

Equation of state of real gases

Kinetic Theory of Gases

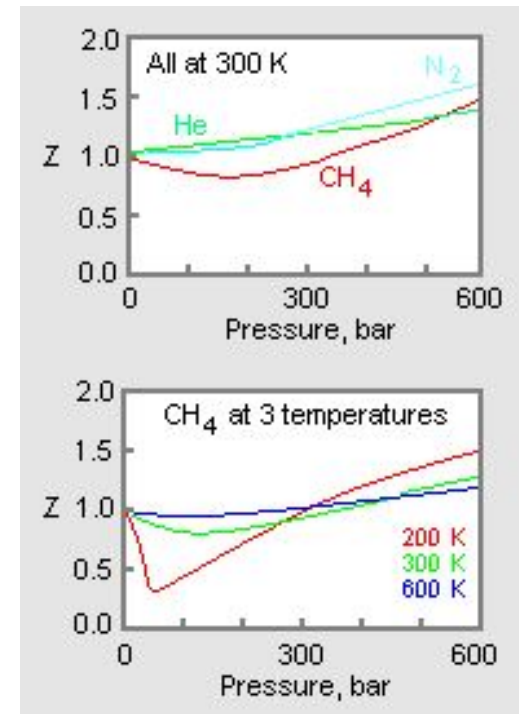
- ❖ A gas consists of a large number of minute particles, called molecules. The molecules are so small that their actual volume is negligible as compared to the total volume occupied by the gas
- ❖ The molecules are in a state of constant rapid motion in all possible directions, colliding with one another and with the walls of the vessel
- ❖ The molecular collisions are perfectly elastic so that there is no net loss of energy when gas molecules collide with one another or against the walls of the vessel
- ❖ There are no attractive forces between molecules or between molecules and the walls of the vessel in which the gas is contained
- ❖ The pressure of a gas is due to the bombardment of the molecules on the walls of the containing vessel

Equation of state of real gases: How it deviate from ideal gas

Compressibility factor Z is defined as

$$Z = \frac{PV}{nRT}$$

- ❖ For ideal gas, Z should be 1.
- ❖ In reality, Z is closer to 1 at very low pressure or at very high temperature.
- ❖ For real gas, Z generally increases with pressure and decreases with temperature.



Equation of state of real gases: Van der Waal correction

Initial assumption about pressure:

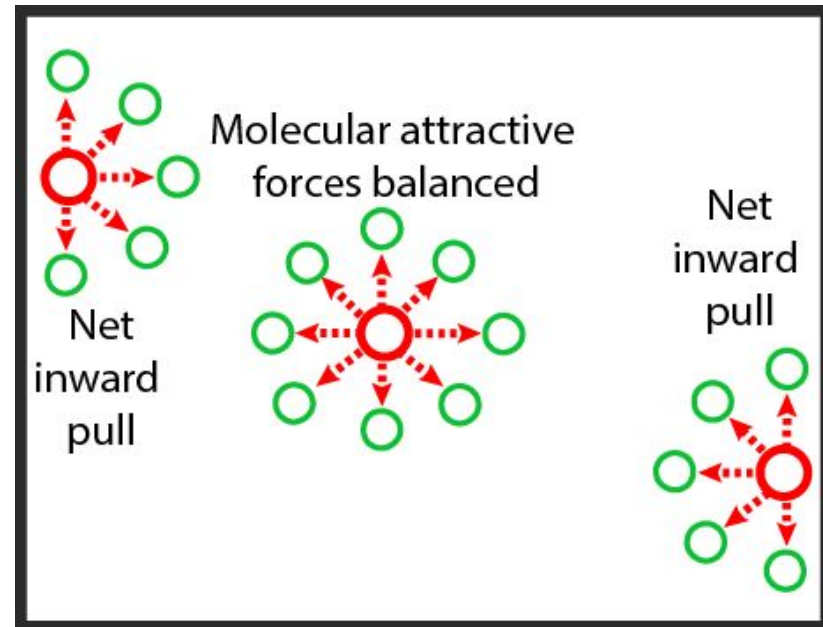
The gas molecules lie apart from each other. There is no attraction force between two gas molecules. The collision between two gas molecules are elastic one.

So the pressure exerted on the wall of the container is the net pressure of the gas.

Van der Waal correction:

For polar molecules dipole-dipole interaction, in mixture of polar and non-polar molecules dipole-induced dipole interaction, even for nonpolar molecules there exists attractive force (London dispersion force) between two gas molecules.

So the total pressure of a gas is the pressure exerted on the wall plus attractive force between two gas molecules.



Equation of state of real gases: Van der Waal correction

Assumption about volume:

The gas molecules are point mass. The actual volume of the sum of all gas molecules can be neglected with respect to total volume.

