STATES OF MATTER: GASES AND LIQUIDS

- Chemical properties of a substance do not change with change in its physical state; but the rate of reaction is affected by the change in the physical state.
- There are three physical states of matter. All the states of matter are different in nature of molecular forces present and molecular interactions.

Intermolecular forces

- Intermolecular forces: These are the forces of repulsion and attraction between particles like atoms and molecules.
- > Attractive intermolecular forces are known as van der Waals forces.
- Johannes van der Waals propounded the deviation of real gases from ideal behaviour through the van der Waals forces.
- Van der Waals forces are of different types i.e., London forces, dipoledipole forces, dipole-induced dipole forces.

1. London forces or dispersion forces:

- Atoms and non-polar molecules are symmetrical and lack in dipole moment as their electronic charge cloud is symmetrically distributed.
- Momentarily dipole moment can exist in such molecules and atoms. It can be described as follows:

Suppose there are two atoms A and B in the close vicinity of each other. For a moment electronic charge distribution of atom A becomes unsymmetrical.

- Due to this the electron density around atom B gets distorted and eventually a dipole induced in atom B.
- > Temporary dipoles of atom A and B attract each other.
- This type of force of attraction was first propounded by Fritz London. That is why this is known as London force.
- London force is inversely proportional to the sixth power of distance between two interacting particles.

London or dispersion force $\propto 1/r^6$

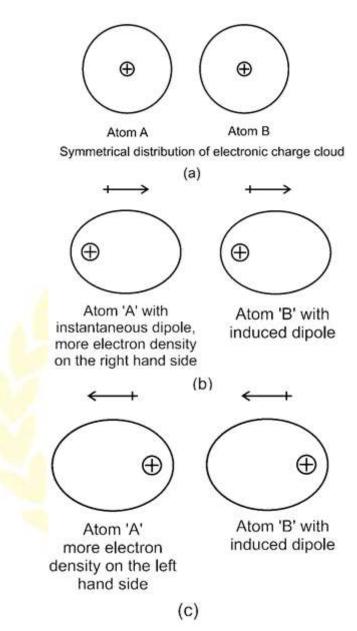


Figure: London or dispersion forces between atoms

- These forces are only for short distances like ~ 500 pm.
- The magnitude of these forces is depends upon the polarisability of particle.

2. Dipole – Dipole Forces

- This kind of force act between the molecules possessing permanent dipole.
- > Ends of the dipoles possess partial charges; which is denoted by Greek letter delta (δ).Partial charges are always less than the unit electronic charge (1.6×10⁻¹⁹ C).

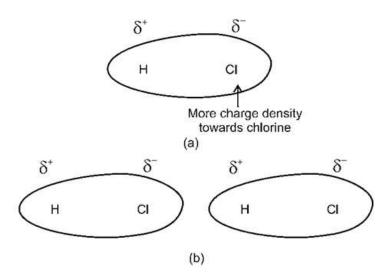


Figure: (a) Distribution of electron cloud in HCl – a polar molecule,(b) Dipole-dipole Interaction between two HCl molecules

- The polar molecules interact with neighboring molecules. Like the electron cloud distribution in the dipole of hydrogen chloride. There is a dipole-dipole interaction between two HCl molecules.
- This interaction is stronger than the London forces but is weaker than ion-ion interaction because only partial charges are involved.
- The attractive force decreases with increase of distance between the dipoles.
- The interaction energy is inversely proportional to distance between polar molecules.
- In case of stationary polar molecules (as in solids):

Dipole-dipole interaction energy $\propto 1/r^3$

In case of rotating polar molecules:

Dipole-dipole interaction energy $\propto 1/r^6$

Here r = distance between polar molecules

3. Dipole - Induced dipole forces:

- This type of attractive forces operates between the polar molecules which have permanent dipole and the molecules lacking permanent dipole.
- Permanent dipole of the polar molecule induces dipole on the electrically neutral molecule by deforming their electronic cloud. Thus an induced dipole is developed in the other molecule. In this

case also interaction energy is proportional to $1/r^6$; where r is the distance between two molecules.

