

The temperature at which its real gas obeys Boyle's law over an appreciable range of pressure is called Boyle point or Boyle temperature. This temperature is characteristic of each gas.

The Boyle temperature (T_B) of a gas can be readily obtained using Vander Waal's equation.

A/c to Vanderwaal's equation for 1-mole of gas -

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

$$\Rightarrow p = \frac{RT}{v-b} - \frac{a}{v^2} \quad \text{--- (2)}$$

On multiplying throughout by v , we get

$$pv = \frac{RT(v)}{v-b} - \frac{a}{v} \quad \text{--- (3)}$$

On differentiating the above eqn - (3) w.r.t p at constant temperature, we get

$$\left[\frac{\partial(pv)}{\partial p}\right]_T = RT \left\{ \frac{1}{v-b} \left(\frac{\partial v}{\partial p}\right)_T + v \frac{-1}{(v-b)^2} \left(\frac{\partial v}{\partial p}\right)_T \right\} + \frac{a}{v^2} \left[\frac{\partial v}{\partial p}\right]_T$$

$$= RT \left[\frac{1}{v-b} - \frac{v}{(v-b)^2} \right] \left[\frac{\partial v}{\partial p}\right]_T + \frac{a}{v^2} \left[\frac{\partial v}{\partial p}\right]_T$$

$$= \left[\frac{RT}{v-b} - \frac{RTv}{(v-b)^2} + \frac{a}{v^2} \right] \left(\frac{\partial v}{\partial p}\right)_T$$

Continue. . . .

Since, $\left(\frac{\partial V}{\partial P}\right)_T$ is always negative i.e. it is not equal to zero, Hence, the expression within square brackets on right hand side is equal to zero. Thus,

$$\frac{RT}{V-b} - \frac{RTV}{(V-b)^2} + \frac{a}{V^2} = 0.$$

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

$$\Rightarrow RT \left[\frac{V-b-V}{(V-b)^2} \right] = -\frac{a}{V^2} \quad \Rightarrow RT \left[\frac{-b}{(V-b)^2} \right] = -\frac{a}{V^2}$$

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

$$\Rightarrow RT = \frac{a}{b} \left[1 - \frac{b}{V} \right]^2$$

Since, at Boyle temperature $T = T_B$.

$$\therefore T_B = \frac{a}{Rb} \left[1 - \frac{b}{V} \right]^2$$

When $P \rightarrow 0$, the volume V will be infinitely large so, that

$$\frac{b}{V} \rightarrow 0.$$

Hence,
$$T_B = \frac{a}{Rb}$$

where, the terms 'a' & 'b' are Vanderwaal's constant and R = gas constant.

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Problems:

Q. (1) show that for Vander Waals gas, the Boyle temperature

$$T_B = \frac{a}{Rb}$$

Q. (2). The Vander Waals constants of a gas are:

$$a = 0.751 \text{ dm}^6 \text{ atm mol}^{-2} \text{ and}$$

$$b = 0.0226 \text{ dm}^3 \text{ mol}^{-1}; \quad R = 0.0821 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}.$$

calculate its critical constants.

Q. (3). calculate ~~the~~ the Boyle temperature for oxygen

assuming that it is a Vander Waals gas.

Given $a = 1.36 \text{ dm}^6 \text{ atm mol}^{-2}$

$$b = 0.0318 \text{ dm}^3 \text{ mol}^{-1}.$$

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

≡ x ≡

Solution :-

Q. (2). :-

We know that,

Critical Volume -

$$V_c = 3b = 3 \times 0.0226 \text{ dm}^3 \text{ mol}^{-1}$$

$$= 0.0678 \text{ dm}^3 \text{ mol}^{-1}.$$

Critical Pressure -

$$P_c = \frac{a}{27b^2} = \frac{0.751 \text{ dm}^6 \text{ atm mol}^{-2}}{27 \times (0.0226 \text{ dm}^3 \text{ mol}^{-1})^2}$$

