

Lecture 12

In this lecture we will cover the following topics:

1. Volume correction
2. Pressure correction
3. van der Waals equation* and slope based understanding
4. Super-saturated, Super-cooled & Super-heated, vapour and liquid
5. Continuity of states
6. Critical state
7. Estimation of V_m
8. Estimation of p_c , V_c , T_c , $\frac{R T_c}{p_c V_c}$
9. Supercritical fluid
10. Home Task

* Named after Johannes Diderik van der Waals

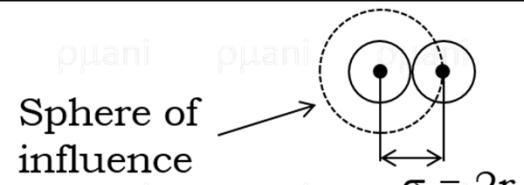
Volume correction:

For each molecule unavailable space = $\frac{1}{2} \times \frac{4}{3} \pi \sigma^3$

$$= \frac{2}{3} \pi (2r)^3 = 4 \times \frac{4}{3} \pi r^3 = 4 b_1$$

⇒ For one mole of gas unavailable space = $b = N_A \times 4 b_1$

(Note: Depends on molecular property -Different for different molecules)



Pressure correction:

Number of molecules striking the wall \propto density of gas molecule (ρ)

Net attractive pull inward \propto density ($= \frac{\text{number}}{\text{unit volume}}$) of gas molecule (ρ)

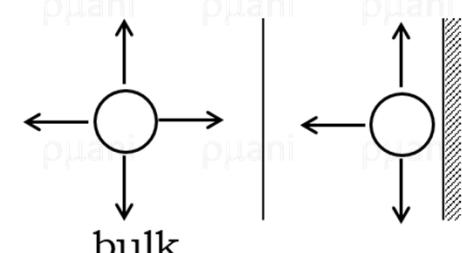
So, net attractive pull (p_i) $\propto \rho^2 \propto \frac{1}{V^2}$

$$\Rightarrow p_i = \frac{a}{V^2} \quad [\text{where } a \text{ is a proportionality constant, depends on molecular properties}]$$

$$\Rightarrow \text{Ideal pressure } (p_{id}) = p_{obs} + p_i = p_{obs} + \frac{a}{V^2}$$

Now, $p V = R T$ (for 1 mole)

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



The van der Waals equation

J. D. van der Waals in 1873 put forward the following equation:

$$p = \frac{n R T}{V - n b} - a \left(\frac{n}{V}\right)^2 \quad \dots \dots \dots \text{(A)}$$

Alternatively, dividing by n

$$p = \frac{p R T}{V_m - b} - \frac{a}{V_m^2} \quad \dots \dots \dots \text{(B)}$$

Justification:

Ideal/perfect gases are assumed to occupy zero volume. But real gases do occupy significant amount of volume. This means in comparison to perfect gases, real gases can occupy a volume ($V - n b$), where, ($n b$) is approximately the total volume occupied by n moles of molecules themselves.

$$p = \frac{n R T}{V - n b}$$

Can V be even smaller than b ?

Repulsive interaction between molecules are taken into account by supposing the molecules behaving as small and impenetrable spheres.

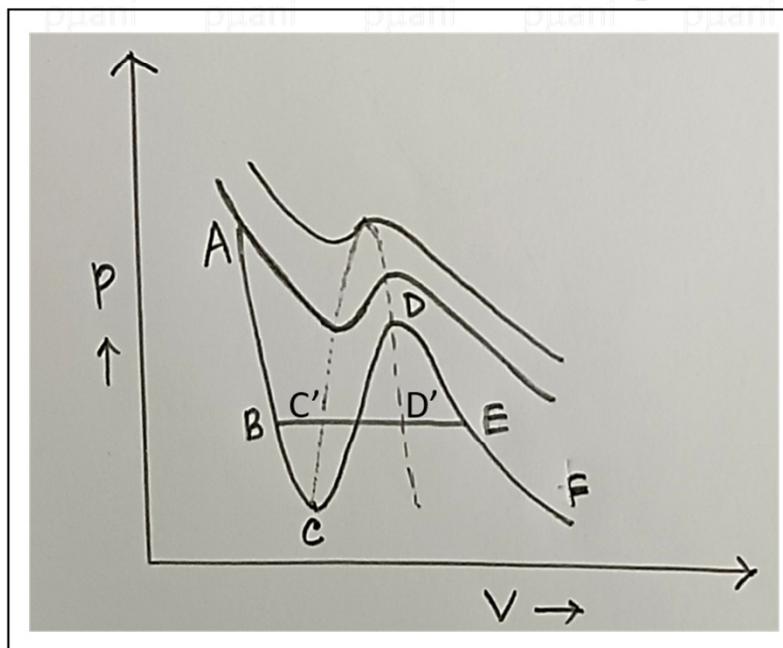
Pressure depends on both frequency of collision with the walls and the force of each collision. Both of the parameters are reduced by attractive forces, which act with a strength proportional to molar concentration $\left(\frac{n}{V}\right)$

The pressure is reduced in proportion to the square of this concentration.

