CM 3230 Thermodynamics, Fall 2014

Lecture 11

1. Equation of State (EOS)

- An equation relating the values of T, P and v (e.g. ideal gas law, etc.)

2. Ideal Gas Law

$$Pv = RT$$

- Assumptions: the molecules are so far apart so that
  a) compared to spaces between molecules, the molecules does not occupy significant volume
  b) there are no intermolecular forces (any collision is also considered perfectly elastic)

3. The Van der Waals Equation

- Adds simple corrections to ideal gas law to approach real gas behavior

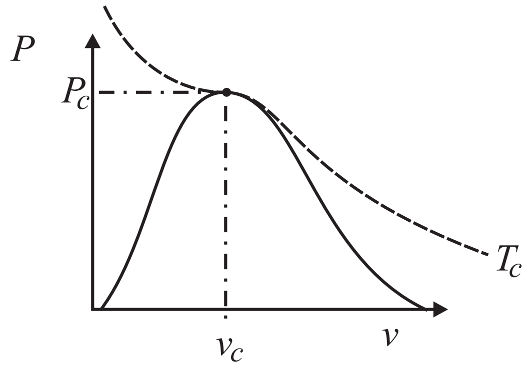
  a) Correction to volume: replace v by $(v - b)$,
  b) Correction to pressure: replace P by $(P + a/v^2)$

$$\left(P + \frac{a}{v^2}\right)(v - b) = RT$$

- Parameters a and b could be obtained experimentally.
- If not available, then use the two assumption of Van der Waals at the critical point:

$$\text{slope is 0 at critical point: } \left(\frac{\partial P}{\partial v}\right)_{\text{critical point}} = 0$$

$$\text{inflection point at the critical point: } \left(\frac{\partial^2 P}{\partial v^2}\right)_{\text{critical point}} = 0$$



Solving the conditions at T_c, P_c and v_c would yield two equations with two unknown a and b. This yields:

$$a = \frac{27}{64}\frac{(RT_c)^2}{P_c} \qquad \text{and} \qquad b = \frac{1}{8}\frac{RT_c}{P_c}$$

- After substituting these values to the Van der Waals model once again,

$$P_r = \frac{8T_r}{3v_r - 1} - \frac{3}{v_r^2}$$

where, $P_r = P/P_c$ (reduced pressure), $T_r = T/T_c$ (reduced temperature), $v_r = v/v_c$(reduced molar volume)

→ an equation that do not depend on substance parameters a or b.
→ this suggests that real gas behavior could described be described more generally without having to specify which gas is being considered, i.e. we arrive at Van der Waals's Principle of Corresponding States:

"Substances behave alike at the same reduced states. Substances at same reduced states are at corresponding states."

➔ If we plot the "compressibility factor" using reduced pressure and reduced temperature, many similar substances should follow the same trends.

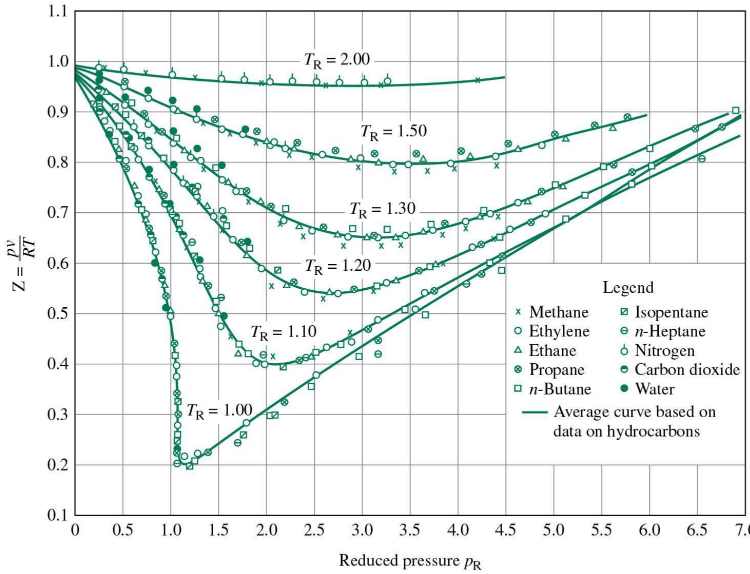


Image from http://www.mae.wvu.edu/~smirnov/mae320/notes.html

4. Cubic Equations of State

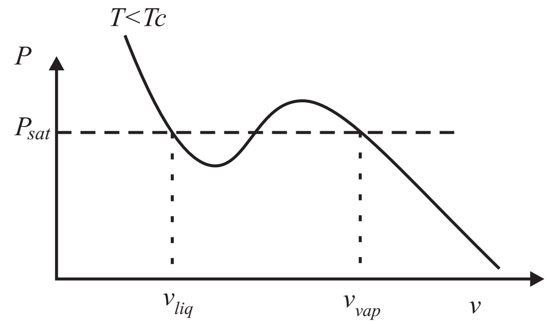
- Van der Waals equation can be rearranged to be

$$v^3 - \left(b + \frac{RT}{P}\right)v^2 + \left(\frac{a}{P}\right)v - \left(\frac{ab}{P}\right) = 0$$

