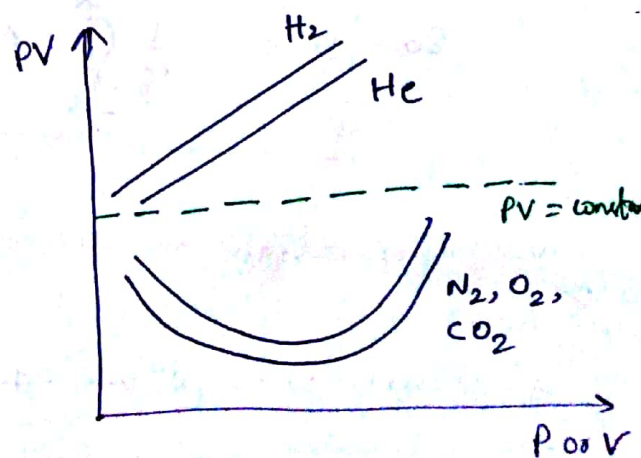


Equation of State for Real Gases

To define the state of a gaseous system completely, we need to know three parameters P , V & T . By equation of state we mean the mathematical relation that express functional form of P, V, T as $f(P, V, T) = 0$. The equation of state of a perfect gas $PV = RT$ is the most simple form of equation of state.

Insufficiency of the perfect gas equation

Boyle found that the perfect gas equation $PV = RT$ does not fit the experimental results and works only at ideal condition i.e. at very high temperature & very low pressure. In indicator diagram (P vs. V) one can obtain isothermals. Experiment by Regnault showed that no gas obeys $PV = \text{constant}$ but either increases with pressure or they decrease & increase with pressure. So modification of perfect gas laws is necessitated.



To explain the gradual increment of PV with P for H_2 , He etc consider the modified equation $P(V-b) = \text{constant}$ or $PV = \text{constant} + Pb$, which increases with P . On the other hand to explain the initial drop of curves for O_2 , N_2 , CO_2 we take $(P + P_i)V = \text{constant}$.
 \therefore In combined form $(P + P_i)(V-b) = \text{constant}$ was noted in 1860.

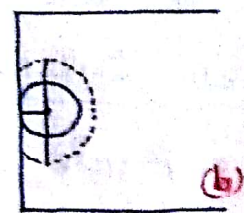
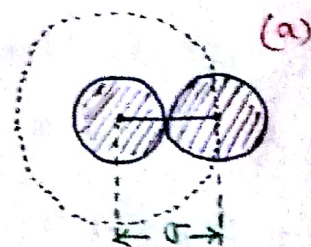
Semiderivation of Vanderwaal's equation

To obtain heuristically an expression for real gas, in 1909, Vanderwaal made a few simplifying assumptions that

- (i) The molecules are rigid spherical objects of diameter σ
- (ii) They attract each other with a weak force that depends only on the intermolecular distance & independent of the orientation of the molecules. To derive, first he considered the effect of finite size of molecules & then considered the weak attractive force & then superposed them which cannot be rigorously justified.

Volume Correction

We know that $\frac{4}{3}\pi\sigma^3$ is the sphere of influence of a molecule, so that center of no other molecule can penetrate it. So if the total space contains N molecules then $(N-1)\frac{4}{3}\pi\sigma^3$ is excluded from the center of others.



\therefore The actual free volume is $V - (N-1)\frac{4}{3}\pi\sigma^3$
 $\approx V - \frac{4}{3}\pi N\sigma^3$ as $N \sim 10^{23} \gg 1$.

\therefore The actual number density is $n_r = \frac{N}{V-2b}$ where $b = \frac{2}{3}\pi N\sigma^3$.

As in figure (b), if we consider the gas to be enclosed in a vessel, then the molecule may approach only to a distance $\sigma/2$ from the wall, as then the surface of the molecule will touch the wall. But since the sphere of influence is of radius σ meaning when a

molecule is at a distance σ , its sphere of influence extends to the wall & therefore the center of no other molecule can lie within the hemisphere $\frac{2}{3}\pi\sigma^3$.

