

1.3 The perfect gas law - a thermal equation of state

As already stated above the perfect gas is a limiting case which strictly holds only for $p = 0$ bar where repulsive or attractive forces between particles are always negligible. Famous scientists have contributed to its equation of state by experimental findings:

- Boyle's law (at const. n, T): $p \propto 1/V$
- Charles's laws (at const. n, p or at const. n, V): $V \propto T$ resp. $p \propto T$
- Avogadro's principle (at const. p, T): $V \propto n$

Combined one finds:

$$p V = n R T \quad (1.3)$$

- n = number of particles in moles; $1 \text{ mol} = 6.022 \times 10^{23}$ molecules
- R = gas constant = $8.314 \text{ J}/(\text{mol K})$
- V_m = molar volume of perfect gas = $V/n = 22.414 \text{ dm}^3\text{mol}^{-1}$
- Determination of R : a) evaluation of perfect gas law at low pressure, b) measurement of the speed of sound and extrapolation to $p = 0$ bar

The partial pressures p_i of perfect gas mixtures just add up, i.e.

$$p_{tot} = \sum_i p_i = \sum_i x_i p_{tot} = \sum_i \frac{n_i}{n_{tot}} \frac{n_{tot} R T}{V_{tot}} = \sum_i n_i \frac{R T}{V_{tot}} \quad (1.4)$$

Here the first equals sign holds for any gas while the second equals sign only holds for a perfect gas. $x_i = n_i/n_{tot}$ is the fraction of component type i in the mixture.

This equation reflects Dalton's law: "The pressure exerted by a mixture of gases is the sum of the pressures that each one would exert if it occupied the container ALONE" (only valid for perfect gases).

A second law which has been found experimentally holds for the (inner) energy U of a perfect gas:

$$U = \frac{3}{2} n R T \quad (1.5)$$

This equation reflects that neither repulsive nor attractive forces act on the molecules; so the energy cannot depend on the distance between particles, i.e. on the volume V , and according to the perfect gas equation not on the pressure p correspondingly.