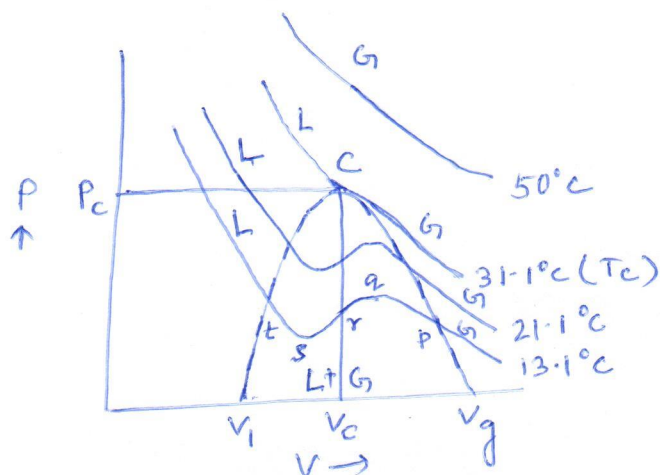


Critical phenomena and Vander Waals equation:

The VDW Equn: for 1 mole gas : $P = \frac{RT}{V-b} - \frac{a}{V^2}$

Taking the values of a and b for CO_2 , it is possible to collect data P and V at temps 13.1°C , 21.1°C , 31.1°C and 50°C and to draw the similar isotherms like that of Andrews. These curves can be called Vander Waals isotherms.



The experimental Andrews isotherms coincide with the Vander Waals isotherms in all the points except the region where the gas and liquid are co-existing. The horizontal lines are replaced by wavy lines.

$$T_c = 31.1^\circ\text{C}, P_c = 72.9 \text{ atm}$$

$$V_c = 94.2 \text{ cc/mol}$$

(VDW isotherm for 1 mole CO_2)

These wavy portion of Vander Waals curves poses two limitations of the VDWE which are not realized in practice. The isotherm, $pqrst$ shows that there are three volumes of the system at a given T and P . Again at the portion srq , it shows that with increase of p , vol. is also increased. These two points show the limitations of VDWE. However, pq and ts may be considered to represent the super saturation and unsaturation of the system.

With increase of temperature, the minimum and maximum points come close to each other and at the critical point, both coalesce. The slope and curvature both are zero at the point. That is

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

Relation between critical constants (P_c , V_c and T_c) and Vander Waals constants (a and b) :-

Differentiating VDWE, $P = \frac{RT}{V-b} - \frac{a}{V^2}$ with respect to V at constant T , we get the slope, $\left(\frac{\partial P}{\partial V}\right)_T = -\frac{RT}{(V-b)^2} + \frac{2a}{V^3}$

and the curvature, $\left(\frac{\partial^2 P}{\partial V^2}\right)_T = \frac{2RT}{(V-b)^3} - \frac{6a}{V^4}$

But, at the critical state, $\left(\frac{\partial P}{\partial V}\right)_T = 0$ and $\left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0$,

and $T = T_c$, $V = V_c$

Putting, we get, $\frac{RT_c}{(V_c-b)^2} = \frac{2a}{V_c^3}$ and $\frac{2RT_c}{(V_c-b)^3} = \frac{6a}{V_c^4}$.

Solving the two equations, we get,

$$V_c = 3b \quad \text{and} \quad T_c = \frac{8a}{27Rb}$$

Again, VDWE at the critical point, $P_c = \frac{RT_c}{V_c-b} - \frac{a}{V_c^2}$

Inserting the value of T_c and V_c , we have, $P_c = \frac{a}{27b^2}$

Thus, the relation between critical constants and VDW const. are

$$V_c = 3b, \quad T_c = \frac{8a}{27Rb}, \quad \text{and} \quad P_c = \frac{a}{27b^2}$$

One property of the gas is critical coefficient, $\frac{RT_c}{P_c V_c}$.

$$\text{Putting } V_c, P_c \text{ and } T_c, \quad \frac{RT_c}{P_c V_c} = \frac{8}{3} = 2.66.$$

Thus, critical coefficient is predicted const. for all VDW gases.

The value of compressibility factor at the critical state,

$$Z_c = \frac{P_c V_c}{R T_c} = \frac{3}{8} \text{ and it is less than 1.}$$

This implies that at the critical state the gas is more compressible.

These values are tested experimentally whether the critical coefficient is const and $= \frac{8}{3}$ for all gases but it is found that it varies from gas to gas and the ~~$Z_{c, \text{Arg}} = 3.66$~~ the average value is about 3.66.

Unique application of these relations is the calculation of the VDW consts a and b .

$b = \frac{V_c}{3}$; V_c is avoided in the relation as it is not easily determined experimentally.

V_c is replaced by using the value of critical coefficient,

$$V_c = \frac{3}{8} \frac{R T_c}{P_c}$$

Therefore, VDW constants are, $b = \frac{1}{8} \frac{R T_c}{P_c}$

$$\text{and } a = \frac{27}{64} \frac{R^2 T_c^2}{P_c}$$

The critical constants of a gas can be determined experimentally and so the values of the VDW constants, a and b can be calculated.

