States of matter

Introduction:

The atmosphere is composed of gases like oxygen, nitrogen, carbon dioxide. The state of matter that we consider atmosphere is a gas. Next most important thing in our life is water. The state of matter of things like water, oil, petrol are liquids. The predominant number of substances that we encounter in our daily lives for example sugar, salt, kitchen vessels are solids. So, these are what we call as states of matter. Typically, the three states of matter that we divide whatever we see around us into. But this division of what we see into three states is in some sense is the convenient thing. But for example, we will have a problem in case we have to give a strict definition of what constitutes a solid, liquid and gas. The reason for this is there are many exceptions. For example, glass appears to be a solid. But in reality, it is actually a super cooled liquid. So, what we need to do then is to characterize this solid, liquid and gas based on some principal characteristics.

The principal characteristics are:

1. **Compressibility:** If I take a substance and apply pressure on it (a static pressure) and how does the volume change is the compressibility of the system. So, this is one characteristic that will allow us in differentiating between solid liquid and gas.

2. **Rigidity:** This is similar to compressibility. Except that what happens here is that at constant volume if you apply some kind of pressure which changes the shape of the body. Then it is called as rigidity. So, ease or convenience or how easy or difficult it is to change the shape of the body keeping the volume constant is what is called as rigidity.

3. **Viscosity:** It is the measure of resistance that a system has to change of shape taking place at finite speeds.

This is that one characterises a state of matter as being a solid liquid or gas.

So, now let us look at some of the characteristic properties of solid, liquid and gas. The advantage of having the characterisation of substances as solid liquid or gas is that you can understand these things in terms of kinetic molecular theory.

1. **Solid:** rigid (if you apply pressure, it doesn't change its shape very quickly), it has a fixed shape and it is not compressible.

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2. **Liquid:** It is not compressible (if I take a liquid in a container and apply a pressure on it, u cannot change the volume of the liquid very much, or you need to increase the pressure very much before it changes the volume), doesn't has a fixed shape, it takes the shape of the container unlike the case of a solid, not rigid, It has a surface(if you put liquid in a container, it has a surface)

3. **Gas:** A gas on the other hand has no surface, it is extremely compressible (that is if I take a glass and apply pressure on it the volume will shrink), it takes the shape of the container (so u confine a gas into container of any shape), but unlike a liquid it has no surface.(So, this difference between a liquid and a gas having a surface or not a surface that is an interface is something of great importance because at the critical point whether it is a gas or a liquid is determined by a surface which differentiates a liquid from a gas. We can understand these solids, liquids, and gases in terms of a kinetic molecular theory.

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So, what is kinetic molecular theory?

Let's consider a solid (a 2D surface) composed of molecules that are structure less circles. All molecules are identical and are packed closely. So, things to notice is that the molecules are in fixed positions. The empty space that we have is very small. And this together characterises how a solid behaves. So, if we apply a pressure on the solid, because the molecules are on top of each other, and empty space is small you cannot compress it. So, what you must notice here is that, for suppose I have taken a crystalline solid for convenience about the fixed position these molecules vibrate. Raise the temperature, the extent of vibration of these molecules will increase (they will be at the same place where they were at the low temperature, but the molecules will vibrate more) This is the kinetic molecular picture of a solid.

Now if you consider a liquid, it looks much the same (consider the same 2D surface, with same size molecules except that now the positions of these molecules are quite random. The molecules are not at fixed positions and these molecules move about this is something that we know from other experiments. So, the molecules are moving about in random, so they are under collision with each other. The empty space is small, it is higher than that we have in a solid, but it is still relatively small (empty space in a liquid may be around 3 percent larger than that of we have in a solid). It's not easy for the molecules to move past each other. So, if you must move past one another, you have to wriggle past one another. As a result of which the viscosity is quite high. It's not higher than solids, but slightly higher than what you see in gases. Because the empty space is small, and molecules are more or less closely packed it is not compressible. So, that's the picture of liquid in the kinetic molecular theory.

Gas, on the other hand looks like this with molecules are completely random with a lot of empty space and moving randomly. When you apply pressure, the gas compresses easily. This is the kinetic molecular theory of gas.

