



# Real Gas

## Objectives:

- To analyze the experimental results considering the ideal behavior – how realistic?
- To understand the reasons behind the deviations of behavior of real gas from the ideal one.
- To construct the equation of state for real gases.
- To check the validity of these equations.

Gas laws have been formulated based on several postulates. Some of these postulates are inadequate and needs modification.

For example,

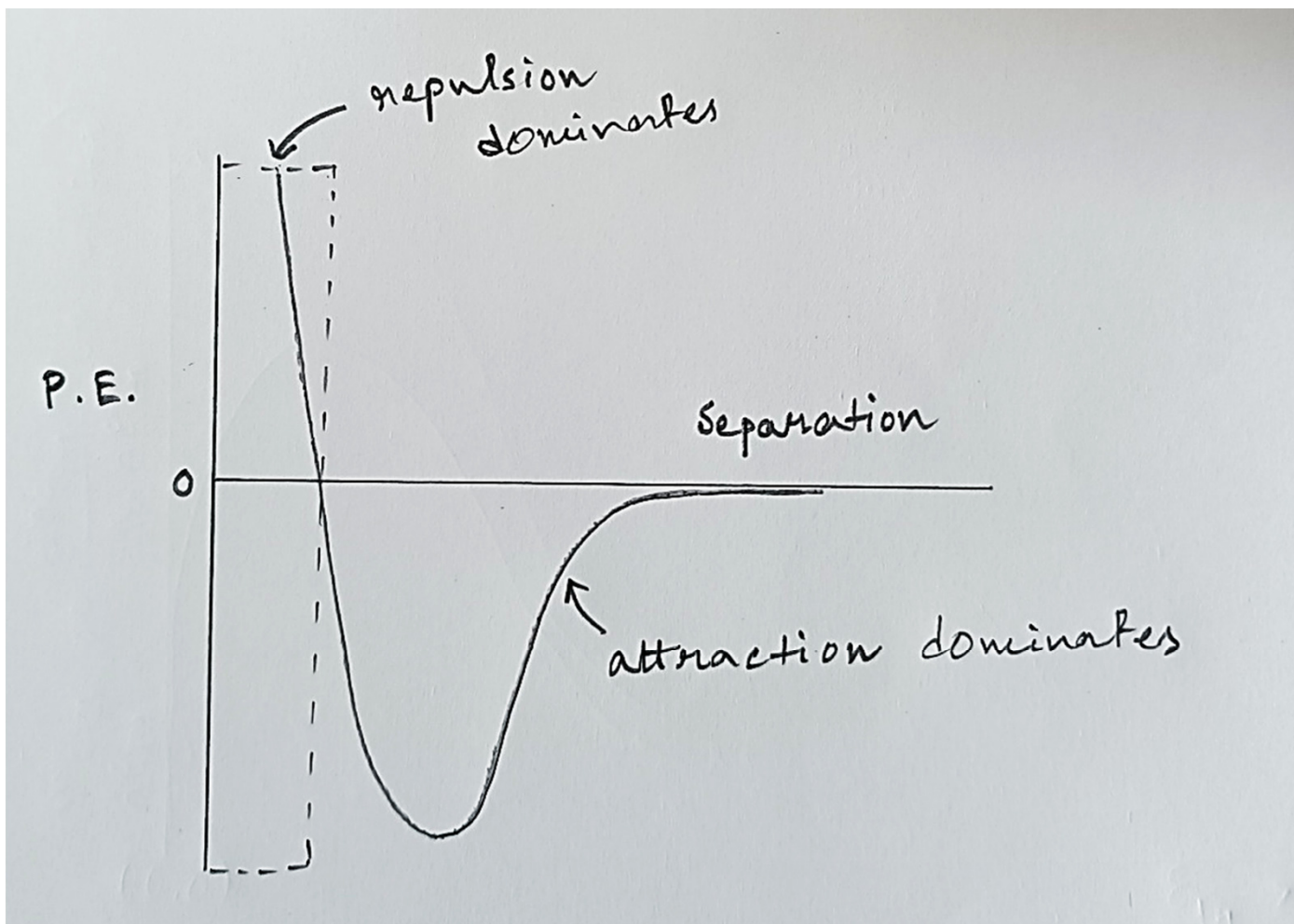
- (a) The molecules were considered as point masses, practically having no volume.
- (b) The molecules of the gas behaves independently, i.e. there exists no force of attraction or repulsion between them.

At 1 atm and room temperature (RT), volume occupied by molecules of 1 mole of a gas is approximately 0.1% of total volume and at 10 atm the volume occupied by gas molecules is about 1%, which is very small but definitely not negligible.

