1.   Details of Module and its structure

Module Detail	
Subject Name	Chemistry
Course Name	Chemistry 01 (Class XI, Semester - 1)
Module Name/Title	States of Matter: Part 4
Module Id	kech_10504
Pre-requisites	Intermolecular forces of attraction, Gas laws, Ideal Gas equation
Objectives	After going through this module, the learner will be able to: • Understand Dalton's law of partial pressure. • Explain Kinetic molecular theory of gases. • Apply gas laws in various real life situations. • Explain the behaviour of real gases.
Keywords	Liquification of gases, Isotherm, Critical Pressure, Critical Volume, Critical temperature, Equilibrium and Standard Vapour pressure, Surface tension, Viscosity, Coefficient of viscosity.

2.   Development Team

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1. **Liquifaction of Gases:** First complete data on pressure - volume - temperature relations of a substance in both gaseous and liquid state was obtained by a scientist from Ireland named Thomas Andrews (1813-85) on carbon dioxide. He devised apparatus capable of applying measured pressures up to 200 times atmospheric pressure to a gas. In this experimental set up, two capillary tubes with uniform diameter were sealed at the upper ends project vertically from a steel casing. The top part of one of the tubes contained the gas to be tested i.e. carbon dioxide, CO_2 (trapped by a thread of mercury) while the top of the other tube was filled with dry air as a control. The mercury in each tube was held in by the water pressure in the casing. The pressure of the water could be increased by turning the screws. Each tube was in its own water bath, the temperature of the control bath was set up at room temperature while the temperature of the test bath could be changed. The volume of gas per mm length was measured before installing the tubes in the casing.

At constant temperature, the pressure of the test gas i.e. CO_2 was increased in steps. The length of both the gas column was measured at increase in pressure and hence the volume of each gas could be determined. The control gas obeys Boyle's law, therefore, its pressure could be calculated from its volume using the expression

$PV = P_oV_o$

where, p and V were the pressure and volume of the control gas while P_o and V_o were the pressure and volume of the control gas at atmospheric pressure. Because the test gas i.e. CO_2 was at the same pressure as the control gas at each step, then the pressure of the test gas could be found. Andrews obtained the readings of pressure and volume at different constant temperatures for a fixed mass of CO_2 and plotted isotherms of carbon dioxide at various temperatures (Fig.1). Later on it was found that real gases behave in the same manner as carbon dioxide. Andrews noticed that at high temperatures isotherms look like that of an ideal gas and the gas cannot be liquified even at very high pressure.
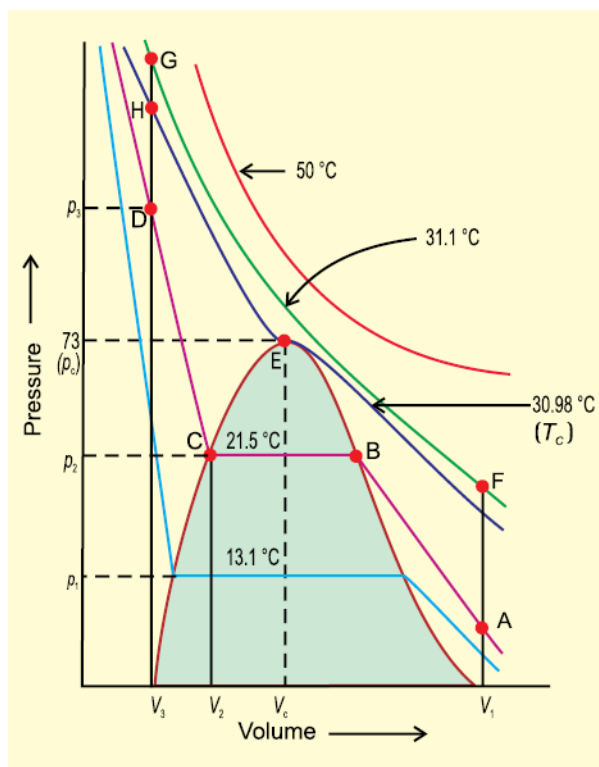
Fig.1. Isotherms of carbon dioxide at various temperatures

(Source: Fig 5.11, page 147, Chapter 5, Textbook NCERT)