Why do different compounds exist in different states of matter? For example, why sugar is solid, oxygen is gas and water is a liquid at room temperature and pressure.

Is it possible to understand why something is a solid, liquid or a gas using this kinetic molecular model? For this one of the best ways to do is to take a particular substance for example ice and conduct some transformation to it.

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We will take ice (which is solid form of water) and we will do an experiment with it.

We will take ice cubes in a container, and we provide heat to it. And as a function of time or heat provided what happens, we start with ice (below its freezing point let's consider -20C below 0) and we provide heat to it using a kitchen flame or Bunsen burner and the temperature starts to rise up to a point where ice (solid) undergoes a change to water (liquid) and when ice (solid) changes to water (liquid) the temperature becomes steady this is the latent heat that we know . at this point we need to provide a lot of heat at constant temperature to make ice(solid) convert to water(liquid). After conversion to liquid water, you continue to provide more heat and the temperature rises after that and it rises upto the point (100°C) where liquid starts converting into steam. When liquid gets converted into steam, the amount of latent heat u need to provide to completely convert into vapor is higher than that of latent heat required to convert from ice to water. After conversion of steam the temperature would again rise.

If you did the same experiment with some other substance like sugar, salt etc. The curve will look the same qualitatively. There will be one point where it breaks and becomes steady and another point where it breaks and becomes steady and so on. All the substances will do same thing, but these points will be different and latent heat required will be different. But the problem with having this characterization is that not all substances will do this kind of behaviour. There are instances that's where this problem of classification will become a problem. In water, alcohol etc these breaks are very clear. Also, there are things that look like solids and do not have these clear-cut breaks. That's one of the reasons why we have problem with this classification. So, what happens is that in the kinetic molecular theory that we have already discussed. Starting with ice (solid) that has molecules closely packed. And as the model suggests as we raise the temperature the molecules vibrate about their fixed positions. If I have a liquid the motion becomes more violent as the temperature increases. So somehow there is something which is

The thing which is making the solid go into this rigid form with molecules stacked on top of each other or close to each other (force of attraction between molecules) which is counter acted by the temperature. Larger the temperature these things are found to vibrate.

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Now let us understand the reason for understanding the force of attraction between molecules that keeps the solid or liquid together and temperature (also called as thermal energy given by RT (where R is the universal gas constant*temp in kelvin)

RT = 8.314 Joule K-1 mol-1*300K = 2.5kJ mol-1 at 300K

If the temperature is higher than what keeps molecules together then you will convert from solid to liquid to gases and the extent of temperature will then decide if it is gas or a liquid.

So, what we need to understand is what is this force of attraction holding the molecules together.

So, this is the intermolecular force of attraction.

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Intermolecular Forces:

Intermolecular forces are the forces of attraction and repulsion between interacting particles have permanent dipole moments. This interaction is stronger than the London forces but is weaker than ion-ion interaction because only partial charges are involved. The attractive forces decrease with the increase of distance between dipoles. The interaction energy is proportional to $1/r^6$ where r is the distance between polar molecules. Ion-Dipole Interaction: This is the force of attraction which exists between the ions (cations or anions) and polar molecules. The ion is attracted towards the oppositely charged end of dipolar molecules. The strength of attraction depends upon the charge and size of the ion and the dipole moment and the size of the polar molecule. For example: Solubility of common salt (NaCl) in water.

•**Ion-induced Dipolar Interactions**

In this type of interaction permanent dipole of the polar molecule induces dipole on the electrically neutral molecule by deforming its electronic cloud. Interaction energy is proportional to $1/r^6$ where r is the distance between two molecules.
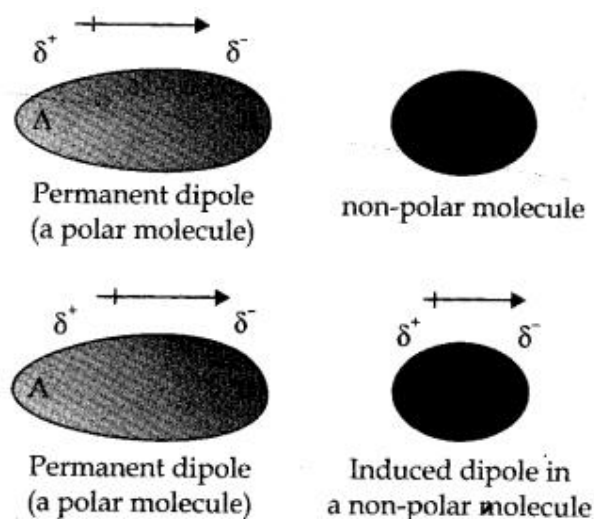