$$= \frac{0.751 \text{ atm}}{27 \times 0.00051076}$$

$$= \frac{0.751 \text{ atm}}{0.01379052}$$

$$= 54.5 \text{ atm}.$$

Similarly,

Critical temperature -

$$T_c = \frac{8a}{27Rb} = \frac{8 \times 0.751 \text{ dm}^6 \text{ atm mol}^{-2}}{27 \times 0.0821 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1} \times 0.0226 \text{ dm}^3 \text{ mol}^{-1}}$$

$$= \frac{6.008 \text{ K}}{0.051}$$

$$\approx 118 \text{ K.}$$

Q. (3). :-

We know that,

Boyle temperature,

$$T_B = \frac{a}{Rb}$$

$$= \frac{1.36 \text{ dm}^6 \text{ atm mol}^{-2}}{0.0821 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1} \times 0.0318 \text{ dm}^3 \text{ mol}^{-1}}$$

$$= \frac{1.36 \text{ K}}{0.002611}$$

$$T_B = 520.88 \text{ K.}$$

X

* Behaviour of Real gases on the basis of Vander Waal's Equation :-

From Vander Waal's Equation -

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

$$\text{or } PV + \frac{aV}{V^2} - Pb - \frac{ab}{V^2} = RT$$

$$\text{or } PV + \frac{a}{V} - Pb - \frac{ab}{V^2} = RT$$

neglecting $\frac{ab}{V^2}$, we have -

$$PV - Pb + \frac{a}{V} = RT = P'V' \quad \text{--- (2)}$$

where $P'V'$ are the ideal pressure & ideal volume of the gas respectively.

* Conditions :-

(1). At low pressure - At low pressure the gas has a large volume. small addition of pressure due to mutual attraction plays an important part while 'b' is negligible as compared to large volume 'V'.
Thus $\frac{a}{V} > Pb$.

$$\text{Let } \frac{a}{V} \cdot Pb = +Z$$

then from eqⁿ - (2)

$$PV + Z = RT = P'V'$$

$$\text{or } PV = RT - Z$$

the observed PV is less than $P'V'$. (show -ve deviation).

(2). At high pressure :-

When pressure is high the volume is small and small volume occupy by molecules themselves cannot be neglected. Hence, the term $Pb > \frac{a}{V}$.

$$\text{let } \frac{a}{V} - Pb = -\gamma$$

then from eqⁿ - (2)

$$PV - \gamma = RT = P'V'$$

$$\therefore PV = P'V' + \gamma$$

i.e. the observed PV is greater than the value expected from an ideal gas. (show +ve deviation)

(3). At ordinary (medium) pressure :-

At medium pressure,

$$Pb = \frac{a}{V}$$

then from eqⁿ - (2)

$$PV = RT = P'V'$$

i.e. gases behave like an ideal gas.

(4). At high temperature :-

At high temperature, V is very large and hence both Pb & $\frac{a}{V}$ will be negligible small. Thus,

from eqⁿ - (2)

$$PV = RT = P'V'$$

i.e. At high temperatures the behaviour of a real gas nearly agree with that expected for ideal gas.

* Critical Phenomenon :-

When temperature of gas is lowered, the kinetic energy of the molecule decreases. The volume occupied by the gas also decreases. At a sufficient low temperature, some of the gas molecules can not resist the force of attraction. Such gas molecules come close and closer and ultimately the gas changes into liquid state.

Increase in pressure also brings the molecule of the gases close together due to decrease in volume. This causes liquification of gas. This phenomenon is called critical phenomenon.

* Critical temperature :-

The highest temperature of the gas at which the gas can be liquified is called critical temperature (T_c).

T_c of CO_2 is $31.1^\circ C \cong 304.1 K$.

* Critical pressure :-

At critical temperature, a certain pressure is needed to liquified the gas is called critical pressure (P_c).

P_c of CO_2 is 73.9 atm.

* Critical volume :-

Volume of 1 mole of a gas at its critical temperature and critical pressure is called critical volume (V_c).

V_c of CO_2 is $0.0956 dm^3/mol$.

Note - Critical temperature (T_c), critical pressure (P_c) and critical volume (V_c) are called critical constant.

