

# HEAT & THERMODYNAMICS

## GASES LAW

Date: \_\_\_\_\_

Page: \_\_\_\_\_

### Boyle's law

It states that, "At constant temperature and other physical condition, volume of given mass of gas is inversely proportional to pressure exerted by gas?"

$$\text{ie: } V \propto \frac{1}{P}$$

$$\text{or, } V = \frac{k}{P}$$

(where,  $k$  is **physics for +2 level** proportionality constant)

$$\text{or, } PV = k = \text{constant}$$

$$\text{or, } P_1 V_1 = P_2 V_2$$

### Charle's law

It states that, "The volume of given mass of gas is increased or decreased by constant fraction of gas at  $0^\circ\text{C}$  at remaining constant pressure?" in every rise or fall in temperature at constant pressure?

We know, the volume of gas is increased when gas is heated from  $0^\circ\text{C}$  to  $\theta^\circ\text{C}$  at constant pressure. Then, we can write.

$$V_\theta = V_0 [1 + \gamma_p \theta]$$

(where,  $\gamma_p$  is cubical expansivity at constant pressure)

experimentally, it's value is found to be 1

$$\text{ie: } (\gamma_p = \frac{1}{273})$$

Then,

$$V_0 = \theta V_0 \left[ 1 + \frac{1}{273} \theta \right]$$

$$\frac{V_0}{V_0} = \frac{[273 + \theta]}{273}$$

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

**physics for +2 level**

Thus, "The volume of given mass of gas is directly proportional to absolute temperature at constant pressure" given by Charles's law.

### Charles's pressure law

It states that, "The pressure of given mass of gas is increased or decreased by constant fraction at  $0^\circ$  in every rise or fall in temperature at constant volume".

We know, the pressure of gas is increased when gas is heated from  $0^\circ\text{C}$  to  $0^\circ\text{C}$  at constant volume. Then, we can write.

$$P_0 = P_0 [1 + \gamma_v^t \theta]$$

(where  $\gamma_v^t$  is cubical expansivity at constant volume)

Experimentally, its value is found to be

$$\frac{1}{273}$$

$$\text{ie: } (\gamma_V = \frac{1}{273})$$

$$P_0 = P_0 \left[ 1 + \frac{1}{273} \theta \right]$$

$$\frac{P_0}{P_0} = \left( \frac{273 + \theta}{273} \right)$$

physics for +2 level

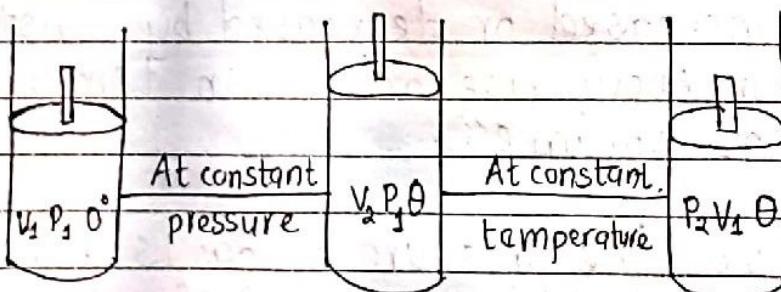
$$\frac{P_0}{P_0} = \frac{T_0}{T_0}$$

$$\therefore P \propto T$$

Thus, "the pressure of given mass of gas is directly proportional to absolute temperature at constant volume" given by Charles.

~~Ans~~

Equality of pressure and volume coefficient



When the gas obey the Boyle's law then, volume and pressure coefficient are equal. ie:  $\gamma_V = \gamma_P$ .