As the temperature is lowered, shape of the curve changes and data shows considerable deviation from ideal behaviour. At 30.98 °C carbon dioxide remains gas upto 73 atmospheric pressure. (Point E in Fig.1). At 73 atmospheric pressure, liquid carbon dioxide appears for the first time. The temperature 30.98 °C is called critical temperature (T_C) of carbon dioxide. This is the highest temperature at which liquid carbon dioxide 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. Further increase in pressure simply compresses the liquid carbon dioxide and the curve represents the compressibility of the liquid. The steep line represents the isotherm of liquid. Even a slight compression results in steep rise in pressure indicating very low compressibility of the liquid. Below 30.98 °C, the behavior of the gas on compression is quite different. At 21.5 °C, carbon dioxide remains as a gas only up to point B. At point B, liquid of a particular volume appears. Further compression does not change the pressure. Liquid and gaseous carbon dioxide coexist and further application of pressure results in the condensation of more gas until the point C is reached. At point C, all the gas has been condensed and further application of pressure merely compresses the liquid as shown by steep line. A slight compression from volume V_2 to V_3 results in steep rise in pressure from P_2 to P_3 (Fig.1). 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. Thus we see that a point like A in the Fig.1 represents gaseous state. 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 constant temperature (isothermal compression) show the same behaviour as shown by carbon dioxide. Also above discussion shows that gases should be cooled below their critical temperature for liquifaction. Critical temperature of a gas is highest temperature at which liquifaction of the gas first occurs. Liquifaction of so called permanent gases (i.e., gases which show continuous positive deviation in Z value) requires cooling as well as considerable compression. Compression brings the molecules in close vicinity and cooling slows down the movement of molecules therefore, intermolecular interactions may hold the closely and slowly moving molecules together and the gas liquifies.

It is possible to change a gas into liquid or a liquid into gas by a process in which always a single phase is present. For example in Fig.1 we can move from point A to F vertically by increasing the temperature, then we can reach the point G by compressing the gas at the constant temperature along this isotherm (isotherm at 31.1°C). The pressure will increase. Now we can move vertically down towards D by lowering the temperature. As soon as we cross the point H on the critical isotherm we get liquid. We end up with liquid but in this series of changes we do not pass through two-phase region. If process is carried out at the critical temperature, substance always remains in one phase.

Thus 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. Liquid and gas can be distinguished only when the fluid is below its critical temperature and its pressure and volume lie under the dome, since in that situation liquid and gas are in equilibrium and a surface separating the two phases is visible. In the absence of this surface there is no fundamental way of distinguishing between two states. At critical temperature, liquid passes into gaseous state imperceptibly and continuously; the surface separating two phases disappears (will be studied in next section). A gas below the critical temperature can be liquified by applying pressure, and is called vapour of the substance. Carbon dioxide gas below its critical temperature is called carbon dioxide vapour. Critical constants for some common substances are given in Table.1.

Table 1. Critical Constants for Some Substances

Substance	T_c /K	P_c /bar	V_c /dm^3 mol^{-1}
H_2	33.2	12.97	0.0650
He	5.3	2.29	0.0577
N_2	126.0	33.9	0.0900
O_2	154.3	50.4	0.0744
CO_2	304.1	73.9	0.0956
H_2O	647.1	220.6	0.0450
NH_3	405.5	113.0	0.0723

Problem 1: Gases possess characteristic critical temperature which depends upon the magnitude of intermolecular forces between the gas particles. Critical temperatures of ammonia and carbon dioxide are 405.5 K and 304.10 K respectively. Which of these gases will liquify first when you start cooling from 500 K to their critical temperature?

Solution: Ammonia will liquify first because its critical temperature will be reached first. Liquifaction of CO_2 will require more cooling.

Problem2: Critical temperature of CO_2 and CH_4 gases are 31.1 ^{0}C and 81.9 ^{0}C respectively. Which of these has strong intermolecular forces & why?

Solution: CO_2 has strong intermolecular forces of attraction than CH_4 because the critical temperature of CH_4 is higher than CO_2 and hence liquefy first.

2. **Liquid State:** Intermolecular forces are stronger in liquid state than in gaseous state. Molecules in liquids are so close that there is very little empty space between them and under normal conditions liquids are denser than gases.

   Molecules of liquids are held together by attractive intermolecular forces. Liquids have definite volume because molecules do not separate from each other. However, molecules of liquids can move past one another freely, therefore, liquids can flow, can be poured and can assume the shape of the container in which these are stored. In the following sections we will look into some of the physical properties of the liquids such as vapour pressure, surface tension and viscosity.

