



## PROPERTIES OF IDEAL GAS AND REAL GAS :-

### 1. Ideal gas :-

An ideal gas is an imaginary substance that obeys the relation  $PV = RT$  or  $pV = RT$ . So the state equation is also known as ideal-gas equation.

At low pressures and high temperatures, the density of a gas decreases. At that time, the gas behaves as an ideal gas.

A factor is introduced to account deviation of ideal gas behaviour is known as compressibility factor. It means a measure of deviation of ideal gas behaviour.

### 2. Real Gas :-

At high pressures, the gases start to deviate from ideal-gas behaviour. So that deviation should be accounted.

The state equation for real gases is given by.

$$PV = ZRT$$

where,

$Z =$  compressibility factor,

$$Z = \frac{Pv}{RT}$$





The compressibility factor can also be expressed as

$$Z = \frac{V_{\text{actual}}}{V_{\text{ideal}}}$$

where,

$V_{\text{actual}}$  = specific volume of real gases.

$V_{\text{ideal}}$  = specific volume of ideal gases.

For ideal gases,  $Z = 1$ .

real gases,  $Z > < 1$ .

### Properties of Ideal Gas :-

An imaginary gas which obeys the equation of state as  $PV = RT$  at all pressures and temperatures is known as ideal gas.

If the pressure of real gas tends to zero or temperature tends to infinity, the real gas behaves as ideal gas.

In equation of state,  $PV = RT$ , volume or pressure remains constant but temperature is 0 K, it means  $T = -273.15^\circ\text{C}$ . So this temperature is called as absolute temperature.

### Enthalpy of an ideal gas :-

Enthalpy = Internal energy + flow energy.

$$h = u + Pv$$

$$h = u + RT$$

$$\because Pv = RT$$

then differentiate.

$$dh = du + RdT$$

$$\because du = C_v dT$$

$$dh = C_v dT + RdT$$

$$\because R = C_p - C_v$$

$$dh = (C_v + R) dT$$

$$C_p = R + C_v$$

$$\boxed{dh = C_p dT}$$

$$C_p = \frac{dh}{dT}$$

In terms of pressure

$$\boxed{C_p = \left( \frac{dh}{dT} \right)_P}$$





Entropy of ideal gas :-

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From first law of thermodynamics.

$$Q = W + \Delta U$$

$$Q = \Delta U + W$$

$$T ds = du + p \cdot dv \quad \text{--- (1)}$$

$$ds = \frac{du}{T} + \frac{p}{T} \cdot dv$$

$$ds = C_v \cdot \frac{dT}{T} + \frac{R}{V} \cdot dv$$

Integrating on both sides,

$$\int ds = \int C_v \cdot \frac{dT}{T} + \int R \cdot \frac{dv}{V}$$

$$S_2 - S_1 = C_v \ln \left( \frac{T_2}{T_1} \right) + R \ln \left( \frac{V_2}{V_1} \right)$$

$$= C_v \ln (T_2 - T_1) + R \ln (V_2 - V_1)$$

$$S_2 - S_1 = C_v \ln \left( \frac{T_2}{T_1} \right) + R \ln \left( \frac{V_2}{V_1} \right)$$

From equation,

$$T \cdot ds = du + p \cdot dv$$

$$= dh - d(pv) + p \cdot dv$$

$$= dh - v dp - p \cdot dv + p \cdot dv$$

$$T \cdot ds = dh - v dp$$

$$ds = \frac{dh}{T} - \frac{v}{T} dp$$

$$ds = C_p \cdot \frac{dT}{T} - \frac{R}{P} \cdot dp$$

Integrating on both side.

$$\int ds = C_p \int_{T_1}^{T_2} \frac{dT}{T} - R \int_{P_1}^{P_2} \frac{dp}{P}$$

$$S_2 - S_1 = C_p \ln (T_2 - T_1) - R \ln (P_2 - P_1)$$

$$S_2 - S_1 = C_p \ln \left( \frac{T_2}{T_1} \right) - R \ln \left( \frac{P_2}{P_1} \right) \quad \text{--- (2)}$$

