

Lecture 15

In this lecture we will cover the following topics:

1. Virial equation
2. Temperature dependence of B
3. van der Waals equation better than ideal gas equation
4. Limitations of van der Waals equation and possible reasons
5. Comparison between van der Waals and Dieterici equation
6. Further improvement of equation

Virial equation:

Kammerlingh-Onnes suggested that $p V$ can be expressed in terms of volume as follows:

$$p V = R T \left(1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \dots \right) \quad \dots \quad (A)$$

Limiting upto the second term,

$$p V = R T + R T \times \frac{B}{V} \quad \dots \quad (B)$$

van der Waals equation

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

$$p = \frac{R T}{V - b} - \frac{a}{V^2}$$

$$= \frac{R T}{V} \times \frac{V}{V - b} - \frac{a}{V^2}$$

$$= \frac{R T}{V} \times \left(1 - \frac{b}{V} \right)^{-1} - \frac{a}{V^2}$$

$$\Rightarrow p V = R T \times \left(1 - \frac{b}{V} \right)^{-1} - \frac{a}{V}$$

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

$$(1 - x)^{-1} = 1 + x + x^2 + x^3 + \dots$$

$$(1 + x)^{-1} = 1 - x + x^2 - x^3 + \dots$$

Limiting upto the second term,

$$\begin{aligned} p V &= R T \times \left(1 + \frac{b}{V}\right) - \frac{a}{V} \\ &= R T + R T \times \left(b - \frac{a}{R T}\right) \times \frac{1}{V} \end{aligned}$$

Comparing the above equation with equation (B) we get,

$$B = b - \frac{a}{R T}$$

Thus it is possible to calculate the value of B from van der Waals constants.

Dieterici equation:

$$\begin{aligned} p &= \frac{R T}{V - b} \times e^{-\frac{a}{R T V}} \\ \Rightarrow p &= \frac{R T}{V} \times \left(1 - \frac{b}{V}\right)^{-1} \times e^{-\frac{a}{R T V}} \\ \Rightarrow p V &= R T \left(1 + \frac{b}{V} + \frac{b^2}{V^2} + \dots\right) \left(1 - \frac{a}{R T V} + \dots\right) \\ &= R T \left[1 + \left(b - \frac{a}{R T}\right) \times \frac{1}{V} - \left(\frac{a b}{R T V^2} + \frac{b}{V^2}\right) + \dots\right] \\ \Rightarrow p V &\simeq R T + \frac{R T}{V} \times \left(b - \frac{a}{R T}\right) \end{aligned}$$

Again comparing the above equation with equation (B), we get,

$$B = b - \frac{a}{R T}$$

Question: Calculate the expression of B from Berthelot's equation: $(p + \frac{a}{TV^2})(V - b) = RT$

Value of B for some gases at 0 °C (in cc/mol unit)

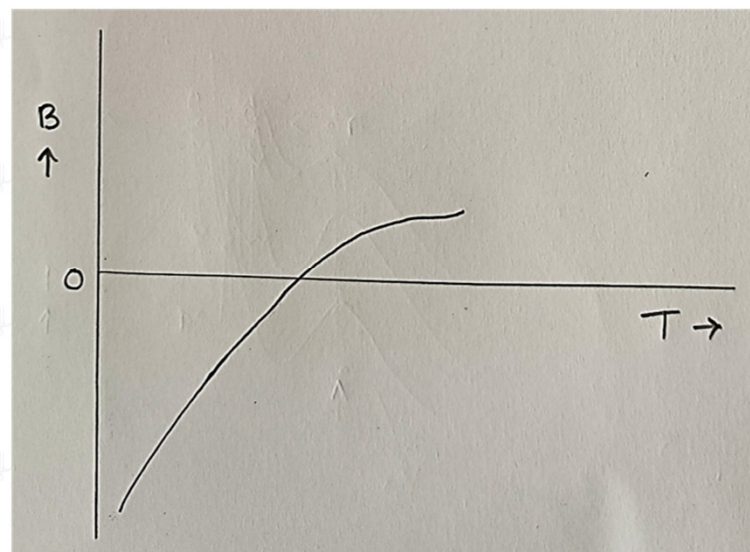
He \rightarrow 12.0 , Ar \rightarrow (-) 21.7 , H₂ \rightarrow 13.7 etc.