Consider a gas having volume  $V_1$ , pressure  $P_1$  at  $0^\circ$  is placed inside a cylinder with movable piston. Now, gas is expand at constant pressure upto temperature  $\theta$ . Then, from charle's law,

then, its volume becomes  $V_2$ . Then, from charle's law,

$$V_2 = V_1 [1 + \gamma_p \Delta \theta]$$

$$\text{i.e. } V_2 = V_1 [1 + \gamma_p \theta] \quad \text{(i)}$$

(where  $\gamma_p$  is volume coefficient)

contracts to its original volume ( $V_1$ )

Now, gas expands at constant temperature, then from Boyle's law,

$$P_1 V_2 = P_2 V_1$$

(from above eqn (i))

$$P_1 V_1 [1 + \gamma_p \theta] = P_2 V_1$$

$$P_2 = P_1 [1 + \gamma_p \theta] \quad \text{(ii)}$$

Then, also from charle's pressure law,

$$P_2 = P_1 [1 + \gamma_v \theta] \quad \text{(iii)}$$

(where  $\gamma_v$  is pressure coefficient)

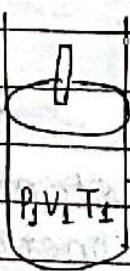
From eqn (iii) & (ii), we get

$$1 + \gamma_p \theta = 1 + \gamma_v \theta$$

$$\therefore \gamma_p = \gamma_v$$

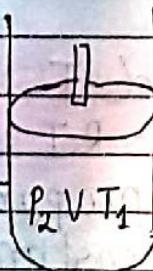
which is required ~~expression~~ relation and is verified.

~~Ideal gas equation / combine gas equation~~



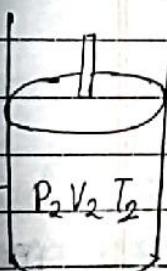
At constant  
temperature

$P_1 V_1 T_1$



At constant  
pressure

$P_2 V_2 T_1$



$P_2 V_2 T_2$

The law which obeys both Charles's law and Boyle's law is called combined gas equation.

Consider one mole gas is placed inside the cylinder with movable piston having pressure  $P_1$ , volume  $V_1$  at temperature  $T_1$ . Now, gas is compressed at constant temperature until its volume and pressure becomes  $V_2$  and  $P_2$ . Then, from Boyle's law,

$$P_1 V_1 = P_2 V \quad \text{--- (i)}$$

$$\text{or, } V = \frac{P_1 V_1}{P_2} \quad \text{--- (ii)}$$

Again, gas is expand at constant pressure until its volume ~~is~~  $V_2$  and temperature  $T_2$ . Then, from Charles's law,

$$\frac{V}{T_1} \rightarrow \frac{V_2}{T_2}$$

(from eqn (i))

$$\frac{P_1 V_1}{T_1} \times \frac{1}{T_1} = \frac{V_2}{T_2}$$

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$\text{ie: } \frac{PV}{T} = \text{constant}$$

$$\text{ie: } PV \propto T$$

$$PV = RT$$

$R$  is proportionality constant called Redbarz constant or gas constant whose value is  $8.31 \text{ J mol}^{-1} \text{ K}^{-1}$ .

# Find the unit of R and its value and its significance.  
Dalton's law / Assumption

For n mole of gas,

$$PV = nRT$$

which is ideal gas equation.

Let, m be the mass of gas and M be the molar mass of gas. Then, number of mole is:

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

$$\therefore PV = \frac{m}{M} \cdot RT$$

$$\text{or, } PV = m r T \quad (\text{where, } r = \frac{R}{M})$$

$$\text{or, } P = \frac{m r T}{V}$$

$$\therefore P = \frac{m}{V} r T$$

### Dalton's law of Partial Pressure

Dalton's law of partial pressure states that, "Total pressure of mixture of two or more non reactive gases enclosed in a vessel is the sum of partial pressure of all component gases under similar condition of temperature."

i.e:

$$P_T = P_A + P_B + P_C$$

Let us consider  $n_A, n_B, n_C$  be the no. of moles of gases A, B & C respectively enclosed in a vessel.

