GASEOUS STATE

Gas laws

(a) Boyle's law

It states that, at constant temperature, the volume of a given mass of a gas is inversely proportional to its pressure.

Thus, if *V* is the volume of the gas at pressure P, then

$V \alpha 1/P$

$V = k/P$

$PV= \text{Constant}$

If V_1 is the volume of the gas at pressure P_1 and V_2 is the volume at pressure P_2 then

$P_1V_1 = P_2V_2$

(b) Charles' law

It states that at constant pressure, the volume of a given mass of a gas is directly proportional to the absolute temperature of the gas.

Mathematically,

$V \alpha T$

$V/T = \text{constant}$, (P, n are constants)
or
$V1/T1 = V2/T2$
where V_1 is the volume of the gas at the temperature T_1 and V_2 is the volume at temperature T_2.

(c) Avogadro's law

It states that equal volumes of all gasses at the same temperature and pressure contain equal number of molecules or moles.

Mathematically,

V α n (P, T are constant)

where, n = the number of moles of gas present in the system.

Ideal gas and non-ideal gas

(a) Ideal gas

A gas which obeys the three gas laws under all conditions of temperatures and pressures is known as an ideal gas or a perfect gas. It is observed that there is no gas which obeys the gas laws or the ideal gas equation under all conditions of temperatures and pressures. However, gasses obey these gas laws fairly well at low pressures and high temperatures.

(b) Non-ideal gas or real gas

A non-ideal gas or real gas is the one which obeys the gas laws only under low pressures and high temperatures. All gasses are non-ideal gasses or real gasses only. They show deviations from ideal behavior when the pressures are too high and temperatures are too low.

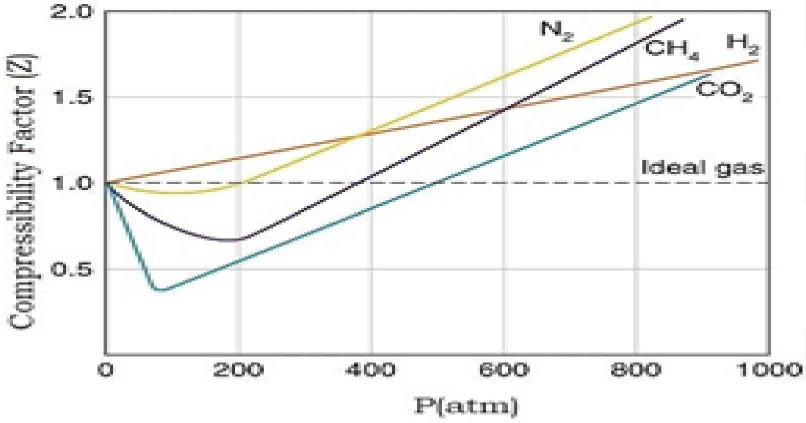
Compressibility factor (Z)

- The compressibility factor is also called compression factor. This factor describes the deviation of a real gas from the ideal behavior. It is denoted by **'Z'**.
- It is defined as the ratio of molar volume of a gas to the molar volume of an ideal gas at the same temperature and pressure.
- It is a useful thermodynamic property for modifying the ideal gas law to account for the real gas behavior. It is mathematically represented as

$$Z = \frac{(PV)observed}{(PV)ideal} = \frac{(PV)observed}{nRT}$$

- For an ideal gas, Z = 1 and is independent of temperature and pressure.
- The deviations from ideality may be shown by a plot of the compressibility factor Z against pressure, P as shown in figure
- The deviations of a real gas from ideal behavior may change the value of Z may be greater or lesser than 1.
- When these deviations become large, then the gas is said to be a real or non-ideal gas.
- Thus, the difference between unity and the value of the compressibility factor of a gas is a measure of the degree of non-ideality of the gas.

Variation of Compressibility Factor for Some gases



Deviation of real gas from ideal behavior:

Real gases show deviations from ideal behavior only under the conditions of high pressures and low temperatures.

These deviations are due to two faulty assumptions that are made in the kinetic molecular theory of gases. They are

(i) The volume occupied by the gas molecules is highly negligible as compared to the total volume of the gas

(ii) The forces of attraction or repulsion among the gas molecules are negligible.

The above two assumptions are true only if the pressure is low or the temperature is high so that the distance between the molecules is sufficiently large.