If the reduction of pressure is written as $P = \frac{nRT}{V-nb} - a\left(\frac{n}{V}\right)^2$ [where 'a' is a positive constant, characteristic of each gas]

Thus,
$$P = \frac{nRT}{V-nb} - a\left(\frac{n}{V}\right)^2$$

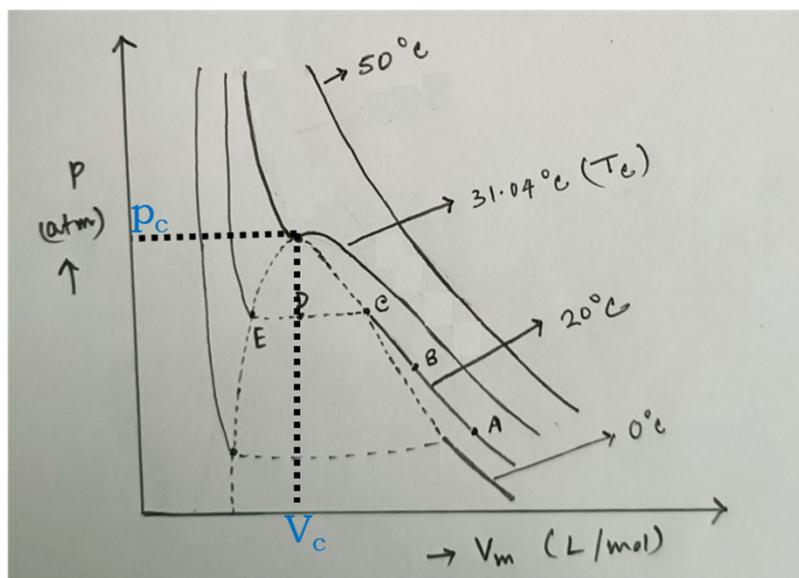
⇒ This is the mathematical formulation of van der Waals equation.



[Slope based understanding of van-der Waals equation (at very low V and very high V region) → will be discussed later].

Critical constants:

When the temperature is low, then with the increase of pressure, at certain point liquid condensation starts from gas and a clearly visible distinguishing surface appears. At a higher temperature, the surface separating the two phases does not appear. This means the length of the horizontal line decreases and merges to a point. This point is known as critical point of the gas.

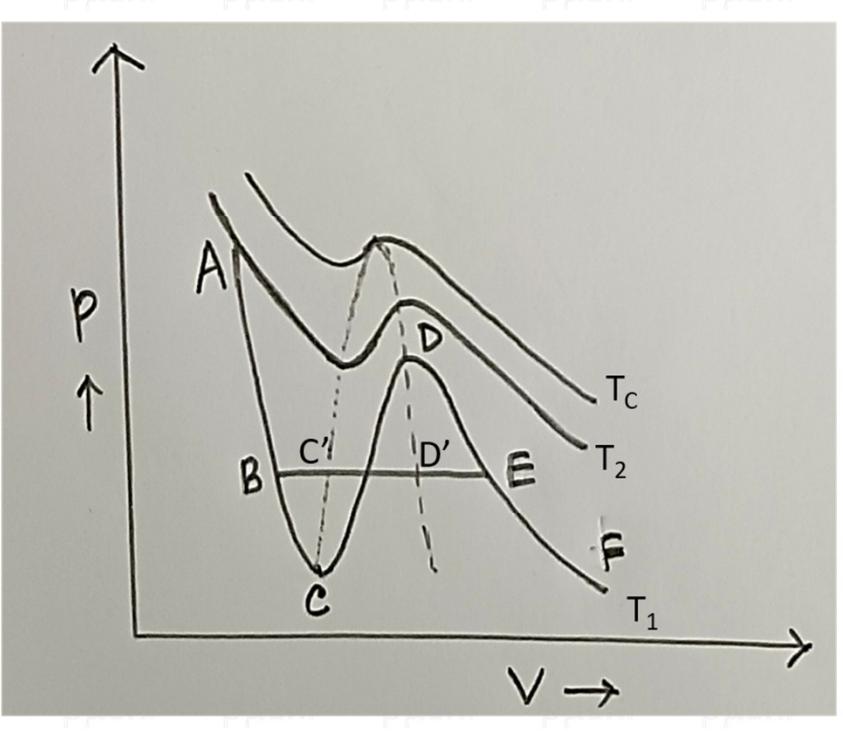


Corresponding temperature, molar volume, pressure are known as **critical temperature (T_c)**, **critical molar volume (V_c)** and **critical pressure (p_c)**.

Above T_c the system remains always in gas phase, no matter what the pressure is. Liquid phase of a substance doesn't appear above critical temperature.

T_c for oxygen is 154.8 K means it is impossible to obtain liquid oxygen by compression alone if the temperature of the system is greater than 154.8 K. In other words, to liquefy it i.e. to obtain a fluid phase that does not occupy the entire volume, the temperature must be lowered below 154.8 K.

