

Critical Constants of the van der Waals Gas

We saw in our discussion of critical phenomena that the mathematical definition of the critical point is,

$$\left(\frac{\partial p}{\partial V} \right)_T = 0, \quad (1)$$

and

$$\left(\frac{\partial^2 p}{\partial V^2} \right)_T = 0. \quad (2)$$

In other words, the critical isotherm on a p - V diagram has a point of inflection. Equations (1) and (2) constitute a set of two equations in two unknowns, V , and T . One can test to see if an approximate equation of state gives a critical point by calculating these two derivatives for the equation of state and trying to solve the pair of equations. If a solution exists (and T and V are neither zero or infinity) then we say that the equation of state has a critical point.

Let's use this test to see if a van der Waals gas has a critical point. First we have to solve the van der Waals equation of state for pressure, p ,

$$p = \frac{nRT}{V - nb} - a \frac{n^2}{V^2}. \quad (3)$$

Now we can take the derivatives in Equations 1 and 2 and set them (independently) equal to zero.

$$\left(\frac{\partial p}{\partial V} \right)_T = -\frac{nRT}{(V - nb)^2} + 2a \frac{n^2}{V^3} = 0 \quad (4)$$

$$\left(\frac{\partial^2 p}{\partial V^2} \right)_T = \frac{2nRT}{(V - nb)^3} - 6a \frac{n^2}{V^4} = 0. \quad (5)$$

In order to stress that from here on the problem is pure algebra, let's rewrite the simultaneous equations that must be solved for the two unknowns V and T (which solutions we will call V_C and T_C),

$$-\frac{nRT}{(V - nb)^2} + 2a \frac{n^2}{V^3} = 0 \quad (6)$$

$$\frac{2nRT}{(V - nb)^3} - 6a \frac{n^2}{V^4} = 0. \quad (7)$$

There are several ways to solve simultaneous equations. One way is to multiply Equation (6) by,

$$\frac{2}{V - nb}$$

to get

$$-\frac{2nRT}{(V - nb)^3} + 4a \frac{n^2}{V^3(V - nb)} = 0. \quad (8)$$

Now add equations (7) and (8). Note that in this addition the terms containing T will cancel out leaving,

$$-\frac{6an^2}{V^4} + 4a \frac{n^2}{V^3(V - nb)} = 0. \quad (9)$$

Divide Equation (9) by $2an^2$ and multiply it by V^3 (and bring the negative term to the other side of the equal sign) to get,

$$\frac{2}{(V - nb)} = \frac{3}{V}, \quad (10)$$

which is easily solved to get

$$V = V_c = 3nb. \quad (11)$$

To find the critical temperature, substitute the critical volume from Equation (11) into one of the derivatives (which equals zero) say Equation (6). This gives,

$$-\frac{nRT}{(3nb - nb)^2} + 2a \frac{n^2}{(3nb)^3} = 0, \quad (12)$$

which "cleans up" to give,

$$\frac{RT}{4} = \frac{2a}{27b}, \quad (13)$$

or

$$T = T_c = \frac{8a}{27bR}. \quad (14)$$

The critical pressure is obtained by substituting V_c and T_c into the van der Waals equations of state as solved for p in Equation (3).

$$\begin{aligned} p_c &= \frac{nRT_c}{V_c - nb} - a \frac{n^2}{V_c^2} \\ &= \frac{nR \left(\frac{8a}{27bR} \right)}{3nb - nb} - a \frac{n^2}{(3nb)^2}. \end{aligned} \quad (15 \text{ a,b})$$

This simplifies to,

$$p_c = \frac{a}{27b^2}. \quad (16)$$

Our conclusion is that the van der Waals equation of state does give a critical point since the set of simultaneous equations (Equations (1) and (2)) has a unique solution.

The van der Waals equation of state is still an approximate equation of state and does not represent any real gas exactly. However, it has some of the features of a real gas and is therefore useful as the next best approximation to a real gas. We will be deriving thermodynamic relationships (equations) using the ideal gas approximation. We can rederive some of these equations using the van der Waals equation of state in order to see how these relationships are affected by gas nonideality. .

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