Fig. 5.1 *Dipole-induced dipole interaction between permanent dipole and induced dipole.*

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• London Forces or Dispersion Forces

As we know that in non-polar molecules, there is no dipole moment because their electronic. charge cloud is symmetrically distributed. But it is believed that at any instant of time, the electron cloud of the molecule may be distorted so that an instantaneous dipole or momentary dipole is produced in which one part of the molecule is slightly more negative than the other part. This momentary dipole induces dipoles in the neighbouring molecules. Thus, the force of attraction exists between them and are exactly same as between permanent dipoles. This force of attraction is known as London forces or Dispersion forces. These forces are always attractive, and the interaction energy is inversely proportional to the sixth power of the distance between two interacting particles, (i.e., $1/r^6$ where r is the distance between two particles).
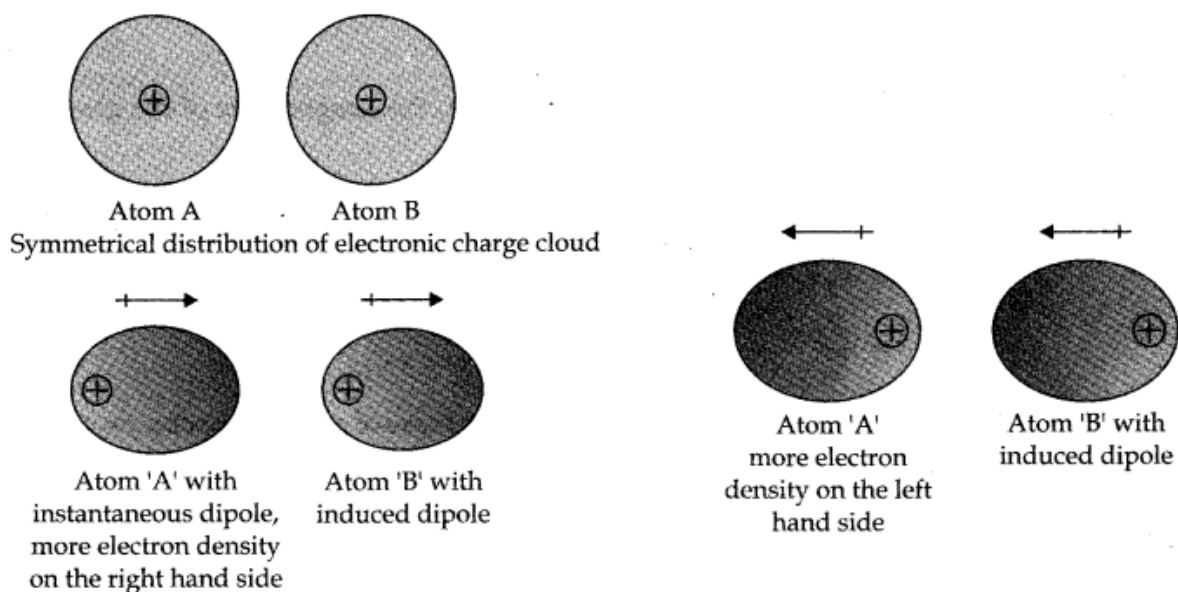
This can be shown by fig. given below.

Atom A   .   Atom B
Symmetrical distribution of electronic charge cloud

Atom 'A' with instantaneous dipole, more electron density on the right hand side

Atom 'B' with induced dipole

Atom 'A' more electron density on the left hand side

Atom 'B' with induced dipole

Fig. 5.2 *Dispersion forces or London forces between atoms.*

Hydrogen bonding:

When hydrogen atom is attached to highly electronegative element by covalent bond, electrons are shifted towards the more electronegative atom. Thus, a partial positive charge develops on

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the hydrogen atom. Now, the positively charged hydrogen atom of one molecule may attract the negatively charged atom of some other molecule and the two molecules can be linked together through a weak force of attraction.

$$- - - H^{\delta+} - - - F^{\delta-} - - - H^{\delta+} - - - F^{\delta-} - - - H^{\delta+} - - - F^{\delta-}$$
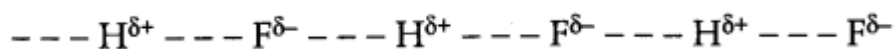
Thermal Energy: The energy arising due to molecular motion of the body is known as thermal energy. Since motion of the molecules is directly related to kinetic energy and kinetic energy is directly proportional to the temperature.