3. **Vapour Pressure:** If an evacuated container is partially filled with a liquid, a portion of liquid evaporates to fill the remaining volume of the container with vapour. Initially the liquid evaporates and pressure exerted by vapours on the walls of the container (vapour pressure) increases (Fig 2). After some time it becomes constant, an equilibrium is established between liquid phase and vapour phase. Vapour pressure at this stage is known as equilibrium vapour pressure or saturated vapour pressure.. Since process of vapourisation is temperature

dependent; the temperature must be mentioned while reporting the vapour pressure of a liquid.
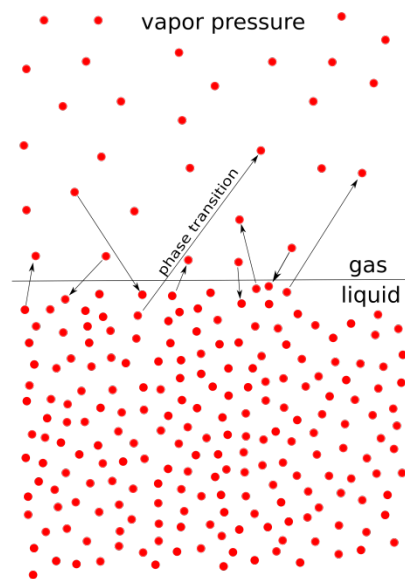

Fig. 2. Phenomenon of Vapour pressure

(Source:

https://upload.wikimedia.org/wikipedia/commons/thumb/6/67/Vapor_pressure.svg/2000px-Vapor_pressure.svg.png)

When a liquid is heated in an open vessel, the liquid vapourises from the surface. At the temperature at which vapour pressure of the liquid becomes equal to the external pressure, vapourisation can occur throughout the bulk of the liquid and vapours expand freely into the surroundings. The condition of free vapourisation throughout the liquid is called boiling. The temperature at which vapour pressure of liquid is equal to the external pressure is called boiling temperature at that pressure. Vapour pressure of some common liquids at various temperatures is given in (Fig. 3). 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. Standard boiling point of the liquid is slightly lower than the normal boiling point because 1 bar pressure is slightly less than 1 atm pressure. The normal boiling point of water is 100 °C (373 K), its standard boiling point is 99.6 °C (372.6 K).

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.
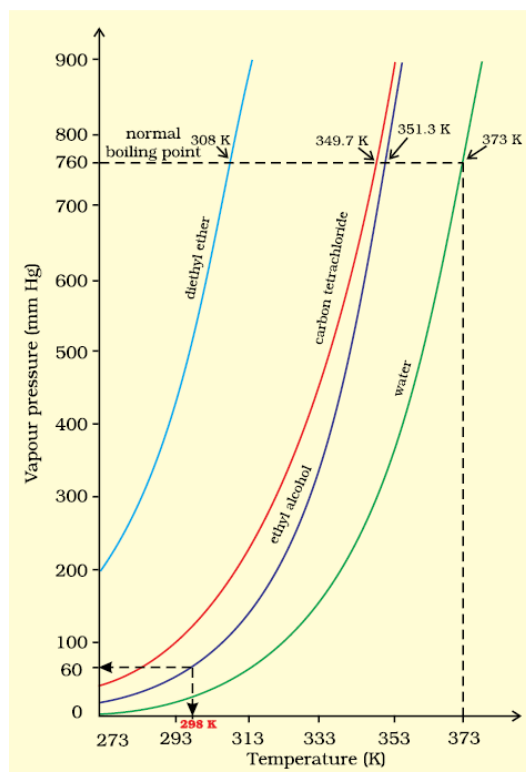
Fig. 3. Vapour pressure vs temperature curve of some common liquids.

(Source: Fig. 5.12, page no. 150, Class XI textbook, NCERT)

Boiling does not occur when liquid is heated in a closed vessel. On heating continuously vapour pressure increases. At first a clear boundary is visible between liquid and vapour phase because liquid is more dense than vapour. As the temperature increases more and more molecules go to vapour phase and density of vapours rises. At the same time liquid becomes less dense. It expands because molecules move apart. When density of liquid and vapours becomes the same; the clear boundary between liquid and vapours disappears. This temperature is called critical temperature about which we have already discussed in previous section.

4. **Surface Tension:** It is well known fact that liquids assume the shape of the container. Why is it then small drops of mercury form spherical bead instead of spreading on the surface? Why do particles of soil at the bottom of river remain separated but they stick together when taken out? Why does a liquid rise (or fall) in a thin capillary as soon as the capillary touches the surface of the liquid? All these phenomena are caused due to the characteristic property of liquids, called surface tension. A molecule in the bulk of liquid experiences equal intermolecular forces from all sides. The molecule therefore does not experience any net force. But for the molecule on the surface of liquid, net attractive force is towards the interior of the liquid (Fig. 4), due to the molecules below it. Since there are no molecules above it.
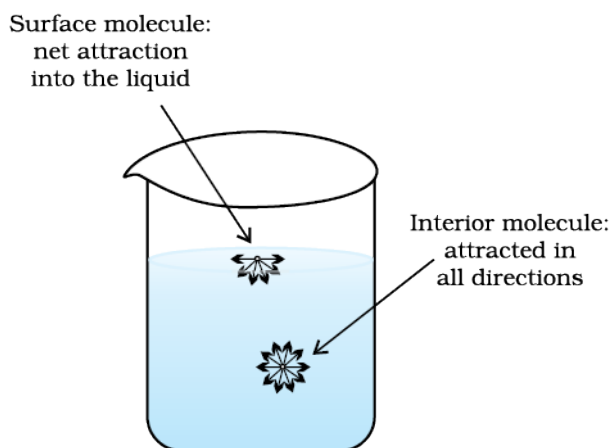
Fig. 4. Forces acting on a molecule on liquid surface and on a molecule inside the liquid (Source: Fig 5.13, page no. 150, Class XI Textbook NCERT)