Q. Choose the correct option out of the followings:-

- (1). At constant T, the product of P & V of a given amount of gas is constant. This is -
(a) Boyle's law (b) Charles's law (c) Avogadro's law (d) Gay-Lussac's law.
- (2). Which of the following is not the value of R?
(a) 1.99 cal $K^{-1} mol^{-1}$ (b) 0.0821 L atm $K^{-1} mol^{-1}$ (c) 9.8 K cal $K^{-1} mol^{-1}$.
(d) 8.314 J $K^{-1} mol^{-1}$.
- (3). 4.4 g of CO_2 contains how many litre of CO_2 at STP?
(a) 2.4 L (b) 2.24 L (c) 44 L (d) 22.4 L
- (4). The compressibility factor of a gas is $Z = \frac{PV}{RT}$. The value of Z of an ideal gas is -
(a) 0 (b) -1 (c) +1 (d) none.
- (5). Vander Waal's equation for a real gas is:
(a) $(P + \frac{a}{V^2})(V + b) = nRT$ (b) $(P + \frac{a}{V^2})(V - b) = nRT$
(c) $(P + \frac{ab^2}{V^2})(V - b) = nRT$ (d) $P = \frac{nRT}{(V - nb)} - \frac{ab^2}{V^2}$
- (6). Gases deviate from ideal behaviour because their molecules?
(a) possess negligible volume (b) are polyatomic (c) are not attracted to one another (d) have force of attraction among them.
- (7). The Unit of Vander Waal's constant 'b' is:
(a) $mol L^{-1}$ (b) $L mol^{-1}$ (c) $atm L^2 mol^{-2}$ (d) $atm mol^{-2} L^{-2}$.
- (8). A gas can be liquefied by pressure alone when its temperature is:
(a) higher than that of critical temperature
(b) lower than that of critical temperature
(c) equal to its critical temperature
(d) none.

CHEMISTRY
MODULE-3
INTERMOLECULAR FORCES
&
PROPERTIES OF GASES

IONIC, DIPOLAR AND VAN DER WAALS INTERACTIONS. EQUATIONS OF STATE OF IDEAL AND REAL GASES, DEVIATION FROM IDEAL BEHAVIOUR. VANDER WAAL GAS EQUATION.

By:- Dr. A. K. GUPTA

The Gas Laws :-

(7)

(1) Boyle's Law - At constant temperature, the pressure of a fixed amount of gas is inversely proportional to its volume.

Thus,

$$P \propto \frac{1}{V} \quad \text{or} \quad P = \frac{K}{V} \quad \text{or} \quad PV = K \quad \text{--- (1)}$$

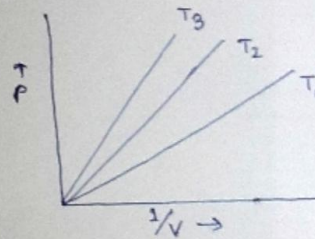
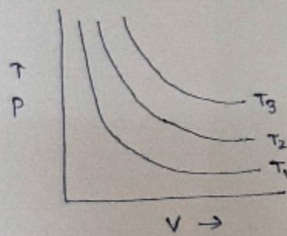
(at constant T & n)

At constant temperature and for a given mass of the gas, the product of Pressure (P) and Volume (V) is constant.

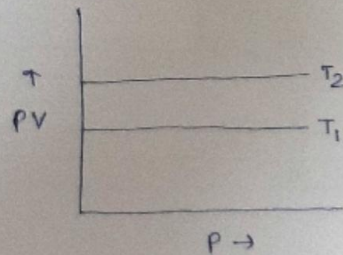
Thus, if for a given mass of gas its volume V_1 at pressure P_1 and volume V_2 at pressure P_2 , then -

$$P_1 V_1 = P_2 V_2 \quad \text{--- (2)}$$

Graph -



$T_3 > T_2 > T_1$



$T_2 > T_1$

$$\text{Density (d)} = \frac{\text{mass (m)}}{\text{Volume (V)}} \quad \text{--- (1)}$$

$$\approx d_1 = \frac{m}{V_1} \quad \& \quad d_2 = \frac{m}{V_2}$$

$$\approx V_1 = \frac{m}{d_1} \quad \& \quad V_2 = \frac{m}{d_2}$$

from eqn - (2)

$$\frac{P_1 m}{d_1} = \frac{P_2 m}{d_2} \quad \approx \quad \boxed{\frac{P_1}{d_1} = \frac{P_2}{d_2}} \quad \text{--- (3)}$$

(2) Charles's law -

The volume of a given mass of a gas increases or decreases by $\frac{1}{273}$ of its original volume at 0°C for every 1°C rise or fall in temperature provided pressure is constant.

