Chapter

2

LAWS OF PERFECT GASES

2.1 PERFECT GAS

A perfect gas or an ideal gas may be defined *as a state of a substance, whose evapora* *from its liquid state is complete.* A perfect gas strictly obeys all the gas laws under all conditi of temperature and pressure. In actual practice, no gas is perfect gas, but some real gases oxygen, nitrogen, hydrogen, air etc. may be regarded as perfect gases within certain tempera and pressure limits.

2.2 LAWS OF PERFECT GASES

There are mainly three variables which control the physical properties of a gas :

(*i*) Temperature of gas (T), (*ii*) Pressure exerted by gas (P), (*iii*) Volume occupied gas (V).

The behaviour of perfect gas undergoing any change in above mentioned variables is gi by various laws which are based upon the experimental results.

(*i*) Boyle's law, (*ii*) Charle's law, (*iii*) Gay-Lussac law.

2.3 BOYLE'S LAW

This law states, "*The absolute pressure of a given mass of a perfect gas varies inverse its volume, provided the temperature remains constant.*" Mathematically,

$$P \alpha \frac{1}{V}$$

or

$$PV = \text{Constant} \quad \ldots$$

The more useful form of the above equation is

$$P_1V_1 = P_2V_2 = P_3V_3 = \ldots\ldots\ldots\ldots = \text{constant.}$$

2.4 CHARLE'S LAW

This law was formulated by a Frenchman Jacques A.C. Charles. This law may be sta the following two ways:

(*i*) "*The volume of a given mass of a perfect gas varies directly as its ab temperature, provided the pressure remains constant.*" Mathematically,

$$V \alpha T \quad \text{or} \quad \frac{V}{T} = \text{Constant}$$

or
$$\frac{V_1}{T_1} = \frac{V_2}{T_2} = \frac{V_3}{T_3} \ldots\ldots\ldots\ldots = \text{Constant}$$

(*ii*) "*All perfect gases change in volume by* $\frac{1}{273}$th *of its original volume at 0°C for every 1°C change in temperature, when the pressure remains constant.*"

Let V_o = Volume of a given mass of gas at 0°C,

and V_t = Volume of the same mass of gas at t °C .

Then, according to the above statement,

$$V_t = V_o + \frac{1}{273} V_o \times t$$

$$= V_o\left(\frac{273+t}{273}\right) = V_o \times \frac{T}{T_o}$$

or
$$\frac{V_t}{T} = \frac{V_o}{T_o} \qquad \ldots(2.3)$$

where T = Absolute temperature corresponding to t °C,

T_o = Absolute temperature corresponding to 0°C.

The above statement shows that the volume of a gas goes on decreasing by $\frac{1}{273}$th of its original volume for every 1°C decrease in temperature. Now at a temperature of –273°C, the volume of the gas would become zero and this temperature is called absolute zero temperature.

2.5 GAY-LUSSAC LAW

This law states that, "*The absolute pressure of a given mass of a perfect gas varies directly as its absolute temperature, provided the volume remains constant.*" Mathematically,

$$P \propto T \quad \text{or} \quad \frac{P}{T} = \text{Constant} \qquad \ldots(2.4)$$

or
$$\frac{P_1}{T_1} = \frac{P_2}{T_2} = \frac{P_3}{T_3} = \ldots\ldots\ldots\ldots\ldots\ldots = \text{Constant.}$$

2.6 GENERAL GAS EQUATION

General gas equation is derived by considering the fact that all the three variables *i.e.* pressure, volume and temperature change simultaneously.

According to Boyle's law

$$P \propto \frac{1}{V} \quad \text{or} \quad V \propto \frac{1}{P}$$

and according to Charle's law

$$V \; \alpha \; T$$

From above two laws, we have

$$V \; \alpha \; \frac{1}{P} \text{ and T both}$$

or $$V \; \alpha \; \frac{T}{P}$$

∴ $$PV \; \alpha \; T$$

or $$PV = CT \qquad \text{...(2.5}$$

where C is a constant and value of C depends upon the mass and other properties of the gas.