We know that,  $R = C_p - C_v$

$$\therefore Q = T ds$$

$$W = p \cdot dv$$

$$\therefore du = C_v \cdot dT$$

$$\frac{du}{dT} = C_v$$

$$pV = RT$$

$$\Rightarrow \frac{p}{T} = \frac{R}{V}$$

$$\therefore h = du + pv$$

$$dh = du + d(pv)$$

$$du = dh - d(pv)$$

$$C_v = u dv - v du$$

$$\therefore dh = C_p dT$$

$$pV = RT$$





Then equation (2) becomes,

$$S_2 - S_1 = c_p \ln \left( \frac{T_2}{T_1} \right) - (c_p - c_v) \ln \left( \frac{P_2}{P_1} \right) \quad (1)$$

$$S_2 - S_1 = c_p \ln \left( \frac{T_2}{T_1} \right) - c_p \ln \left( \frac{P_2}{P_1} \right) + c_v \ln \left( \frac{P_2}{P_1} \right)$$

$$S_2 - S_1 = c_p \ln \left( \frac{T_2/T_1}{P_2/P_1} \right) + c_v \ln \left( \frac{P_2}{P_1} \right)$$

$$S_2 - S_1 = c_p \ln \left( \frac{P_1 T_2}{P_2 T_1} \right) + c_v \ln \left( \frac{P_2}{P_1} \right)$$

$$S_2 - S_1 = c_p \ln \left( \frac{V_2}{V_1} \right) + c_v \ln \frac{P_2}{P_1}$$

### Equation of State of Ideal Gas :-

An ideal gas is a substance which obeys the law of  $Pv = \bar{R}T$   
or  $PV = \bar{R}T$

where,  $p$  = pressure of the gas.

$v$  = specific volume of the gas.

$V$  = total volume of the gas.

$\bar{R}$  = universal gas constant =  $8.314 \text{ kJ/mole}\cdot\text{K}$ .

$$R = \frac{\bar{R}}{M}$$

$T$  = Absolute temperature in K.

If we consider mass of the gas  $m$ , the equation of state becomes

$$Pv = Nm \bar{R} T \quad (\text{or}) \quad PV = Nm \bar{R} T.$$

For example :-

gas constant  $R$  for air  $R = \frac{\bar{R}}{M} = \frac{8.314}{28.97}$

$$R = 0.287 \text{ kJ/kg}\cdot\text{K}$$

gas constant  $R$  for oxygen,

$$R = \frac{\bar{R}}{M} = \frac{8.314}{32}$$

$$R = 0.26 \text{ kJ/kg}\cdot\text{K}$$





① Boyle's law :-

Boyle's law states the volume of given mass of a gas varies inversely with its absolute pressure when the temperature remains constant.

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

$$PV = \text{constant}$$

for example,

$$P_1 V_1 = P_2 V_2 \quad (\text{applicable for isothermal process})$$

② Charles's law :-

Charles's law states "the volume of given mass of a gas varies directly with its absolute temperature when the pressure remains constant."

$$V \propto T$$

$$\frac{V}{T} = C \quad \text{constant}$$

for example,

State 1,  $\frac{V_1}{T_1} = C$       State 2,  $\frac{V_2}{T_2} = C$

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

$$\frac{V_1}{V_2} = \frac{T_1}{T_2} \quad (\text{applicable for constant pressure process})$$

Charles's law also states the pressure of give mass of a gases directly with its absolute temperature when the volume remains constant.

$$P \propto T$$

$$\frac{P}{T} = C \quad [\text{Constant pressure}]$$

State 1,  $\frac{P_1}{T_1} = C$

State 2,  $\frac{P_2}{T_2} = C$

$$\therefore \frac{P_1}{T_1} = \frac{P_2}{T_2}$$

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

$$\text{So, } \therefore \frac{P_1}{P_2} = \frac{T_1}{T_2} \quad [\text{constant volume process}]$$





③ Joule's law :-

Joule's law states, "the internal energy of a given quantity of a gas depends only on the temperature."

$$\Delta U = C_v \Delta T$$

④ Regnault's law :-

Regnault's law states, "the two specific heats  $c_p$  and  $c_v$  of a gas do not change with the change of temperature and pressure".  $c_p$  and  $c_v$  of a gas always remain constant.

⑤ Avogadro's law :-

Avogadro's law states, "Equal volumes of different perfect gases at the same temperature and pressure contain equal number of molecules."

It can be stated, "The volume of one gram mole of all gases at the pressure of 760 mm Hg and temperature of  $0^\circ\text{C}$  is the same, and is equal to 22.4 litres."

$$\text{kg mole of a gas} = 22.4 \times 10^{-3} \text{ m}^3$$

$$1 \text{ kg mole of a gas} = 22.4$$

$$\bar{R} = 8314.3 \text{ J/mole kg}\cdot\text{K}$$

⑥ Characteristic gas equation :-

General gas equation for ideal gas is

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

Taking  $R$  as constant

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

$$PV = RT$$

Consider mass 'm'

$$PV = mRT$$





### Properties of Real Gas :-

The gas which does not obey the law of equation of state is known as REAL GAS. The specific heats, compressibility factor, which vary with pressure and temperature. The enthalpy and internal energy are functions of pressure and temperature.

$$PV = ZRT$$

where,

$Z$  = compressibility factor.