∴ If we consider an elementary volume dV in the neighbourhood of the wall, then $\frac{2}{3}\pi n_r \sigma^3$ is the fraction of volume unavailable for the center of other molecules. So if dV_a is the amount of dV existing as free space, then

$$dV_a = dV - \frac{2}{3}\pi\sigma^3 n_r dV = dV \left(1 - \frac{\frac{2}{3}\pi N \sigma^3}{V - 2b}\right) = dV \left(1 - \frac{b}{V - 2b}\right)$$

the actual number of molecules in dV is $n_r dV_a$

$$= \frac{N}{V - 2b} \left(1 - \frac{b}{V - 2b}\right) dV = \frac{NdV}{V - 2b} \frac{\left(1 - \frac{b}{V - 2b}\right)\left(1 + \frac{b}{V - 2b}\right)}{\left(1 + \frac{b}{V - 2b}\right)}$$

$$= \frac{NdV}{V - 2b} \frac{1}{1 + \frac{b}{V - 2b}} \quad \left(\text{as } \frac{b^2}{(V - 2b)^2} \ll 1\right)$$

$$= \frac{NdV}{V - b}$$

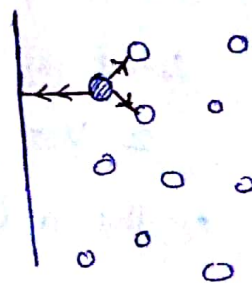
If we would've considered the molecules as geometrical point mass objects, then the number of molecules in dV would be $\frac{N}{V} dV$

So finite size correction is $V - b$ and ~~the~~ volume correction is

$$b = \frac{2}{3}\pi\sigma^3 N = 4 \times \frac{4}{3}\pi N \left(\frac{\sigma}{2}\right)^3 = 4 \times \text{Total volume of all molecules.}$$

Pressure Correction

The molecule attract with a cohesive force that varies inversely as some power of the distance between them, which is negligible at long distance. On average, molecule get zero force due to isotropicity except near a surface. Parallel to surface forces will still balance but not perpendicular to it, so uncompensated inward force \perp to boundary. Force on single molecule \propto number of attracting molecule/cc.



Also force acting/unit area of surface \propto number of molecules in that area of surface. Hence cohesive force/unit area of the surface is $\propto n^2 = \left(\frac{N}{V}\right)^2$ where N is the total number of molecules & V is the total volume. $\therefore P_i \propto \frac{1}{V^2} = \frac{a}{V^2}$. This cohesive pressure is called internal pressure or intrinsic pressure & acts only in the boundary layer of any solid or fluid giving rise to surface tension in liquids & tensile force in solids. It opposes the kinetic pressure but assists the external pressure in keeping the substance together. So it opposes the outward motion & decreases the momentum & hence the pressure. So P is replaced by $P + \frac{a}{V^2}$ as if the external pressure is increased.

So for one mole gas $\boxed{\left(P + \frac{a}{V^2}\right)(V-b) = RT}$ Vanderwaals equation of state.

Constant volume method of finding "a" and "b"

From ~~the~~ VW equation, $P = \frac{RT}{V-b} - \frac{a}{V^2}$

$$\therefore \left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V-b}$$

or

$$\boxed{b = V - \frac{R}{\left(\frac{\partial P}{\partial T}\right)_V}}$$

Therefore "a" and "b" can be obtained by observing the rate

$$\boxed{a = V^2 \left\{ T \left(\frac{\partial P}{\partial T}\right)_V - P \right\}}$$

of increase of pressure with temperature as in constant volume gas thermometer very accurately. But they vary with temperature.

| Gas | a in atm cm ⁶ ($\times 10^{-6}$) | b in cc ($\times 10^{-6}$) |
|-----------------|--|---------------------------------|
| He | 6.8 | 106 |
| Ar | 268.0 | 143 |
| O ₂ | 273.0 | 143 |
| N ₂ | 272.0 | 173 |
| CO ₂ | 717.0 | 191 |
| NH ₃ | 833.0 | 168 |

At N.T.P.