However, if the pressure is high or the temperature is low, the gas molecules come closer together. Under these conditions:

a. The forces of attraction or repulsion between the molecules are to be considered.

b. The volume of the gas is so small that the volume occupied by the gas molecules cannot be neglected.

van der Waals equation of state

Inorder to understand the behavior of real gases vander wall proposed an equation this equation is known as vander waals equation.

This gives a simple physical picture for the difference between a real gas and an ideal gas. vander Waals obtained the equation for real gases by applying the corrections for volume and pressure as follows.

(a) Correction for the volume

Suppose v is the actual volume occupied by one mole of the gas molecules. Since the gas molecules are in motion, it has been found that the effective volume occupied by the gas molecules is four times the actual volume (4v). Let it be represented by b.

The volume b is called co-volume or excluded volume.

Thus, the free space available for the movement of gas molecules is (V-b).

Hence in the ideal gas equation V should be replaced by (V-b).

(b) Correction for the force of attraction- pressure correction

A gas molecule present in the interior of the gas, say molecule A in figure. is attracted equally by all other gas molecules surrounding it. Hence the net force of attraction exerted on such a molecule by the other molecules is zero.

However, for a molecule lying near the wall of the container, say molecule B in figure, the molecules lying inside the bulk of the gas exert some net inward pull.

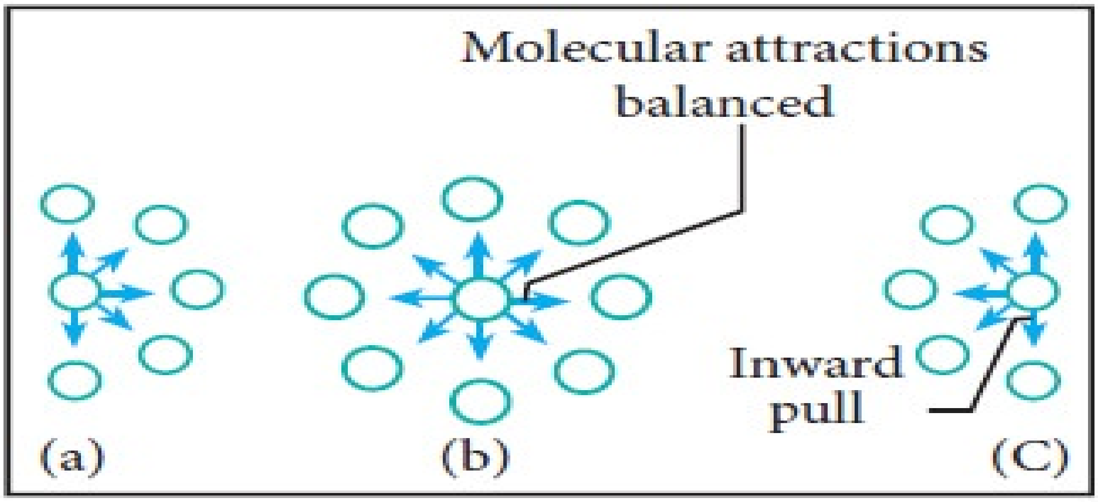


Figure. 6.10 Inter-molecular forces of attraction

Thus, the effect of such inward pull is ‘dragging back’ of the molecule. Consequently the pressure with which the gas molecule strikes the wall of the vessel is less than the pressure that would have been exerted if there were no such inward pull.

Thus, the ideal pressure would be greater than the observed pressure by a factor ‘p’.

$$\text{Corrected pressure} = P + p$$

Where, p is the correction factor due to the inward pull.

This inward pull on the gas molecules present near the wall depends upon:

(i) Number of molecules surrounding the molecule,

(ii) Total number of molecules.

Each of these factors in turn depends upon the density (d) of the gas.Hence correction factor,

$$p \ \underline{\alpha}\ d^2$$

But for a given mass of the gas $d \ \underline{\alpha}\ 1/v$

$$p \ \underline{\alpha}\ 1/v^2$$

$$p = a/v^2$$

Where *a* is a constant and it depends on the nature of the gas.

Substituting the corrected volume and corrected pressure in the ideal gas equation PV = RT for one mole of the gas, the equation is

$$(P + a/v^2)(V-b) = RT .$$

- This equation is known as van der Waals equation. The constants a and b are called van der Waals constants.
- The values of a and b depend upon the nature of the gas and are independent of the tempera- ture and pressure.
- vander Waals constant 'a' represents the magnitude of inter- molecular forces of attraction.
- The constant 'b' represents the effective size of the molecules.