### Properties :-

1. Intermolecular forces.
2. Shape factor.

### Equation of state :-

#### ① Vander waal's equation :-

The equation of state for real gases is given by

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

For ideal gas, the constant  $a$  and  $b$  are zero.

The values of  $a$  and  $b$  are dependent upon the type of fluid or gases used.

If we consider molar volume in analysis, the equation of state becomes,

$$\left(P + \frac{a}{V^2}\right)(V - b) = \bar{R}T$$

where,  $V$  = Molar volume

$\bar{R}$  = Universal gas constant = 8.314 J/mole.K

The values of  $a$  and  $b$  is theoretically determined by

$$a = \frac{27R^2(T_c)^3}{64P_c}$$

$$b = \frac{RT_c}{8P_c}$$

where,  $T_c$  = critical temperature.

$P_c$  = critical pressure.





Limitations :-

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1. The study had not been made closely under actual conditions and its validity bias failed.
2. The values of  $a$  and  $b$  are assumed as constant but they will vary with temperature which is found experimentally.
3. At critical point, the Vander waal's equation,

for real gases  $\frac{P_c V_c}{RT_c} = \frac{Z}{B}$

Ideal gases  $\frac{P_c V_c}{RT_c} = 1$

But experimentally,  $\frac{P_c V_c}{RT_c}$  changes from 0.2 to 0.3 for most of the gases.

② Beattie - bridgeman equation of state :-

This equation is based on five experimentally determined constraints in the form of.

$$P = \frac{R_a T}{V^2} \left(1 - \frac{C}{V T^3}\right) (V + B) - \frac{A}{V^2}$$

where,  $A = A_0 \left(1 - \frac{a}{V}\right)$ ,  $B = B_0 \left(1 - \frac{b}{V}\right)$

It is accurate for densities values upto 0.8  $\rho_{cr}$ .

$\rho_{cr}$  = density of the substance at critical point.

③ Benedict - webb - Rubin equation of state :-

The equation of state is expressed as.

$$P = \frac{R_u T}{V} + \left( B_0 R_u T - A_0 - \frac{C_0}{T^2} \right) \frac{1}{V^2} + \frac{b R_u T - a}{V^3} + \frac{ax}{V^6} + \frac{c}{V T^2} \left(1 + \frac{d}{V^2}\right) e^{-\frac{d}{V^2}}$$

This can take substances at densities upto about 2.5  $\rho_{cr}$ .

④ Viral equation of state :-

Viral (or) virtual expansions are only applicable to gases of low and medium densities.

The equation of state of a substance is given by.

$$P = \frac{RT}{V} + \frac{a(T)}{V^2} + \frac{b(T)}{V^3} + \frac{c(T)}{V^4} + \frac{d(T)}{V^5} + \dots$$

The coefficient of  $a(T)$ ,  $b(T)$ ,  $c(T)$ ,  $d(T)$ , ... are viral coefficients. The viral coefficient will vanish when the pressure becomes zero. Finally the equation of state reduces to the ideal gas equation.





### Compressibility Factor :-

The perfect gas equation is

$$PV = RT$$

But for real gas, a correction factor has to be introduced in the perfect gas equation to take into account the deviation of the real gas from the perfect gas equation. This factor is known as compressibility factor ( $Z$ ).

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

The general compressibility chart is plotted with compressibility factor ( $Z$ ) versus reduced pressure ( $P_r$ ) for various values of reduced temperature ( $T_r$ ).

The equation of state for real gas at any state becomes

$$PV = ZRT$$

Similarly, the equation of state for the same real gas at critical point becomes.

$$P_c V_c = Z_c R T_c$$

### Compressibility chart :-

The general compressibility chart is plotted with compressibility factor ( $Z$ ) vs reduced pressure ( $P_r$ ) for various values of reduced temperature ( $T_r$ ).

The following observations can be made from the generalized compressibility chart.

- \* At very low pressures ( $P_r \ll 1$ ), the gases behave as an ideal gas.
- \* At high temperature ( $T_r > 2$ ), ideal gas behaviour is assumed as with good accuracy of pressures.
- \* The deviation of a gas from ideal-gas behaviour is the greatest in the vicinity of critical point.

For different gases, the behaviour changes on the basis thermal properties like reduced pressure and reduced temperature.