Vander Waal's equation from Clausius virial theorem

In an entirely different approach, Clausius deduced rigorously the equation for a real gas, using Newtonian concept of classical dynamics. If x, y, z denote the coordinate of a molecule in an arbitrary reference frame and f_x, f_y, f_z denote the force components, then

$$m \frac{d^2 x}{dt^2} = f_x, \quad m \frac{d^2 y}{dt^2} = f_y, \quad m \frac{d^2 z}{dt^2} = f_z$$

$$\text{as } \frac{d^2}{dt^2} (x^2) = 2 \frac{d}{dt} \left(x \frac{dx}{dt} \right) = 2 \left(\frac{dx}{dt} \right)^2 + 2x \frac{d^2 x}{dt^2}$$

$$\therefore x \frac{d^2 x}{dt^2} = \frac{1}{2} \frac{d^2}{dt^2} (x^2) - \left(\frac{dx}{dt} \right)^2, \quad \text{similarly for } y \text{ and } z.$$

$$\therefore m x \frac{d^2 x}{dt^2} = f_x x \Rightarrow m \left\{ \frac{1}{2} \frac{d^2}{dt^2} (x^2) - \left(\frac{dx}{dt} \right)^2 \right\} = f_x x$$

$$\text{or } \frac{m}{2} \left(\frac{dx}{dt} \right)^2 = \frac{m}{4} \frac{d^2}{dt^2} (x^2) - \frac{1}{2} f_x x, \quad \text{similarly for } y \text{ and } z.$$

Adding all components, $\frac{1}{2} m \left\{ \left(\frac{dx}{dt} \right)^2 + \left(\frac{dy}{dt} \right)^2 + \left(\frac{dz}{dt} \right)^2 \right\} = \frac{m}{4} \frac{d^2}{dt^2} (x^2 + y^2 + z^2) - \frac{1}{2} (x f_x + y f_y + z f_z)$
we get the K.E. of a molecule.

Summing over all molecule and taking average over sufficiently long interval τ , we get

$$\frac{1}{2} \sum_i^{\tau} m v^2 = \frac{m}{4} \sum_i^{\tau} \frac{d^2}{dt^2} (r^2) - \frac{1}{2} \sum_i^{\tau} x f_x + y f_y + z f_z \quad \left[\frac{\tau}{X} = \frac{1}{\tau} \int_0^{\tau} x dt \right]$$

In steady state, $\frac{1}{2} \sum_i^{\tau} m v^2$ and $\frac{1}{2} \sum_i^{\tau} \vec{r} \cdot \vec{f}$ are approximately constant throughout the motion. But $\frac{m}{4} \frac{1}{\tau} \int_0^{\tau} \sum_i^{\tau} \frac{d^2}{dt^2} (r^2) dt = \frac{m}{4\tau} \int_0^{\tau} \sum_i^{\tau} \frac{d}{dt} \left(2\vec{r} \cdot \frac{d\vec{r}}{dt} \right) dt$

$$= \frac{m}{2\tau} \left[\sum_i^{\tau} \vec{r} \cdot \frac{d\vec{r}}{dt} \right]_0^{\tau} = 0 \quad \text{as } \vec{r} = \frac{d\vec{r}}{dt} \text{ fluctuates irregularly}$$

with time and using the Brownian motion concept, $\frac{\tau}{\tau} \cdot \frac{d\vec{r}}{dt} = 0$. Remember in Einstein's theory (Langevin equation)

$$m \frac{dv}{dt} = -\alpha v + F_B(t), \quad \begin{aligned} \frac{\tau}{\tau} F_B &= 0 & (\text{Markovian}) \\ \frac{\tau}{v} F_B &\neq 0 = \alpha k_B T & (\text{non-Markovian}) \end{aligned}$$

inertial viscous Brownian

$$\therefore \boxed{\frac{1}{2} \sum_i m \overline{v^2} = -\frac{1}{2} \sum_i \vec{r} \cdot \vec{F}}_{\text{KE}} \quad \text{virial}$$

Virial theorem states that average kinetic energy of translation of the

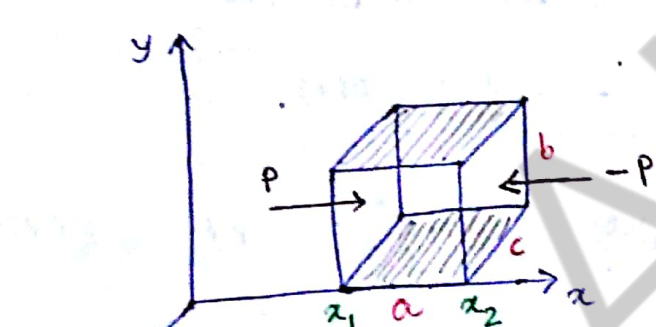
molecules of a gas in the steady state is equal to its virial.