If v is the volume of a unit mass of the gas, then the above constant C is represented by another constant R which is known as characteristic gas constant or simply gas constant. Thus the general gas equation may be written as :

$$Pv = RT \qquad \text{...(2.6}$$

In general, equation 2.5 can be written as

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_1} = \text{...........} = \text{Constant}$$

If m is the mass of a gas in kg, then the equation (2.6) can be written as:

$$PV = mRT \qquad (\because mv = V)\text{...(2.7}$$

The above correlation is the equation of state for any arbitrary amount of gas and is valid for a perfect gas only.

The unit of R may be calculated from equation (2.7).

i.e. $$R = \frac{PV}{mT}$$

$$= \frac{N/m^2 \times m^3}{kg \times K} = \frac{Nm}{kg\ K} \text{ or } \frac{J}{kg\ K}$$

The values of R, though constant for a particular gas, are different for different gases. In S.I unit, value of R for atmospheric air is taken as 287 J/kg K or 0.287 kJ/kg K.

2.7 AVOGADRO'S LAW

This law states, "*Equal volume of all gases will have equal number of molecules, under identical conditions of temperature and pressure.*"

According to this law, $1m^3$ of hydrogen will contain the same number of molecules as $1m^3$ of oxygen when temperature and pressure is same. We know that molecular mass of hydrogen is 2 and that of oxygen is 32. As $1m^3$ of these two gases have equal number of molecules, therefore, mass of one molecule of oxygen will be $\frac{32}{2}$ = 16 times the mass of hydrogen molecule. In other words, the density of oxygen is 16 times the density of hydrogen. Hence Avogadro's law indicates that the density of any two gases is directly proportional to their molecular masses at the same temperature and pressure.

At normal temperature and pressure (N.T.P.) *i.e.* at 0°C and 1.01325 bar, the density of oxygen is 1.429 kg/m^3

$$\therefore \quad \text{Specific volume of oxygen at N.T.P., } V = \frac{1}{1.429}\,\text{m}^3/\text{kg}$$

$$\text{Volume of 32 kg (or 1 kg-mol) of oxygen at N.T.P} = \frac{1}{1.429} \times 32 = 22.4\ \text{m}^3$$

In this way, it can be proved that volume of 1 kg mol of any gas at N.T.P is 22.4 m^3.

2.8 UNIVERSAL GAS CONSTANT

The universal gas content or molar constant (generally denoted by R_u*) of a gas is the product of the gas constant and the molecular mass of gas. Mathematically.*

$$R_u = MR \qquad \text{...(2.8)}$$

where M = Molecular mass of gas in kg mole

and R = Gas constant.

In general form, $R_u = M_1R_1 = M_2R_2 = M_3R_3 = \ldots\ldots\ldots\ldots$

We know that $Pv = MRT$ (For 1 kg mole)

or $$Pv = R_uT \qquad \text{...(2.9)}$$

or $$R_u = \frac{Pv}{T} = \frac{10135 \times 22.413}{273} = 8314.3\ \text{J/kg mole/K}$$

2.9 REGNAULT'S LAW

This law states, "*The two specific heats* C_P *(specific heat at constant pressure) and* C_v *(specific heat at constant volume) of a gas do not change with the change of temperature and pressure.*"

As the specific heats of a gas vary with the temperatures, therefore, Regnault's law gives the approximate results only. The variation in the results can be as high as 20% in engineering practice due to variation in specific heat with the increase in temperature.

2.10 SPECIFIC HEAT

The specific heat of a substance may be defined as *the amount of heat required to raise the temperature of its unit mass through one degree.* All the liquids and solids have only one specific heat while a gas has mainly two types of specific heats.

2.10.1 Specific Heat at Constant Pressure (C_P)

It is the amount of heat required to raise the temperature of a unit mass of a gas through on degree, when its pressure is kept constant.

