

Van der Waals' Equation of State

→ For 1 mole of an ideal gas :

① Boyle's law: $P \propto \frac{1}{V}$ [T = constant]

② Charles law: $V \propto T$ [P = constant]

Using ① and ② :

$$PV = RT$$

Andreev's experiments on CO₂

→ compressibility of gases while attempting to liquefy them.

The experiments carried out on compressing CO₂ gave following results:

1) At 48°C, the isotherm shows the behaviour of a perfect gas.

2) As the temperature is lowered, the behaviour deviates from that of perfect gas.

3) At 31.4°C, a kink appears in the PV curve and cohesion suggests that a gas can be liquefied under compression. Above this temperature, liquefaction is not possible, no matter how high the pressure may be.

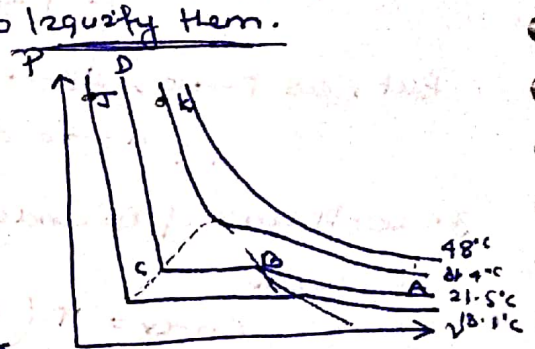
4) As the temperature is further lowered, the kink spreads into a straight line parallel to x-axis which shows that liquefaction can take place and on compression and over a large range of volume the liquid and saturated vapour exists. From A to B, CO₂ behaves as a gas, from B to C the gas compressed at constant pressure to the liquid and vapour coexists and at C the liquid phase exists which is almost incompressible.

5) As the temperature further decreased, the flat portion increases implying that liquid and vapour phase coexists for larger range of volume.

The temperature at which kink appears is called critical temp. and the pressure at which liquefaction starts is called critical pressure. The corresponding volume is called critical volume.

Important points:

- ① Gas can't be liquefied unless it is cooled upto or below the critical temperature.
- ② There exists a continuity of liquid and gaseous states i.e. they are two distinct stages of a continuous phenomenon.



eg: At point K , let us consider two isotherms s.t. $T_1 < T_2$. For $P > P_c$, at point K the substance is a gas and at J the same substance is a liquid i.e. if a substance is cooled at constant pressure, the substance changes from a gaseous state to a liquid state.

Van der Waals' eqn of state

Assumptions:

- ① Gaseous molecules are finite in size and spherical and can't be assumed to be point masses.
- ② The molecules attract one another with a force which depends on distance between them.
- ③ The no. of collisions with the walls of the container are exactly the same for both point and finite size molecules.

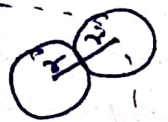
a) Correction for finite size:

Consider one mole of a gas enclosed in a container of volume V . If we consider molecules size under consideration, the volume available to a single molecule for free movement will be somewhat less than V which is the volume which is available when we assume point masses.

Let us consider the radius of spherical reduction in volume by $(\frac{V-b}{V})$. Hence, total volume available for one mole of gas will be $\frac{V-b}{V}$ we assume

$$P(V-b) = RT$$

Let us consider the radius of each molecule to be r . At the instant of collision, the centre to centre distance of 2 colliding molecules be $2r = d$;



This means that around any molecule, a spherical volume of $V = \frac{4}{3}\pi r^3$ will be unavailable for other molecules and is called sphere of exclusion and its volume is 8 times that of molecule. Let us

consider filling a container with N molecules one by one. i.e. to

- Volume available to 1st sphere $\equiv V_1$
 " " " 2nd " $\equiv V - V_1$
 " " " Nth " $\equiv V - (N-1)V_1$

\therefore Average volume available is:

$$\bar{V} = \frac{1}{N} \sum_{i=1}^N V - (i-1)V_1$$

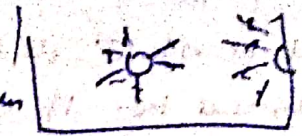
$$= \frac{1}{N} \left[NV - \frac{(N-1) \cdot N \cdot V_1}{2} \right]$$

For large N :

$$\bar{V} = V - \frac{NV_1}{2} = V - 4V_m \quad \text{when } V_m = \frac{4}{3}\pi r^3 = \text{vol of 1 molecule}$$

$$b = 4NV_m$$

⑤ Correction for intermolecular attraction



From our assumption that, molecules attract one another with a central force, we can see from fig that the molecule in the interior of the gas is attracted ~~from~~ equally from all sides and hence net force on it is zero. But for the molecules colliding with the surface, there is a net inward force and hence the ~~pressure~~ momentum ~~transfer~~ ^{imparted} by it on the walls is less than that of a perfect gas. Therefore, the intermolecular forces lead to reduction in pressure. This is called cohesive pressure.