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• The Gaseous State

Physical Properties of Gaseous State

(I) Gases have no definite volume and they do not have specific shape,

(II) Gases mix evenly and completely in all proportions without any mechanical aid.

(III) Their density is much lower than solids and liquids.

(IV) They are highly compressible and exert pressure equally in all directions.

• Boyle's Law (Pressure-Volume Relationship)

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

$$V \propto \frac{1}{P} \quad \text{(At constant temp.)}$$

$$V = \frac{K}{P}$$

or $\qquad PV = K \quad$ (constant)

Here, V is the volume, P is the pressure.

$$K = \text{constant of proportionality.}$$

The value of constant K, depends upon the amount of gas, the temperature of the gas and the units in which P and V are expressed.

Let V_1 be the volume of the gas at a pressure P_1. By keeping the temperature constant, if the pressure is increased to P_2 then the volume will decrease to V_2. According to the law,

$$P_1 V_1 = P_2 V_2 = \text{constant.}$$

or $\qquad \dfrac{P_1}{P_2} = \dfrac{V_2}{V_1}$

Charles' law:

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

$$V \propto T$$

or $$\frac{V}{T} = \text{constant.}$$

Let V_1 be the volume of a gas at temperature T_1. Pressure remains constant.
If the temperature of the gas increased to T_2, then the volume will also increase to V_2. Therefore, according to law,

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

• Gay Lussac's Law (Pressure-Temperature Relationship):

At constant volume, pressure of a given mass of a gas is directly proportional to the temperature.

Mathematically,

$$P \propto T$$

$$\Rightarrow \quad \frac{P}{T} = \text{constant. (At constant volume, and mass)}$$

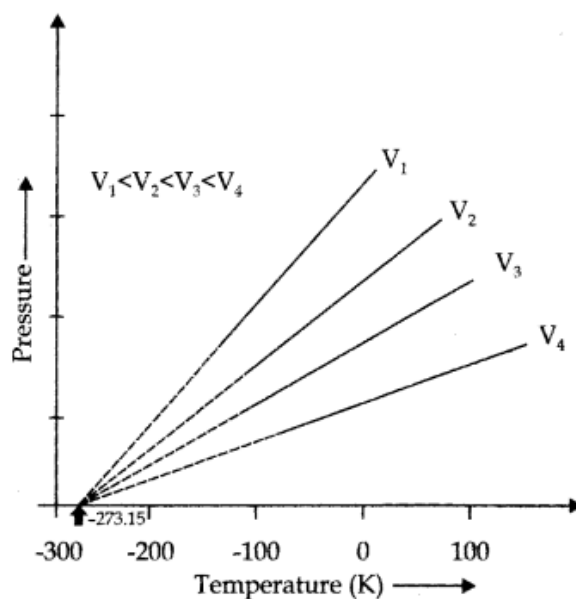Pressure Vs. temperature (Kelvin) graph at constant molar volume is shown in figure.

Fig. 5.3 Pressure vs temperature (K) graph (Isochores) of a gas.

Isochore: Each line of graph is called isochore.

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• **Avogadro Law (Volume-Amount Relationship):**

Avogadro's law states that equal volumes of all gases under the same conditions of temperature and pressure contain equal number of molecules.

V α n

Where n is the number of moles of the gas.

Avogadro constant: The number of molecules in one mole of a gas $= 6.022 \times 10^{23}$

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Ideal Gas: A gas that follows Boyle's law, Charles' law, and Avogadro law strictly, is called an ideal gas.

Real gases follow these laws only under certain specific conditions. When forces of interaction are practically negligible.

• Ideal Gas Equation

This is the combined gas equation of three laws and is known as ideal gas equation.