Second point needs some more discussion. Molecules do interact with each other specially at high pressure and at low temperature. Whether the interaction is attractive or repulsive depends on the separation between molecules. The variation of potential energy (i.e. attraction or repulsion) can be understood from the following considerations.

Different cases based on intermolecular distance:

- When the separation between molecules is very large then two molecules are almost non-interacting (at very low pressure).
- At moderate separation (at moderate pressure) i.e. when each molecule is distant from other molecule by a few diameters of the molecule, the attractive force starts predominating.
- When the separation between molecules is quite small (at very high pressure), i.e. separation is of the order of molecular diameter the repulsive force starts predominating.
- Attractive forces assist compression and repulsive force assists expansion. At high pressure when repulsive force predominates, gas molecules become less compressible.
- How will the plot of potential energy vs. distance look like?



[This curve came much later ! ]

## Deviations from Ideality: Differences between ideal behaviour from the experimental one

### (a) Coefficient of thermal expansion ( $\alpha$ ):

$$\alpha = \frac{1}{V} \left( \frac{\delta V}{\delta T} \right)_p$$

We know,  $V = \frac{n R T}{p}$

$$\Rightarrow \left( \frac{\delta V}{\delta T} \right)_p = \frac{n R}{p}$$

$$\Rightarrow \alpha = \frac{1}{V} \times \frac{n R}{p} = \frac{1}{T}$$

How was the experiment performed?

i.e.  $\alpha$  is dependent only on temperature and should be independent on nature of the gas. But the value of  $\alpha$  are different for different gas. For example,  $\alpha$  value for hydrogen and  $\text{CO}_2$  are  $2.78 \times 10^{-7}$  and  $3.49 \times 10^{-7}$  respectively at  $0^\circ\text{C}$  and 500 atm.

### (b) Coefficient of compressibility ( $\beta$ ) or Isothermal compressibility:

$$\beta = - \frac{1}{V} \left( \frac{\delta V}{\delta p} \right)_T$$

We know,  $V = \frac{n R T}{p} \Rightarrow \left( \frac{\delta V}{\delta p} \right)_T = - \frac{n R T}{p^2}$

$$\Rightarrow \beta = - \frac{1}{V} \times - \frac{n R T}{p^2} = \frac{1}{p}$$

How was the experiment performed?

So, by similar logic,  $\beta$  value should depend on pressure only and should be independent on the nature of the gas.



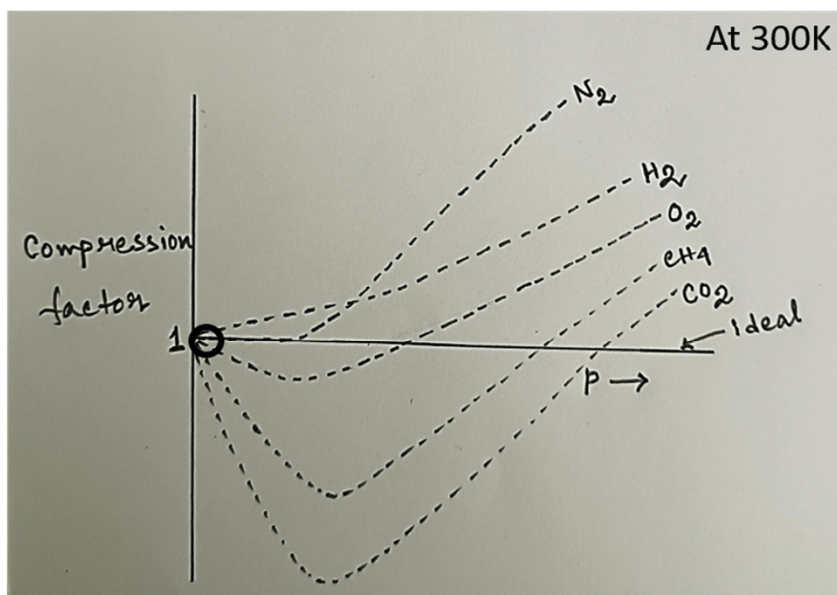
Regnault and Amagot worked extensively in this direction.

