

1.2: Virial Equations

It is often useful to fit accurate pressure-volume-temperature data to polynomial equations. The experimental data can be used to compute a quantity called the **compressibility factor**, Z , which is defined as the pressure-volume product for the real gas divided by the pressure-volume product for an ideal gas at the same temperature.

We have

$$(PV)_{ideal\ gas} = nRT$$

Letting P and V represent the pressure and volume of the real gas, and introducing the molar volume, $\bar{V} = V/n$, we have

$$Z = \frac{(PV)_{real\ gas}}{(PV)_{ideal\ gas}} = \frac{PV}{nRT} = \frac{P\bar{V}}{RT}$$

Since $Z = 1$ if the real gas behaves exactly like an ideal gas, experimental values of Z will tend toward unity under conditions in which the density of the real gas becomes low and its behavior approaches that of an ideal gas. At a given temperature, we can conveniently ensure that this condition is met by fitting the Z values to a polynomial in P or a polynomial in \bar{V}^{-1} . The coefficients are functions of temperature. If the data are fit to a polynomial in the pressure, the equation is

$$Z = 1 + B^*(T)P + C^*(T)P^2 + D^*(T)P^3 + \dots$$

For a polynomial in \bar{V}^{-1} , the equation is

$$Z = 1 + \frac{B(T)}{\bar{V}} + \frac{C(T)}{\bar{V}^2} + \frac{D(T)}{\bar{V}^3} + \dots$$

These empirical equations are called **virial equations**. As indicated, the parameters are functions of temperature. The values of $B^*(T)$, $C^*(T)$, $D^*(T)$, ..., and $B(T)$, $C(T)$, $D(T)$, ..., must be **determined for each real gas** at every temperature. (Note also that $B^*(T) \neq B(T)$, $C^*(T) \neq C(T)$, $D^*(T) \neq D(T)$, etc. However, it is true that $B^* = B/RT$.) Values for these parameters are tabulated in various compilations of physical data. In these tabulations, $B(T)$ and $C(T)$ are called the **second virial coefficient** and **third virial coefficient**, respectively.

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