# UNIT-II Gaseous state

Gas Laws are the fundamental relationships describing how the pressure (P), volume (V), temperature (T), and sometimes the amount of gas (n) are related for an ideal gas. They are derived from experimental observations and can be expressed mathematically.

## 1. Boyle's Law (Pressure–Volume Law)

Statement: At constant temperature, the volume of a fixed mass of gas is inversely proportional to its pressure.

$P \propto \frac{1}{V}$ (T constant)

$PV=\text{constant}$

## 2. Charles's Law (Volume–Temperature Law)

Statement: At constant pressure, the volume of a fixed mass of gas is directly proportional to its absolute temperature (in Kelvin).

$V \propto T$(P constant)

$VT=\text{constant}$

## 3. Gay-Lussac's Law (Pressure–Temperature Law)

Statement: At constant volume, the pressure of a fixed mass of gas is directly proportional to its absolute temperature.

$P \propto T$(V constant)

$PT=\text{constant}$

## 4. Avogadro's Law (Volume–Mole Law)

Statement: At constant temperature and pressure, the volume of a gas is directly proportional to the number of moles of gas.

$V \propto n$ (P, T constant)

$\frac{V}{n}$ = constant

## 5. Combined Gas Law

By combining Boyle's, Charles's, and Gay-Lussac's laws:

$\frac{PV}{T}$ = constant

## Ideal Gas Equation

By adding Avogadro's law to the combined gas law, we get:
$PV= nRT$
Where:
P = pressure , V = volume , n = number of moles, R = universal gas constant (8.314 J $mol^{-1}K^{-1}$ & T = absolute temperature (K)
All gases are real gases. They show more and more deviations from the gas laws (i.e. from ideal behaviour) as the pressure is increased or temperature is decreased.
As mentioned above, gases tend to show ideal behaviour as the temperature increases above their boiling points. Thus at ordinary temperature, the most nearly ideal (perfect) gases are those which have very low boiling points, i.e. $N_2$, $H_2$, $O_2$ etc. On the other hand, the most easily liquefiable and highly soluble gases (e.g., $CO_2$, $SO_2$, $NH_3$ etc.) show much larger deviations from ideal behaviour.

## Deviations from Boyle's law.

According to Boyle's law, PV=Constant at constant temperature

This means that at a given temperature, the product PV should be constant at all pressures; and thus the plot of PV versus P at constant temperature should be a horizontal line in diagram

However this is an ideal behaviour which no real gas shows in practice. All gases give either of the following two types of curves.

(i) For gases like hydrogen and helium, the product PV continuously increases with increase of pressure

(ii) For gases like CO and $CH_4$, the product PV first decreases with increase of pressure, reaches a minimum value and then begins to increase.

These curves lead to the following conclusions.
(a) At low pressure, PV for all gases, except $H_2$ and He, has a lower value than that for an ideal gas.
(b) At high pressure, PV for all gases including $H_2$ and He has a higher value than that for an ideal gas.
(c) As pressure approaches zero, all gases tend to behave as ideal gases.

Alternatively, the magnitude and the nature of deviation from Boyle's law may be observed from the plots of $\frac{PV}{nRT}$ (Compressibility factor, denoted by Z) versus pressure,P at constant temperature.

Compressibility factor, $Z=\frac{PV}{nRT}$

At constant temperature T, $Z \propto PV$

Remember that at all temperatures and pressures, Z=1

The plots of compressibility factor Z versus P at different temperatures for nitrogen gas are shown in the diagram below

The plots lead to the following conclusions.

As the temperature increases, the dip in the curves becomes smaller and smaller. At a particular temperature (50°C in case of $N_2$) the curve seems to remain almost horizontal and Z is much closer to one for an appreciable range of pressure (0 to 100 atmosphere in the present case).

*This temperature at which a real gas behaves like an ideal gas over an appreciable pressure range is called Boyle's temperature* or *Boyle's point*. Below this temperature, the value of Z at first decreases, approaches a minimum and then increases continuously with increase in pressure. Above this temperature, the value of Z increases continuously with increase in pressure.

**Thus from the above observation, we may conclude that Boyle's law is obeyed only at very low pressure and moderately high temperature.**

## Deviation from Charle's law.

According to Charle's law, the coefficient of expansion of volume of every gas should be same *(i.e.,*$\frac{1}{273}$ *= 0.003663 of its volume at 0°C)* at all pressures. However, in practice this is found to be only at low pressure and considerable deviation sets in with the increase in pressure.Further the gases which are more easily liquefiable show larger deviations (similarity with Boyle's law).

## Deviation from Avogadro's law.

According to Avogadro's law, *1 mole of every gas should occupy a volume of 22.4 litres at N.T.P.*, which is not found to be true in any real gas. Again as in the above two gas laws, the deviations are more (i) in case of easily liquefiable gases *(e.g.,* $NH_3$ *and* $C_2H_5Cl$*)*, and (ii) at lower temperature and higher pressures.