Then, total number of moles ( $n_T$ ) will be

$$n_T = n_a + n_b + n_c \quad (i)$$

From ideal gas equation,

$$PV = nRT$$

$$n = \frac{PV}{RT}$$

For gas A,

$$n_A = \frac{P_a V}{RT}$$

For gas B,

$$n_b = \frac{P_b V}{RT}$$

For gas C,

$$n_c = \frac{P_c V}{RT}$$

Total gas of mixture i.e. mixture of gas,

$$n_T = \frac{P_T V}{RT}$$

Substituting value of  $n_a$ ,  $n_b$ ,  $n_c$  &  $n_T$  in eqn (i)  
we get,

$$\frac{P_T V}{RT} = \frac{P_a V}{RT} + \frac{P_b V}{RT} + \frac{P_c V}{RT}$$

$$\left(\frac{V}{RT}\right) P_T = \frac{V}{RT} (P_a + P_b + P_c)$$

$$\therefore P_T = P_a + P_b + P_c$$

This is proved mathematically.

The gas constant R

$$R = \frac{PV}{nT} = \frac{1 \text{ atm } 22.41}{1 \text{ mol } 273 \text{ K}}$$

$$= 0.08205 \frac{\text{Latm}}{\text{mol} \cdot \text{K}}$$

When S.I. units are desirable,  $P = 101325 \text{ N/m}^2$  (Pa for pascal) instead of 1 atm - The

### Significance of R:

It signifies the amount of work done by the gas per mole per kelvin.

Date: \_\_\_\_\_

Page: \_\_\_\_\_

volume is  $0.0224 \text{ m}^3$ . The numerical value and units for R are

$$R = \frac{101325 \text{ N}}{\text{m}^2} \cdot \frac{0.0224 \text{ m}^3}{\text{mol} \cdot \text{K}}$$
$$= 8.314 \text{ J}$$
$$= 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$$

Note:  $1 \text{ latm} = 0.001 \text{ m}^3 \times 101325 \text{ N} = \frac{101.325 \text{ J}}{\text{m}^2}$

### Unit of R

From ideal gas equation we get,

$$R = \frac{PV}{nT} \quad \text{--- (i)}$$

The unit of P = Pa = N/m<sup>2</sup>

The unit of V = l = m<sup>3</sup>

The unit of T = K

unit of n = mol

so,

The S.I unit of R = Pa l

K mol

$$= \frac{\text{N} \times \text{m}^3}{\text{m}^2 \text{ K mol}}$$

$$= \frac{\text{Nm}}{\text{K mol}}$$

$$= \text{J mol}^{-1} \text{ K}^{-1}$$

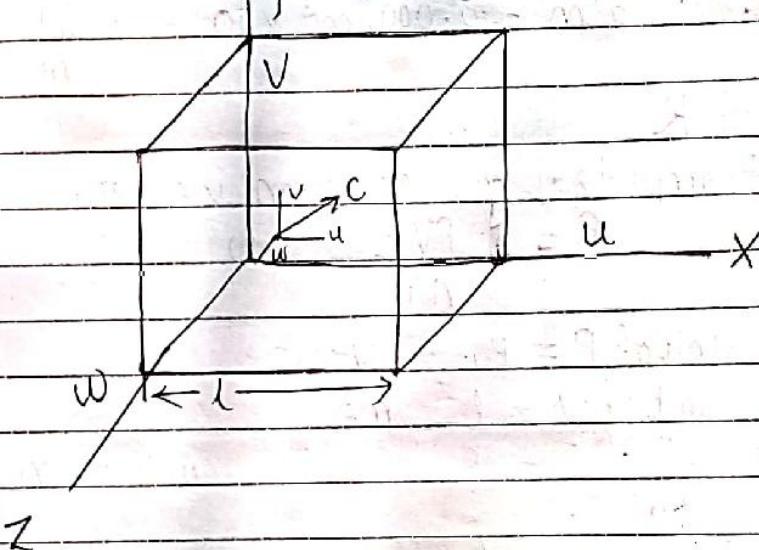
### Assumptions of Kinetic Molecular Theory of Gas

- 1) Collision between gas molecules as well as wall of container is elastic.
- 2) Intermolecular force of attraction and repulsion between gas molecules are negligible.
- 3) The time taken for collision is negligible.