Now, F_x , F_y and F_z include all the forces that act on the molecule.

These forces can be broadly categorized as.

1. The force of impact on the molecule due to collision with the walls of the vessel.
2. The force due to collision between two molecules.
3. The force of attraction between molecules within some distance.

We consider the contribution of 1 to the virial. Imagine the gas confined in a box of dimension a , b , and c with faces cutting x axes at x_1 & x_2 . If the pressure exerted by the gas is P , then



$$\sum F_x \text{ at } x_1 = Pbc$$

$$\sum F_x \text{ at } x_2 = -Pbc.$$

$$\therefore -\frac{1}{2} \sum F_x x = \frac{1}{2} Pbc (x_2 - x_1)$$

$$= \frac{1}{2} Pabc = \frac{1}{2} PV. \text{ where}$$

$V = abc$ is the volume of the box. Similarly $-\frac{1}{2} \sum F_y y = \frac{1}{2} PV$ and $-\frac{1}{2} \sum F_z z = \frac{1}{2} PV$ for two other faces. \therefore Total contribution by the forces acting on the wall is $\frac{3}{2} PV$.

For an ideal gas, contribution from 2 and 3 is neglected, because there is no cohesive force, nor they've a finite size, then,

$$\frac{1}{2} m N \bar{c}^2 = \frac{3}{2} PV = \frac{3}{2} RT \quad (\text{using Virial theorem})$$

$$\therefore \boxed{P = \frac{1}{3} m n \bar{c}^2}$$

Equation of state for real gases

Now we incorporate point 2 and 3 but we do not know the nature of forces. For simplicity, let's assume isotropically so that the force is fully radial, say $\phi(r)$, with $\phi(r) = -\frac{dE}{dr}$ where E is the P.E. due to intermolecular force. Let the coordinates of the center of two molecules be (x, y, z) and (x', y', z') . Then the components (F_x, F_y, F_z) and (F_x', F_y', F_z') of the forces acting are

$$F_x = \phi(r) \left(\frac{x-x'}{r} \right)$$

$$F_x' = \phi(r) \left(\frac{x'-x}{r} \right). \text{ Therefore the}$$

contribution to $\sum F_x x$ by these forces is $F_x x + F_x' x' = \frac{\phi(r)}{r} (x-x')^2$

Similarly for the y and z components. So the total contribution is

$$-\frac{1}{2} \sum \frac{\phi(r)}{r} \left[\underbrace{(x-x')^2 + (y-y')^2 + (z-z')^2}_{r^2} \right] = -\frac{1}{2} \sum r \phi(r).$$

Hence from the virial theorem, we get $\frac{1}{2} m N \bar{c}^2 = \frac{3}{2} pV - \frac{1}{2} \sum r \phi(r)$

But $\frac{1}{2} m \bar{c}^2 = \frac{3}{2} k_B T$, \therefore $pV = N k_B T + \frac{1}{3} \sum r \phi(r)$

Evaluation of $\sum r \phi(r)$

According to MB distribution with P.E. we know

$$N_c = N_0 \left(\frac{m}{2\pi k_B T} \right)^{3/2} 4\pi c^2 e^{-(\frac{1}{2} m c^2 + E)/k_B T} dc.$$

\hookrightarrow no. of molecules when P.E. = 0. $\approx N_0 e^{-E/k_B T}$

Let us calculate the contribution of one molecule to the virial.