- Induced dipole moment depends upon the dipole moment present in the permanent dipole and the polarisability of the electrically neutral molecule.
- Molecules with larger size can be easily polarized. High polarisability increases the strength of attractive interactions.

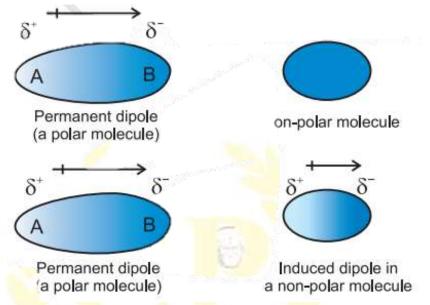


Figure: Dipole - induced dipole interaction between permanent dipole and induced dipole

4. Hydrogen bond:

- This is special case of dipole-dipole interaction.
- It is formed between hydrogen and F⁻,O and N.
- Energy of hydrogen bond varies between 10 to 100 kJ mol⁻¹.
- Hydrogen bonds are powerful force in determining the structure and properties of many compounds. Example: proteins and nucleic acids.
- Strength of the hydrogen bond is determined by the columbic interaction between the lone pair of electrons on electronegative atom of one molecule and the hydrogen atom of other molecule.

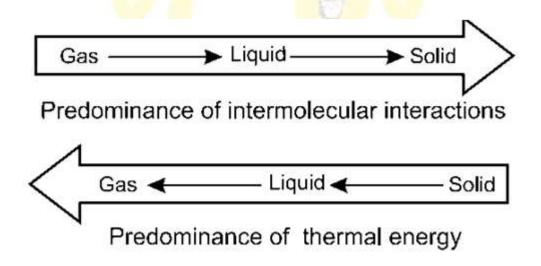
$$\stackrel{\delta_+}{H-}\stackrel{\delta_-}{F}\cdots\stackrel{\delta_+}{H-}\stackrel{\delta_-}{F}$$

Thermal energy:

- Thermal energy is the energy of a body arising from motion of its atoms or molecules.
- It is directly proportional to the temperature of the substance.
- It is the measure of average kinetic energy of the particles of the matter and is thus responsible for movement of particles.

Intermolecular forces versus thermal energy

- When molecular interactions are very weak, molecules do not stick together to make liquid or solid unless thermal energy is reduced by lowering the temperature.
- Gases do not liquefy on compression only, although molecules come very close to each other and intermolecular forces operate to the maximum.
- > When thermal energy of molecules is reduced by lowering the temperature; the gases can be very easily liquefied.
- Predominance of thermal energy and the molecular interaction energy of a substance in three states is described as follows :



The Gaseous State

- Gas is the simplest state of matter.
- Our life we remain immersed in the ocean of air which is a mixture of gases.

- We spend our life in the lowermost layer of the atmosphere called troposphere, which is held to the surface of the earth by gravitational force.
- The thin layer of atmosphere is vital to our life. It shields us from harmful radiations and contains substances like O₂, N₂, CO₂, water vapour, etc.
- In periodic table only 11 elements exist as gases under normal conditions; which are hydrogen, nitrogen, oxygen, fluorine, chlorine, helium, neon, argon, krypton, xenon and radon.
- Characteristic of gaseous state:
 - Gases are highly compressible.
 - Gases exert pressure equally in all directions.
 - Gases have lower density than the solids and liquids.
 - The volume and the shape of gases are not fixed. These assume volume and shape of the container.
 - Gases mix evenly and completely in all proportions without any mechanical aid.

The Gas Law

- Robert Boyle propounded a law which is known as Boyle's Law to describe the properties of gases.
- Later Jaccques Charles and Joseph Lewis Gay Lussac to discover additional gas laws.
- Avogadro and others provided lot of information about gaseous state.