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. Therefore, liquids tend to have minimum number of molecules at their surface. If surface of the liquid is increased by pulling a molecule from the bulk, attractive forces will have to be overcome. This will require expenditure of energy. The energy required to increase the surface area of the liquid by one unit is defined as surface energy. Its dimensions are $J\ m^{-2}$. 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 (Gamma). It has dimensions of $kg\ s^{-2}$ and in SI unit it is expressed as $N\ m^{-1}$. The lowest energy state of the liquid will be when surface area is the minimum. Spherical shape satisfies this condition, that is why mercury drops are spherical in shape. This is the reason that sharp glass edges are heated for making them smooth. On heating, the glass melts and the surface of the liquid tends to take the rounded shape at the edges, which makes the edges smooth. This is called fire polishing of glass.

Liquid tends to rise (or fall) in the capillary because of surface tension. Liquids wet the things because they spread across their surfaces as thin film. Moist soil grains are pulled together because surface area of thin film of water is reduced. It is surface tension which gives stretching property to the surface of a liquid. On flat surface, droplets are slightly flattened by the effect of gravity; but in the gravity free environments drops are perfectly spherical.

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.

5. **Viscosity:** It is one of the characteristic properties 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 we choose any layer in the flowing liquid (Fig. 5), the layer above it accelerates its flow and the layer below this retards its flow.
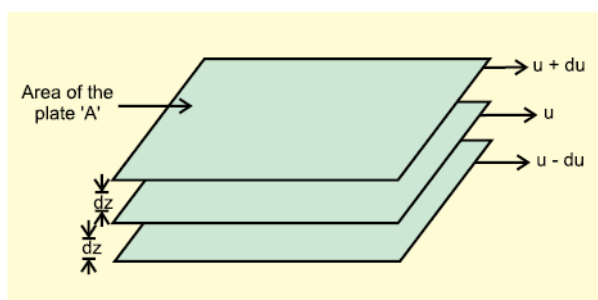
Fig. 5. Gradation of velocity in the laminar flow

(Source: Fig 5.13, page no. 151, Class XI Textbook, NCERT)

If the velocity of the layer at a distance dz is changed by a value du then velocity gradient is given by the amount $\dfrac{du}{dz}$. 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.

(A is the area of contact)

$F \propto \dfrac{du}{dz}$ (where, $\dfrac{du}{dz}$ is velocity gradient; the change in velocity with distance)

$F \propto A.\dfrac{du}{dz}$

$F = \eta.A.\dfrac{du}{dz}$

'η' is proportionality constant and is called coefficient of viscosity. Viscosity coefficient is the force when velocity gradient is unity and the area of contact is unit area. Thus 'η' is measure of viscosity. SI unit of viscosity coefficient is 1 newton second per square metre (N s m^{-2}) = pascal second (Pa s = 1kg m^{-1}s^{-1}). In cgs system the unit of coefficient of viscosity is poise (named after great scientist Jean Louise Poiseuille).

1 poise = 1 g cm^{-1}s^{-1} = 10^{-1}kg m^{-1}s^{-1}

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. It is so viscous that many of its properties resemble solids. However, property of flow of glass can be experienced by measuring the thickness of windowpanes of old buildings. These become thicker at the bottom than at the top.

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.

6. **Summary:** This module explained the phenomenon of liquification of gases. At high pressure and low temperature intermolecular forces start operating strongly between the molecules of gases because they come close to each other. Under suitable temperature and pressure conditions gases can be liquified. Liquids may be considered as continuation of gas phase into a region of small volume and very strong molecular attractions. Some properties of liquids e.g., surface tension and viscosity are due to strong intermolecular attractive forces. The pressure exerted by the vapor/liquid equilibrium in the closed container is called the vapor pressure. Vapour pressure of a liquid increases with increase in temperature.