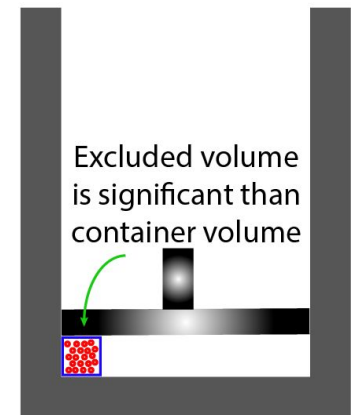
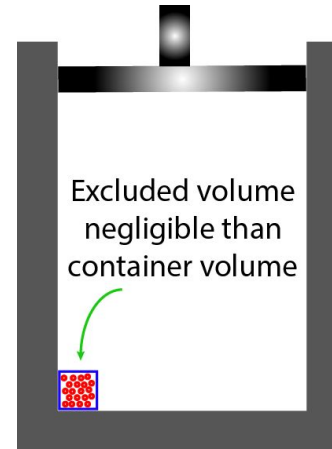
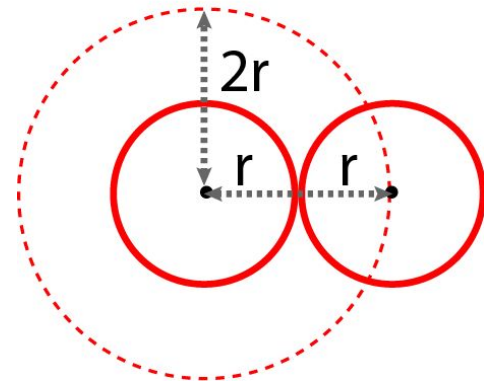
So the volume of the gas is the volume of the container that it is in.

Van der Waal correction:

Gas molecules are rigid spheres with finite volume that can be measured.

So the total volume of a gas is the container volume minus the volume of all the gas molecules.

Excluded volume



Equation of state of real gases: Van der Waal correction

Correction about pressure and volume:

Intermolecular attraction is proportional to square of density.

$$p \propto \rho^2$$

$$p = a \cdot \frac{n^2}{V^2} \text{ as } \rho = n/V, \text{ where } a = \text{constant}$$

Considering two molecules, excluded volume

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

$$V = 8 \left(\frac{4}{3} \pi r^3 \right)$$

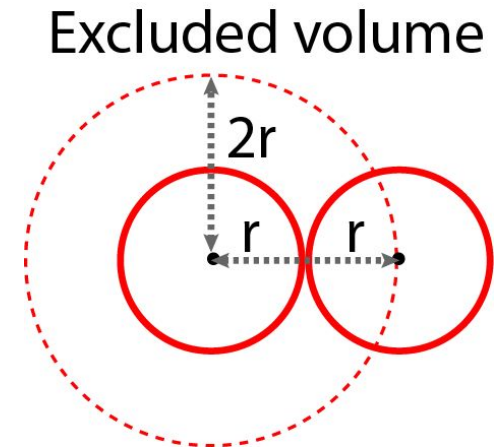
$$V = 8 \cdot V_m$$

$$V = 4 \cdot V_m \text{ for single molecule, so for } n \text{ mole}$$

$$V = n \cdot (4 \cdot V_m) = nb$$

Hence the final Van der Waal equation is,

$$\left(p + \frac{n^2 a}{V^2} \right) (V - nb) = nRT$$



Equation of state of real gases: Van der Waal correction

Comment about a and b values:

For H_2 and He, a and b values are small so the equation deviate very slightly from ideal gas equation, while for other gases significant deviation is observed.

Gas	a ((L ² ·atm)/mol ²)	b (L/mol)
He	0.03410	0.0238
Ne	0.205	0.0167
Ar	1.337	0.032
H_2	0.2420	0.0265
N_2	1.352	0.0387
O_2	1.364	0.0319
Cl_2	6.260	0.0542
NH_3	4.170	0.0371
CH_4	2.273	0.0430
CO_2	3.610	0.0429

Equation of state of real gases: The Clausius equation

The Clausius equation is a three-parameter (a, b, c) equation used to model real gases

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

$$\text{where } a = \frac{27R^2T_c^3}{64p_c}$$

$$b = V_c - \frac{RT_c}{4p_c}$$

$$c = \frac{3RT_c}{8p_c} - V_c$$

T_c = critical temperature

V_c = critical volume

p_c = critical pressure

Critical phenomena

- ❑ If temperature is lowered then volume of the gas as well as kinetic energy of the gas decreases, allowing the molecules to come closer.
- ❑ Similar effect happens when pressure is increased, although temperature change will have a dominant effect over pressure.
- ❑ At a sufficiently lower temperature, the gas molecules cannot surpass the intermolecular attraction force and they come even closer. Then, a gaseous to liquid state change occurs.
- ❑ For example, SO_2 liquifies at $-8\text{ }^\circ\text{C}$ at 1 atm pressure, while it can be liquefied at $20\text{ }^\circ\text{C}$ at 3.3 atm pressure.
- ❑ Above a certain temperature, gas cannot be liquefied no matter how high the pressure is (remember T is dominant over p)

Critical phenomena

Critical temperature:

The exact temperature above which a particular gas cannot be liquefied whatever high the pressure may be.

For example, CO_2 cannot be liquefied above $31.1\text{ }^\circ\text{C}$ at any pressure, so this is the critical temperature for CO_2 .

Critical pressure:

At critical temperature a certain pressure is required for the liquefaction of the gases, known as critical pressure.

For example, at $31.1\text{ }^\circ\text{C}$, the critical pressure for CO_2 is 73 atm.

Critical volume:

The volume occupied by 1 mole of gas at its critical temperature and critical pressure is known as critical volume.

For example, at $31.1\text{ }^\circ\text{C}$ and 73 atm, the critical volume for CO_2 is 94 ml.