Concept of Supersaturated, Supercooled, and Superheated liquid and vapour:



ABCDEF → Plot as per van der Waals eqn. (Theoretical)

ABC'D'EF → Experimentally obtained plot.

BC, DE → Can be attained experimentally, though difficult.

CD → Experimentally not possible.

DE → Supersaturated vapour

BC → Supersaturated liquid

DE → Supercooled vapour

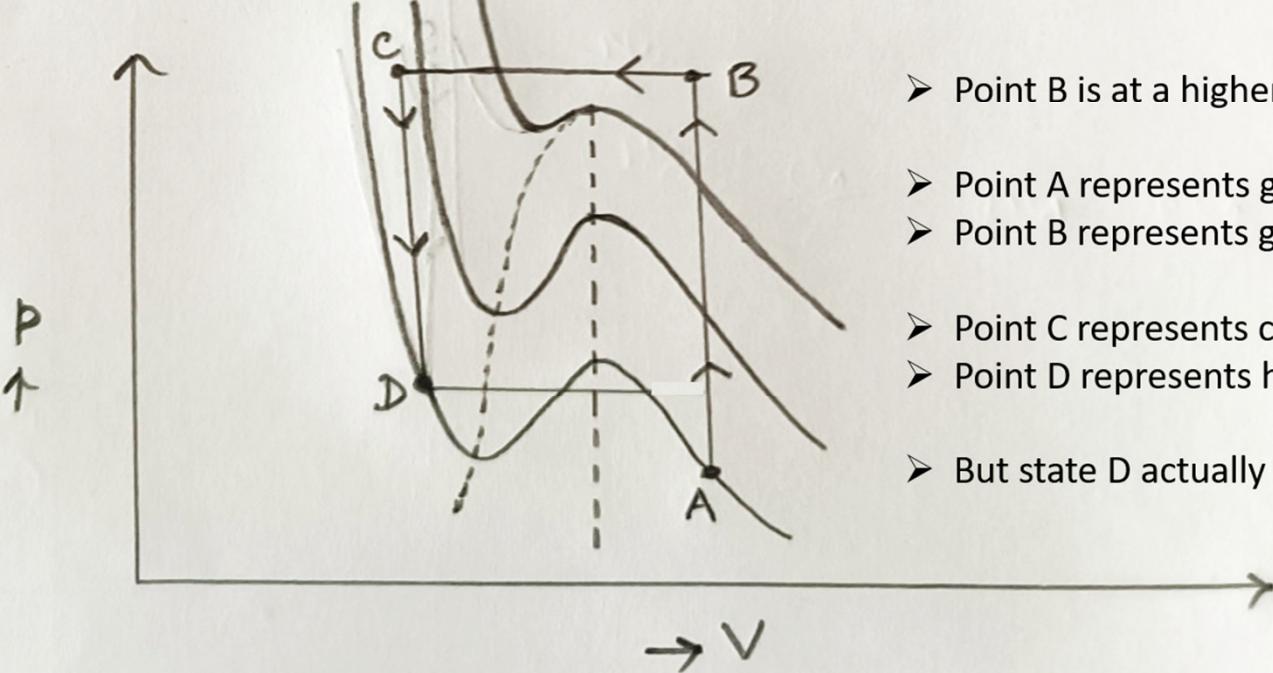
BC → Superheated liquid

The liquid should boil at the point B under the given pressure at the temperature T_1 , but in the region BC the system still remains in the liquid state. Moreover, temperature at each point on the BC line should normally exist on the isotherms of lower temperature, but in fact they actually present on the theoretical curve at a higher temperature. Thus, the state of the system corresponding to line BC represents the “superheated liquid”.

Similarly, the state of the system corresponding to line DE represents the “supercooled vapour”.

Continuity of state:

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- Point B is at a higher temperature ($>T_c$) than for point A ($<T_c$).
- Point A represents gas/vapour state
- Point B represents gas/vapour state
- Point C represents compressed gas/vapour.
- Point D represents highly compressed gas/vapour.
- But state D actually represents liquid state.

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- Thus, highly compressed gas = liquid state.
- Coinage of the term Fluid.

Estimation of molar volume of a van der Waals gas using the following equation:

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

$$\Rightarrow p = \frac{RT V_m^2 - a V_m + a b}{(V_m - b) \times V_m^2}$$

$$\Rightarrow p V_m^3 - p b V_m^2 = R T V_m^2 - a V_m + a b$$

dividing by p

$$\Rightarrow V_m^3 - \left(b + \frac{R T}{p}\right) V_m^2 + \left(\frac{a}{p}\right) V_m - \frac{a b}{p} = 0$$

This is a cubic equation w.r.t. V_m .

When 'a' and 'b' values are known (as well as p and T), then by solving the above equation, it is possible to calculate V_m . ('a' and 'b' are empirical parameters instead of precisely defined molecular properties).