At constant T and n : $V \propto \dfrac{1}{P}$ Boyle's law

At constant P and n : $V \propto T$ Charles' law
At constant P and T : $V \propto n$ Avogadro law.

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

$$V = \frac{RnT}{P}$$

or
$$\boxed{PV = nRT}$$

R is called gas constant. It is also called Universal Gas Constant.

$$\boxed{R = \frac{PV}{nT}} \qquad R = \frac{1 \text{ atom} \times 22400 \text{cm}^3}{1 \text{ mol} \times 273K}$$

$$= 82.1 \text{ cm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$$

• Dalton's Law of Partial Pressure

When two or more non-reactive gases are enclosed in a vessel, the total pressure exerted by the gaseous mixture is equal to the sum of the partial pressure of individual gases.

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Let P_1, P_2, and P_3 be the pressure of three non-reactive gases A, B, and C. When enclosed separately in the same volume and under same condition.

$$P_{Total} = P_1 + P_2 + P_3$$

Where, $P_{Total} = P$ is the total pressure exerted by the mixture of gases.

• **Aqueous Tension**

Pressure of non reacting gases are generally collected over water and therefore are moist. Pressure of dry gas can be calculated by substracting vapour pressure of water from total pressure of moist gas.

$$P_{2Dry\ gas} = P_{Total} - Aqueous\ Tension$$

• **Partial Pressure in terms of Mole Fraction**

Let at the temperature T, three gases enclosed in the volume V, exert partial pressure P_1, P_2 and P_3 respectively, then

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$$P_1 = \frac{n_1 RT}{V}$$

$$P_2 = \frac{n_2 RT}{V}$$

$$P_3 = n_3 \frac{RT}{V}$$

$$P_{total} = P_1 + P_2 + P_3$$

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

$$\frac{P_1}{P_{total}} = \left(\frac{n_1}{n_1 + n_2 + n_3}\right)\frac{RTV}{RTV}$$

$$= \frac{n_1}{n} = x_1$$

Where $(n = n_1 + n_2 + n_3)$

$\therefore$ $P_1 = n_1 P_{total}.$

• **Kinetic Molecular Theory of Gases**

(i) Gases consist of large number of very small identical particles (atoms or molecules),

(ii) Actual volume occupied by the gas molecule is negligible in comparison to empty space between them.

(iii) Gases can occupy all the space available to them. This means they do not have any force of attraction between their particles.

(iv) Particles of a gas are always in constant random motion.

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(v) When the particles of a gas are in random motion, pressure is exerted by the gas due to collision of the particles with the walls of the container.

(vi) Collision of the gas molecules are perfectly elastic. This means there is no loss of energy after collision. There may be only exchange of energy between colliding molecules.

(vii) At a particular temperature distribution of speed between gaseous particles remains constant.

(viii) Average kinetic energy of the gaseous molecule is directly proportional to the absolute temperature.

• **Deviation from Ideal Gas Behaviour**

Real Gas:

A gas which does not follow ideal gas behaviour under all conditions of temperature and pressure, is called real gas.

Deviation with respect to pressure can be studied by plotting pressure V_s volume curve at a given temperature. (Boyle's law)
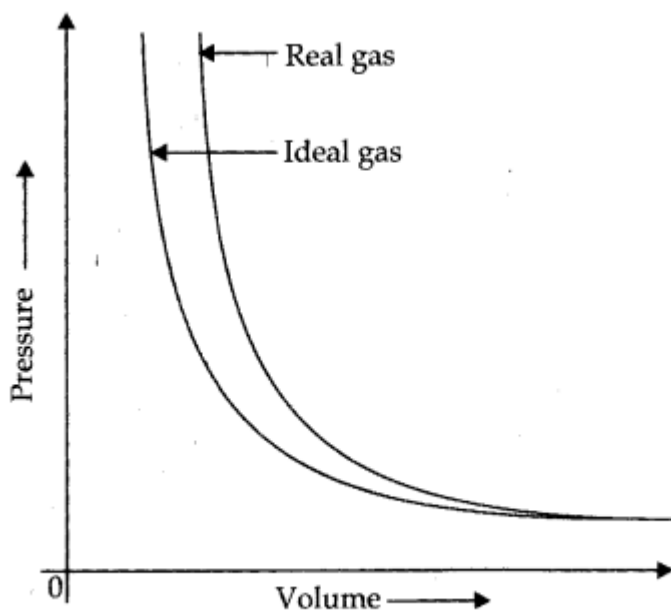
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Fig. 5.4 *Plot of pressure vs volume for real gas and ideal gas.*

Compressibility factor (Z): Deviation from ideal behaviour can be measured in terms of compressibility factor, Z.