- 4) Gravitational force of attraction upon gas molecule are negligible.
- 5) Volume of a single molecule is negligible in comparison to total volume of gas.

~~SMP~~

Pressure exerted by a gas



Consider 'n' no. of mole of gas is placed in a cube having length 'l'. The molar mass of gas is 'M' which is identical for all moles of gas. Let,  $u, v, w$  are the velocity of gas molecule along  $x, y$  &  $z$  axis respectively. Then, resultant velocity of gas molecule is,

$$c = \sqrt{u^2 + v^2 + w^2}$$

and,

mass of gas in a cube is  $m = n \times M$

Let,  $u_1, u_2, \dots, u_n$  be the velocity of gas molecules along  $x$ -axis. Then, change in momentum of one particle molecules when return from another wall of cube is:

$$\Delta P_x = M(u_1 - Mu_1 - (-Mu_1))$$

$$= 2Mu_1$$

Let,  $\Delta t$  be the time taken by that molecules.  
Then,

$$\Delta t = \frac{s}{u} = \frac{l}{u_1}$$

$$= \frac{2l}{u_1}$$

And,

force experienced by 1st molecule along the  $x$ -axis is:

$$F_{x1} = \frac{\Delta P_{x1}}{\Delta t_1}$$

$$= 2Mu_1$$

$$= \frac{2l}{u_1}$$

$$= \frac{Mu_1^2}{l}$$

Similarly, force experienced by other <sup>gas</sup> molecules along the  $x$ -axis are;  $Mu_2^2, Mu_3^2, \dots, Mu_n^2$

Total force of gas along  $x$ -axis is

$$F_x = \frac{Mu_1^2}{l} + \frac{Mu_2^2}{l} + \frac{Mu_3^2}{l} + \dots + \frac{Mu_n^2}{l}$$

Then, total pressure exerted by gas along  $x$ -axis

$$P_x = \frac{F_x}{A} = \frac{F}{l^2}$$

Then,

$$P_x = \frac{M}{l^3} [u_1^2 + u_2^2 + u_3^2 + \dots + u_n^2]$$

Similarly,

pressure exerted along  $y$ -axis is

$$P_y = \frac{M}{L^3} [v_1^2 + v_2^2 + v_3^2 + \dots + v_n^2]$$

again, pressure exerted along  $z$ -axis is

$$P_z = \frac{M}{L^3} [w_1^2 + w_2^2 + w_3^2 + \dots + w_n^2]$$

Average pressure exerted by gas is:

$$P = \frac{P_x + P_y + P_z}{3}$$

$$= \frac{M}{3L^3} [u_1^2 + u_2^2 + \dots + u_n^2 + v_1^2 + v_2^2 + \dots + v_n^2 + w_1^2 + w_2^2 + \dots + w_n^2]$$

(Volume of cube =  $L^3$ )

$$= \frac{M}{3V} (u_1^2 + u_2^2 + u_3^2 + \dots + u_n^2 + v_1^2 + v_2^2 + \dots + v_n^2 + w_1^2 + w_2^2 + \dots + w_n^2)$$

$$\text{or, } P = \frac{nM}{3V} \left( c_1^2 + c_2^2 + c_3^2 + \dots + c_n^2 \right)$$

( $nM$  = mass of gas)

$$\text{or, } P = \frac{m}{3V} \bar{c}^2$$

[where,  $\bar{c}^2 = (c_1^2 + c_2^2 + c_3^2 + \dots + c_n^2)/n$  is called mean of square velocity called root mean square velocity written as  $C_{rms}$ ]

$$P = \frac{1}{3} \frac{m}{V} C_{rms}^2$$

$$P = \frac{1}{3} \frac{m}{V} C_{rms}^2$$

which is required expression for pressure exerted by a gas.