Boyle's Law

According to Robert Boyle at constant temperature, the pressure of a fixed amount of gas varies inversely with its volume. This is known as Boyle's law. Mathematically, it can be written as:

$$p \propto \frac{1}{V}$$
$$p = k_1 \frac{1}{V}$$

Here k_1 = proportionality constant

Its value depends upon the amount of gas, temperature of the gas.

On rearranging the above equation:

It means that at constant temperature, product of pressure and volume of a fixed amount of gas is constant.

If a fixed amount of gas at constant temperature T occupying volume V_1 At pressure p_1 undergoes expansion, so that volume becomes V_2 and pressure becomes p_2 , then according to Boyle's law –

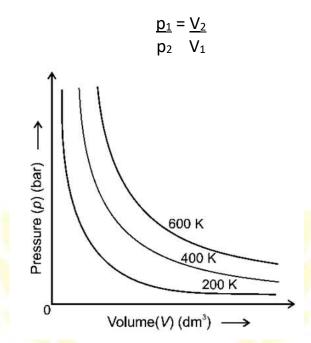
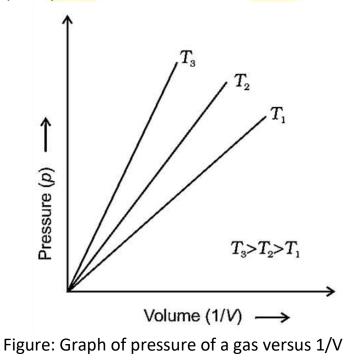


Figure: Graph of pressure versus Volume at different temperature



 $p_1V_1 = p_2V_2 = \text{constant}$

- Gases become denser at high pressure. A relationship can be obtained between density and pressure of a gas by using Boyle's law:
- By definition, density 'd' is related to the mass 'm' and the volume 'V' by the relation is as follows:

If we put value of V in this equation from Boyle's law equation:

This means that at a constant temperature; pressure is directly proportional to the density of a fixed mass of the gas.

Example: A balloon is filled with hydrogen at room temperature. It will burst if pressure exceeds 0.3 bar. If at 1 bar pressure the gas occupies 2.27 L volume, up to what volume can the balloon be expanded? **Solution:** According to Boyle's Law

$$p_1V_1 = p_2V_2$$

If p1 is 1 bar, V_1 will be 2.27 L If $p_2 = 0.2$ bar, then $V_2 = p_1V_1$ P_2 $V_2 = 1 \text{ bar x } 2.27L = 7.566$ 0.3 bar

Since balloon bursts at 0.3 bar pressure, the volume of balloon should be less than 7.56 L.

Charles's Law

- Charles and Gay Lussac propounded that for a fixed mass of a gas at constant pressure, volume of a gas increases on increasing temperature and decreases on cooling.
- According to them for each degree rise in temperature, volume of a gas increases by 1/273.15 of the original volume of the gas at 0 °C. Thus if volumes of the gas at 0 °C and at t °C are V₀ and V_t respectively:

$$V_{t} = V_{0} + \frac{t}{273.15} V_{0}$$

$$\Rightarrow V_{t} = V_{0} \left(1 + \frac{t}{273.15} \right)$$

$$V_{t} = V_{0} \left(\frac{273.15 + t}{273.15} \right)$$

✤ A new scale of temperature such that t °C on new scale is given by

O °C will be given by

$$T_0 = 273.15$$

- This new temperature scale is called the Kelvin temperature or Absolute temperature scale.
- If we write $T_t = 273.15 + t$ and $T_0 = 273.15$ in the above equation we obtain the relationship:

$$V_{t} = V_{o} \left(\frac{T_{t}}{T_{o}}\right)$$
$$\Rightarrow \frac{V_{t}}{V_{o}} = \frac{T_{t}}{T_{o}}$$

Thus we can write:

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

$$\frac{V_1}{T_1} = \frac{V_2}{T_1}$$
$$\frac{V}{T_1} = \text{constant} = k_2$$
$$T$$