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

For ideal gas $Z = 1$

For real gas $Z \neq 1$

When

$Z > 1$ Real gases show positive deviation from ideality

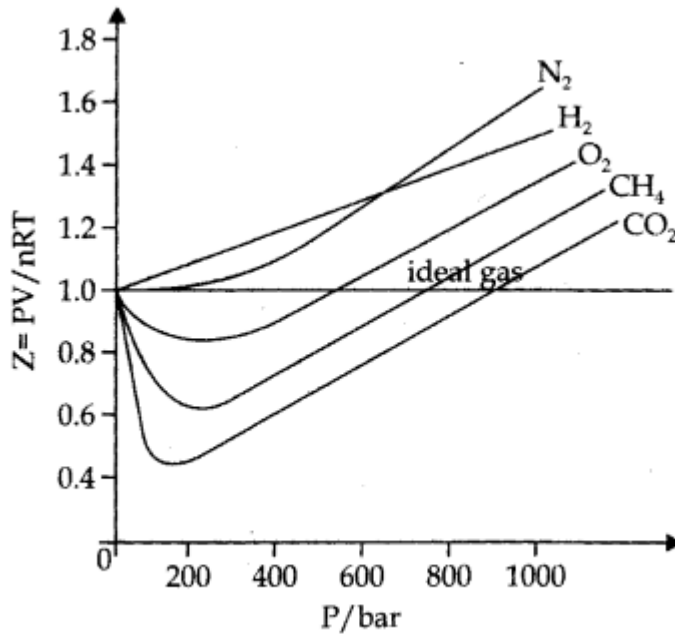$Z < 1$ The gas show more compressibility and deviation is regarded as negative deviation.

Fig. 5.5 *Variation of compressibility factor for some gases.*

• Van der Waals Equation:

For one mole of a gas $\left(P + \dfrac{a}{V^2} \right)(V - b) = RT$

Where V is a constant for molecular attraction while 'V is a constant for molecular volume.

(a) There is no force of attraction between the molecules of a gas.

(b) Volume occupied by the gas molecule is negligible in comparison to the total volume of the gas.

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Above two assumptions of the kinetic theory of gas were found to be wrong at very high pressure and low temperature.

• Liquefaction of Gases

Liquefaction of gases can be achieved either by lowering the temperature or increasing the pressure of the gas simultaneously.

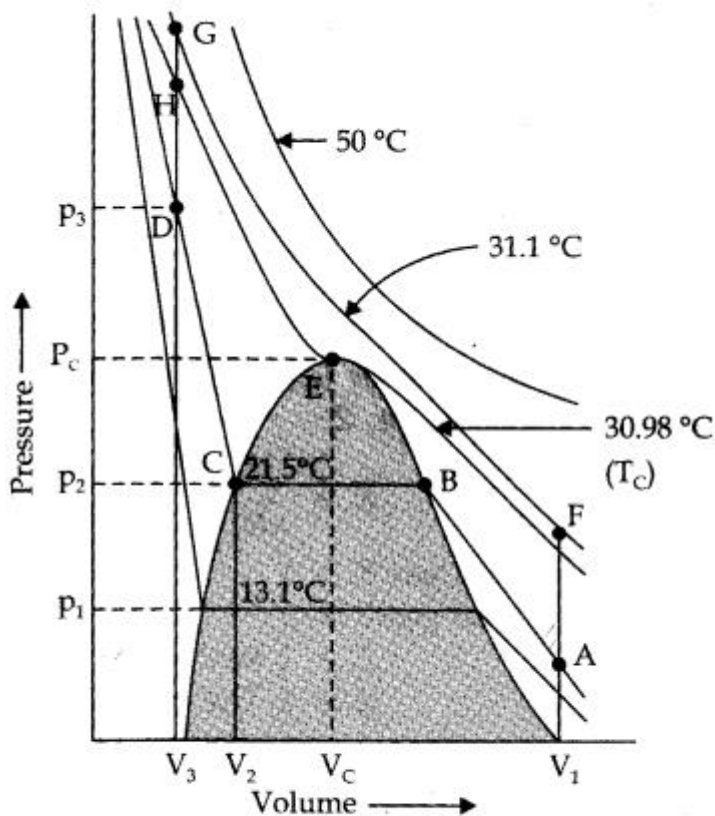Thomas Andrews plotted isotherms of CO_2 at various temperatures shown in figure.