This cohesive pressure is proportional to no. of molecules per unit volm of surface layer (on which the inward forces act) and the no. of mol/volume in the next layer which causes the inward force i.e.

$$\Delta p \propto \left(\frac{N}{V}\right)^2$$

$$\Rightarrow \Delta p = \frac{a' N^2}{V^2} \quad \text{Let } a' N^2 = a$$

$$\therefore \Delta p = \frac{a}{V^2}$$

∴ In ideal gas eqn, we must replace p by sum of the observed pressure for a real gas and a ~~for~~ the drop caused by intermolecular attraction.

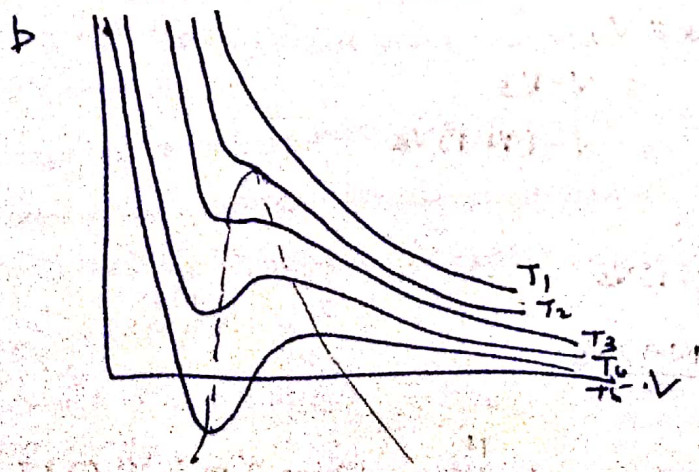
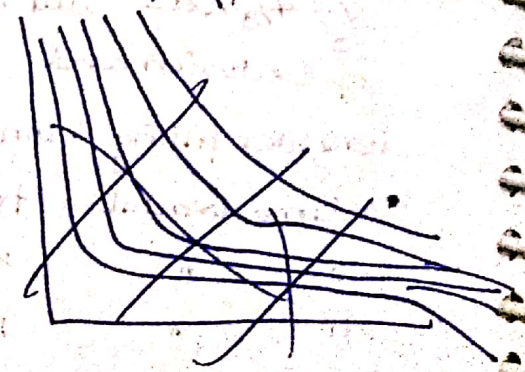
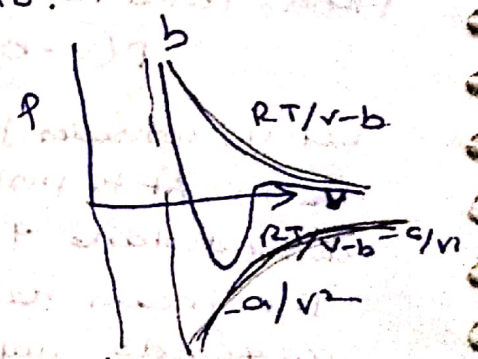
∴ The eqn of state for an ideal gas modifies to:

$$\left(p + \frac{a}{V^2}\right)(V-b) = RT$$

a, b: van der Waals constants; \hookrightarrow van der Waals eqn of state

For large V, van der Waals eqn \rightarrow ideal gas eqn.

van der Waals eqn for diff. temp.



Discussion

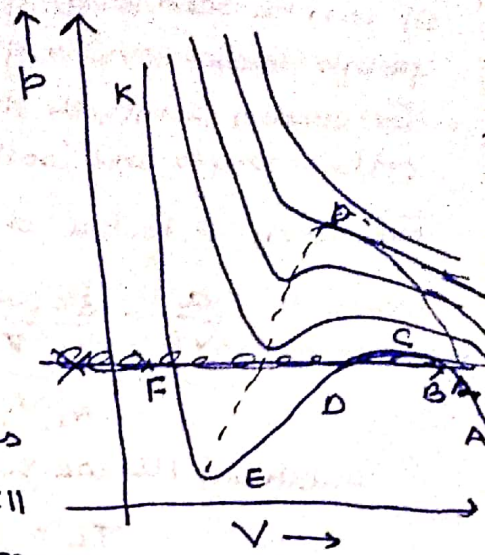
We can rewrite Vander Waals eqn as:

$$P = \frac{RT}{V-b} - \frac{a}{V^2} \quad \text{--- (1)}$$

When expanded in powers of V , we get,

$$PV^3 - (Pb + RT)V^2 + a(V-b) = 0 \quad \text{--- (2)}$$

From this we note that:



