

16.4: The Law of Corresponding States

van der Waals assumed that all real gases at corresponding states should behave similarly. The corresponding state that van der Waals chose to use is called the reduced state, which is based on the deviation of the conditions of a substance from its own critical conditions. We can define reduced quantities:

$$P_r = \frac{P}{P_c}$$

$$V_r = \frac{V}{V_c}$$

$$T_r = \frac{T}{T_c}$$

By substitution into the van der Waals equation we find:

$$\left(P_r + \frac{3}{\bar{V}_r^2} \right) \left(\bar{V}_r - \frac{1}{3} \right) = \frac{8}{3} T_r \quad (16.4.1)$$

Which means the critical parameters for a gas can be expressed in terms of a and b parameters:

$$V_c = 3b$$

$$P_c = \frac{a}{27b^2}$$

and:

$$T_c = \frac{8a}{27bR}$$

The formation of the van der Waals equation of state in terms of the critical parameters in Equation 16.4.1 is a universal equation for all gases. Although the actual pressures and volumes may differ, two gases are said to be in corresponding states if their reduced pressure, volume, and temperature are the same. What it says is that the behavior of all gases (and liquids!!) is pretty much the same, except for a scaling factor that is related to the critical point of the substance. The compressibility value (Z) of $3/8$ at the critical point for the van der Waals equation is actually not in such good agreement with measurement. This is why the more complicated Redlich-Kwong and Peng-Robertson expressions are better, although the idea is the same. Hence, all one needs to know to describe any fluid's behavior is its critical point. For example, argon behaves much the same at 300 K as ethane does at 600 K because these temperatures correspond to twice their respective critical temperatures (150.72 K and 305.4 K, respectively) so $T_r = 2.0$.

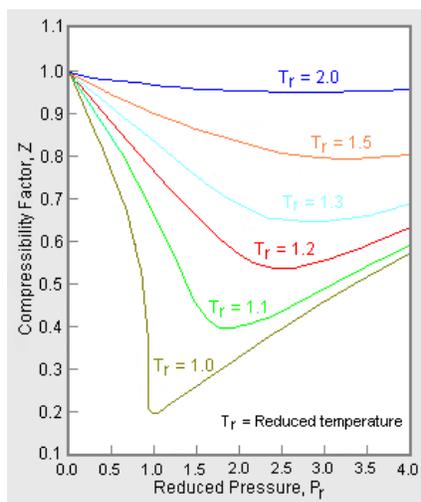


Figure 16.4.1 : Example of a generalized compressibility factor graph (Public domain; [Milton Beychok](#))

We can rewrite the universal expression for compressibility Z using reduced variables and plot measured values of Z versus the reduced pressure, P_r (see Figure 16.4.1). As you can see, very different gases/liquids like nitrogen and water can be made to coincide if their properties are plotted relative to their critical points rather than in absolute terms. The compressibility factor Z can also be cast into the form of corresponding states showing that Z also can be expressed as a universal function of V_r and T_r or any other two reduced quantities:

$$Z = \frac{\bar{V}_r}{\bar{V}_r - \frac{1}{3}} - \frac{9}{8\bar{V}_r T_r}$$

Van der Waals did not stop here. He went on to describe the root cause of condensation of gases into liquids at lower temperatures: the attractive interactions between the molecules.

Contributors and Attributions

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