### Avg. Kinetic theory of gases.

From ideal gas eqn **physics for +2 level**

$$PV = RT \quad [\text{for 1 mole}] \quad (\text{i})$$

Also, pressure exerted by gas is:

$$\text{or, } P = \frac{1}{3} S C_{\text{rms}}^2$$

$$\text{or, } P = \frac{m}{3V} C_{\text{rms}}^2$$

$$\text{or, } P = \frac{nM}{3V} C_{\text{rms}}^2$$

for 1 mole of gas

$$P = \frac{M}{3V} C_{\text{rms}}^2$$

$$PV = \frac{3M}{3} C_{\text{rms}}^2 \quad (\text{ii})$$

from eqn (i) & (ii)

$$\frac{1}{3} M C_{\text{rms}}^2 = RT$$

$$\frac{1}{2} M C_{\text{rms}}^2 = \frac{3}{2} RT$$

(Here,  $\frac{1}{2} M C_{\text{rms}}^2$  is the average K.E of 1 mole. So,  $\frac{1}{2}$  K.E of gas per mole is  $\frac{3}{2} RT$ .

If, the mass of the molecules  $M$  and  $N$  is the no. of molecules in one mole of gas. Then,

$$\frac{3}{2} RT = \frac{1}{2} N \cdot m C_{\text{rms}}^2$$

$$\frac{3}{2} \frac{RT}{N} = \frac{1}{2} M C_{rms}^2$$

$$\frac{3}{2} K T = \frac{1}{2} M C_{rms}^2$$

(where  $K = \frac{R}{N_A}$  is called Boltzmann constant)

whose value is,  $K = 1.38 \times 10^{-23} \text{ J mol}^{-1} \text{ K}^{-1}$

(Here, the term  $\frac{1}{2} M C_{rms}^2$  is called average kinetic energy  $^2$  per mole of the gas)

$$\therefore \text{Av. K.E} = \frac{3}{2} K T$$

### Interpretation of Temperature

From the kinetic theory of gases, the average kinetic energy per mole of the gas is  $\frac{1}{2} M C_{rms}^2 = \frac{3}{2} K T$ . This shows that the av.

kinetic energy of the gas is directly proportional to absolute temperature.

If  $T = 0$ . Then,

K.E per mole also equals to 0. Thus, at absolute zero temperature molecule of the gas are at completely rest.

### Root mean square speed / velocity

Root mean square speed of a gas is defined as the square root of the mean square velocity of the gas molecules.

$$\text{i.e. } C_{rms} = \sqrt{\bar{C}^2}$$

$$\text{or if } C_{\text{rms}} = \sqrt{\frac{C_1^2 + C_2^2 + C_3^2 + \dots + C_n^2}{n}}$$

From, kinetic theory of gases

$$P = \frac{1}{3} s C_{\text{rms}}^2$$

$$C_{\text{rms}} = \sqrt{\frac{3P}{s}}$$

$$C_{\text{rms}} = \sqrt{\frac{3P}{s}}$$

### physics for +2 level

From average kinetic energy,

$$\frac{1}{2} m C_{\text{rms}}^2 = \frac{3}{2} kT$$

$$C_{\text{rms}} = \sqrt{\frac{3kT}{m}}$$

$$C_{\text{rms}} = \sqrt{\frac{3kT}{m}}$$

Similarly,

$$\frac{1}{2} M C_{\text{rms}}^2 = \frac{3}{2} RT$$

$$C_{\text{rms}} = \sqrt{\frac{3RT}{M}}$$

(Since, R, M & 3 are constant. Then,  $C_{\text{rms}} \propto \sqrt{T}$ )

For two different root mean square velocity,

$$C_1 = \sqrt{T_1 m_1 / (3R)}$$

$$C_2 = \sqrt{T_2 m_2 / (3R)}$$

$$C_1 / C_2 = \sqrt{T_1 / T_2} \cdot \sqrt{m_1 / m_2}$$