

1.10 Van-der-Waals (vdW) equation

For the virial coefficients describing real gases a meaningful physical interpretation is missing. For the Van-der-Waals equation (developed already 1873) the key idea was a "slight" modification of the perfect gas equation by introducing two additional physically meaningful parameters: the (co-)volume b occupied by molecules and a change in pressure induced by the interaction of particles, represented by a parameter a , i.e.

$$pV = nRT \quad \Rightarrow \quad \left(p + \frac{an^2}{V^2} \right) (V - nb) = nRT \quad (1.12)$$

Today a and b are typically interpreted as purely empirical fitting parameters (mostly determined via critical constants as discussed in section 1.11.1), i.e. in strict sense they do not really point to attractive/repulsive forces, resp. co-volume. a and b are independent of T , i.e. they represent the properties of gases for all temperatures.

To get a feeling for the magnitude of the co-volume we take into account that the minimal distance between pairs of two molecules in a gas is determined by $2r$ where r is the radius of the gas molecules, so the ratio of the volume V_{mol} of each molecule to the occupied volume V_{occ} by molecules is determined by

$$V_{mol} = \frac{4}{3}\pi r^3 \quad , \quad V_{occ} = \frac{4}{3}\pi \frac{(2r)^3}{2} \quad \Rightarrow \quad V_{occ} = 4V_{mol} \quad (1.13)$$

The factor 2 in the denominator of the second equation shows up because pairs of molecules have to be taken into account.

Since the interaction between TWO particles depends consequently on the SQUARE of the particle concentration the internal pressure has the parameter dependence

$$\frac{an^2}{V^2} \quad (1.14)$$

In summary the vdW Eq. (1.12) is found having a cubic dependency on V ; so in general for each pressure three solutions of V are found:

- For the critical isotherm all solutions coinciding.
- For the supercritical isotherm one real and two imaginary solutions exist.
- For the subcritical isotherm three real solutions exist.