Thus, if V_0 and V_t are the volume of the gas at 0°C & $t^\circ\text{C}$ then

$$V_t = V_0 + \frac{t}{273} V_0 \quad \text{--- (1)}$$

$$\approx V_t = \frac{V_0(273 + t)}{273} \quad \text{--- (2)}$$

Since, $T_0 = 0^\circ\text{C} = 273\text{K}$

$$\approx T = t + 273$$

Thus from eqn - (2)

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

$$\frac{V_0}{T_0} = \frac{V_t}{T} \quad \approx \quad \frac{V}{T} = \text{Constant} \quad \text{--- (3)}$$

Thus, At constant pressure, the volume of a given mass of a gas is directly proportional to its absolute temperature (T).

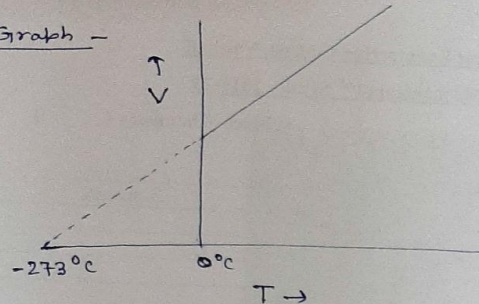
$$V \propto T \quad (\text{at constant } P \ \& \ m)$$

$$\approx V = kT \quad \text{--- (4)}$$

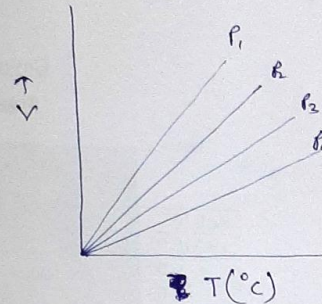
at two different volumes -

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \quad \text{--- (4)}$$

Graph -



(3)



Density -

$$d = \frac{m}{V} \quad \text{or} \quad d_1 = \frac{m}{V_1} \quad \& \quad d_2 = \frac{m}{V_2}$$

$$\text{or} \quad d_1 V_1 = m \quad d_2 V_2 = m$$

$$d_1 V_1 = d_2 V_2$$

$$\frac{V_1}{V_2} = \frac{d_2}{d_1}$$

from eqⁿ (4)

$$d_1 T_1 = d_2 T_2 \quad \text{--- (5)}$$

Thus, at constant Pressure, density of a gas is inversely proportional to absolute temperature (T).

Problems -

- (1) 100 ml of a gas has pressure of 600 mm. What will be the volume of the gas if (a) P is doubled (b) P is halved. (50 & 200 ml) Ans.
- (2) T is keeping constant.
- (3) Pressure of a gas filled in a closed cylinder at 273K is 4 atm. Calculate the temperature of the gas when its pressure is 5 atm. (341.25 K) Ans.

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CHEMISTRY
MODULE-3
INTERMOLECULAR FORCES
&
PROPERTIES OF GASES

IONIC, DIPOLAR AND VAN DER WAALS INTERACTIONS. EQUATIONS OF STATE OF IDEAL AND REAL GASES, DEVIATION FROM IDEAL BEHAVIOUR. VANDER WAAL GAS EQUATION.

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SEM - 2nd.
Module - 3.

