

From Perry's, 5th Edition, page 4-61

Correlations for Constants in Equations of State. The principle of corresponding states and its modifications provide methods for the estimation of values for the constants in equations of state. Probably the most useful generalization is based on the work of Pitzer and coworkers (see Lewis, Randall, Pitzer, and Brewer, "Thermodynamics," 2d ed., appendix 1, McGraw-Hill Book Co., New York, 1961) who refined the usual generalized correlation based on reduced temperature T_r and reduced pressure P_r by incorporating a third parameter, known as the acentric factor ω . This factor is defined for a pure material with reference to its vapor or saturation pressure P^{sat} as follows:

$$\omega = -\log_{10} (P_r^{\text{sat}})_{T_r=0.7} - 1.000 \quad (4-286)$$

where $P_r^{\text{sat}} = P^{\text{sat}}/P_c$ and $T_r = T/T_c$.

In addition to generalized correlations for compressibility factor and the usual configurational properties, Pitzer et al. developed a generalized correlation for second virial coefficients which is very useful in conjunction with the simplest of the virial equations, Eq. (4-259), which may be written

$$Z = 1 + \left(\frac{P_c B}{RT_c} \right) \frac{P_r}{T_r} \quad (4-287)$$

The quantity $P_c B/RT_c$ is dimensionless, and may be regarded as a reduced second virial coefficient. The correlation proposed by Pitzer et al. is simply

$$\frac{P_c B}{RT_c} = B^0 + \omega B^1 \quad (4-288)$$

where

$$B^0 = \delta^0(T_r) = 0.1445 - \frac{0.330}{T_r} - \frac{0.1385}{T_r^2} - \frac{0.0121}{T_r^3} \quad (4-289)$$

and

$$B^1 = \delta^1(T_r) = 0.073 + \frac{0.46}{T_r} - \frac{0.50}{T_r^2} - \frac{0.097}{T_r^3} - \frac{0.0073}{T_r^8} \quad (4-290)$$

The temperature derivative of B can also be determined from these equations. Differentiation of Eq. (4-288) gives

$$\frac{P_c}{RT_c} \left(\frac{dB}{dT} \right) = \frac{dB^0}{dT} + \omega \frac{dB^1}{dT}$$

But $T = T_c T_r$ and $dT = T_c dT_r$. Substitution for dT on the right-hand side of the last equation leads to

$$\frac{P_c}{R} \left(\frac{dB}{dT_r} \right) = \frac{dB^0}{dT_r} + \omega \frac{dB^1}{dT_r} \quad (4-291)$$

where all terms are dimensionless and the derivatives on the right follow directly from Eqs. (4-289) and (4-290):

$$\frac{dB^0}{dT_r} = \frac{0.330}{T_r^2} + \frac{0.277}{T_r^3} + \frac{0.0363}{T_r^4} \quad (4-292)$$

$$\frac{dB^1}{dT_r} = \frac{-0.46}{T_r^2} + \frac{1.00}{T_r^3} + \frac{0.291}{T_r^4} + \frac{0.0584}{T_r^9} \quad (4-293)$$

The functions represented by Eqs. (4-289), (4-290), (4-292), and (4-293) can of course be plotted vs. T_r for convenience in hand calculations, but for computer calculations the equations themselves are employed. Values for ω can be determined from vapor-pressure data and Eq. (4-286). This has been done for many substances, and tables of values are available. (See, for example, Prausnitz, Eckert, Orye, and O'Connell, "Computer Calculations for Multicomponent Vapor-Liquid Equilibria," appendix B-1, Prentice-Hall, Englewood Cliffs, N.J., 1967.)