Average number of other molecules lying within r and $r+dr$ from this molecule is $4\pi r^2 dr n$ & the force exerted by them is $\phi(r)$. So the contribution of one molecule to $r \phi(r)$ is

$\int_0^\infty 4\pi r^3 n_0 e^{-E/k_B T} \phi(r) dr$ and so the contribution of N molecules is $\frac{N}{2} \int_0^\infty 4\pi r^3 n_0 \phi(r) e^{-E/k_B T} dr$ where division by 2 is to avoid the double-counting. Substituting $n_0 = \frac{N}{V}$ and $\phi(r) = -\frac{\partial E}{\partial r}$ we have

$$\text{contribution of } N \text{ molecules} = \frac{2\pi N^2}{V} \int_0^\infty r^3 e^{-E/k_B T} dr \phi(r)$$

$$\text{Now } \int e^{-E/k_B T} \phi(r) dr = - \int e^{-E/k_B T} \frac{\partial E}{\partial r} dr = -k_B T \int e^{-E/k_B T} d(E/k_B T) \\ = k_B T e^{-E/k_B T} + \text{Constant}, \quad (\text{constant} = -k_B T)$$

\therefore Integrating by parts $\left[\int u dv = uv - \int v du \right]$

$$\frac{2\pi N^2}{V} \left[\left\{ r^3 (k_B T e^{-E/k_B T} + \text{constant}) \right\}_0^\infty - \int_0^\infty 3r^2 (k_B T e^{-E/k_B T} + \text{constant}) dr \right] \\ = \frac{2\pi N^2}{V} 3k_B T \int_0^\infty r^2 (1 - e^{-E/k_B T}) dr = \sum r \phi(r).$$

Substituting this to real gas equation of state, we obtain

$$PV = Nk_B T + \frac{2\pi N^2}{V} k_B T \int_0^\infty r^2 (1 - e^{-E/k_B T}) dr.$$

To evaluate the integral, we assume that molecules are rigid spheres of diameter σ , so $E = \infty$ for $r < \sigma$
 $= \text{small}$ for $r > \sigma$

$$\therefore \int_0^\sigma r^2 dr + \int_0^\infty r^2 (1 - e^{-E/k_B T}) dr = \frac{1}{3} \sigma^3 + \int_0^\infty \frac{\sigma^2 E dr}{k_B T}$$

$$\therefore \boxed{PV = RT + \frac{RT}{V} \left(b - \frac{a}{RT} \right)} \quad \text{with}$$

$$\boxed{b = \frac{2}{3} N \pi \sigma^3} \\ \boxed{a = -2\pi N^2 \int_0^\infty E \sigma^2 dr}$$

Note that "b" is identical to VW constant and "a" is positive (as E is negative). Thus the second virial coefficient obtained from virial theorem is $\frac{RT}{V} \left(b - \frac{a}{RT} \right)$

from VW equation $\left(p + \frac{a}{V^2} \right) (V - b) = RT$ we have

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

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

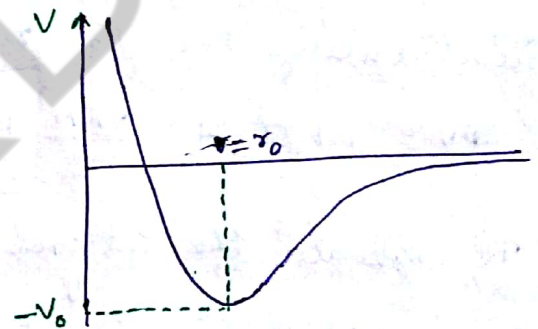
This equation agrees with the earlier obtained expression (using virial theorem) upto second virial coefficient. Third virial coefficient isn't correct & do not agree with Clausius' virial theorem. So VW equation is theoretically correct upto $\frac{1}{V}$ term & no further.

Nature of molecular force

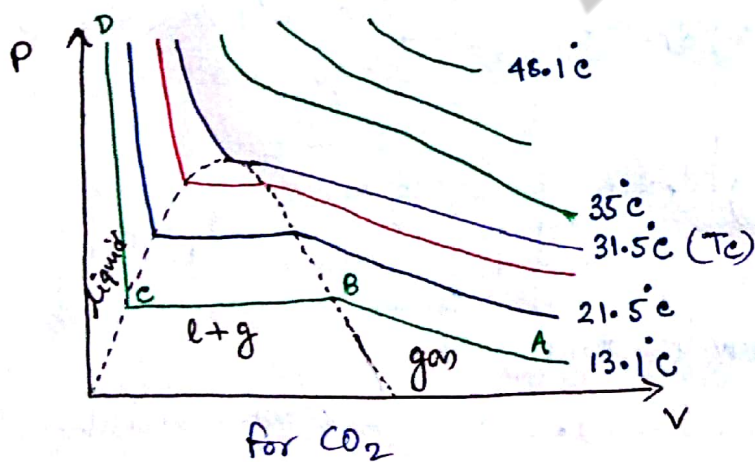
The force of interaction between the molecules of a gas is a very complicated phenomena. It is found that the force is attractive when the molecules are far apart & strongly repulsive when they are closeby. Lennard & Jones showed by taking fluctuating dipole-dipole interaction that the P.E. without any charge is