For n moles of the gas

vander Waals equation for n moles of a gas is

$$[P + a(n/v)^2][V - nb] = nRT .$$

Significance of van der Waals Constants

(i). It is observed that the values of '*a*' for the easily liquefiable gases,

such as SO_2, NH_3, H_2S, CO_2 are greater than those for the perma- nent gases like N_2, O_2 H_2 and He.

Moreover, the value of 'a' increases with the ease of liquefaction of the gas.

It is observed that a gas which is more easily liquefiable has greater intermolecular forces of attraction. Hence '*a*' is a measure of the intermolecular forces of attraction in a gas.

(ii). The 'b' is the effective volume of the gas molecules. The constancy in the value of *b* for any gas over a wide range of temperature and pressure confirms that the gas molecules are incompressible.

The values of a and b for some gases are shown in table

Gas	a (atm L^2 mol^{-2})	b (L mol^{-1})
He	0.034	0.0237
H_2	0.245	0.0266
N_2	1.36	0.0318

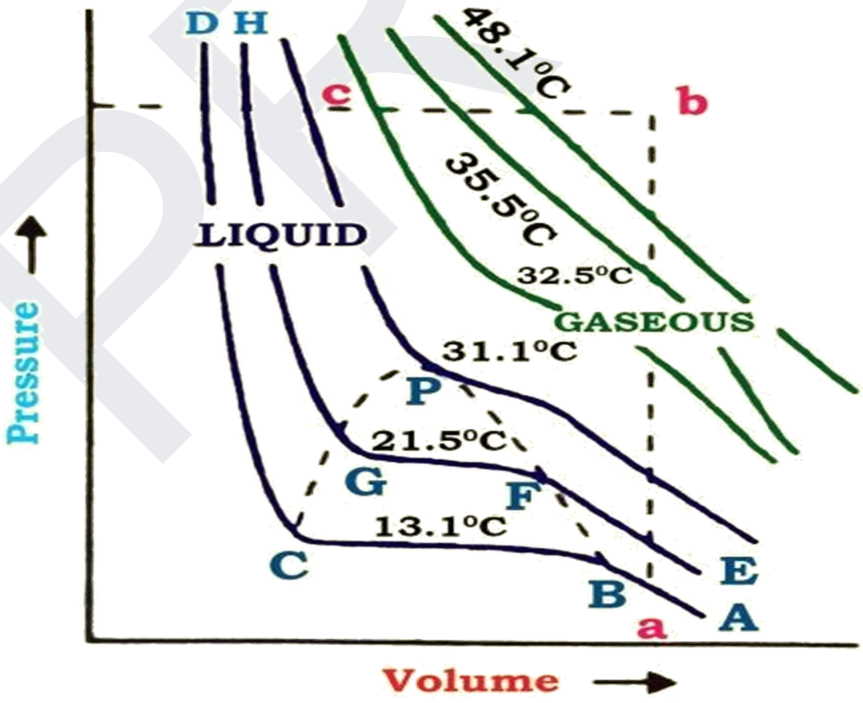
CO_2	1.39	0.0391

Limitations of van der Waals equation

Although van der Waals equation is much more accurate than the ideal gas equation, appreciable deviations have been observed at too low temperatures or too high pressures. This is due to the fact that the values of ‘a’ and ‘b’ do not remain constant over the entire ranges of temperature and pressure and hence the van der Waals equation is also valid over the specific ranges of temperature and pressure.

Andrews Isotherms of Carbon Dioxide

- The curves representing the variations of volume and pressure at constant temperature are called isotherms *(Greek, iso = equal; thermos = warm).*
- The plot of P vs V at constant Temperature is called an isotherm.
- Thomas Andrews was the first to study the effect of pressure on the volume of carbon dioxide at different temperatures.
- Andrews measured the volume of carbon dioxide at different pressures, at constant temperature of carbon dioxide.
- A number of such isotherms were obtained at different temperatures.



- At the temperature of 13.1ºC at low pressure, carbon dioxide exists as a gas as shown at the point A.
- As the pressure is increased, the volume of the gas decreases along the curve AB.
- At the point B, the liquefaction of the gas starts. Hence the volume decreases rapidly along BC because the liquid has much less volume than the gas.
- At the point C, the liquefaction is complete. Now the increase of pressure has very little effect upon the volume because liquids are hardly compressible. Hence a steep curve CD is obtained.
- Thus, along the portion AB, carbon dioxide exists only as gas.
- Along the portion BC, the liquid and the vapour are in equilibrium with each other.
- Along CD, carbon dioxide exists only as liquid.
- The isotherm EFGH at 21.5°C is similar to that at 13.1°C except that the horizontal portion over which the liquefaction occurs is shorter. In fact, as the temperature is raised this portion becomes smaller and smaller and finally at 31.1°C, it is reduced only to a point.

