

The Reduced van der Waals Equation of State

The van der Waals equation of state is

$$\left(p + \frac{n^2 a}{V^2}\right)(V - nb) = nRT \quad (1)$$

where n is the mole number, a and b are constants characteristic of a particular gas, and R the gas constant. P , V , and T are as usual the pressure, volume, and temperature. Here we are expressing the van der Waals equation in molar quantities; but as usual, we can replace nR by Nk and write it in terms of molecular quantities.

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

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

We set $n = 1$ mole for convenience and investigate these relations. 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

$$p = \frac{RT}{V - b} - \frac{a}{V^2}. \quad (2)$$

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

$$\left(\frac{\partial p}{\partial V}\right)_{T_c} = -\frac{RT_c}{(V_c - b)^2} + \frac{2a}{V_c^3} = 0 \quad (3)$$

$$\left(\frac{\partial^2 p}{\partial V^2}\right)_{T_c} = \frac{2RT_c}{(V_c - b)^3} - \frac{6a}{V_c^3} = 0. \quad (4)$$

Now we solve both Eq. (3) and Eq. (4) for RT_c .

$$RT_c = \frac{2a(V - b)^2}{V_c^3} \quad (5)$$

$$RT_c = \frac{3a(V_c - b)^3}{V_c^4} \quad (6)$$

Equating the right hand sides of these last two equations, we obtain

$$2a = 3a \frac{V_c - b}{V_c}$$

$$2V_c = 3V_c - 3b \quad \text{or finally,}$$

$$V_c = 3b \tag{7}$$

We substitute this result back into Eq. (5) to obtain

$$RT_c = \frac{2a(3b - b)^2}{(3b)^3} \quad \text{or}$$

$$RT_c = \frac{8a}{27b} \tag{8}$$

We substitute both of these results back into Eq. (2) to obtain

$$p_c = \frac{RT_c}{V_c - b} - \frac{a}{V_c^2} = \frac{\frac{8a}{27b}}{2b} - \frac{a}{9b^2} \quad \text{or}$$

$$p_c = \frac{8a}{27b^2} \tag{9}$$

Note that we have at this point found the critical quantities p_c , V_c , and T_c in terms of the constants a and b . We collect these three results as follows:

$$p_c = \frac{8a}{27b^2}$$

$$V_c = 3b$$

$$RT_c = \frac{8a}{27b} \tag{10}$$

Next, we define the following “reduced” quantities:

$$\tilde{p} = \frac{p}{p_c}; \quad \tilde{V} = \frac{V}{V_c}; \quad \tilde{T} = \frac{T}{T_c}. \tag{11}$$

Thus the molar van der Waals equation,

$$\left(p + \frac{a}{V^2} \right) (V - b) = RT,$$

becomes

$$\left(\frac{8a}{27b^2} \tilde{p} + \frac{a}{9b^2 \tilde{V}^2} \right) (3b\tilde{V} - b) = R \frac{\tilde{T}}{R} \frac{8a}{27b}.$$

Collecting terms and simplifying, we at last obtain the reduced van der Waals equation,

$$\left(\tilde{p} + \frac{3}{\tilde{V}^2}\right)(3\tilde{V} - 1) = 8\tilde{T}. \quad (12)$$

Exercise: Plot the isotherms of the reduced van der Waals equation and confirm that there is a point of inflection for the critical temperature, $\tilde{T} = 1$.

This equation, which implies that the equation of state for any van der Waals gas takes exactly the same form, is sometimes called the Law of Corresponding States. In fact, that law is a good deal more general. As the graph I will hand out in class shows, experimental data for a wide range of substances fall on the same curves if P , V , and T are measured in terms of the reduced quantities defined above. (The graph is taken from Stanley's book on critical phenomena, cited below.)

It is of interest to consider the "compressibility ratio" $Z_c = \frac{P_c V_c}{RT_c}$. For an ideal gas, this quantity is of course one. For a van der Waals gas,

$$Z_c = \frac{\frac{a}{27b^2}(3b)}{\frac{8a}{27b}} = \frac{3}{8} = 0.375. \quad (13)$$

This result should hold for any van der Waals gas. If we compare this prediction to the results of critical point measurements of real gases, we find something like the following table:

Fluid	$Z_c = \frac{P_c V_c}{RT_c}$
water	0.230
carbon dioxide (CO ₂)	0.275
nitrogen (N ₂)	0.291
hydrogen (H ₂)	0.304

For a more complete list (and discussion), see H. Eugene Stanley, *Introduction to Phase Transitions and Critical Phenomena*, Oxford, 1971, page69ff.

The moral is that although the van der Waals gas is clearly an improvement on the ideal gas—it at least predicts a phase transition, and shows the "scaling" features that can be found in reduced plots of real gases—it is by no means a highly accurate description.