Fig. 5.6 *Isotherms of carbon dioxide at various temperatures*

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Critical Temperature (T_c): It is defined as that temperature above which a gas cannot be liquified however high pressure may be applied on the gas.

$T_c = 8a/27Br$

(Where a and b are van der Waals constants)

Critical Pressure (P_c): It is the pressure required to Liquify the gas at the critical temperature.

$Pc = a/27b^2$

The volume occupied by one mole of the gas at the critical temperature and the critical pressure is called the critical volume (V_c).

For Example. For CO_2 to Liquify.

$T_c = 30.98°C$

$P_c = 73,9$ atm.

$V_c = 95\text{-}6 \text{ cm}^3/\text{mole}$

All the three are collectively called critical constants.

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• Liquid State

Characteristics of Liquid State

(i) In liquid, intermolecular forces are strong in comparison to gas.
(ii) They have definite volume but irregular shapes or we can say that they can take the shape of the container.

(iii) Molecules of liquids are held together by attractive intermolecular forces.

Vapour Pressure: The pressure exerted by the vapour of a liquid, at a particular temperature in a state of dynamic equilibrium, is called the vapour pressure of that liquid at that temperature.

Vapour Pressure depends upon two factors:

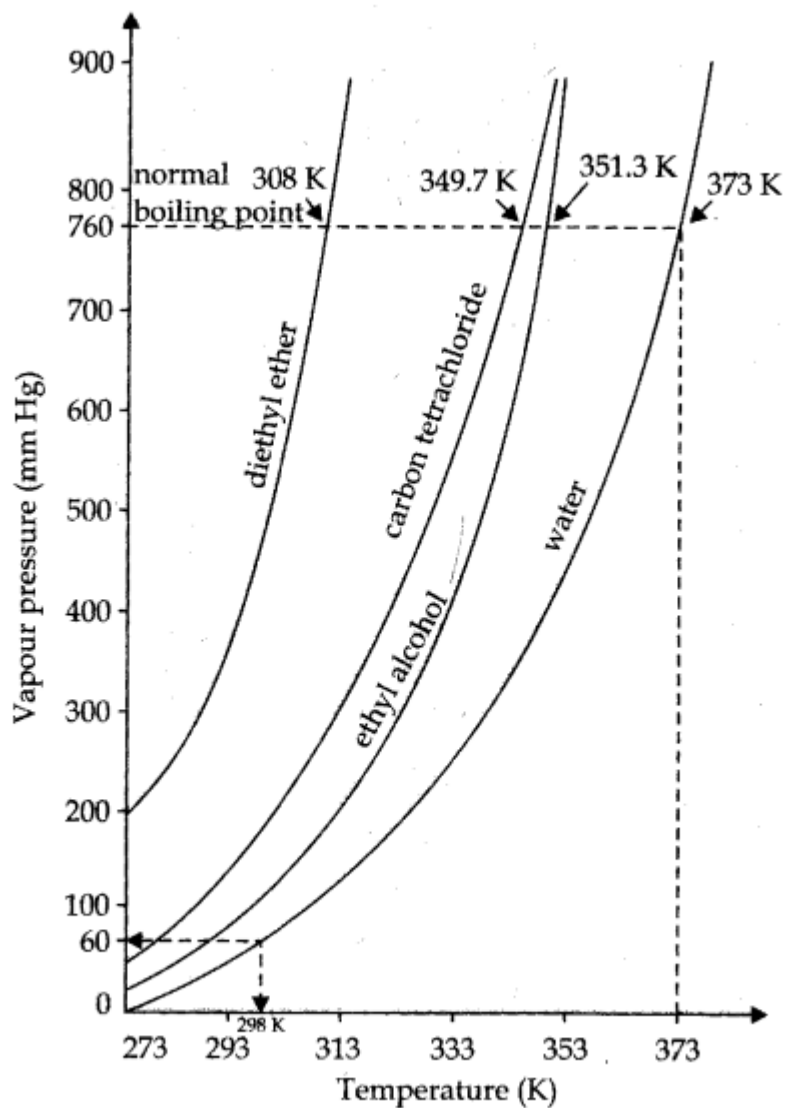(i) Nature of Liquid

(ii) Temperature

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Fig. 5.7 *Vapour pressure vs temperature curve of some common liquids.*

• **Surface Tension**

It is defined as the force acting per unit length perpendicular to the line drawn on the surface of liquid.

S.I. unit of Surface Tension = Nm^{-1}

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Surface Tension decreases with increase in temperature, because force acting per unit length decreases due to increase in kinetic energy of molecules.

• Viscosity

It is defined as the internal resistance to flow possessed by a liquid. The liquids which flow slowly have very high internal resistance, which is due to strong intermolecular forces and hence are said to be more viscous.