Question. Estimate the molar volume of CO_2 at 500 K and 100 atm considering it as van der Waals gas.

$$a = 3.640 \text{ atm L}^2 \text{ mol}^{-2}$$

$$b = 4.267 \times 10^{-2} \text{ L mol}^{-1}$$

Answer: $V_m = 0.370 \text{ L/mol}$

Slope based understanding of the plot based on van der Waals equation:

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

$$\left(\frac{\delta p}{\delta V}\right)_T = (-) \frac{RT}{(V-b)^2} + \frac{2a}{V^3}$$

Relative magnitude of $\left|\frac{RT}{(V-b)^2}\right|$ and $\left|\frac{2a}{V^3}\right|$ will dictate the magnitude of slope [(+)ve or (-)ve]

- (a) When T is high, V is very small : Then the first term is $>>$ in magnitude than the second term. Thus, the slope is (-) ve but magnitude is large.
- (b) When T is high and V is large : Then the first term is $>$ in magnitude than the second term. Thus, the slope is (-) ve but magnitude is small. (At higher volume the second term falls off more rapidly than the first term)
- (c) Intermediate volume section is **complicated**.

Cubic equation leading to three roots of V, one maximum, one minimum and the third root lies in the region where $V < b$, which is physically not feasible. (V is 30 times b).

Question: How will you explain Amagat's plot using van der Waals equation?

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

$$\Rightarrow pV - pb + \frac{a}{V} - \frac{ab}{V^2} = RT$$

Estimation of critical constants from van-der Waals equation

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

$$\Rightarrow \left(\frac{\delta p}{\delta V}\right)_T = -\frac{RT}{(V-b)^2} + \frac{2a}{V^3} \quad \dots \dots \dots \text{(i)}$$

$$\text{and } \left(\frac{\delta^2 p}{\delta V^2}\right)_T = \frac{2RT}{(V-b)^3} - \frac{6a}{V^4} \quad \dots \dots \dots \text{(ii)}$$

By definition [vide calculus class], at the critical point both $\left(\frac{\delta p}{\delta V}\right)_T$ and $\left(\frac{\delta^2 p}{\delta V^2}\right)_T$ are zero

$$\text{i.e. } \frac{RT_c}{(V_c-b)^2} = \frac{2a}{V_c^3} \quad \dots \dots \dots \text{(iii)}$$

$$\text{and } \frac{2RT_c}{(V_c-b)^3} = \frac{6a}{V_c^4} \quad \dots \dots \dots \text{(iv)}$$

dividing equation (iv) by equation (iii)

$$\Rightarrow \frac{2}{V_c-b} = \frac{3}{V_c} \Rightarrow \boxed{V_c = 3b}$$

$$\text{From equation (iii), } \frac{RT_c}{(3b-b)^2} = \frac{2a}{(3b)^3}$$

$$\Rightarrow T_c = \frac{2a \times 4b^2}{R \times 27b^3} \Rightarrow \boxed{T_c = \frac{8a}{27Rb}}$$

$$p_c = \frac{RT_c}{V_c-b} - \frac{a}{V_c^2} = R \times \frac{8a}{27Rb} \times \frac{1}{2b} - \frac{a}{9b^2}$$

$$p_c = \frac{8a - 6a}{54b^2}$$

$$\boxed{p_c = \frac{a}{27b^2}}$$

$$\boxed{\text{Critical coefficient} = \frac{RT_c}{p_c V_c} = 2.66}$$

Lecture 13

Explanation of Amagat's plot in terms of van der Waals equation

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

$$\Rightarrow p V_m = RT + p b - \frac{a}{V_m} + \frac{ab}{V_m^2}$$

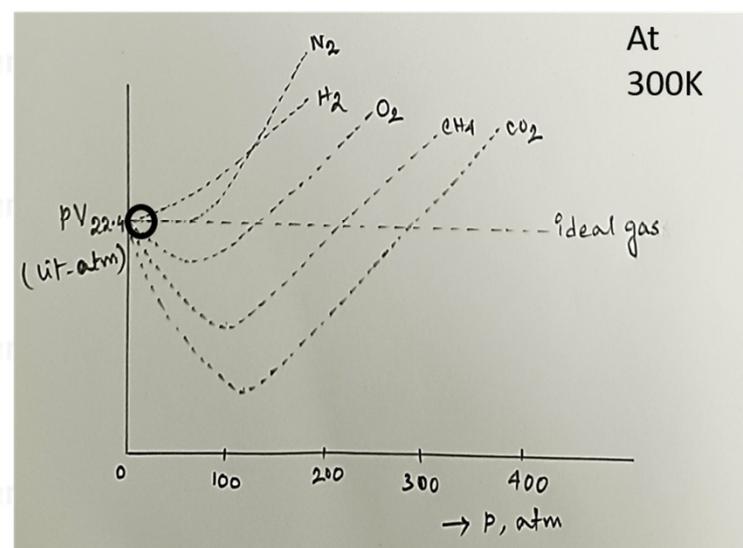
$$\Rightarrow p V_m \approx RT + p b - \frac{a}{V_m} \quad [a, b \text{ are small, so last term is neglected}]$$

$$\Rightarrow p V_m = RT + p b - \frac{a}{V_m}$$

Let us now consider four different cases observed for most of the gases.

