.

Generally, the value of M of a gas is determined from the comparison with O_2 at the same temp.

For example, $(\frac{d}{P})_{P \rightarrow 0}$ for CH_3F is 1.5177, while that for O_2 is 1.4177 at the same temp.

$$\text{Thus, } M_{CH_3F} = M_{O_2} \times \frac{(\frac{d}{P})_{P \rightarrow 0} \text{ for } CH_3F}{(\frac{d}{P})_{P \rightarrow 0} \text{ for } O_2}$$

$$= 32 \times \frac{1.5177}{1.4177} = 34 \text{ gm/mol}$$

This is the correct molar mass for methyl fluoride determined by limiting density method.

Abnormal vapour density:-

Vapour density of a substance is defined as the ratio of the density of the gaseous state of the substance and density of hydrogen under same temp. and Pr. It is unitless quantity and expected vapour density $D_0 = \frac{M_0}{2}$, where M_0 is the molecular formula weight of the substances.

$$V.P = \frac{\text{Density of the gaseous state of the substance}}{\text{Density of } H_2 \text{ under same temp and Pr.}}$$