Temperature variation of B: (For Ar)

T (K)	85	100	150	200	250	300	400	500	600	1000
B (cc/mol)	- 251	- 184	- 86	- 47	- 28	- 16	- 1	7	12	22

When we plot:

	H ₂	O ₂	N ₂
a (atm L ² mol ⁻²)	0.244	1.36	1.39
b (L mol ⁻¹)	0.027	0.032	0.039



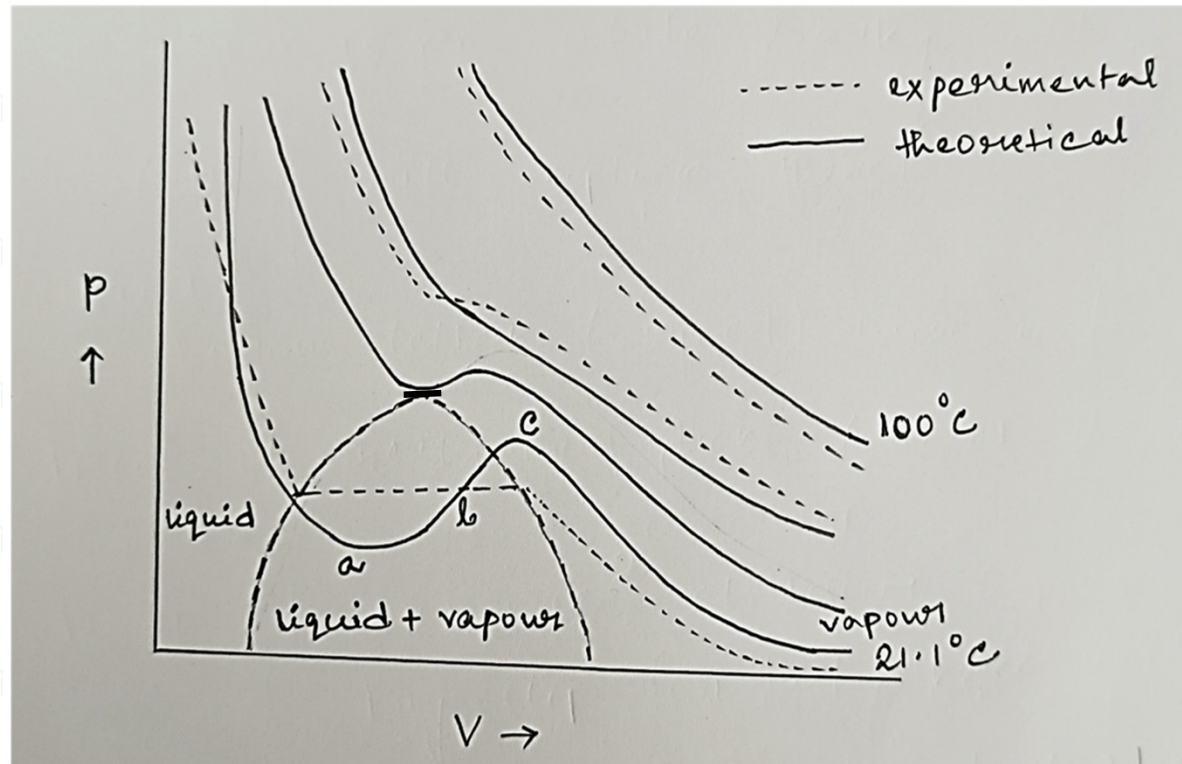
Validity of van der Waals equation:

At higher temperature, both experimental and theoretical curves match quite well with each other.