- (i) At a very low pressure: Both (pb) and (a/V_m) can be neglected in comparison to RT .
- (ii) At low pressure: The term (a/V_m) increases more rapidly than (pb) , so pV_m decreases more and more from RT , thus the influence of (a/V_m) is higher than (pb) , and "a" is related to attractive pull, which means attractive pull operates even at low pressure, and at low pressure the distance between molecule is large, thus attraction can be considered as long range force.

Gas	a (lit ² atm mol ⁻²)	b (lit mol ⁻¹)
He	0.034	0.0237
H ₂	0.244	0.0266
N ₂	1.390	0.0391
O ₂	1.360	0.0318
Cl ₂	6.493	0.0562
NH ₃	4.17	0.0371



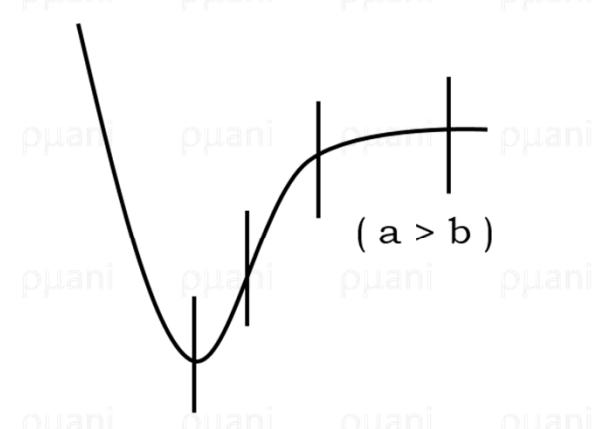
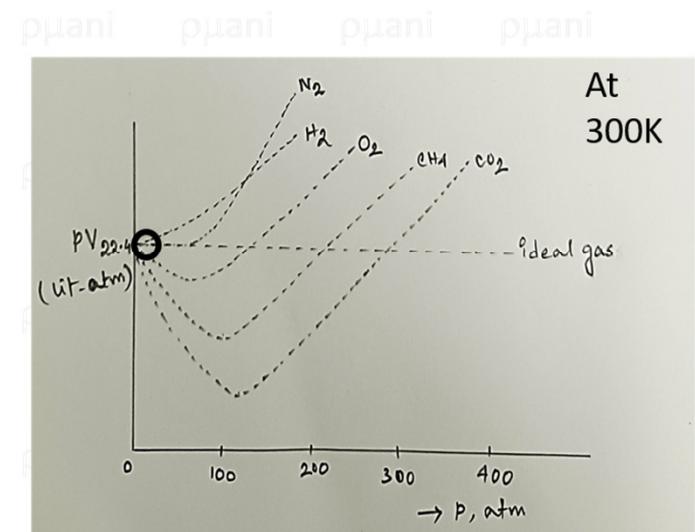
(iii) At moderately high pressure: In this range the gap between the molecules is small, hence increase in pressure does not increase much change in volume. This means, (pb) increases more rapidly than (a/V_m) , hence the curve exhibits positive slope after crossing the minimum till it crosses the magnitude of RT (when $(pb) = (a/V_m)$).

Intermolecular gap \sim molecular dimension ; $V \propto \frac{1}{p}$

(iv) At very high pressure: At very high pressure regime, the intermolecular separation is quite small and the magnitude of (a/V_m) is much smaller than (pb) . Under this circumstance repulsive interaction becomes more prominent than the attractive interaction. Thus, repulsion can be considered as a short range force. Thus, term "a" is related to attraction and term "b" is related to repulsion.

Thus, when attraction prevails the plot goes below the ideal gas line and when repulsion becomes more important then the plot shown positive deviation and ultimately goes above the ideal gas line.

For H_2 and He the intermolecular attraction is quite low. Hence even at low pressure and ordinary temperature, pV_m vs. p plot goes always above the ideal gas line.



Explanation of Amagat's plot in terms of van der Waals equation: Boyle temperature

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

$$\Rightarrow p V_m = RT + p b - \frac{a}{V_m} + \frac{ab}{V_m^2}$$

$$\approx p V_m \simeq RT + p b - \frac{a}{V_m} \quad [a, b \text{ are small, so last term is neglected}]$$

$$\Rightarrow p V_m = RT + p b - \frac{a}{V_m}$$

$$\Rightarrow Z = 1 + \frac{b}{V_m} - \frac{a}{V_m \times RT}$$

$$\Rightarrow Z = 1 + \left(b - \frac{a}{RT}\right) \times \frac{1}{V_m}$$

van der Waals equation reads as

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

$$\Rightarrow p V = \frac{RTV}{V - b} - \frac{a}{V}$$

$$\left(\frac{\delta(pV)}{\delta p}\right)_T = \left[\frac{RT}{V - b} - \frac{RTV}{(V - b)^2} + \frac{a}{V^2} \right] \left(\frac{\delta V}{\delta p}\right)_T = \left[-\frac{RTb}{(V - b)^2} + \frac{a}{V^2} \right] \left(\frac{\delta V}{\delta p}\right)_T$$