Thus $V = k_2 T$

- The value of constant k₂ is determined by the pressure of the gas, its amount and the units in which volume V is expressed.
- According to Charles' law, which states that pressure remaining constant, the volume of a fixed mass of a gas is directly proportional to its absolute temperature.
- ✤ He stated that for all gases, at any given pressure, graph of volume versus temperature (in celsius) is a straight line and on extending to zero volume, each line intercepts the temperature axis at 273.15 °C.
- Slopes of lines obtained at different pressure are different but at zero volume all the lines meet the temperature axis at 273.15 °C.
- Each line of the volume versus temperature graph is known as isobar.

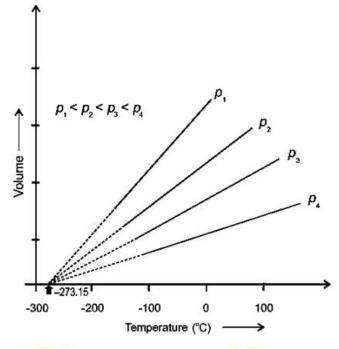


Figure: Volume versus Temperature (°C) graph

Absolute zero temperature - All the gases get liquefied before temperature is reached to a lowest hypothetical or imaginary temperature at which gases are supposed to occupy zero volume is called Absolute zero.

Gay Lussac's Law

Gay Lussac propounded that at constant volume, pressure of a fixed amount of a gas varies directly with the temperature.

р ∝ Т

<u>p</u> = constant = k₃ T

If we draw a graph of pressure versus temperature (Kelvin) g at constant molar volume, each line of this graph is called isochore.

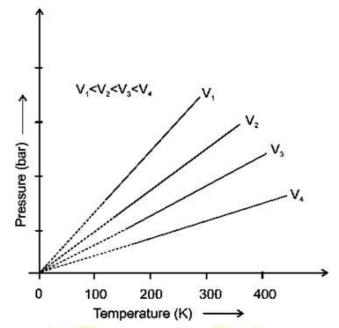


Figure: Pressure versus temperature graph of a gas

Avogadro Law

According to this law equal volumes of all gases under the same conditions of temperature and pressure contain equal number of molecules.

V ∝ n Here n = number of moles of the gas

 $V = k_4 n$

The number of molecules in one mole of a gas has been determined to be 6.022 ×10²³ and is known as Avogadro constant.

5	
Ar	22.37
CO ₂	22.54
N ₂	22.69
02	22.69
H ₂	22.72
Ideal gas	22.71

Table: Molar volume of some gases at 273.15K and 1 bar

Number of moles of a gas can be calculate as follows:

Here m = mass of the gas under investigation M = molar mass

After rearrangement

$$M = k_4 \underline{m} = k_4 d$$

Here d= density of gas

- A gas that follows Boyle's law, Charles' law and Avogadro law strictly is called an ideal gas. Such a gas is hypothetical.
- It is assumed that intermolecular forces are not present between the molecules of an ideal gas.
- Real gases follow these laws only under certain specific conditions when forces of interaction are practically negligible.

Ideal gas equation

The ideal gas equation is as follows:

At constant T and n; $V \propto \underline{1}$	Boyle's Law
p	U
At constant <mark>p and</mark> n; V \propto T	Cha <mark>rles</mark> 's Law
At constant p and T; $V \propto n$	Avogadro Law
Thus V∝ <u>nT</u> p V = R <u>nT</u> P	
R = gas constant	

pV= nRT for ideal gas equation

This equation will be applicable to any gas, under those conditions when behaviour of the gas approaches ideal behaviour.