If m kg of a gas is heated from temperature T_1 to temperature T_2 at constant pressure, the amount of heat supplied to gas is given by

$$Q = mC_P (T_2 - T_1) \quad \text{...(2.1}$$

The value of C_P for air in S.I. unit is 1 kJ/kg K.

2.10.2 Specific Heat at Constant Volume (C_V)

It is the amount of heat required to raise the temperature of a unit mass of a gas through on degree, when its volume is kept constant.

If m kg of a gas is heated at constant volume from temperature T_1 to temperature T_2, the amount of heat supplied to gas is given by

$$Q = mC_V (T_2 - T_1) \quad \text{...(2.1}$$

The value of C_V for air in S.I. unit is 0.72 kJ/kg K.

As stated by Regnault's law, the specific heats C_P and C_V of a perfect gas are assumed t remain constant at all temperatures, but they increase considerably with the rise in the temperature for real gases.

The value of C_P is always greater than C_V and, therefore, their ratio of C_P and C_V will b greater than one.

i.e.

$$\gamma = \frac{C_P}{C_V} > 1 \quad \text{...(2.12}$$

The value of γ for air is 1.4.

2.11 RELATIONSHIP BETWEEN SPECIFIC HEATS C_P AND C_V

Let us consider m kg of a gas enclosed in a container and is being heated at constan pressure.

Let T_1 = Initial temperature of the gas,
T_2 = Final temperature of the gas,
V_1 = Initial volume of gas,
V_2 = Final volume of gas,
C_P = Specific heat at constant pressure,
C_V = Specific heat at constant volume,
P = Absolute constant pressure.

We know that heat supplied to the gas at constant pressure,

$$Q = mC_P (T_2 - T_1) \quad \text{...(}$$

We also know that a part of this heat is utilised in doing external work, while the remaining part of heat is used in increasing the internal energy of gas.

i.e. $$Q = W + dU \qquad \ldots(ii)$$

Now heat utilised for external work,

$$W = P(V_2 - V_1) \qquad \ldots(iii)$$

and increase in internal energy

$$dU = mC_v\,(T_2 - T_1) \qquad \ldots(iv)$$

Putting the values of W and dU in equation (*ii*)

$$\therefore \quad Q = P(V_2 - V_1) + mC_V\,(T_2 - T_1) \qquad \ldots(v)$$

Using characteristic gas equation, we have

$$PV_1 = mRT_1 \qquad \text{(For initial condition)}$$

$$PV_2 = mRT_2 \qquad \text{(For final condition)}$$

$$\therefore \quad P(V_2 - V_1) = mR\,(T_2 - T_1) \qquad \ldots(vi)$$

Putting the value of $P(V_2 - V_1)$ from equation (*vi*) in equation (*v*), we get

$$Q = mR(T_2 - T_1) + mC_V\,(T_2 - T_1)$$

Now putting the value of Q from equation (*i*) in above equation, we get

$$mC_P\,(T_2 - T_1) = mR\,(T_2 - T_1) + mC_V\,(T_2 - T_1)$$

or $$C_P = R + C_V$$

or $$C_P - C_V = R \qquad \ldots(2.13)$$

The equation 2.13 may be written as

$$C_V\left[\frac{C_P}{C_V} - 1\right] = R$$

or $$C_V\,(\gamma - 1) = R$$

$$\therefore \quad C_V = \frac{R}{\gamma - 1} \qquad \ldots(2.14)$$

The value of R in S.I. unit is taken as 287 J/kg K or 0.287 kJ/ kg K.

The equation (2.13) may also be written as

$$C_P = C_V + R$$

Dividing both sides by C_V, we get

$$\frac{C_P}{C_V} = 1 + \frac{R}{C_V}$$

or $$\gamma = 1 + \frac{R}{C_V} \qquad \ldots(2.15)$$

Let M = Molecular mass of the gas,

and R_u = Universal gas constant.

Then, from equation (2.8), we get