Gas	a (lit ² atm mol ⁻²)	b (lit mol ⁻¹)
He	0.034	0.0237
H ₂	0.244	0.0266
N ₂	1.390	0.0391
O ₂	1.360	0.0318
Cl ₂	6.493	0.0562
NH ₃	4.17	0.0371

At Boyle temperature, $\left[\frac{\delta(pV)}{\delta p} \right]_T = 0$

$$\text{So, } \frac{a}{V^2} = \frac{RT_B b}{(V-b)^2} \quad [\text{as } \left(\frac{\delta V}{\delta p} \right)_T \neq 0]$$

$$\Rightarrow T_B = \frac{a}{Rb} \times \left(\frac{V-b}{V} \right)^2$$

As $p \rightarrow 0$, V is large, so $V-b \approx V$

$$\Rightarrow T_B = \frac{a}{Rb}$$

We know that, $T_C = \frac{8a}{27Rb}$

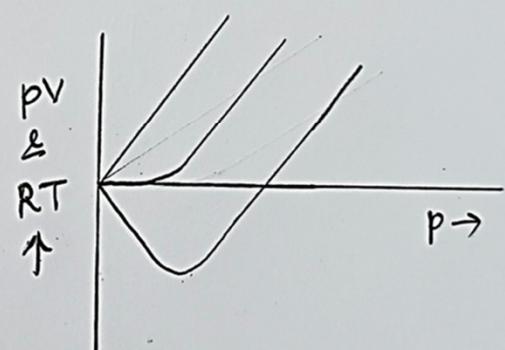
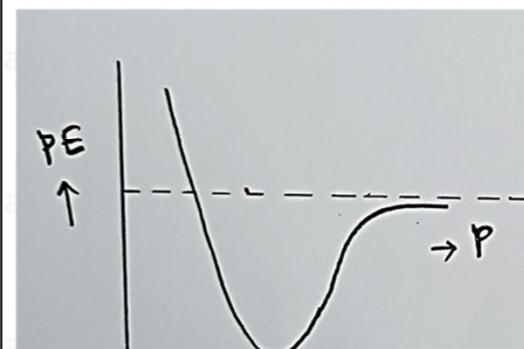
$$\Rightarrow \frac{T_B}{T_C} = \frac{8}{27} = 3.375$$

We know that at Boyle temperature,

real gas behaves like an ideal gas as $p \rightarrow 0$

i.e. at T_B and $p \rightarrow 0$, $\left[\frac{\delta(pV)}{\delta p} \right]_T = 0$

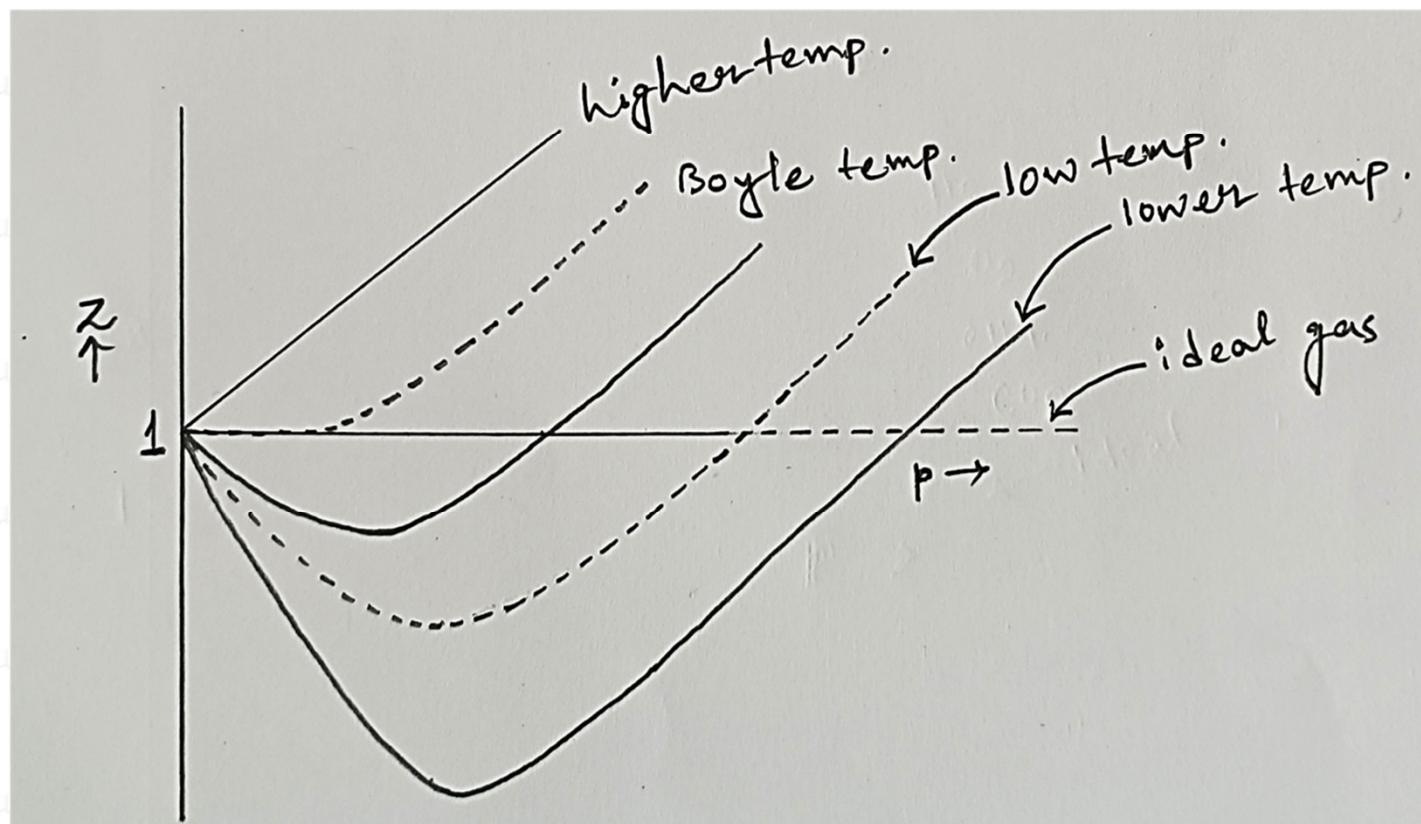
Correlating "a" with attraction and "b" with repulsion



