CBE 246  Pure Component Props

For determination of fundamental equations from experimental data, one needs (a) PVT data (b) P^3 or C^3

PVT Equations of State (EOS)

→ Ideal gas \( \frac{PV}{RT} \) good to 1% or better at near-atmospheric conditions for many gases

→ Virial equation of state (density expansion)

\[
Z = \frac{PV}{RT} = 1 + B(T) \rho + C(T) \rho^2 + \ldots
\]

* \( B(T), C(T) \ldots \) are "virial coefficients"

* Virial equation based on Stat. mechanical theory, can relate coefficients to intermolecular forces:
  low T  \( B(T) < 0 \), attractions dominate
  high T  \( B(T) > 0 \), repulsions dominate

* Unfortunately, equation does not converge for liquids

* Useful for gases at moderate pressures (a few bars)

→ van der Waals EOS , 1873  [1910 Nobel in Physics]

\[
P = \frac{RT}{V-b} - \frac{a}{V^2}
\]

\( a \) causes \( P \) to decrease rel. to ide. value / due to attractions

\( b \) increases \( P \) rel. to ide. value (due to repulsions)

Values for specific substances obtained from criticality conditions
\[ (\frac{\partial P}{\partial V})_T = 0 = (\frac{\partial^2 P}{\partial V^2})_T \]

\[ \alpha = \frac{\partial P}{\partial V} \bigg|_T \Rightarrow \frac{RT_c}{(V_c-b)^2} = \frac{2\alpha}{V_c^3} \tag{1} \]

\[ \beta = \frac{\partial^2 P}{\partial V^2} \bigg|_T \Rightarrow \frac{2RT_c}{(V_c-b)^3} = \frac{6\alpha}{V_c^4} \tag{2} \]

Divide (ii) \( \div \) (i) \( \Rightarrow \frac{2}{V_c-b} = \frac{3}{V_c} \Rightarrow b = \frac{V_c}{3} \)

Substitute in (i) : \( \alpha = \frac{a}{8} V_c \frac{RT_c}{V_c} \)

Substitute \( \alpha, b \) in vdw EOS: \( P_c = \frac{RT_c}{2} - \frac{a}{8} \frac{RT_c}{V_c} \)

\[ \Rightarrow P_c = \frac{3RT_c}{8V_c} \Rightarrow Z_c = \frac{P_c V_c}{RT_c} = \frac{3}{8} \text{ "universal"} \]

The prediction that all fluids have a critical compressibility factor \( Z_c = 3/8 \) is not very accurate, but helped establish the principle of corresponding states.

Solving for \( V_c = \frac{3RT_c}{8P_c} \) and substituting,

\[ b = \frac{RT_c}{8P_c} \quad \alpha = \frac{2TR^2T_c^2}{64P_c} \]

\( \text{commonly used to obtain } a, b \text{ from exp. measured } T_c, P_c \)

vdw EOS qualitatively correct, captures vapor-liquid transition, critical point, but quantitatively inadequate.

Empirical Modifications used for engineering calculations:
Redlich-Kwong, 1944: \[ P = \frac{RT}{V-b} - \frac{a}{V(V+b)} \]

Peng-Robinson, 1976: \[ P = \frac{RT}{V-b} - \frac{a(T_j)}{V(V+b) + b(V-b)} \]

\( w \): "acentric factor" related to vapor pressure

All of these equations can be reduced to a cubic polynomial in volume - e.g. vdW EOS

\[ P = \frac{RT}{V-b} - \frac{a}{V^2} \Rightarrow PV^3 - (Pb + RT)V^2 + aV - ab = 0 \]

\[ \Rightarrow \text{cubic equation of state} \]

For higher accuracy (e.g. NIST Webbook) complex, multiparameter expressions directly by \( A(T,V) \) are used instead of cubic EOS.

Ideal-gas heat capacities

\[ C_P^{IG} = C_v^{IG} + R \]

\( C_P, C_v \) generally dependent on \( T \)

How do isolated molecules store energy?

\[ C_v^{IG} = \frac{du}{dT} \rightarrow \text{motion in each of 3 directions of space} \]

\( R \) to the heat capacity

For monoatomic gases - e.g. Ar

\[ C_v = \frac{3R}{2}, \text{indep. of } T; \quad C_P = \frac{5R}{2} \]
CBE 246  Pure Component Properties

→ vibrations - each contributes 3R, but because of strong bonds these are not excited at room T for gases such as N₂, O₂
→ rotations - each contributes R/2

For diatomic gases, e.g. O₂
\[ \frac{5R}{2} \]
two rotations

Empirical expressions from fitting exp. data -
"Shomate Equation"
\[ C_p = a + b \frac{T}{10^3} + c \frac{T^2}{10^6} + d \frac{T^3}{10^9} + e \left( \frac{10^3}{T} \right)^2 \]
C_p in J/(mol K)  T in K