The Reduced van der Waals Equation of State

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The van der Waals equation of state

- $$\left(P + \frac{a}{V^2}\right)(V - b) = Nk_B T \qquad (1)$$

  where a and b are constants characteristic of a particular gas, and k_B the Boltzmann constant. P, V, and T are as usual the pressure, volume, and temperature.

- It turns out that if we examine the isotherms of a van der Waals gas on a $P - V$ plot, one sees a point of inflection on the isotherm corresponding to the critical point of a gas. In other words, we have

$$\left(\frac{\partial P}{\partial V}\right)_{T=T_c} = 0 \quad \text{and} \quad \left(\frac{\partial^2 P}{\partial V^2}\right)_{T=T_c} = 0. \qquad (2)$$

Critical point

- Our goal is to derive a "reduced" form of the van der Waals equation that will not include the constants a and b.
- We first write the van der Waals equation in the form

$$P = \frac{Nk_B T}{V - b} - \frac{a}{V^2}. \tag{3}$$

- Next we find the first and second derivatives and set each one equal to zero:

$$\left(\frac{\partial P}{\partial V}\right)_{T=T_c} = -\frac{Nk_B T_c}{(V_c - b)^2} + \frac{2a}{V_c^3} = 0, \tag{4}$$

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_{T=T_c} = \frac{2Nk_B T_c}{(V_c - b)^3} - \frac{6a}{V_c^4} = 0. \tag{5}$$

- Solving these we find $V_c = 3b$, $Nk_B T_c = 8a/27b$, and $P_c = 8a/27b^2$.

Reduced equation of state

- Next, we define the following "reduced" quantities: $\bar{P} = P/P_c$, $\bar{V} = V/V_c$, and $\bar{T} = T/T_c$.
- Then van der Waals equation in terms of reduced parameters reads as

$$\left(\bar{P} + \frac{3}{\bar{V}^2}\right)(3\bar{V} - 1) = 8\,\bar{T}. \tag{6}$$

Compressibility ratio

- It is of interest to consider the "compressibility ratio"

$$Z_c = \frac{P_c V_c}{N K_B T_c}. \tag{7}$$

- For an ideal gas, this quantity is of course one. For a van der Waals gas, $Z_c = 3/8$.