Gas	T_B (K)
He	22.64
H_2	110.0
N_2	327.2
O_2	405.9
CO_2	714.8
NH_3	995.0

Question: How will Z vs. p curve will look like for H₂ (and He and N₂) if the measurement is done at 20K and 30K? Convert these plots into P vs. V plot for each gases.

Gas	T _B (K)
He	22.64
H ₂	110.0
N ₂	327.2
O ₂	405.9
CO ₂	714.8
NH ₃	995.0



Dieterici equation:

Volume correction: Same as that of the van der Waals equation.

Pressure correction:

$$\rho = \rho_0 e^{-\frac{A}{RT}}$$

ρ is the density of the gas at the surface and ρ_0 is in the bulk, A is the amount of work needed per mole to overcome the attractive force

$$A \propto \frac{1}{V} \Rightarrow A = \frac{a}{V} \quad [A \propto \text{density} ; \text{ so, } A \propto \frac{1}{V}]$$

$$p \propto \rho \text{ and } p_0 \propto \rho_0$$

$$\text{So, } p = p_0 \times e^{-\frac{a}{RTV}}$$

p_0 is the ideal pressure ; Ideal pressure \times free space = R T (for 1 mole of gas)

$$\text{So, } p_0 (V_m - b) = R T$$

$$\Rightarrow \frac{p}{e^{-\frac{a}{RTV_m}}} \times (V_m - b) = R T$$

$$\Rightarrow p (V_m - b) = R T \times e^{-\frac{a}{RTV_m}}$$

Time average force of attraction that a molecule feels at the bulk = 0, hence, a molecule at the bulk will behave as an ideal gas molecule

Existence of such field of force will not affect the velocity distribution or K.E. distribution, however will affect the spatial distribution of molecules

Connection with Boltzmann distribution $e^{-\frac{a}{RTV}}$

This is the [Dieterici equation](#).

Dieterici equation

[Emperical equation, later derived by Jeans; see Jeans, Dynamical Theory of Gases 126 (1916)]

Dieterici equation has the following functional form

$$p = \frac{RT}{V-b} \times e^{-\frac{a}{RTV}} \dots \dots \dots \quad (A)$$

On expanding the exponential function,

$$\begin{aligned} p &= \frac{RT}{V-b} \left[1 - \frac{a}{RTV} + \frac{1}{2} \left(\frac{a}{RTV} \right)^2 - \dots \dots \dots \right] \\ &= \frac{RT}{V-b} - \frac{a}{V(V-b)} \quad (\text{neglecting the other terms}) \\ &= \frac{RT}{V-b} - \frac{a}{V^2 - Vb} \end{aligned}$$

At low pressure V is very large, i.e. $V^2 - Vb \approx V^2$, then

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

This is the van der Waals equation.