→ for fixed T and P there are three roots possible.

i) One real root, 2 complex roots → only one value for v
ii) Three equal roots → critical point
iii) Three real roots: $v_1 > v_2 > v_3$ → yields $v_{liq} = v_3$ and $v_{vap} = v_1$

→ can use Antoine equation to find saturated pressure for a given T, then use the cubic equation to find the roots



→ Alternatively, we can use Maxwell's equal area principle to find P_{sat}, v_{liq} and v_{vap},

$$P_{sat}\left(v_{vap} - v_{liq}\right) = \int_{v_{liq}}^{v_{vap}} P \ dv$$

- Improvements to Van der Waals: replace the term $1/v^2$ by other approximation

a) Redlich-Kwong

$$P = \frac{RT}{v-b} - a\frac{1}{(v+b)v\sqrt{T}}$$

$$a = \left[0.4275\sqrt{T_c}\right]\frac{(RT_c)^2}{P_c}$$

$$b = 0.08664\ \frac{RT_c}{P_c}$$

b) Soave-Redlich-Kwong

$$P = \frac{RT}{v-b} - a\frac{\alpha_{SRK}}{(v+b)v}$$

$$\alpha_{SRK} = \left[1 + (0.480 + 1.574\omega - 0.176\omega^2)\left(1-\sqrt{T_r}\right)\right]^2$$

where ω is the acentric factor (see appendix A for values of typical substances)

c) Peng-Robinson

$$P = \frac{RT}{v-b} - a\frac{\alpha_{PR}}{(v+b)v + b(v-b)}$$

$$\alpha_{PR} = \left[1 + (0.37464 + 1.54226\omega - 0.26992\omega^2)\left(1 - \sqrt{T_r}\right)\right]^2$$

$$a = 0.457235\ \frac{(RT_c)^2}{P_c}$$

$$b = 0.077796\ \frac{RT_c}{P_c}$$

- Mixing Rules for n components

a) Van der Waals: let $a_{ij} = \sqrt{a_i a_j}$, then

$$a_{mix} = \sum_{i=1}^{n}\sum_{j=1}^{n} a_{ij} y_i y_j \qquad b_{mix} = \sum_{i=1}^{n} b_i y_i$$

b) Other cubic equation of state: let $(a\alpha)_{ij} = \sqrt{(a\alpha)_i (a\alpha)_j}$, then

$$(a\alpha)_{mix} = \sum_{i=1}^{n}\sum_{j=1}^{n} (a\alpha)_{ij} y_i y_j \qquad b_{mix} = \sum_{i=1}^{n} b_i y_i$$

5. Virial Equation of State

Let z be the "compressibility factor" defined as

$$z = \frac{Pv}{RT}$$

- Then a series approximation is given in two forms:
  a) "Explicit in molar volume" form

$$z = 1 + \frac{B}{v} + \frac{C}{v^2} + \frac{D}{v^3} + \cdots$$

Example: Beattie-Bridgeman equation of state (cf. page 241) for B, C and D

b) "Explicit in pressure" form

$$z = 1 + B'P + C'P^2 + D'P^3 + \cdots$$

- Mixing Rules for n components :

$$B_{mix} = \sum_{i=1}^{n}\sum_{j=1}^{n} B_{ij}\, y_i\, y_j \quad ; \quad C_{mix} = \sum_{i=1}^{n}\sum_{j=1}^{n}\sum_{k=1}^{n} C_{ijk}\, y_i\, y_j y_k$$

6. **Compressiblity Charts (e.g. Lee-Kesler) p. 245-246**

$$z = z^{(0)} + \omega\, z^{(1)}$$

Remarks:

i) Curves are based on reduced T isotherms.
ii) The horizontal axis is reduced pressures but on log scales.
iii) For subcritical values (i.e. $T_r < 1$ and $P_r < 1$), note whether the desired values are for the vapor or liquid state
iv) Can also use tables given in Appendix C.1 and C.2

7. **Equations of State for Liquids and Solids** (see table 4.4, p. 245, for values at $20°C$, 1 bar)

- Thermal expansion coefficient, β

$$\beta = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P$$

- Isothermal compressibility, κ

$$\kappa = -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T$$