Inversion Curve

Finally, consider the inversion curve for a van der Waals gas. We considered a Joule-Thompson (or Joule-Kelvin) process, in which a gas expands at constant enthalpy across a Joule-Thompson valve. We define the Joule-Thompson coefficient μ as

$$\mu \equiv \left(\frac{\partial T}{\partial p} \right)_H \quad (14)$$

To calculate this quantity, we consider

$$dH = TdS + Vdp. \quad (15)$$

We substitute the second TdS equation to obtain

$$dH = C_p dT - T \left(\frac{\partial V}{\partial T} \right)_p dp + Vdp$$

or, collecting terms,

$$dH = C_p dT + \left(V - T \left(\frac{\partial V}{\partial T} \right)_p \right) dp. \quad (16)$$

Since H is constant, $dH = 0$, whereupon Eq. (16) reduces to

$$\mu = \left(\frac{\partial T}{\partial p} \right)_H = - \frac{V - T \left(\frac{\partial V}{\partial T} \right)_p}{C_p} = \frac{V(\alpha T - 1)}{C_p} \quad (17)$$

where $\alpha \equiv \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p$ is the coefficient of thermal expansion. As we have seen, $\mu > 0$

implies the gas will become cooler, $\mu < 0$ implies the gas will actually warm up. Thus, $\mu = 0$, the equation of the inversion curve, is the curve that divides these two regions. Refer to the graph of temperature vs. pressure for hydrogen to understand how this situation plays out experimentally.

Exercise: Show that for an ideal gas, μ is always zero.

Exercise: Various approximation schemes lead to the result in for low densities, the inversion curve is given approximately by

$$kT_i = \frac{2a}{b} \quad (18)$$

Confirm this result by working through G&T page 287 carefully and in detail. Be sure you see how they introduce the low density approximation. Note that they implicitly define a density $\rho = N/V$. See Reif for a similar approach.

By comparison with Reif's experimental graph for nitrogen, persuade yourself that this result is not especially descriptive.

It is straightforward to find the inversion curve for a van der Waals gas. We start with the molar van der Waals equation of state,

$$p = \frac{RT}{V-b} - \frac{a}{V^2}$$

and calculate the expansion coefficient, as follows:

$$0 = \left(\frac{\partial p}{\partial T} \right)_p = \frac{R}{V-b} + \left\{ -\frac{RT}{(V-b)^2} + \frac{2a}{V^3} \right\} \left(\frac{\partial V}{\partial T} \right)_p.$$

We obtain after a little algebra the result

$$\begin{aligned} \left(\frac{\partial V}{\partial T} \right)_p &= \frac{\frac{R}{V-b}}{-\frac{RT}{(V-b)^2} + \frac{2a}{V^3}} \\ &= \frac{V-b}{T - \frac{2a}{R} \frac{(V-b)^2}{V^3}}. \end{aligned} \tag{19}$$

Hence the expansion coefficient is given by

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p = \frac{V-b}{VT - \frac{2a}{R} \left(\frac{V-b}{V} \right)^2} \tag{20}$$

We seek the inversion curve: $\mu = 0 \Rightarrow \alpha T - 1 = 0$. Using Eq. (20), it is straightforward to show

$$(V-b)T = VT - \frac{2a}{R} \left(\frac{V-b}{V} \right)^2,$$

which after a few lines of algebra reduces to

$$b = \frac{2a}{kT} \left(\frac{V-b}{V} \right)^2 \tag{21}$$

This result for the inversion curve is considerably more plausible than the approximate form cited above. To put it into a convenient form, we use reduced van der Waals quantities. It follows from Equations (10) and (11) above that

$$V = 3b\tilde{V}$$

$$RT = \frac{8a}{27b}\tilde{T}.$$

We substitute as follows into Eq. (21):

$$b = \frac{2a}{\frac{8a}{27b}\tilde{T}} \left(\frac{3b\tilde{V} - b}{3b\tilde{V}} \right)^2,$$

which after a little algebra reduces to

$$\frac{4\tilde{T}}{3} = \frac{(3\tilde{V} - 1)^2}{\tilde{V}^2} \quad (22)$$

Equation (22) is the equation of the reduced inversion curve. It is convenient to write it in terms of p and T . We will do so, in the process dispensing with the tilde symbol (\sim) for simplicity. We first note that, taking the square root of Eq. (22),

$$\sqrt{\frac{4T}{3}} = \frac{(3V - 1)}{V} \Rightarrow \frac{1}{V} = 3 - \sqrt{\frac{4T}{3}}.$$

We use this result to substitute into the reduced van der Waals equation [Eq. (12) above], which we write as

$$p = \frac{8T}{3V - 1} - \frac{3}{V^2};$$

we obtain

$$p = \frac{8T}{\sqrt{\frac{4T}{3}}V} - \frac{3}{V^2}$$

or

$$p = \frac{8T}{\sqrt{\frac{4T}{3}}} \left(3 - \sqrt{\frac{4T}{3}} \right) - 3 \left(3 - \sqrt{\frac{4T}{3}} \right)^2.$$

After several lines of algebra, we obtain at last the result

$$p = 9 - 12(\sqrt{T} - \sqrt{3})^2 \quad (23)$$

which gives us the inversion curve for the van der Waals equation in a useful form. If we solve for T as a function of p and make a graph, the resulting curve is qualitatively similar to the experimental inversion curve for nitrogen in Reif's book!