1) The eqn (2) is cubic in volume ' V '. That means for each pair of values of P and T , V will have three values, either all of them real or one real and two imaginary. For low temperatures, three real roots exist, they become equal at $T = T_c$ and above this temperature one real and two imaginary roots exist.

2) It can be seen that for large V , $P \rightarrow 0$ and for $V \rightarrow b$, $P \rightarrow \infty$ which implies that the isotherms will decrease upwards.

3) For CO_2 at various temperatures, the general form of isotherms is shown in figure. These curves are different from those observed in Andrews. Vander Waals predicts maxima and minima in the straight line region of Andrews' curve at low temperatures.

Let us consider one of the isotherms at low temperatures. Portion AB and FK represents gaseous and liquid states respectively. However portion BC represents superheated vapour while portion EF represents superheated liquid. Both of them correspond to metastable equilibrium and doesn't appear in Andrews curve.

The portion CDE of these theoretical curves indicates that volume should decrease with decrease in pressure which is practically infeasible.

The eqn of locus of maxima and minima shown by dotted curve can be obtained by putting $\left(\frac{\partial P}{\partial V}\right)_T = 0$.

$$\therefore \left(\frac{\partial P}{\partial V}\right)_T = \frac{-RT}{(V-b)^2} + \frac{2a}{V^3} = 0$$

$$\Rightarrow T = \frac{2a(V-b)^2}{RV^3}$$

It can be seen that this is also cubic in ' V ' and it can be seen here will be 3 real or 1 real and 2 imaginary values of V for maxima and minima. Putting T is (1), we get,

$$P = \frac{2a(V-b)}{V^3} - \frac{a}{V^2} = \frac{a(V-2b)}{V^3} \rightarrow \text{eqn of curve passing through maxima \& minima}$$

It can be seen that the isotherms below P cut the dotted curve at two points ~~coexist~~ and a gas can be liquefied by changing pressure only. For critical point, the two points coalesce into one. This must be the critical point and isotherm passing through this must be critical isotherm. For point P to be the point of maximum in the dotted curve, we:

$$\frac{a}{v^2} - \frac{3a(v-2b)}{v^4} = 0$$

$$\Rightarrow \boxed{V_c = 3b}$$

Substituting this we get

$$T_c = \frac{8a}{27Rb}$$

$$\Rightarrow P_c = \frac{a}{27b^2}$$

$$\therefore \frac{P_c V_c}{R T_c} = \frac{R T_c}{P_c V_c} = \frac{8}{3} = Z_c \rightarrow \text{critical coefficient}$$

Onnes proposed the eqn of state as:

$$pV = A + Bp + Cp^2 + \dots$$

From Vanderwaal eqn, we have,

$$pV = RT \left(1 - \frac{b}{V}\right)^{-1} - \frac{a}{V}$$

$$= RT \left(1 + \frac{b}{V} + \frac{b^2}{V^2} + \dots\right) - \frac{a}{V}$$

$$\Rightarrow pV = RT + \frac{RTb-a}{V} + \frac{RTb^2}{V^2} + \dots$$

$$\Rightarrow \boxed{A = RT, B = RTb - a, C = RTb^2}$$

virial coefficients; Vanderwaal gives just 3 virial coefficients

At the Boyle temp, 2nd virial coeff goes to zero

$$\text{i.e. } B = 0$$

$$\Rightarrow \boxed{T_b = \frac{a}{Rb}}$$

$$\therefore \boxed{T_b = \frac{27}{8} T_c}$$

Reduced eqn of state:

To write van der Waal eqn in a form that is applicable to all gases we introduce reduced pressure, reduced volume, reduced temperature

$$p_r = \frac{p}{p_c}, \quad v_r = \frac{V}{V_c}, \quad T_r = \frac{T}{T_c}$$

$$\Rightarrow \left(p_r p_c + \frac{a}{v_r^2 v_c^2} \right) (v_r v_c - b) = R T_r T_c \rightarrow \text{Reduced eqn of state as the loc of corresponding states.}$$