Volume of one mole of an ideal gas under STP conditions (273.15 K and 1 bar pressure) is 22.710 L mol⁻¹. Value of R for one mole of an ideal gas can be calculated under these conditions as follows:

$$R = \frac{(10^{5} \text{ Pa})(22.71 \times 10^{-3} \text{ m}^{3})}{(1 \text{ mol})(273.15 \text{ K})}$$
$$R = 8.314 \text{ Pa m}^{3} \text{ K}^{-1} \text{ mol}^{-1}$$
$$R = 8.314 \text{ J k}^{-1} \text{ mol}^{-1}$$

If temperature, volume and pressure of a fixed amount of gas vary from T₁, V₁ and p₁ to T₂, V₂ and p₂ then:

$$\frac{P_1V_1}{T_1} = \frac{p_2V_2}{T_2}$$

Density and Molar mass of a gaseous substance:

$$\frac{n}{V} = \frac{p}{V}$$
By replacing n by m/M:

$$\frac{m}{M} = \frac{p}{MV}$$
MV RT

$$\frac{d}{M} = \frac{p}{M}$$
Molar mass of a gas:

$$M = \frac{dRT}{P}$$

Dalton's Law of Partial Pressure

- According to this law total pressure exerted by the mixture of nonreactive gases is equal to the sum of the partial pressures of individual gases.
- In a mixture of gases the pressure exerted by the individual gas is known as partial pressure.

$$\mathbf{P}_{\text{Total}} = \mathbf{p}_1 + \mathbf{p}_2 + \mathbf{p}_3 + \dots$$
 (at constant T, V)

Here P_{Total} = total pressure exerted by the mixture of gases P₁, p₂, p₃ etc. are partial pressures of gases.

- Gases are generally collected over water and therefore are moist. Pressure of dry gas can be calculated by subtracting vapour pressure of water from the total pressure of the moist gas which contains water vapours also.
- > Pressure exerted by saturated water vapour is called aqueous tension.

Partial pressure in terms of mole fraction

Suppose at the temperature T, three gases, enclosed in the volume V, exert partial pressure p₁, p₂ and p₃ respectively:

$$P_{1} = \frac{n_{1}RT}{V}$$

$$P_{2} = \frac{n_{2}RT}{V}$$

$$P_{3} = \frac{n_{3}RT}{V}$$

Here n_1 , n_2 , and n_3 are number of moles of these gases. Thus:

$$P_{Total} = p_1 + p_2 + p_3$$
$$= n_1 \frac{RT}{V} + n_2 \frac{RT}{V} + n_3 \frac{RT}{V}$$

$$= (n_1 + n_2 + n_3) \frac{RT}{V}$$

On dividing p_1 by p_{Total} we get -

$$\frac{p_1}{p_{\text{total}}} = \left(\frac{n_1}{n_1 + n_2 + n_3}\right) \frac{\text{RTV}}{\text{RTV}}$$

$$= \underline{n_1} = \underline{n_1} = x_1$$

n_1+n_2+n_3 n

Here $n = n_1 + n_2 + n_3$

x₁ =mole fraction of first gas

p1 =x1 pTotal

For other two gases:

 $p_2 = x_2 p_{Total}$ and $p_3 = x_3 p_{Total}$

Here p_1 and x_1 are partial pressure and mole fraction of first gas.

Kinetic molecular theory of gases

Postulates of kinetic molecular theory:

- 1. Gases consist of large number of identical particles i.e. atoms or molecules that are so small and so far apart on the average that the actual volume of the molecules is negligible in comparison to the empty space between them. They are considered as point masses. This assumption explains the great compressibility of gases.
- 2. There is no force of attraction between the particles of a gas at ordinary temperature and pressure. Gases expand and occupy all the space available to them.
- 3. Particles of a gas are always in constant and random motion. If the particles were at rest and occupied fixed positions, then a gas would have had a fixed shape which is not observed normally.
- 4. Particles of a gas move in all possible directions in straight lines. During their random motion, they collide with each other and with the walls of the container. Pressure is exerted by the gas as a result of collision of the particles with the walls of the container.
- 5. Collisions of gas molecules are perfectly elastic. This means that total energy of molecules before and after the collision remains same. There may be exchange of energy between colliding molecules, their individual energies may change, but the sum of their energies remains constant. If there were loss of kinetic energy, the motion of molecules will stop and gases will settle down. This is contrary to what is actually observed.
- 6. Different particles in the gas have different speeds and hence different kinetic energies. This assumption is reasonable because as the particles collide, we expect their speed to change. Consequently, the particles must have different speeds, which go on changing constantly.
- 7. In kinetic theory, it is assumed that average kinetic energy of the gas molecules is directly proportional to the absolute temperature. On heating a gas at constant volume, the pressure increases. Eventually kinetic energy of the particles increases and these strike the walls of the container more frequently, thus, exerting more pressure.

