States of Matter

Topic: Critical Phenomenon (PV Isotherm of Real Gases and Continuity of States)

Study Material
For
B.Sc (Ist Semester)
Chemistry Students

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PV Isotherms of Real Gases Chapter No. 04

The Ideal Gas Law assumes that a gas is composed of randomly moving, non-interacting point particles. This law sufficiently approximates gas behaviour in many calculations, real gases exhibit complex behaviours that deviate from the ideal model. Isotherms refer to the different curves on the graph, which represent a gaseous state at different pressure and volume conditions but at *constant temperature*. **"*Iso* means same and *therm* means temperature hence called as *isotherm*".**

In 1869, Thomas Andrews carried out an experiment in which P -V relations of carbon dioxide gas were measured at different temperatures (**Figure 1**).

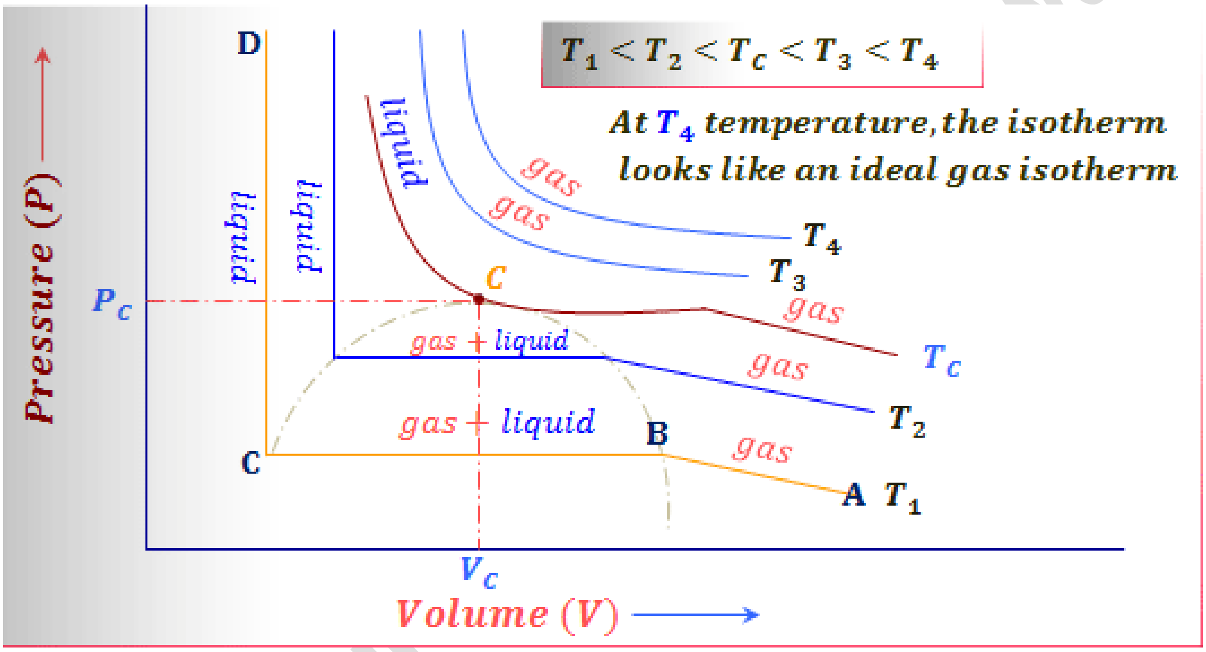

Figure 1. P-V isotherm of CO_2 gas

Following observations are made from this graph:

1. At high temperatures, such as T_4, the isotherms look like those of an ideal gas.

2. At low temperatures, the curves have altogether different appearances. Consider, for example, a typical curve ABCD.

3. As the pressures increase, the volume of the gas decreases (curve A to B). The point A represents CO_2 in gaseous state occupying certain volume under a certain pressure

4. At the point, B liquefaction begins and the volume decreases rapidly as the gas is converted to a liquid with much higher density. This conversion takes place at constant pressure (P).

5. At point C, liquefaction is complete and further increase of pressure produces only a small decrease in volume (cure CD). Thus, curve CD is evidence of the fact that the liquid cannot be easily compressed afterwards. Thus, we note that at curve AB

CO_2 is gas, curve BC represents CO_2 is partly liquid and partly gas and curve CD shows CO_2 is in liquid state only.

Similarly, curve at temperature T_2 displays similar behaviour except that now the liquefication started at higher temperature. Since $T_2 > T_1$ so the tendency of a gas to get converted into liquid state decreases which is obvious from small flattened curve at temperature T_2.

With further increase in temperature from T_1 to T_4 the liquification of gas becomes more and more difficult.

For CO_2 gas above 31.1 ^oC the isotherm is continuous and there is no evidence of liquification at all. Andrew concluded that if the temperature of CO_2 gas is above 31.1 ^oC it cannot be liquified no matter how high the pressure may be.

Andrew called this temperature (31.1 ^oC) as **Critical Temperature (T_c).** The gases which have very low critical temperature (below ordinary temperature) are called **Permanent Gases** such as N_2, O_2, H_2 etc.

The gases which have critical temperature within the range of ordinary temperature are called **Ordinary gases** such as HCl, NH_3, CO_2 etc.

Continuity of States

On the basis of isotherm (**Figure 2**) given by Thomas Andrews it is possible to convert CO_2 gas into liquid and vice-versa without any discontinuity that is, without having more than one phase present at any time. The area under the boundary curve CGXFB both gaseous and liquid states co-exist but outside this area only either liquid or gaseous state can alone exist.

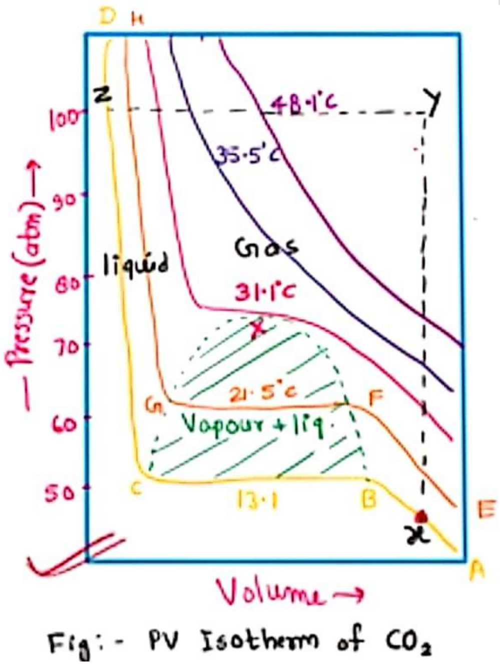

Figure 2.

Suppose a certain volume of CO_2 (represent by point X on 13.1 ^oC isotherm ABCD) is heated at constant volume to a temperature at which pressure increases to point Y. The gas now be cooled at the same pressure, the temperature and volume both will decrease along YZ and CO_2 will exist as liquid.

During this transition from gas to liquid, there has never been more than one phase present at any time. As the temperature decreases from Y to Z, the volume of gas decreases gradually till the molecules are close enough for the Van der waals force of attraction to cause their condensation into liquid state.

Thus, the process of transition from gaseous state to liquid state or vice-versa therefore is regarded as continuous, this is called as **Continuity of State.**