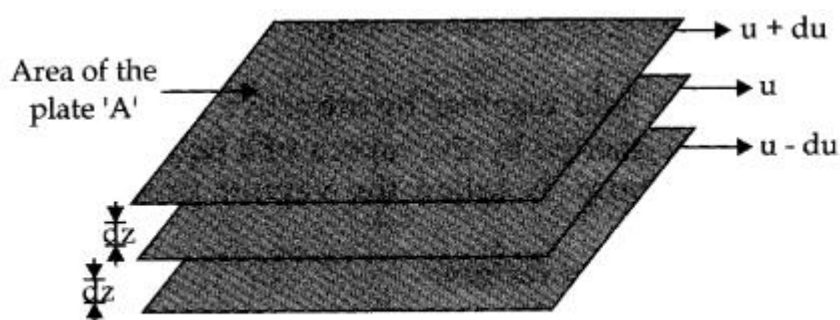

Fig. 5.8 *Gradation of velocity in the laminar flow.*

When liquid flows, the layer immediately below it tries to retard its flow while the one above tries to accelerate.

Thus, force is required to maintain the flow of layers.

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This force

$$f \propto A \quad \text{(A is area of contact)}$$

$$f \propto \frac{du}{dz} \quad (\frac{du}{dz} \text{ is velocity gradient } i.e., \text{ the change in velocity with distance.)}$$

$$f \propto A \frac{du}{dz}$$

$$f = \eta A \frac{du}{dz}$$

Where 'η' is proportionality constant and is called coefficient of viscosity.
SI unit of viscosity coefficient = 1 newton second per square metre

$$= Nsm^{-2} = \text{Pascal Second.}$$

In C.G.S system, the unit of coefficient of viscosity is poise.

$$1 \text{ poise } = 1g \, cm^{-1} \, s^{-1}.$$

Effect of Temp, on Viscosity: 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.

• **Boyle's Law:** It states that, under isothermal conditions pressure of a given mass of a gas is inversely proportional to its volume.

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

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or $\quad\quad PV$ = constant

or $\quad\quad P_1 V_1 = P_2 V_2$

- **Charles' Law:** It states that, pressure remaining constant, volume of a fixed amount of a gas is directely proportional to its absolute temperature.

$$V \propto T$$

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

- **Avogadro law:** It states that, equal volumes of all gases under same conditions of temperature and pressure contain equal number of molecules.

- **Ideal gas equation:**

$$PV = nRT$$

Where $\quad\quad R$ = Universal Constant.

- **Dalton's law of partial pressures:** It states that, total pressure exerted by a mixture of non-reacting gases is equal to the sum of partial pressures exerted by them.

$$P = P_1 + P_2 + P_3 \ldots \ldots$$

- **van der Waals equation**

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

- **Critical Temperature:** $(T_c) = \dfrac{8a}{27\,Rb}$

Critical pressure $\quad\quad (P_c) = \dfrac{a}{27b^2}$

Critical volume $\quad\quad V_c = 3b$