Behaviour of real gases: deviation from ideal gas behaviour

➤ It is an actual pressure-volume-temperature relationship of gases.

If we plot a graph between pV and p at constant pressure we will obtain straight line parellal to x-axis for ideal gases.

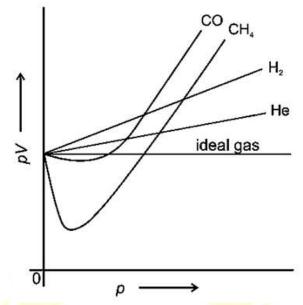


Figure: Plot of pV versus p for real gas and ideal gas.

- > For H₂ and He, as the pressure increases the value of pV also increases.
- In case of other gases like CO and CH₄; first there is a negative deviation from ideal behaviour, the pV value decreases with increase in pressure and reaches to a minimum value characteristic of a gas. After that pV value starts increasing. The curve then crosses the line for ideal gas and after that shows positive deviation continuously. The real gases do not follow ideal gas equation perfectly under all conditions.
- The pressure versus volume plot shows different behaviour of ideal and real gases.

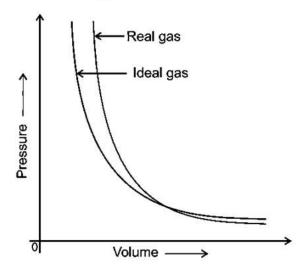


Figure: Plot of pressure and volume for ideal and real gas.

- The real gases do not follow Boyle's law, Charles law and Avogadro law perfectly under all conditions.
- The two postulates of kinetic theory do not hold good. These are as follows:
 - 1. There is no force of attraction between the molecules of a gas.
 - 2. Volume of the molecules of a gas is negligibly small in comparison to the space occupied by the gas.
- According to above first assumption gases never liquefy but on cooling and compression gases do liquefy.
- According to second assumption in pressure versus volume graph the real gases line should coincide the ideal gas line. But real gases show deviations from ideal gas law because molecules interact with each other. At high pressure, molecules do not strike the walls of the container with full impact because these are dragged back by other molecules due to molecular attractive forces. This affects the pressure exerted by the molecules on the walls of the container. Thus, the pressure exerted by the gas is lower than the pressure exerted by the ideal gas.

$$p_{ideal} = p_{real} + \frac{an^2}{n^2}$$

Here $\frac{an^2}{V^2}$ = Correction term a = Constant

At high pressure volume occupied by the molecules also becomes significant because instead of moving in volume V, these are now restricted to volume (V–nb).

Here nb = Total volume occupied by the molecules

b = constant.

The pressure volume relationship is as follow:

$$\left(p + \frac{\mathrm{a}n^2}{V^2}\right)(V - n\mathrm{b}) = n\mathrm{R}T$$

This equation is known as van der Waals equation.

In this equation n = number of moles of the gas a and b = van der Waals constants

Value of constant **a** is measure of magnitude of intermolecular attractive forces within the gas and is independent of temperature and pressure.

The deviation from ideal behaviour can be measured in terms of compressibility factor Z, is as follows:

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Z = p<u>V</u>
nRT
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- ➤ For ideal gas Z = 1 at all temperatures and pressures because pV = n RT.
- > The graph of Z versus p will be a straight line parallel to pressure axis.