## *Causes Of Deviations From Ideal Behaviour*

We have observed that the gases obey the ideal gas equation *(PV = nRT)* only at low pressure or high temperature. However, if the pressure is high or the temperature is low, the real gases show deviations from the ideal behaviour. The reason for the derivation is the following two *faulty assumptions* made during the derivation of kinetic gas equation on the bases of which gas laws are derived.

*(i) The volume occupied by the gas molecules is negligibly small as compared to the total volume of the gas.*
*(ii) The forces of attraction between gas molecules are negligible.*

However, the above two assumptions are true only at low pressure or high temperature so that the distance between the molecules is large. In case, the pressure is high or the temperature is low, the gas molecules come close together and the above two assumptions do not hold. Hence, *it is necessary to apply suitable corrections to the ideal gas equation so as to make it applicable to real gases.*

## Van der Waals' equation of state.

### Necessity For Van Der Waal's Equation

*As mentioned earlier, the ideal gas equation is not obeyed by the real gases at high pressures or low temperatures. In case, the pressure is high or the temperature is low, the gas molecules come close together and the above two assumptions do not hold. Hence, it is necessary to apply suitable corrections to the ideal gas equation so as to make it applicable to real gases.*

### Definition – Van der Waals' Equation of State

The van der Waals equation of state is a modified form of the ideal gas equation that accounts for the finite size of gas molecules and the intermolecular forces between them. It is expressed as:

$$(P+\frac{an^2}{V^2})\ (V-nb) = nRT$$

For one mole (n=1):

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

Here: P = pressure of the gas , V = volume of the gas ,T = absolute temperature ,R = universal gas constant, n = number of moles , a = van der Waals constant accounting for attractive forces between molecules b = van der Waals constant accounting for finite volume of molecules

### Derivation:

From Ideal gas law For nnn moles of an ideal gas: PV=nRT

This assumes (i) molecules have negligible volume and (ii) no intermolecular forces. For real gases these assumptions fail at high pressures / low temperatures, so corrections are needed.

### 2. Correction for finite molecular size (volume correction)

Real gas molecules occupy finite volume. If b is the excluded volume per mole (volume effectively occupied by one mole of molecules so unavailable for motion), the volume available for motion of n moles is approximately

$V_{available} = V-nb$.

Replace V by V−nb in the ideal gas law.

### 3. Correction for intermolecular attraction (pressure correction)

Attractive forces between molecules reduce the momentum transfer to the container walls, so the observed pressure PPP is less than the pressure the gas would exert if no attractions were present. The correction term is taken proportional to the square of the molar density because attractive interactions depend on the number of pairs.

$P_{ideal} \approx (P+\frac{an^2}{V^2})$

where a is a constant measuring strength of attraction (units : $p_a\ m^6.mol^{-2}$ in SI)

### 4. Substitute corrected pressure and volume available into ideal gas law PV=nRT

$(P+\frac{an^2}{V^2})\ (V-nb) = nRT$

This is the van der Waals equation (general form).

5. One-mole form

For one mole (n=1n=1n=1) the equation simplifies to:

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

6. Physical meaning of constants

a: measure of strength of attractive forces (larger a → stronger attractions → larger deviation from ideality).

b: effective excluded volume per mole (roughly 4 × molecular volume for hard spheres).

## Critical Phenomena & Critical Constants

### Critical Phenomena:

When a gas is compressed at a constant temperature, it eventually condenses into a liquid. However, **above a**

***certain temperature****, the gas cannot be liquefied by pressure alone, the boundary between liquid and gas disappears, and both phases become indistinguishable.*

*The temperature, pressure, and volume at this state are called critical constants.*

*At the critical point,*

- *The densities of the liquid and vapour become equal.*
- *Surface tension between phases becomes zero.*
- *Distinction between liquid and gas phases vanishes.*
- ***Critical Constants:***
- *Critical Temperature ($T_c$): The temperature above which a gas cannot be liquefied, no matter how much pressure is applied.*
- *Critical Pressure ($P_c$): The minimum pressure required to liquefy a gas at its critical temperature.*
- *Critical Volume ($V_c$): The volume occupied by one mole of a gas at the critical temperature and pressure.*

## Relationship between critical constants and van der Waals' constants.

***van der Waals' equation for 1 mole Gas is** $(P+\frac{a}{V^2})(V-b) = RT$*

***Multiply the above equation throughout by $V^2$:***

$$V^2[(P+\frac{a}{V^2})(V-b)] = V^2.RT$$

$$V^2[PV-Pb+\frac{a}{V}-\frac{ab}{V^2}] = V^2.RT$$

$$PV^3-PbV^2+aV-ab= V^2.RT$$

***Dividing the above equation throughout by P***

$$V^3-bV^2+\frac{aV}{P}-\frac{ab}{P}=\frac{RTV^2}{P}$$

***Arranging the above Equation in the descending powers of V***

$$V^3-bV^2-\frac{RTV^2}{P}+\frac{aV}{P}-\frac{ab}{P}=0$$

$V^3-V^2(b+\frac{RT}{P})+\frac{a}{P}V-\frac{ab}{P}=0$*. This is a third order Equation V and has 3 roots /3 solutions.*

*From the theoretical isotherms of $CO_2$, below the critical temperature there are three values of V for every value of P, while at the critical temperature, there is only one value of V for every value of P.*