In the isotherms above, 31.1°C the horizontal portion completely disappears. This shows that above 31.1°C the liquefaction of the gas does not take place at all, however high the applied pressure may be. Thus 31.1°C is the **critical temperature** of carbon dioxide.

The pressure required to liquefy the CO2 gas at 31.1°C is found to be 72.9 atmospheres.
This is called **critical pressure** of CO2.

It has been found that in case of all other gases similar isotherms are obtained. However, lengths of the horizontal portions and the peak of the dotted parabola are different depending upon the nature of the gas.

Continuity of State

- Intermixing of gaseous state into the liquid state and vice versa is known as 'Continuity of State'.
- If the ends of the horizontal portions of the different isotherms are joined together a parabolic curve (shown by dotted lines in Figure) is obtained.
- The peak of this parabola represents the critical point. Within the parabola the liquid and the vapour exist together in equilibrium.
- Outside the parabola, the substance exists only as a gaseous under the conditions represented on the right side and only as liquid under the conditions represented on the left side.

- A careful reveal that below the critical temperature it is possible to change a substance from gaseous state to liquid state without having both the phases present together at any stage.
- The change of state from gaseous to liquid state is continuous. Thus it is referred to as the continuity of state.

Critical Phenomena

The term critical phenomenon refers to the peculiar behavior of a substance when it is at or near the point of a continuous phase transition (critical point).

A continuous phase transition, in turn, may be defined as a point at which a substance changes from one state to another without any discontinuity or jump in its density.

The specific temperature above which, a gas cannot be converted into liquid whatever high pressure is applied on the gas. This temperature is called "critical temperature (Tc)" and the temperature above which the gas cannot be converted into liquid even by application of high pressure.

This critical temperature (Tc) is a characteristic property of a gas.

The minimum pressure required to convert gas into liquid at this critical temperature is called "critical pressure (Pc)".

The volume occupied by 1 mole of gas at critical temperature (Tc) and critical pressure (Pc) is called "critical volume (Vc)"

Therefore, every gas will have Tc, Pc and Vc.

Critical constants of some gases are shown in the table

Gas	**Tc (K)**	**P_c** (atm)	**V_c** (ml)
He	5.2	2.26	60.63
H_2	33.2	12.8	64.51
O_2	154.3	49.7	74.42
CO_2	304.3	72.9	95.65

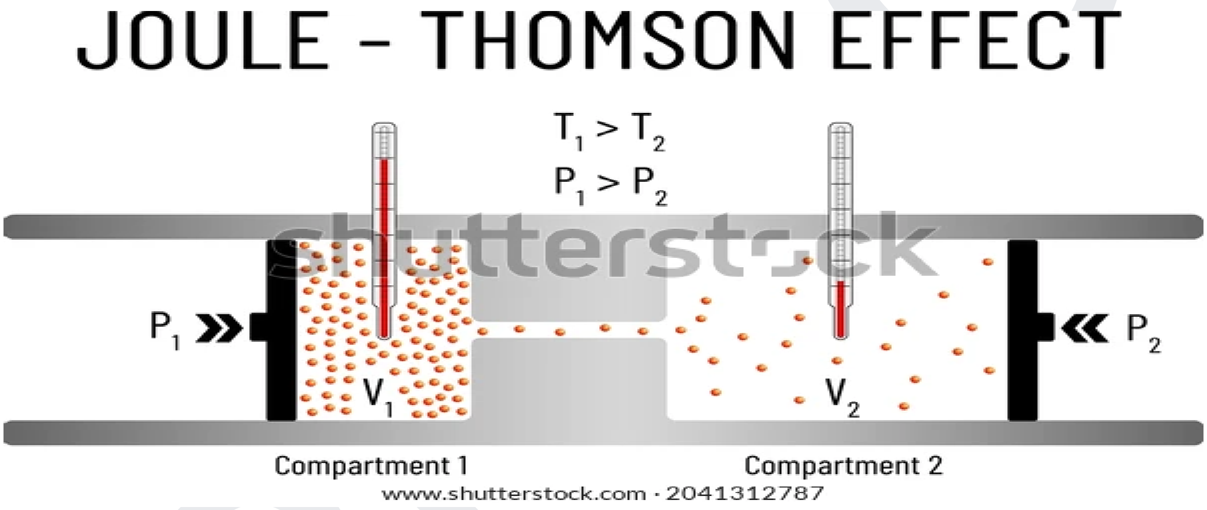
Relationship between Critical Constants and van der Waals constants:

Write down from the running notes

Joule – Thomson effect

Joule and Thomson observed that when a gas under high pressure is allowed to expand into a region of low pressure under adiabatic conditions, the gas gets appreciably cooled. This phenomenon is known as the Joule – Thomson effect.