Reduced form of VDW eqn. of state:

VDWE can be expressed in terms of their reduced variables in stead of T, P and V . The reduced variables are defined as the actual variables divided by the corresponding critical const.s.

Thus, reduced Pr., $\pi = \frac{P}{P_c}$

reduced Temp., $\theta = \frac{T}{T_c}$ and reduced vol. $\phi = \frac{V}{V_c}$

Replacing P, V , and T in the VDWE by corresponding reduced variables, we have

$$\left[\pi P_c + \frac{a}{(\phi V_c)^2} \right] (\phi V_c - b) = R \theta T_c$$

Inserting the value of critical const.s, $V_c = 3b$, $T_c = \frac{8a}{27Rb}$ and $P_c = \frac{a}{27b^2}$ in the above eqn., we get the reduced form of VDWE : $\left(\pi + \frac{3}{\phi^2} \right) (3\phi - 1) = 8\theta$

The important feature of the eqn. is that it is independent of VDW const.s, a and b . Thus, it appears that the eqn. is independent of the nature of the gas and general as it is in ideal gas eqn. But it is not true. The characteristic gas const.s now remain in disguise within the reduced variables (π, ϕ , and θ) as these variables contain critical constants (P_c, V_c and T_c) and these are characteristic const.s. of the gas. Thus, it is not that generality lost in VDWE is regained in this form.

Limitations of VDWE:

- ① The equn. predicts $V_c = 3b$ but the mean value is $V_c = 2b$
- ② VDWE suggests, $\frac{RT_c}{P_c V_c} = \frac{8}{3} = 2.66$, but the average value is 3.66.
- ③ $\frac{T_D}{T_c} = \frac{27}{8} = 3.375$, but the value is 2.98.

So, we can conclude that VDWE explains the behavior of the real gas qualitatively but it fails to explain quantitatively.

Kammerlingh - Onnes Virial Equation:

The equn. of state of a gas can be satisfactorily expressed as a power series of vol. or pr. as suggested by H. Kammerlingh - Onnes in 1901 as,

$$PV = RT \left[1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \dots \right]$$

$B = 2^{\text{nd}}$ virial coefficient and is most important in the expression.

B, C, D is the virial coefficients and dependent on T and on the nature of the gas, their values are small in magnitude. virial equn. as power series of P is given by

$$PV = RT [1 + B_1 P + C_1 P^2 + D_1 P^3 + \dots]$$

VDWE of real gas can be recast in virial form as follows;

$$P = \frac{RT}{V-b} - \frac{a}{V^2} \Rightarrow PV = \frac{RTV}{V-b} - \frac{a}{V}$$

$$\Rightarrow PV = \frac{RT}{(1-\frac{b}{V})} - \frac{a}{V}$$

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

$$\text{or } PV = RT \left(1 + \frac{b}{V} + \frac{b^2}{V^2} + \frac{b^3}{V^3} + \dots\right) - \frac{a}{V}$$

$$\approx RT \left(1 + \frac{b}{V}\right) - \frac{a}{V} \approx RT + RT \left(b - \frac{a}{RT}\right) \frac{1}{V}$$

So, the virial form of VDWE as power series of v is

$$Z \approx 1 + \left(b - \frac{a}{RT}\right) \frac{1}{v}$$

The 2nd virial coefficient, $B = b - \frac{a}{RT}$.

Thus, evaluation of B is possible from a and b .

At the Boyle temp, T_B , $B = 0$, Thus, $b - \frac{a}{RT_B} = 0$

$$\text{or } T_B = \frac{a}{Rb}$$

Therefore, the virial form of the VDWE can produce the expression of T_B .

The above virial form can easily be expressed as power series of P by replacing $v = \frac{RT}{P}$ (taking approximation for small term).

So the form is,
$$Z = 1 + \frac{1}{RT} \left(b - \frac{a}{RT}\right) P$$

A more rigorous mathematical treatment can be exercised to get a form consisting of 3rd virial coefficient. This form is

$$Z = 1 + \frac{1}{RT} \left(b - \frac{a}{RT}\right) P + \frac{a}{(RT)^3} \left(2b - \frac{a}{RT}\right) P^2$$

It can be shown that the 2nd virial coefficient is -ve, while 3rd virial coefficient is +ve.

Thus, when P is low, 2nd term dominates and Z decreases with increase of P but when P is high, the 3rd term dominates and Z increases with the increase of P in the Z vs. P diagram.

A complete description of Z vs. P curve is obtained by this virial form of VDWE. More accurate form of VDWE is

$$Z = 1 + \frac{1}{RT} \left(b - \frac{a}{RT}\right) P + \frac{a}{(RT)^3} \left(2b - \frac{a}{RT}\right) P^2 + \frac{aP^2}{(RT)^4} \left[3b^2 - \frac{2a^2}{(RT)^2}\right]$$