$$V(r) = -\frac{A}{r^6} + \frac{B}{r^{12}}$$

where r is intermolecular distance and A & B are constants.



Andreev's Experiments & inferences



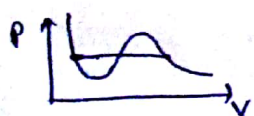
Isothermals:

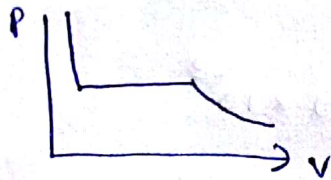
- AB \rightarrow P increases, v decreases
- BC \rightarrow v decreases without P changing (Lever rule)
- CD \rightarrow almost negligible change of V , P shoots up

"Critical Opalescence" 1910
Einstein's final theoretical investigation on Brownian motion.

liquefaction of gas. Vanderwaal's equation gives a curve as

Thomson hypothesized but Maxwell's construction was

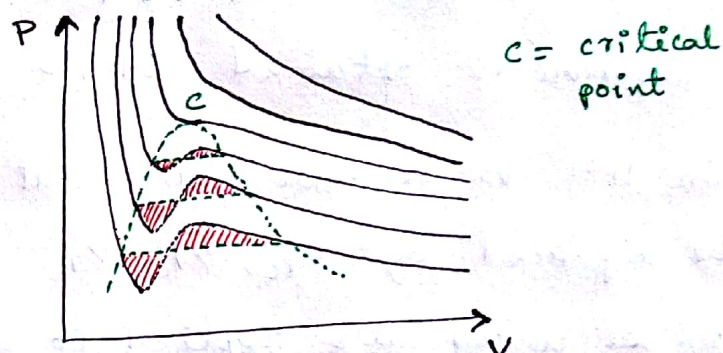
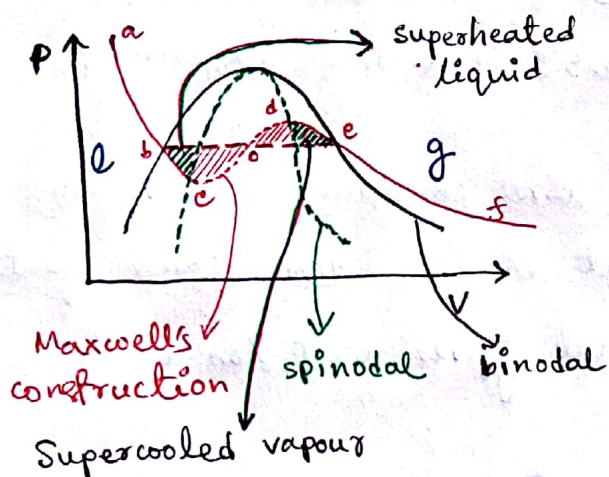




so that ambiguity can be removed, $\frac{\partial P}{\partial V} > 0$.

$$(P + \frac{a}{V^2})(V-b) = RT \Rightarrow P = \frac{RT}{V-b} - \frac{a}{V^2}$$

$$\text{or } \frac{dP}{dV} = -\frac{RT}{(V-b)^2} + \frac{2a}{V^3}, \quad \frac{\partial^2 P}{\partial V^2} = -\frac{2RT}{(V-b)^3} - \frac{6a}{V^4}$$



Critical constants & the law of corresponding states

From pictures above we find that there are three points b, c, e where P is same for three values of V which becomes one at point C. So the temperature at which maximum & minimum coalesce is the critical temperature & corresponding pressure & volume is the critical pressure & critical volume. To evaluate P_c, V_c, T_c we see that at C, $\frac{\partial P}{\partial V} = 0$

