

Real (non-ideal) gases

Virial expansion

The equation of state of a gas may be expressed as a **virial expansion**, a power series with successive terms of decreasing size. For n moles this takes the form

$$\frac{pV}{nRT} = 1 + \frac{nB}{V} + \frac{n^2C}{V^2} + \dots \quad (1)$$

Usually we take $n = 1$ so that V is the volume of one mole. The coefficients B and C are known as **virial coefficients**¹ and are functions of temperature in general.

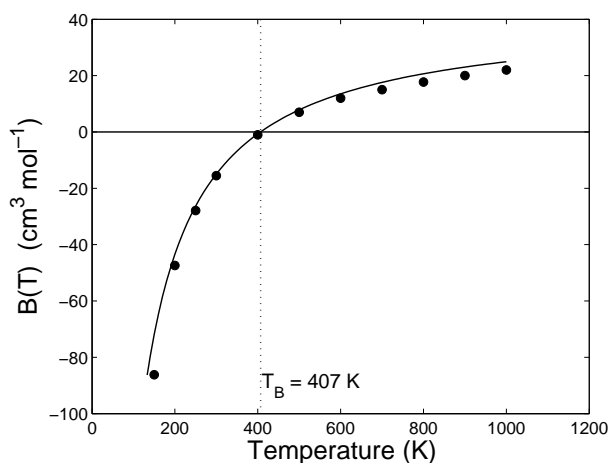
The temperature $T = T_B$ at which $B(T) = 0$ is known as the **Boyle temperature**. At this temperature the behaviour of the gas is close to that of an ideal gas.

Van der Waals equation

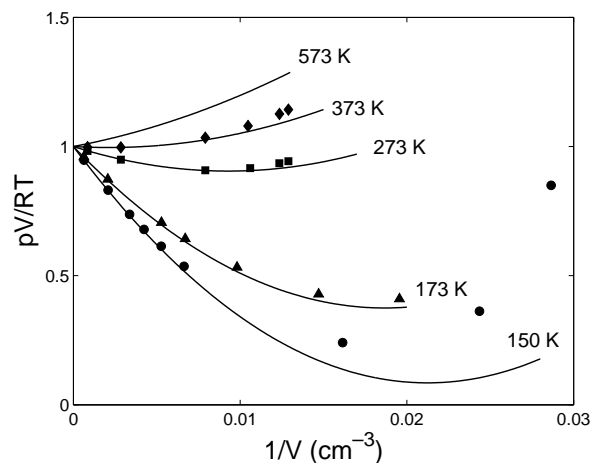
A reasonable approximation to the equation of state of many real gases is

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT \quad (\text{for one mole}) \quad (2)$$

This is the **van der Waals equation**.² Although it is not the most accurate analytic approximation to the equation of state of real gases, the van der Waals equation is useful because it is relatively easy to handle mathematically, and because the a/V^2 and b terms can be derived from a physical model. The a/V^2 term corrects for the attractive forces between the molecules which make the measured pressure less than the true pressure, and b is the effective volume of the molecules whereupon $V - b$ is the true volume available for the molecules to move in.



Second virial coefficient for argon. The line is calculated from the van der Waals expression $B(T) = b - a/RT$ with $a = 1.42 \times 10^5 \text{ J cm}^3 \text{ mol}^{-1}$ and $b = 42 \text{ cm}^3$. The Boyle temperature T_B is indicated. Data points are from J. H. Dymond and E. B. Smith, *The Virial Coefficients of Pure Gases and Mixtures* (Clarendon, Oxford, 1980).



Virial plots for argon. The lines are calculated from eqn (1) with values of $B(T)$ and $C(T)$ calculated by E.M. Mas *et al.*, *J. Chem. Phys.* **110** (1999) 6694. The critical temperature for Ar is $T_c = 151 \text{ K}$, which explains the poor agreement with the data at 150 K.

¹after *vis*, the latin word for force

²Johannes Diderik van der Waals (1837–1923)

Critical point

The critical point of a gas is the point in the $p - T$ phase diagram at which the liquid–vapour phase boundary terminates. The values of temperature, pressure and volume at the critical point are denoted by T_c , p_c and V_c . For $T < T_c$, there exists a phase in which the gas is condensed into a liquid in equilibrium with its vapour.

At the critical point, the pV isotherm has zero slope and curvature, i.e.

$$\left(\frac{\partial p}{\partial V}\right)_{T=T_c} = \left(\frac{\partial^2 p}{\partial V^2}\right)_{T=T_c} = 0. \quad (3)$$

For the van der Waals gas it can be shown from (2) that

$$T_c = \frac{8a}{27Rb}; \quad p_c = \frac{a}{27b^2}; \quad V_c = 3b.$$

Dieterici's equation

Dieterici's eqn gives similar behaviour to van der Waals' eqn but differs in the details. It is

$$p(V - b) = RT \exp\left(-\frac{a}{RTV}\right) \quad (\text{for one mole}) \quad (4)$$

The critical point is at

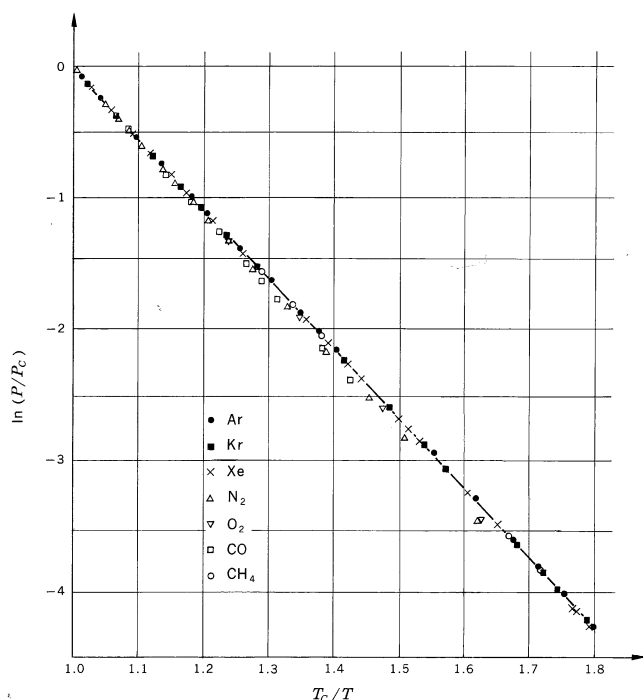
$$T_c = \frac{a}{4Rb}; \quad p_c = \frac{a}{4e^2b^2}; \quad V_c = 2b.$$

Law of corresponding states

A **law of corresponding states** expresses the fact that it is possible to collapse data from all simple fluids onto the same curve when plotted in **reduced coordinates**, i.e. coordinates scaled by their values at the liquid–gas critical point:

$$\tilde{T} = \frac{T}{T_c}; \quad \tilde{p} = \frac{p}{p_c}; \quad \tilde{V} = \frac{V}{V_c}.$$

It works because the thermodynamics of fluids depends on the intermolecular potential, which has the same basic shape for most materials.



Law of corresponding states for the temperature variation of the vapour pressure of seven simple molecular fluids. The data are expressed in terms of reduced temperature and reduced pressure, and the points all fall on a universal curve described by the equation $\ln(p/p_c) = 5.4(1 - T_c/T)$. [From E.A. Guggenheim, *Thermodynamics* (Interscience, 1967).]