However, below critical temperature there appears deviation between theoretical and experimental results. For example, at 21.1°C , on going from a to b to c, both pressure and volume increases. This phenomenon can't be achieved experimentally. Thus we observe a plateau.

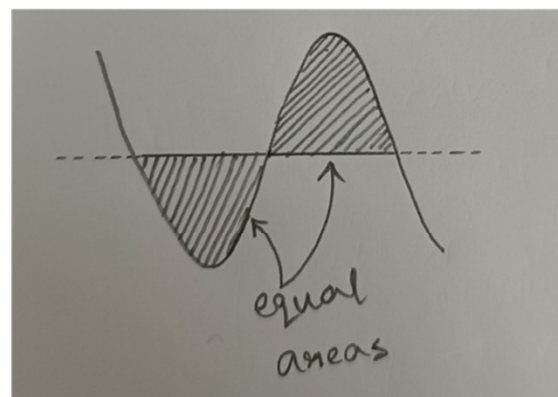
The van der Waals fails to explain experimental observation very accurately at lower temperature.

\Rightarrow For CO_2



Actually since both pressure and volume can't increase simultaneously, so the loops (see the figure beside) are replaced by a straight line so that area below and above the line is equal.

These loops are known as van der Waals loops.



Gas	Temperature	Observed pressure (atm)	Pressure using ideal equation (atm)	Pressure using van der Waals equation (atm)
H ₂	100 °C	75	72.3	75.7
		100	95.0	100.8
CO ₂	100 °C	75	92.3	73.2
		100	133.5	95.8

Limitations of van-der Waals equation:

- 1) van der Waals curve does not represent real experimental situation much below T_c .
- 2) a and b values are not the same for each gas. Even for same gas the magnitude of a and b vary with temperature.
- 3) According to van der Waals equation, ' b ' is equal to four times the volume of one molecule, but in reality the value is nearly $4\sqrt{2}$ times.

- a) Magnitude of intermolecular forces vary in complex manner both with temperature and pressure. But in van der Waals equation, only first order terms are considered for entire range of pressure and temperature.
- b) van der Waals equation does not consider the existence of a threshold velocity necessary to overcome the attractive force and hit the wall. Molecules having low velocity may not overcome attractive force and hit the wall.
- c) van der Waals equation considered only binary collision but at high pressure / low volume / low temperature conditions ternary collisions do take place.

Comparison between van der Waals equation and Dieterici equation:

Parameters	Experimental value (average)	Van der Waals	Dieterici
$\frac{V_c}{b}$	2.0	3.0	2.0
$\frac{R T_c}{p_c V_c}$	3.6	2.66	3.695
$\frac{T_B}{T_c}$	2.98	3.375	4.0

The constants 'a' and 'b' can be expressed in terms of critical constants. For different equations these expressions are different and tabulated below:

Equations	a	b
van der Waals	(i) $3 p_c V_c^2$ (ii) $\frac{27}{64} \frac{R^2 T_c^2}{p_c}$	(i) $\frac{1}{3} V_c$ (ii) $\frac{1}{8} \frac{R T_c}{p_c}$
Dieterici	(i) $2 R T_c V_c$ (ii) $e^2 p_c V_c^2$	(i) $\frac{1}{2} V_c$ (ii) $\frac{1}{e^2} \times \frac{R T_c}{p_c}$

In summary, van der Waals equation is a much simpler equation of state (in comparison to Dieterici or Berthelot's equations) and can be used with a fair amount of accuracy to understand the behaviour of real gases. However, at very high pressure, van der Waals equation yields erroneous results.

Further improvement:

A more accurate two parameter equation of state for gases is the [Redlich-Kwong equation](#) that has the following functional form:

$$\left[p + \frac{a}{\bar{V}(\bar{V}+b) T^{\frac{1}{2}}} \right] (\bar{V} - b) = R T$$

This equation is useful for a very wide range of p and T.