Pressure as a function

In sec. 6.3.3, pressure was introduced as a function of temperature and volume.

An ideal gas is the most primitive example; here the function is

$$\hat{P}(V,T) = \frac{nRT}{V} \quad \text{(ideal gas)}. \tag{1}$$

A van der Waals fluid gives a slightly more complex function, cf. eq. (5.1) or (5.2) in the book. The former is

$$\hat{P}(V,T) = \frac{nRT}{V-bn} - \frac{an^2}{V^2} \quad \text{(van der Waals)}. \tag{2}$$

Yet more complex but still explicit is the function given by the **Beattie-Bridgeman** gas state equation (Hála, 1975):

$$\hat{P}(V,T) = \frac{nRT(1-\varepsilon)}{V^2}(V+Bn) - \frac{An^2}{V^2} \quad \text{(Beattie}-\text{Bridgeman)}. \tag{3}$$

The symbols A, B, ε are given by:

$$A = A_0\left(1-\frac{an}{V}\right), \tag{4}$$

$$B = B_0\left(1-\frac{bn}{V}\right), \tag{5}$$

$$\varepsilon = \frac{cn}{VT^3}. \tag{6}$$

A_0, B_0, a, b, c are constants specific for each gas. Their number is thus five, whereas van der Waals equation has only two constants.

Somewhere between the van der Waals and Beattie-Bridgman equations is the **Redlich-Kwong** equation with two constants (they have the same symbols as the van der Waals equation but are different; Hála, 1975) proposed for gases, again:

$$\hat{P}(V,T) = \frac{nRT}{V-bn} - \frac{an^2}{T^{0.5}V(V+bn)} \quad \text{(Redlich}-\text{Kwong)}. \tag{7}$$

Another function is represented by **virial equations** of state describing a gas at low and moderate pressures (DeVoe, 2001). These equations may be derived from statistical theory, but their parameters are mostly determined empirically. Expressed as a pressure function:

$$\hat{P}(V,T) = \frac{nRT}{V}\left(1+\frac{Bn}{V}+\frac{Cn^2}{V^2}+\cdots\right) \quad \text{(virial expansion)}. \tag{8}$$

The coefficients $B, C, \ldots$ are called the second, third, ... virial coefficients and are functions of temperature (different for different gaseous substances). They are zero for an ideal gas; the first virial coefficient is 1 as (8) indicates.

Fairly often in practice, we want to **invert the function** $\hat{P}(V,T)$ for volume, i.e., to express volume as a function of pressure (and temperature) and to use pressure as an independent variable instead of volume in thermodynamic equations (cf. eq. (10.12) in the book):

$$\hat{f}(V,T) \xrightarrow{\text{inversion of } \hat{P}(V,T)} \hat{f}\left(\check{V}(P,T),T\right) \equiv \check{f}(P,T). \tag{9}$$

This is not always easy, as noted on pages 55 and 110 in the book. Evidently, the ideal gas state equation (1) is invertible in its whole domain:

$$\check{V}(P,T) = \frac{nRT}{P} \quad \text{(ideal gas)}. \tag{10}$$

This is not the case with the van der Waals function (equation), see p. 55 in the book, again. Expressing volume from it, we obtain a cubic equation for volume, not an explicit function. Locally, this equation can be solved and up to three values of volume for given values of pressure and temperature (and a specified molar amount) obtained. Perhaps only one of them would be physically acceptable and local inversion can then be useful (once more, p. 110 in the book). A similar and more complex situation appears with the Beattie-Bridgeman and Redlich-Kwong equations.

Virial equations are alternatively expressed in terms of powers of pressure (DeVoe, 2001), thus giving directly the "inverted" function:

$$\hat{P}(V,T) = \frac{nRT}{V}(1 + B'P + C'P^2 + \cdots) \quad \text{(alternative virial expansion)}. \tag{11}$$

Remember that technically this is just a different equation not the inversion of the function (8). It can be inverted easily, in contrast to (8):

$$\check{V}(P,T) = \frac{nRT}{P}(1 + B'P + C'P^2 + \cdots) \quad \text{(alternative virial expansion)}. \tag{12}$$

At low pressures, van der Waals equation transformed to the form

$$PV = n\left(RT - \frac{an}{V} + bP + \frac{abn^2}{V^2}\right) \tag{13}$$

can be simplified by neglecting the last (small) term and using nRT/P in place of V (Hála, 1975):

$$PV = nRT + n\left(b - \frac{a}{RT}\right)P. \tag{14}$$

This gives the following function for volume:

$$\check{V}(P,T) = \frac{nRT}{P} + n\left(b - \frac{a}{RT}\right) \quad \text{(van der Waals at low pressures)}.. \tag{15}$$

References

DeVoe H. *Thermodynamics and Chemistry*. Upper Saddle River: Prentice Hall, 2001.

Hála E. *Úvod do chemické termodynamiky*. Prague: Academia, 1975. (*Introduction to chemical thermodynamics*. In Czech).