BRANCH - IT/ME/C/LT

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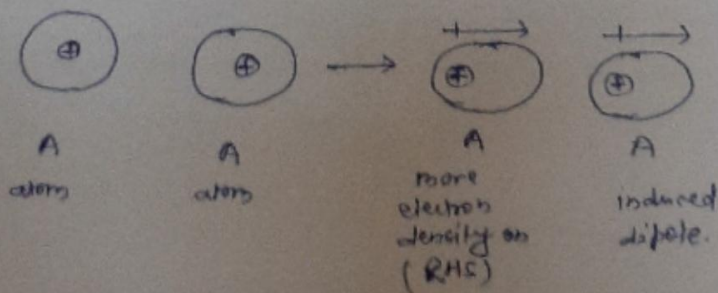
Intermolecular forces and properties of gases -

* Introduction - The force present between the molecules of the substances are called intermolecular forces. These forces are present in all kinds of molecules. Greater is the strength of intermolecular forces, higher is the boiling and melting point of the substances. These intermolecular forces are collectively called van der Waals forces. These forces include :-

- (1). London forces or Dispersion forces
- (2). Dipole - dipole forces
- (3). Dipole - induced dipole forces
- (4). Ion - induced dipole forces
- (5). Ion - dipole interaction
- (6). Hydrogen bonding.

(1). London force or Dispersion forces -

This type of force acting between two non-polar molecule such as N_2 , O_2 , F_2 etc or monoatomic gases such as He, Ne, Ar etc. This type of forces arises due to motion of an electron.



This is temporary effect. These are the weakest intermolecular forces.

The interaction energy $\phi(r) = \frac{C}{r^6}$. (2)

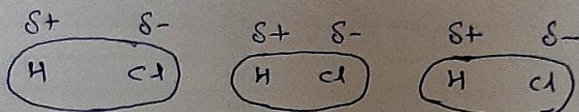
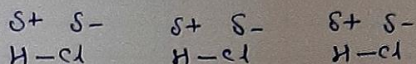
Where, $C =$ Constant, depends upon the ionisation energy of two molecule.

$r =$ the distance between two particles.

(2). Dipole-dipole forces :-

These forces occurs among polar molecule ($A-B$) which have permanent dipoles. The +ve pole of the molecule attracts the -ve pole of the molecule.

eg- HCl , HBr , HF .



↑
more charge density towards Cl.

In case the molecule contain more atoms, the magnitude of these forces depends upon the geometry of the molecule. The polarity of the molecules is expressed in terms of dipole moment (μ).

eg- H_2S PH_3

mol. mass = 34 34

$\mu = 1.10D$ $\mu = 0.55D$

Thus, dipole-dipole interaction are larger in H_2S .

The m.p. and b.p is higher of H_2S than PH_3 .

The interaction energy $\phi(r) = \frac{C}{r^3}$ (stationary polar molecule)

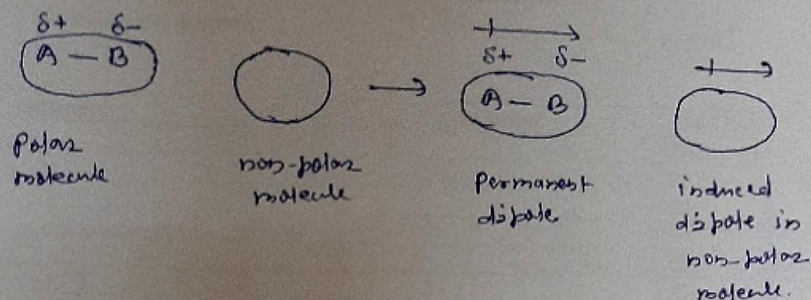
and " " " $\phi(r) = \frac{C}{r^6}$ (rotating polar molecule)

(3) Dipole-induced dipole forces:-

(2)

This type of attractive forces occurs between a polar molecule having permanent dipole and non-polar molecule which have no dipole.

eg- NH_3 and C_6H_6 .

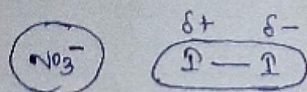


$$\text{The interaction energy } \phi(r) = \frac{C}{r^6}$$

(4) Ion-induced dipole forces:-

This type of force acting between an ion and a non-polar molecule. A non-polar molecule may be polarised by an ion near it. The strength of such interactions depends upon the charge of the ion and polarisability of the non-polar molecule.

eg- NO_3^- ion polarises non-polar I_2 molecule.



(5) Ion-dipole interactions:-

This type of interaction occurs between an ion and a polar molecule. When an ionic compound dissolved in water, it dissociates to give cations & anions. The polar water molecules are attracted by the cations as well as anions of the ionic compound. This process is called hydration of ions.

