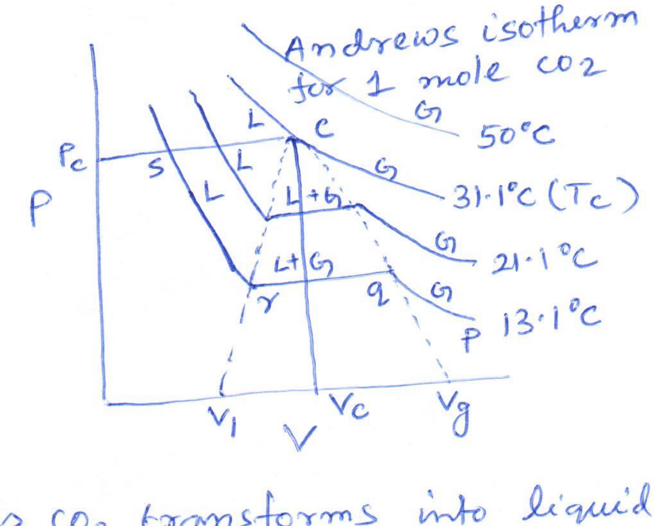
Critical Phenomena - Andrews' curve :

A gas can be liquefied by lowering of temp. and increasing Pr. But influence of temp. is more important. Most gases are liquefied at ordinary Pr. by suitably lowering of temp. But a gas can not be liquefied unless its temp. is below a certain value depending on the nature of the gas. This temp. of the gas is called its critical temp. (T_c) and above which the gas can not be liquefied what ever high Pr. may be applied to.

A gas can only be liquefied when the temp. is kept below T_c of the gas. The Pr. required to liquefy the gas at its T_c is called critical Pr. (P_c) and the vol. occupied by 1 mole at T_c and P_c is called critical vol (V_c).

These critical constants can be illustrated from the Andrews curves. These curves are obtained by drawing P vs. V at diff. temp.s. T. Andrews (1869), in his experiment with 1 mole CO_2 collected data of P vs. V at various temp.s.

Let us discuss the isotherm (it is the curve describing the relation of P and V at const. T) at 13.1°C (below T_c), pqrs. The point p represents the gaseous CO_2 at low P. As P is increased, V is correspondingly decreased according to Boyle's law. At the point q, the gaseous CO_2 begins to liquefy and the Pr. at the point is the saturation vapour pr. of CO_2. As the vol. is decreased, more of the gaseous CO_2 transforms into liquid CO_2 but P remains unchanged. This isothermal conversion continues up to r when all the gaseous CO_2 is converted into liquid CO_2.



Now the curve rs is very steep as the liquid is highly incompressible.

when the temp. 21·1°c is taken for the study, similar curve is obtained except the liquid begins to form at higher saturation pr. and the range of vol. over which condensation occurs is smaller.

At still higher temp. of 31·1°c, the plateau shrinks to a point and this temp. is the critical temp (T_c) of the gas. when the temp. is further increased to 50°c, the isotherm approaches more closely to that of ideal gas; no plateau is observed and no liquid is formed.

The dotted line encloses a dome-shaped area within which liquid and gas are co-existent. The highest point c of the area indicates the critical point. on the right side of the area, gas alone is present and at the left liquid.

Condition of the critical point (c):

The critical point is the limiting point of a series of horizontal two-phase lines. so the slope of the horizontal lines as well as the limiting point (c) is

$$\left(\frac{\partial P}{\partial V}\right)_T = 0$$

Again along the critical temp. isotherm, the slope is zero at the critical point (c) and is -ve on either side of the point. Thus the slope is maximum (zero value is greater than -ve values) at the critical point. This slope is function of v and its derivative with respect to v is again zero at the point.

That is, $$\left[\frac{\partial}{\partial V}\left(\frac{\partial P}{\partial V}\right)_T\right]_T = \left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0 \text{ at the point.}$$

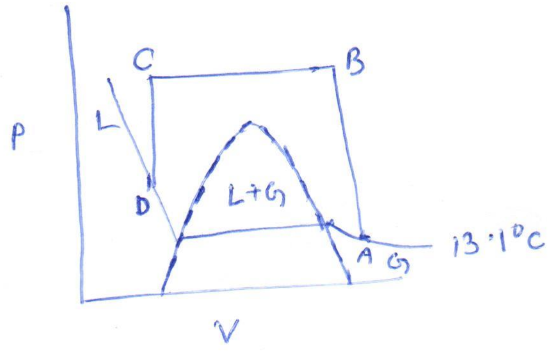
Thus, the condition of the critical point is given by

$$\left(\frac{\partial P}{\partial V}\right)_T = 0 \quad \text{and} \quad \left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0 .$$

That means, both slope and curvature at the point is zero.

Continuity of states:

In the Andrews P-V diagram, the area in which the phases, gas and liquid coexist, are shown by dashed line. In the adjoining figure, A and D lie on the same isotherm at 13.1°C temp., below the T_c of CO_2. The point A clearly indicates the gaseous state, and point D indicates the liquid state. These two states are sharply defined and the dashed area which contains liquid-gas in equilibrium are also well-defined. But it is possible to shift from the gaseous state point A to the liquid state point D continuously without passing through the discontinuous dashed area.



Two-phase region and continuity of states.

Let the gas at the ~~same~~ state point A is heated to B at constant volume along AB. Then the gas is gradually cooled at constant pressure along BC, the volume is reduced considerably. The gas is again cooled at constant volume until the state point D is reached. No where in the process liquid would appear. At D, the system is highly compressed gas. But the curve shows that this state point is for the liquid state. Thus, there is hardly any difference betwn. the liquid state and the gaseous state and there is no line of demarcation betwn. the two phases. This is the continuity of states. The point D we may refer as liquid state or highly compressed gaseous state. In the absence of discontinuity there is no fundamental way of distinguishing liquid or gas. The gas is continuously transferred to the liquid without passing the usual process of condensation.