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, $\overline{V}=V/n$, we have

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

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 $\overline{V}^{-1}$. The coefficients are functions of temperature. If the data are fit to a polynomial in the pressure, the equation is

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

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

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

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