This means at low pressure, both the equations will behave similarly.

$$\begin{aligned} e^x &= 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \frac{x^4}{4!} + \dots \dots \dots \\ e^{-x} &= 1 - x + \frac{x^2}{2!} - \frac{x^3}{3!} + \frac{x^4}{4!} - \dots \dots \dots \end{aligned}$$

$$\begin{aligned} 100 - 0.1 &= 99.9 \\ 100 (100 - 0.1) &= 9990 \end{aligned}$$

From equation (A) we get (assuming $\frac{a}{RT} = C$)

$$\begin{aligned} \left(\frac{\delta p}{\delta V}\right)_T &= -\frac{RT}{(V-b)^2} \times e^{-\frac{C}{V}} + \frac{RT}{V-b} \times \frac{C}{V^2} \times e^{-\frac{C}{V}} \\ &= -\frac{p}{V-b} + p \times \frac{C}{V^2} \quad [\text{using equation (A)}] \end{aligned}$$

$$\begin{aligned} \left(\frac{\delta^2 p}{\delta V^2}\right)_T &= -\frac{1}{V-b} \times \left(\frac{\delta p}{\delta V}\right)_T + \frac{p}{(V-b)^2} + \frac{C}{V^2} \times \left(\frac{\delta p}{\delta V}\right)_T - \frac{2pC}{V^3} \\ &= \left(\frac{\delta p}{\delta V}\right)_T \left[\frac{C}{V^2} - \frac{1}{V-b} \right] + p \left[\frac{1}{(V-b)^2} - \frac{2C}{V^3} \right] \end{aligned}$$

At the critical point, both $\left(\frac{\delta p}{\delta V}\right)_T$ and $\left(\frac{\delta^2 p}{\delta V^2}\right)_T$ are equal to zero.

$$\text{This means, } \frac{p_c}{V_c - b} = \frac{p_c C}{V_c^2}$$

$$\Rightarrow \frac{C}{V_c^2} = \frac{1}{V_c - b} \quad \dots \dots \dots (1)$$

$$\text{and } \frac{2C}{V_c^3} = \frac{1}{(V_c - b)^2} \quad \dots \dots \dots (2)$$

$$\begin{aligned} \text{Combining equation (1) and (2) } [(1) \div (2)] \text{ we get, } \frac{V_c}{2} &= V_c - b \\ \Rightarrow \boxed{V_c = 2b} \end{aligned}$$

From equation (1) we get (as $C = \frac{a}{RT}$)

$$\frac{a}{RT_c} \times \frac{1}{(2b)^2} = \frac{1}{b}$$

$$\Rightarrow T_c = \frac{a}{4bR}$$

$$p_c = \frac{RT_c}{V_c - b} \times e^{-\frac{a}{RT_c V_c}}$$

$$= \frac{R}{2b - b} \times \frac{a}{4bR} \times e^{-\frac{a}{R} \times \frac{4bR}{a} \times \frac{1}{2b}}$$

$$\Rightarrow p_c = \frac{a}{4b^2} \times e^{-2}$$

Thus, critical coefficient $\frac{RT_c}{p_c V_c} = R \times \frac{a}{4bR} \times \frac{4b^2}{a} \times e^2 \times \frac{1}{2b} = \frac{1}{2} \times e^2 = 3.695$

$$\text{Critical coefficient} = \frac{RT_c}{p_c V_c} = 3.695$$

Boyle Temperature from Dietirici equation (T_B)

$$p = \frac{RT}{V-b} \times e^{-\frac{a}{RTV}}$$

Multiplying both side by V

$$pV = \frac{RTV}{V-b} \times e^{-\frac{a}{RTV}}$$

$$\Rightarrow \left(\frac{\delta(pV)}{\delta p} \right)_T = \left[\left(\frac{RT}{V-b} - \frac{RTV}{(V-b)^2} \right) e^{-\frac{a}{RTV}} + \frac{RTV}{V-b} \times \frac{a}{RTV^2} \times e^{-\frac{a}{RTV}} \right] \left(\frac{\delta V}{\delta p} \right)_T$$

We know, $\left(\frac{\delta V}{\delta p} \right)_T \neq 0$

At Boyle temperature, $\left(\frac{\delta(pV)}{\delta p} \right)_T = 0$

$$\frac{RT}{V-b} - \frac{RTV}{(V-b)^2} + \frac{RTV}{V-b} \times \frac{a}{RTV^2} = 0$$

$$\Rightarrow \frac{RTV}{V-b} \left[\frac{1}{V} - \frac{1}{V-b} + \frac{a}{RTV^2} \right] = 0$$

$$\Rightarrow \frac{a}{RTV^2} = \frac{1}{V-b} - \frac{1}{V} = \frac{b}{V(V-b)}$$

$$\Rightarrow T = \frac{a}{Rb} \times \frac{V-b}{V}$$

At Boyle Temperature, $p \rightarrow 0$, this means $(V - b) \approx V$

$$\Rightarrow T_B = \frac{a}{Rb}$$

$$\frac{T_B}{T_c} = 4.0$$

Berthelot equation:

Berthelot equation has the following functional form

$$p = \frac{RT}{V - b} - \frac{a}{TV^2}$$

Question: Calculate critical constants based on Berthelot equation.

Question: Write an expression of p_c , T_c , V_c , $\frac{RT_c}{p_c V_c}$, T_B , $\frac{T_B}{T_c}$ corresponding to Berthelot equation.

Saha-Bose equation*:

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

*Megh Nath Saha and Satyendra Nath Bose