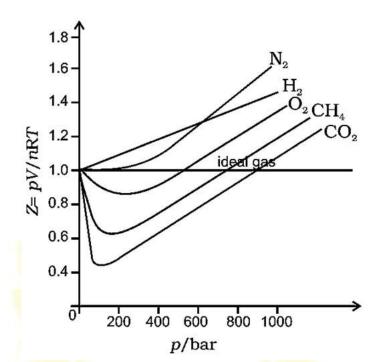


Figure: Variation of compressibility factor for some gases

- For gases which deviate from ideality, value of Z deviates from unity. At very low pressures all gases shown have Z ≈1 and behave as ideal gas.
- At high pressure all the gases have Z > 1. These are more difficult to compress. At intermediate pressures, most gases have Z < 1.</p>
- Gases show ideal behaviour when the volume occupied is large so that the volume of the molecules can be neglected in comparison to it.

Liquefaction of gases

- Thomas Andrews plotted isotherms of carbon dioxide at various temperatures.
- He noticed that at high temperatures isotherms look like that of an ideal gas and the gas cannot be liquefied even at very high pressure. As the temperature is lowered, shape of the curve changes and data show considerable deviation from ideal behaviour.

- At 73 atmospheric pressure, liquid CO₂ appears for the first time. The temperature 30.98°C is called critical temperature (T_c) of CO₂. This is the highest temperature at which liquid CO₂ is observed. Above this temperature it is gas.
- Volume of one mole of the gas at critical temperature is called critical volume (V_c) and pressure at this temperature is called critical pressure (p_c). The critical temperature, pressure and volume are called critical constants.

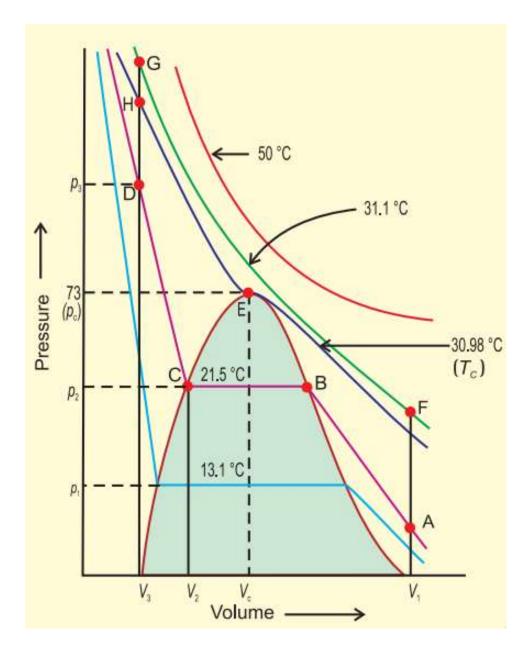


Figure: Isotherms of CO₂ at various temperatures

> A slight compression from volume V_2 to V_3 results in steep rise in pressure from p_2 to p_3 .

- Below 30.98 °C (critical temperature) each curve shows the similar trend. Only length of the horizontal line increases at lower temperatures. At critical point horizontal portion of the isotherm merges into one point.
- A point like D represents liquid state and a point under the dome shaped area represents existence of liquid and gaseous carbon dioxide in equilibrium.
- All the gases upon compression at isothermal compression show the same behaviour as shown by CO₂.
- There is continuity between the gaseous and liquid state. The term fluid is used for either a liquid or a gas to recognize this continuity. Thus a liquid can be viewed as a very dense gas.
- When liquid and gas are in equilibrium and a surface separating the two phases is visible. At critical temperature, liquid passes into gaseous state imperceptibly and continuously; the surface separating two phases disappears.
- A gas below the critical temperature can be liquefied by applying pressure, and is called vapour of the substance. CO₂ gas below its critical temperature is called CO₂ vapour.

Liquid state:

- In case of liquids intermolecular forces are stronger compare to gases.
- Liquid particles can move freely and liquid can be poured, can acquire shape of container in which stored.
- There are some physical properties of liquid such as vapour pressure, surface tension and viscosity etc.