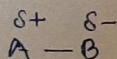
Problems :-

(5)

- (1). Why H_2O is in liquid state but H_2S in gaseous state ?
- (2). which type of H-bonding exists between ^(a) o-nitro phenol and ^(b) p-nitro phenol.
- (3). Why density of H_2O is maximum at $4^\circ C$?
- (4). Which type of intermolecular forces exists in the following molecule?
 - (a) H_2S or HCl (b) NH_3 or H_2O (c) CH_4 or SiH_4 .
 - (d) He or Ne (f) Cl_2 or CCl_4 .

* Dipole moment (μ) -

A covalent bond formed between two dissimilar atoms is always polar.



A polar bond has two poles +ve and -ve. Like a magnet. Thus, dipole moment is the net ~~charge~~ displacement of electronic charge in a particular direction.

$$\mu = \text{charge } (q) \times \text{interatomic spacing } (d)$$

$$\text{or } \boxed{\mu = q \times d}$$

Unit - Debye (D) = 10^{-18} esu-cm

SI unit -

$$\text{Debye (D)} = 3.3 \times 10^{-30} \text{ Coulomb-metre.}$$

Important points:-

- (1). If a molecule contains only one polar bond, it must have dipole moment and is always polar.
eg. HCl , HBr , HF , HI etc.

(2). If a molecule contains two or more polar bonds, its molecule may or may not have dipole moment. Thus the molecule may and may not be polar. It depends on the geometry of the molecule. (6)

eg CH_4 , BeH_2 , CO_2 , CCl_4 , CS_2 etc. are non polar while SO_2 , H_2O , H_2O_2 , NH_3 , NF_3 , CH_3Cl , CH_3OH etc are polar.

Problems -

- (1) Which out of NH_3 & NF_3 has higher dipole moment and why?
- (2) Why BeH_2 molecule has zero dipole moment although the Be-H bond is polar?
- (3) Which of the following molecules are polar.
(a) SO_3 , SO_2 , CO_2 , NF_3 , H_2S , O_3 , H_2O_2 , BF_3 , H_2O .

-x-

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(3) Gay-Lussac's Law :-

At constant volume and for a given mass of a gas, pressure is directly proportional to absolute temperature (T).

$$\text{Thus, } P \propto T \text{ (at constant } V \text{ \& } n) \quad \text{--- (1)}$$

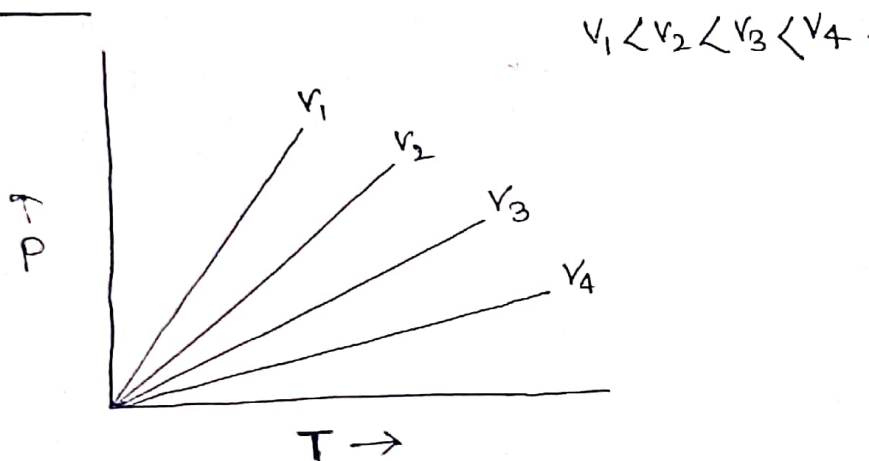
$$\approx P = K \cdot T$$

$$\approx \frac{P}{T} = K = \text{constant.}$$

for two different pressures-

$$\boxed{\frac{P_1}{T_1} = \frac{P_2}{T_2}} \quad \text{--- (2)}$$

Graph :-

(4) Avogadro's Law :-

Equal volumes of all the gases under the same conditions of temperature & pressure contain equal number of molecules.

