

For determination of fundamental Equations from experimental data, one needs (a) PVT data (b) (C_p) or (C_v)

PVT Equations of State (EOS)

→ Ideal gas $\underline{PV} = RT$ good to 1% or better at near-atmospheric conditions for many gases

→ Virial equation of state (density expansion)

$$\underline{Z} \equiv \frac{\underline{PV}}{RT} = 1 + B(T)\rho + C(T)\rho^2 + \dots$$

* $B(T)$, $C(T)$... 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 bar)

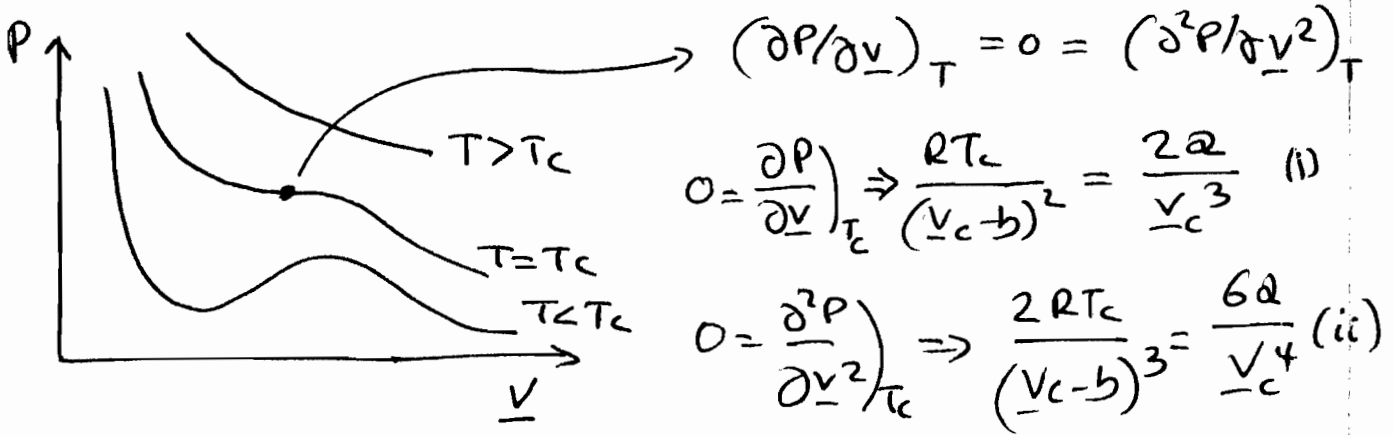
→ van der Waals EOS, 1873 [1910 Nobel in Physics]

$$P = \frac{RT}{\underline{V}-b} - \frac{a}{\underline{V}^2} \quad \left[\begin{array}{l} a \text{ causes } P \text{ to decrease rel.} \\ \text{to I.G. value / due to attractions} \end{array} \right.$$

$$a, b > 0$$

$$\left[\begin{array}{l} b \text{ increases } P \text{ rel. to I.G.} \\ \text{value / due to repulsions} \end{array} \right.$$

Values for specific substances obtained from criticality conditions



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

$$\text{Substitute in (i): } a = \frac{9}{8} V_c RT_c$$

$$\text{Substitute } a, b \text{ in vdW EOS: } P_c = \frac{RT_c}{\frac{2}{3} V_c} - \frac{9}{8} \frac{RT_c}{V_c} \rightarrow$$

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

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,

$$b = \frac{RT_c}{8P_c} \quad a = \frac{27R^2 T_c^2}{64P_c} \quad \left. \begin{array}{l} \text{commonly used to} \\ \text{obtain } a, b \text{ from} \\ \text{exp. measured } T_c, P_c \end{array} \right\}$$

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

Empirical Modifications used for engineering calculations:

CBE 246 Pure Component Props.

(3)

* Redlich-Kwong, 1949:
$$P = \frac{RT}{\underline{v}-b} - \frac{a/\sqrt{T}}{\underline{v}(\underline{v}+b)}$$

* Peng-Robinson, 1976:
$$P = \frac{RT}{\underline{v}-b} - \frac{Q(T;w)}{\underline{v}(\underline{v}+b)+b(\underline{v}-b)}$$

w: "acentric factor" related to vapor pressure

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

$$P = \frac{RT}{\underline{v}-b} - \frac{Q}{\underline{v}^2} \Rightarrow P\underline{v}^3 - (Pb + RT)\underline{v}^2 + Q\underline{v} - Qb = 0$$

→ Cubic equations of state ←

For higher accuracy (e.g. NIST webBook) complex, multiparameter expressions directly for $\underline{A}(T, \underline{v})$ are used instead of cubic EOS.

Ideal-gas heat Capacities

$$C_p^{IG} = C_v^{IG} + R$$

C_p^{IG}, C_v^{IG} generally depend on T

How do isolated molecules store energy?

$$C_v^{IG} = \frac{du}{dT}$$

→ motion in each of 3 directions of space - each contributes $\frac{R}{2}$ to the heat capacity

For monoatomic gases - e.g. Ar

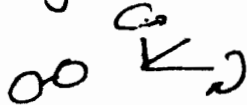
$$C_v^{IG} = \frac{3R}{2}, \text{ indep. of } T; \quad C_p^{IG} = \frac{5R}{2}$$

→ vibrations - each contributes R , but because of strong bonds these are not excited at room T for gases such as N_2, O_2

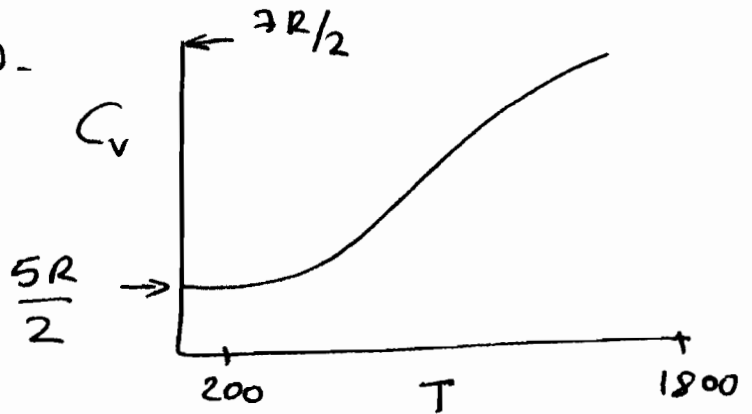
→ rotations - each contributes $R/2$

For diatomic gases.

e.g. O_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 $J/(mol \cdot K)$ T in K