Vapour pressure:

- Initially the liquid evaporates and pressure exerted by vapours on the walls of the container (vapour pressure) increases.
- After some time equilibrium is established between liquid phase and vapour phase. Vapour pressure at this stage is known as equilibrium vapour pressure or saturated vapour pressure.
- The temperature at which vapour pressure of liquid is equal to the external pressure is called boiling temperature at that pressure.

- At 1 atm pressure boiling temperature is called normal boiling point. If pressure is 1 bar then the boiling point is called standard boiling point of the liquid.
- At high altitudes atmospheric pressure is low. Therefore liquids at high altitudes boil at lower temperatures in comparison to that at sea level.
- Since water boils at low temperature on hills, the pressure cooker is used for cooking food.
- In hospitals surgical instruments are sterilized in autoclaves in which boiling point of water is increased by increasing the pressure above the atmospheric pressure by using a weight covering the vent.
- When density of liquid and vapours becomes the same; the clear boundary between liquid and vapours disappears. This temperature is called critical temperature.

Surface tension:

- It is a characteristic property of liquids.
- Due to this property small drops of mercury form spherical bead instead of spreading on the surface and a liquid rise in a thin capillary as soon as the capillary touches the surface of the liquid.
- Surface tension is defined as the force acting per unit length perpendicular to the line drawn on the surface of liquid. It is denoted by Greek letter γ. It has dimensions of kg s⁻² and in SI unit it is expressed as N m⁻¹.
- Liquids tend to minimize their surface area. The molecules on the surface experience a net downward force and have more energy than the molecules in the bulk, which do not experience any net force.

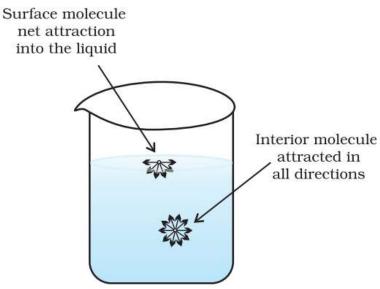


Figure: Forces acting on a molecule on liquid surface and on a molecule inside the liquid

- The energy required to increase the surface area of the liquid by one unit is defined as surface energy. Its dimensions are J m⁻².
- The magnitude of surface tension of a liquid depends on the attractive forces between the molecules.
- When the attractive forces are large, the surface tension is large.
- Increase in temperature increases the kinetic energy of the molecules and effectiveness of intermolecular attraction decreases, so surface tension decreases as the temperature is raised.

Viscosity:

- It is a characteristic property of liquids.
- Viscosity is a measure of resistance to flow which arises due to the internal friction between layers of fluid as they slip past one another while liquid flows.
- Strong intermolecular forces between molecules hold them together and resist movement of layers past one another.
- When a liquid flows over a fixed surface, the layer of molecules in the immediate contact of surface is stationary. The velocity of upper layers increases as the distance of layers from the fixed layer increases. This type of flow in which there is a regular gradation of velocity in passing from one layer to the next is called laminar flow.
- If the velocity of the layer at a distance dz is changed by a value du then velocity gradient is given by the amount.

du/dz A force is required to maintain the flow of layers. This force is proportional to the area of contact of layers and velocity gradient i.e.

 $F \propto A$ (A is the area of contact)

Here du/dz is velocity gradient.

Here η = Coefficient of viscosity

- SI unit of viscosity coefficient: 1 newton second per square metre (N s m⁻²) = pascal second (Pa s = 1kg m⁻¹s⁻¹).
- In cgs system the unit of coefficient of viscosity is poise.

- Greater the viscosity, the more slowly the liquid flows. Hydrogen bonding and van der Waals forces are strong enough to cause high viscosity. Glass is an extremely viscous liquid.
- Viscosity of liquids decreases as the temperature rises because at high temperature molecules have high kinetic energy and can overcome the intermolecular forces to slip past one another between the layers.