In other words -

At constant T & P, the volume of gas depends upon the number of moles of the gas.

$$\text{Thus, } V \propto n \quad \approx V = K \cdot n \quad \text{--- (1)}$$

Again, $n = \frac{m}{M} = \frac{\text{given mass}}{\text{Molar mass}}$

$\approx V = \frac{K \cdot m}{M} \quad \approx M = \frac{K m}{V}$

$\approx M = K \cdot d \quad \left(d = \frac{m}{V} \right)$

Thus, density of the gas is directly proportional to its molar mass.

Problems :-

① Volume of a gas at 400 K is 10 L. Calculate the decrease in volume of the gas. when it cooled to -23°C . Pressure remains constant. (V = 3.75 L) Ans.

② At what temperature on Celsius scale will the volume of a given mass of a gas at 0°C becomes half of its volume. Pressure remains constant. ($T_2 = -136.5^\circ\text{C}$) Ans.

-x-

* An Ideal Gas :-

Those gases which obeys Boyle's law, Charles's law and Avogadro's law under all conditions of temperature & pressure is called an ideal gas. Such a gas is hypothetical. There are some deviations in ideal gases. Therefore, no gas is perfectly ideal.

* An Ideal gas equation :-

A/c to Boyle's law -

$P \propto \frac{1}{V} \quad \approx P = \frac{K}{V} \quad \approx PV = K \quad \text{--- (1)}$

(at constant T & n)

A/c to Charles's law -

$V \propto T \quad \approx V = K \cdot T \quad \approx \frac{V}{T} = K \quad \text{--- (2)}$

(at constant P & n)

A/c to Avogadro's law -

$$V \propto n \quad \approx \quad V = k \cdot n \quad \approx \quad \frac{V}{n} = k \quad \text{--- (2)}$$

On combining eqs- (1), (2) & (3) -

$$V \propto \frac{nT}{P} \quad \approx \quad V = \frac{RnT}{P}$$

$$\approx \quad \boxed{PV = nRT} \quad \text{--- (4)}$$

Eqn- (4) is called an ideal gas equation. There are four variables (P, V, T, n) in the ideal gas equation and it describes the state of any gas. Therefore, it is also called equation of state.

'R' is called Universal gas constant. Value of R is same for all the gases.

for two different P, T & V at fixed amount of gas -

$$\boxed{\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}} \quad \text{--- (5)}$$

The equation which gives simultaneous effect of pressure and temperature on the volume of fixed amount of the gas is known as an ideal gas equation or equation of state.

* Density

Since,

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

$$PV = nRT \quad \approx \quad PV = \frac{WRT}{M} \quad \approx \quad P = \frac{WRT}{VM}$$

$$\approx \quad P = \frac{dRT}{M} \quad \approx \quad M = \frac{dRT}{P}$$

for two different gas at equal amount

$$\boxed{\frac{P_1}{d_1 T_1} = \frac{P_2}{d_2 T_2}} \quad \text{--- (6)} \quad (\text{at constant } R \text{ \& } M)$$

Value of gas constant (R) in different units:-

(13)

→ At STP -

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

$$R = 0.083 \text{ bar dm}^{-1} \text{ K}^{-1} \text{ mol}^{-1}$$

→ CGS -

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

→ SI unit - $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$.

Problems :-

① Volume of a gas at a certain temperature and pressure is one litre. If pressure is doubled and temperature is made half. Calculate the volume of the gas.

$$(V_2 = 0.25 \text{ L}) \text{ Ans.}$$

② Density of a gas at STP is 1.43 g/L . What is the density at 290 K & 800 mm Hg .

$$(d_2 = 1.42 \text{ g/L}) \text{ Ans.}$$

③ Calculate the density of ammonia in g/L at 5 atm pressure & at 30°C .

$$(3.42 \text{ g/L}) \text{ Ans.}$$

④ Density of gas at 74.5 cm Hg pressure and 338 K is 1.56 g/L . What is the molar mass of the gas?

Hint.

$$P = \frac{74.5}{76}$$

$$d = 1.56 \text{ g/L}$$

$$T = 338 \text{ K}$$

$$(M = 44.1 \text{ u}) \text{ Ans.}$$

—x—

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