Compression factor ( $Z$ ) =  $\frac{p V_m}{R T} = 1$  (for perfect gas)

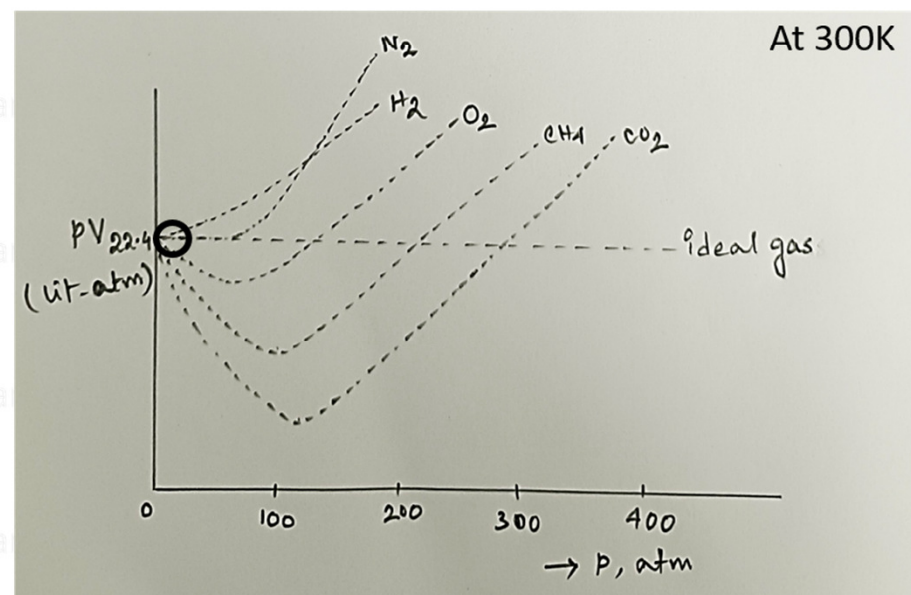
Experiments on real gases show different values of compression factor.

Regnault → 1847 (upto 400 atm)

Amagot → 1897 (upto 3000 atm)



or



Amagot went to mines to perform experiments at high pressure (3000 atm) in 1897.

At zero/very low pressure all gases behave ideally.

At intermediate pressure, compression factor  $< 1$  which means attractive forces are dominant and favours compression.

However, at higher pressure, compression factor  $> 1$  which means they are difficult to compress.

### VIRIAL coefficients:

pV isotherm pattern has been observed to be dependent on temperature.

For carbon dioxide, at higher temperature and large  $V_m$ , pV isotherm behaves similar to that of the ideal gas.

At lower temperature the curve for  $\text{CO}_2$  shown deviation from ideality, which can be accounted for by the following equation:

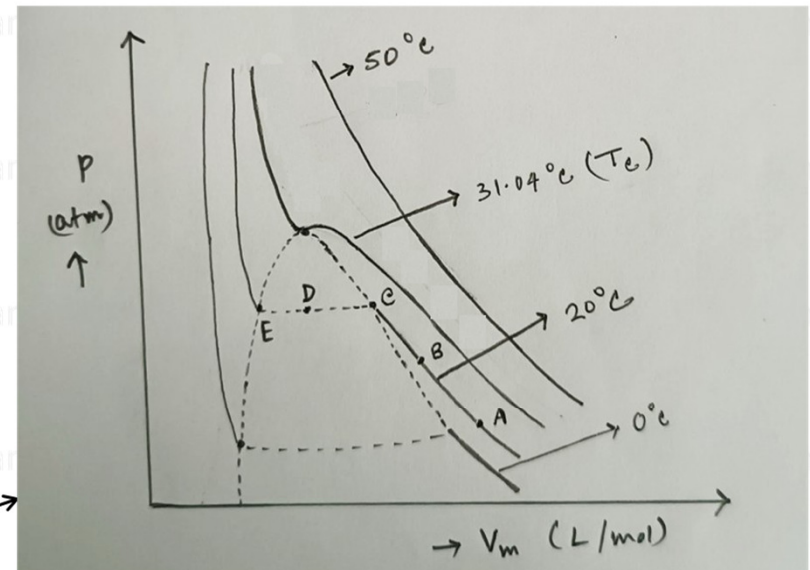
$$p V_m = R T (1 + B' p + C' p^2 + \dots) \quad \dots\dots\dots(A)$$

$$\text{or, } p V_m = R T \left( 1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \dots \right) \quad \dots\dots\dots(B)$$

Equations (A) and (B) are termed as virial equation of state

[ virial → Latin word : meaning → force]

Andrews experiment (with  $\text{CO}_2$ ) in 1863.





The coefficients, B, C, ..... etc. which depend on temperature are known as second, third, ..... virial coefficients.