The cooling in this effect is due to the internal work done by the gas molecules in breaking the attractive forces between molecules.



Joule – Thomson coefficient: It is the number of degrees of temperature change produced by a drop of one atmospheric pressure under the conditions of constant enthalpy.

$$\mu = \left(\frac{\partial T}{\partial P}\right)_H$$

(a) The value of ì depends on the nature of the gas, temperature and pressure of the gas before expansion.

(b) For all real gases, it is equal zero at some point called the inversion point.

The effect is greater at lower temperature and takes place at constant enthalpy.

Inversion Temperature (T_i)

According to the Joule – Thomson effect, the gases become cooler during the expansion process. This will happen only if they are below a certain temperature called inversion temperature (T_i).

It is represented by the equation,

$$Ti = 2a/Rb$$

Where, T_i is known as the inversion temperature and is depen- dent on the van der Waals constants ‘a’ and ‘b’ of the gas.

Most of the gases have positive Joule – Thomson coefficients and hence they cool at room temperature.

Hydrogen and Helium when subjected to Joule – Thomson effect at room temperature, they warm up instead of cooling on sudden expansion.

However, when hydrogen is first cooled to –80°C, it behaves normally towards Joule – Thomson effect. Hence –80°C is the inversion temperature of hydrogen. Helium has the inversion temperature of –240°C.

Applications of Joule – Thomson Effect

The cooling produced in the Joule-Thomson expansion has made it a very valuable tool in refrigeration.

The effect is applied in **Linde's** technique in the petrochemical industry, where the cooling effect is used to liquefy gases.

It is also used in many cryogenic applications, such as, for the production of liquid nitrogen, oxygen and argon.

JOULE THOMSON EFFECT

The phenomenon of change of temperature produced when a gas is made to expand adiabatically from a region of high pressure to a region of extremely low pressure is known as the **Joule-Thomson effect**".

- At room temperature, all gases except hydrogen, helium, and neon cool upon expansion by the Joule–Thomson process when being throttled through a porous plug. These three gases experience the same effect but only at lower temperatures.
- Joule-Thomson effect is also called adiabatic expansion of gases.
- Joule and Thomson observed that when a gas at high pressure is allowed to expand to low pressure region, the gas gets cold.
- If a gas is compressed to about 200 atmospheres pressure and then allowed to expand through an orifice into a container that is at low pressure, the gas expands and gets cold.
- The reason for this is that at high pressure the intermolecular distances are so low that the molecules experience the faces of attraction.
- When the gas expands the intermolecular distances must increase for which molecules must do some work or lose some kinetic energy to overcome the intermolecular attractions. Kinetic energy of a gas is directly proportional to its absolute temperature.
- Hence by losing kinetic energy the gas gets cold and this phenomenon is called "JouleThomson effect".

Joule-Thomson Coefficient:

Joule and Thomson introduces the term Joule-Thomson coefficient, represented by 'μ_{JT}' for expressing the change in temperature produced by change in pressure during adiabatic expansion of a real gas.

They defined μ_{JT} by the expression

$$\mu_{JT} = \left(\frac{\partial T}{\partial P} \right)_H$$

i. If μ_{JT} is positive, the gas cools on adiabatic expansion.

ii. If μ_{JT} is negative, the gas warms up on adiabatic expansion at room temperature.

iii. If μ_{JT} is equal to zero, the gas neither cools nor warms up on adiabatic expansion.

Inversion Temperature (Ti):

At a particular pressure, every gas has a definite temperature at which Joule- Thomson coefficient μ_{JT} becomes zero ($\mu_{JT} = 0$). This temperature is called “inversion temperature (T_i)”. Below this temperature μ_{JT} is positive (i.e., gas undergoes cooling on adiabatic expansion) and above this temperature μ_{JT} is negative (i.e., gas undergoes heating on adiabatic expansion). This inverse temperature is written as

$$Ti = \frac{2a}{Rb}$$

(where a, b are the Vander Waals constants)

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