Equation for the points of maxima-minima (dotted graph) is

$$\frac{RT}{(V-b)^2} = \frac{2a}{V^3} \quad \text{or} \quad T = \frac{2a(V-b)^2}{RV^3} \quad \text{--- (1)}$$

$$\therefore P = \frac{R}{V-b} \cdot \frac{2a(V-b)^2}{RV^3} - \frac{a}{V^2} = \frac{2a(V-b)}{V^3} - \frac{a}{V^2} \quad \text{--- (2)}$$

$$\text{At the critical point, } \left. \frac{dP}{dV} \right|_{V=V_c} = 0 = \frac{2a}{V_c^3} - \frac{6a(V_c-b)}{V_c^4} + \frac{2a}{V_c^3}$$

$$\text{or, } 2aV_c - 6aV_c + 6ab + 2aV_c = 0$$

$$\text{or } \boxed{V_c = 3b}$$

$$\text{from (1), } T_c = \frac{2a \cdot 4b^2}{R \times 27b^3} = \frac{8a}{27Rb}$$

$$\text{or } \boxed{T_c = \frac{8a}{27Rb}}$$

$$\text{from (2), } P_c = \frac{2a \times 2b}{27b^3} - \frac{a}{3b^2} = \frac{a}{27b^2}$$

$$\text{or } \boxed{P_c = \frac{a}{27b^2}}$$

At 1 cc at STP, $a = 0.00874 \text{ atm-cm}^6$, $b = 0.0023 \text{ cc}$ for CO_2
($T = 273\text{K}$), $P = 1\text{atm}$, $V = 1\text{cc}$.

Using VW equation $(P + \frac{a}{V^2})(V-b) = RT$,

$$(1 + \frac{0.00874}{1^2})(1 - 0.0023) = 273R, \therefore R = 3.687 \times 10^{-3}$$

$$\therefore T_c = \frac{8a}{27Rb} = \frac{8 \times 0.00874}{27 \times 3.687 \times 10^{-3} \times 0.0023} = 305.5^\circ K = 32.5^\circ C.$$

Experiments obtained $31.1^\circ C$ & $30.9^\circ C$ (Andrews experiment).

In 1881, van der Waal found that the three constants a, b, R can be replaced by $P/P_c, V/V_c, T/T_c$ so that the non-dimensional equation can be universally applied to all real gases that has an indicator diagram of VW.

If $P/P_c = P^*, V/V_c = V^*, T/T_c = T^*$ are reduced (P, V, T) then

$$(P + \frac{a}{V^2})(V-b) = RT \Rightarrow (P^*P_c + \frac{a}{V_c^2 V^{*2}})(V^*V_c - b) = RT_c T^*$$

$$\text{Substituting } P_c, V_c, T_c, \left(\frac{a}{27b^2} P^* + \frac{a}{9b^2 V^{*2}}\right)(3bV^* - b) = RT^* \frac{8a}{27Rb}$$

$$\therefore \boxed{\left(P^* + \frac{3}{V^{*2}}\right)\left(V^* - \frac{1}{3}\right) = \frac{8}{3} T^*}$$

The states of two substances for which their values of (P^*, V^*, T^*) are equal are called "corresponding states". Clearly critical states of all bodies are their corresponding states. If two reduced parameters of any two substances are same, then the third reduced parameter must be identical for them. This is called the "law of corresponding states".

$$(P^*)_{CO_2} = (P^*)_{SO_2} \text{ \& } (V^*)_{CO_2} = (V^*)_{SO_2} \text{ then } (T^*)_{CO_2} = (T^*)_{SO_2}$$

- HW**
1. Calculate VW constants " a " and " b " for a gm-mole of He gas using $T_c = 5.3 K$, $P_c = 2.25 \text{ atm}$ & $R = (273)^{-1} \text{ litre atmosphere } ^\circ$.
 2. Calculate P_c & T_c of He gas using $a = 6.15 \times 10^{-5} \text{ atm-cm}^6$, $b = 9.95 \times 10^{-6} \text{ cc per gm-molecule}$, where pressure is 1 atm & volume is volume of gas at S.T.P.