Third virial coefficient is less important than second virial coefficient (and so on ..... ) as  $\frac{C}{V_m^2} \ll \frac{B}{V_m}$

Units of virial coefficients: cc/mol

Typical values of B' (at 273 K) for CO<sub>2</sub> is -149.7 cc/mol

At 600 K, B for CO<sub>2</sub> = -12.4 cc/mol

Although real gases tend to behave like ideal gas as  $p \rightarrow 0$

However,  $\frac{dZ}{dp} = 0$  (As  $Z = 1$  at all pressure), but for real gas,

$$\frac{dZ}{dp} = B' + 2 p C' + \dots \simeq B' \text{ as } p \rightarrow 0$$

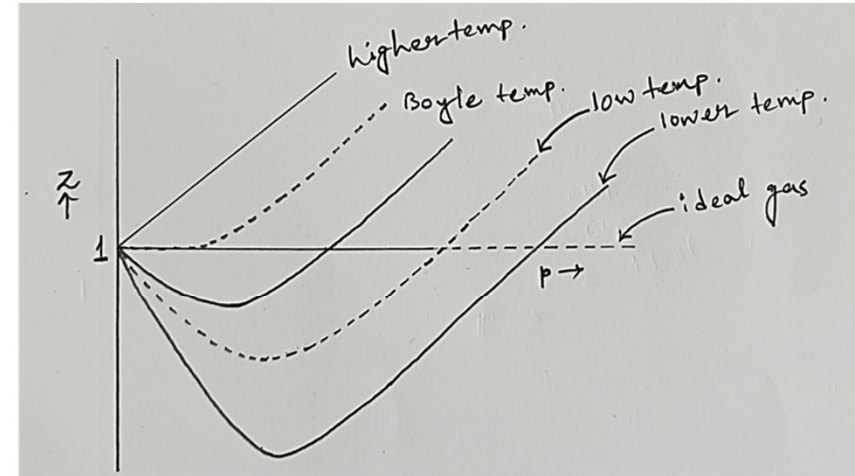
$$\frac{dZ}{d\left(\frac{1}{V_m}\right)} = B \text{ as } V_m \rightarrow \infty$$

B' will be shown to be dependent on 'a' and 'b' ;  $B = b - \frac{a}{RT}$

$B'$  is not necessarily zero, so the slope of  $Z$  vs.  $p$  curve does not necessarily approach zero (the ideal gas value).

Because virial coefficients depend on temperature, there may be a temperature at which  $Z \rightarrow 1$  with zero slope at low temperature or high  $V_m$ .

At this temperature real gas behave like ideal gas as  $p \rightarrow 0$



As temperature increases,  $Z$  vs.  $p$  curve becomes more shallow hence at Boyle temperature ( $T_B$ ) the curve touches the ideal curve for a long range of  $p$ .

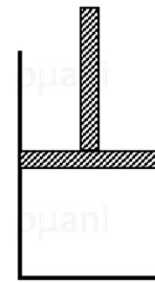
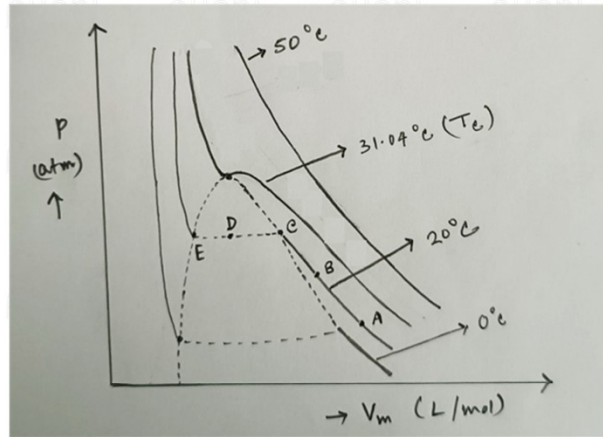
**Thus, at Boyle temperature,  $B = 0$  as  $p \rightarrow 0$ .**

Thus,  $p V_m = R T_B$  follows over a more extended range of pressure at Boyle temperature than at any other temperature, because the first term after 1, i.e.  $\frac{B}{V_m}$  in the virial equation is zero and  $\frac{C}{V_m^2}$  or higher terms are negligibly small.

Gas	$T_c$	$T_B$
Hydrogen	31K	116K
He	5K	23K
$N_2$	127K	332K
$CO_2$	304K	600K

## Condensation:

pV isotherm at certain temperature can be used to explain condensation. At 20 °C say, at point A, the pressure rises as V decreases following Boyle's law.



At 'C' (at high pressure and low volume) all similarity to ideal gas ends. This stage is represented by line CDE. There is a reduction of volume without significant change in pressure. At any point on line CDE liquid appears and the piston slides down.

As volume decreases from C to E, volume of liquid increases. Thus at C, gas gets condensed to liquid, i.e. phase separation appears. The pressure corresponding to line CDE, at which both liquid and gas are present in equilibrium is known as [vapour pressure](#) of that liquid at that particular temperature.

At E, the sample is entirely liquid, and a further reduction in volume requires a great increase of pressure.

Question: How does the vapour pressure of a real gas depend on temperature?

What are the reasons behind the departure of experimental findings from the ideal behavior?

What could be the possible sources or error?

What are the handles?

Is the volume correct ? Is the pressure correct? Do we need correction in both volume and pressure ?