*Since at the critical temperature, the three values of V (i.e. three roots of van der Waals equations) become identical for a particular value of P and represented by Vc i.e.,*

*$V=V_C$ at critical temperature*

$(V-V_C)^3 = 0$

$$V^3-3V_CV^2+3V_C^2V-V_C^3=0$$

*Under critical condition $T=T_C$ and $P=P_C$*

*Substituting these values in the van der Waals' equation*

$$V^3-V^2(b+\frac{RT_C}{P_C})+\frac{a}{P_C}V-\frac{ab}{P_C}=0$$

*At critical point the equations*

$V^3-3V_CV^2+3V_C^2V-V_C^3=0$ *and* $V^3-V^2(b+\frac{RT_C}{P_C})+\frac{a}{P_C}V-\frac{ab}{P_C}=0$ *must be identical. Hence the coefficients of similar power terms of V must be equal i.e.,*

$V^3-3V_CV^2+3V_C^2V-V_C^3=0$ *and*

$$V^3-(b+\frac{RT_C}{P_C})V^2+\frac{a}{P_C}V-\frac{ab}{P_C}=0$$

*Compare the coefficients of similar power terms of V*

$$3V_C=(b+\frac{RT_C}{P_C}) \quad ..........1$$

$$3V_C^2=\frac{a}{P_C} \quad ..........2$$

*and* $V_C^3=\frac{ab}{P_C}$ ..........3

*Divide Eqn 3 with Eqn 2*

$$\frac{V_C^3}{3V_C^2}=\frac{\frac{ab}{P_C}}{\frac{a}{P_C}}=\frac{ab}{P_C} X \frac{P_C}{a}=b$$

$$V_C=3b$$

*Substituting the value of $V_C$ in Eqn* $3V_C^2=\frac{a}{P_C}$

$$(3 X (3b)^2=\frac{a}{P_C}$$

$$P_C=\frac{a}{27b^2}$$

*Now Substituting the value of $V_C$ & $P_C$ in Eqn* $3V_C=(b+\frac{RT_C}{P_C})$

$$3 X 3b=(b+\frac{RT_C}{\frac{a}{27b^2}})$$

$$9b=(b+\frac{RT_C.27b^2}{a})$$

$$8b=\frac{RT_C.27b^2}{a}$$

$$T_C=\frac{8a}{27bR}$$

$V_C=3b$ ; $P_C=\frac{a}{27b^2}$ ; $T_C=\frac{8a}{27bR}$ *are the relation between the critical constants and van der Waals' constants*

*To get the internal relation among critical constants $P_C$, $V_C$ and $T_C$*

*Take* $\frac{T_C}{P_C \cdot V_C} = \frac{\frac{8a}{27bR}}{\frac{a}{27b^2} \cdot 3b} = \frac{8a}{27bR}\frac{27b^2}{3ab} = \frac{8}{3R}$

$$P_C \cdot V_C = \frac{3}{8}RT_C$$

## *Joule–Thomson Effect*

### *Definition:*

*The **Joule–Thomson effect** (or Joule–Kelvin effect) is the change in temperature of a real gas (or liquid) when it is allowed to expand adiabatically (no heat exchange) through a porous plug or a valve from a region of high pressure to a region of low pressure, without performing external work.*

- ***For ideal gases*** *→ No change in temperature (because internal energy depends only on temperature).*

*Joule–Thomson coefficient = 0.*

- ***For real gases*** *→ Temperature may increase or decrease depending on the initial temperature and pressure.*
- *The temperature change occurs due to the change in potential energy of intermolecular forces.*

### *Mathematical Expression:*

*The **Joule–Thomson coefficient** is given by:*

$\mu_{JT} = (\frac{\partial T}{\partial P})_H \frac{\mu_{JT}}{}$ *Where:* $\mu_{JT}$ *= Joule–Thomson coefficient (K/Pa or K/bar)*

*T = temperature P = pressure H = enthalpy (constant during the process)*

### *Interpretation:*

- *If* $\mu_{JT} > 0$ *: Gas cools on expansion (most gases below inversion temperature).*
- *If* $\mu_{JT} < 0$ *: Gas warms on expansion (most gases above inversion temperature).*

***Example:***

- *Oxygen, nitrogen, and CO₂ cool during expansion at room temperature.*
- *Hydrogen and helium warm during expansion at room temperature (because their inversion temperature is much lower than room temperature).*

## *Inversion Temperature*

### *Definition:*

*The **inversion temperature** (TiT_iTi) is the temperature at which the Joule–Thomson coefficient changes sign – i.e., the temperature above which a gas warms on expansion, and below which it cools on expansion.*

***Condition:***

*At inversion temperature:*

$\mu_{JT} = 0$

### *Physical Meaning:*

- ***Below*** $T_i$*: Expansion → cooling (basis of gas liquefaction by Linde's process).*
- ***Above*** $T_i$*: Expansion → heating.*

### *Applications:*

- *Liquefaction of gases (Linde and Claude processes).*
- *Understanding natural gas pipeline cooling.*
- *Cryogenics and refrigeration engineering.*