Isotherms

Isotherms are plots of the pressure of a gas as a function of volume at a fixed constant temperature. The isotherms for an ideal gas are hyperbolae

\[ P = \frac{RT}{\bar{V}} \]

where \( \bar{V} \) is the molar volume \( (V/n) \). We know that at sufficiently low temperatures, any real gas, when compressed, must undergo a transition from gas to liquid. The signature of such a transition is a discontinuous change in the volume, signifying the condensation of the gas into a liquid that occupies a significantly lower volume.

Figure \( \PageIndex{1} \): Ideal gas isotherms for one mole of the gas and at select temperatures. (public domain).

The isotherms for the van der Waals Equation of state are shown in Figure \( \PageIndex{2} \). At sufficiently high temperature, the isotherms approach those of an ideal gas. However, we also see something strange in some of the isotherms. Specifically, we see a region in which \( P \) and \( V \) increase together, and we know that this cannot actually happen in a real gas. It should be clear that many approximations and assumptions go into the derivation of the van der Waals equation so that some of the important physics is missing from the model. Hence, we should not be surprised if the van der Waals equation has some unphysical behavior buried in it.
Figure \(\PageIndex{2}\): Different isotherms (curves of constant temperature) of the van der Waals equation of state using parameters \(a\) and \(b\) computed for carbon dioxide. The dashed line from A to B is drawn in accordance with Maxwell's equal area rule. The carbon dioxide molecule (CO\(_2\)) has \(p_C = 7.37\) MPa and \(T_C = 304.1\) K = 31 °C, which gives \(a = 0.366\) m\(^6\) Pa and \(b = 42.9\) \(10^{-6}\) m\(^3\). The critical pressure is at 73.7 bar = 7370 kPa.

For large volumes, the pressures are low and the fluid obeys approximately the ideal gas law \(pV = nRT\) for all temperatures shown. If we decrease the volume (go to the left in the figure along an isotherm), the pressure rises. Consider the (blue) isotherm of 10 °C, which is below the critical temperature. Decrease the volume until we reach the point B, where condensation (formation of liquid CO\(_2\)) starts. At this point the van der Waals curve is no longer physical (excluding the possibility of the occurrence of an oversaturated, metastable gas), because in reality from B to the left (to smaller volume), the pressure stays constant—equal to the vapor pressure of the liquid. The real physical behavior is given by the dashed blue line of gas-liquid coexistence.

Unfortunately, the van der Waals equation does not correctly predict the gas-liquid coexistence behavior, and hence, it must be added in \textit{ad hoc}. This is done by drawing a horizontal line through the isotherm (Figure \(\PageIndex{2}\)). The vertical position of the line is chosen so that the area above the line (between the line and the isotherm) and below the line (again between the line and the isotherm) is exactly the same. In this way, we entirely remove the artifact of the unphysical increase of \(\langle P\rangle\) with \(\langle V\rangle\) when we compute the compressional work on the gas from \(\langle\int P(V) \, dV\rangle\), to be discussed in our section on thermodynamics. This horizontal line is called the \textit{tie line}.

The areas, bounded by the 10 °C isotherm (blue curve), below and above the coexistence line are equal. This is the content of \textit{Maxwell's equal-area rule}. Decreasing the volume further, we end at point A where all molecules are now in the liquid phase, no molecules are remaining in the gas phase. When the volume is diminished of a vessel that contains only liquid, the pressure rises steeply, because the compressibility of a liquid is considerably smaller than that of a gas.

If one follows the (green) 31 °C curve of critical temperature, one meets a horizontal point of inflection (first and second derivatives of \(p\) with respect to \(V\) are zero). Note that the figure exhibits two isotherms of temperature higher than the critical temperature, if they are followed no liquid-gas phase transition will be seen; the higher pressure fluid will resemble a liquid, while at lower pressures the fluid will be more gas-like. At temperatures higher than the critical temperature no gas-liquid interface appears any longer. Although the maxima and minima in the van der Waals curves
below the critical point are not physical, the equation for these curves, derived by van der Waals in 1873, was a great scientific achievement.

Note

Even today it is not possible to give a single equation that describes correctly the gas-liquid phase transition.

As it happens, there is exactly one isotherm along which the van der Waals equation correctly predicts the gas-to-liquid phase transition. Along this isotherm, the volume discontinuity captured by the tie line is shrunk down to a single point (so that there is no possibility of an increase of \(\sqrt{P/V}\)). This isotherm, in fact, corresponds to the highest possible temperature at which such a transition can occur. As we approach this isotherm from higher temperatures, this isotherm is a kind of dividing line between the system's remaining a gas at all value of \(\sqrt{P/V}\) and the system's actually undergoing a gas-to-liquid transition. Hence, this isotherm is called the critical isotherm (the green curve in Figure \(\PageIndex{2}\)): The temperature of this isotherm is called the critical temperature, denoted \(T_c\). The point at which the curve flattens out, signifying the phase transition, is called the critical point. If we draw a curve through the isotherms joining all points of these isotherms at which the tie lines begin, continue the curve up to the critical isotherm, and down the other side where the tie lines end, this curve reaches a maximum at the critical point. This is illustrated below:

The shape of the critical isotherm at the critical point allows us to determine the exact temperature, pressure, and volume at which the phase transition from gas to liquid will occur. At this point, the isotherm is both horizontal and flat. This means that both the first and second derivatives of \(\sqrt{P/V}\) with respect to \(V\) must vanish:

\[
\frac{\partial P}{\partial V} = 0, \quad \frac{\partial^2 P}{\partial V^2} = 0
\]

Substituting the van der Waals equation into these two conditions, we find the following:

\[
\begin{align*}
-\frac{nRT}{(V - nb)^2} + \frac{2an^2}{V^3} &= 0 \\
\frac{nRT}{(V - nb)^3} - \frac{6an^2}{V^4} &= 0
\end{align*}
\]

Hence, we have two equations in two unknowns \(V\) and \(T\) for the critical temperature and critical volume. Once these are determined, the van der Waals equation, itself, allows us to determine the critical pressure.

To solve the equations, first divide one by the other. This gives us a simple condition for the volume:

\[
\begin{align*}
\frac{V - nb}{2} &= \frac{V}{3} \\
3V - 3nb &= 2V \quad \Rightarrow \quad V &= 3nb \equiv V_c
\end{align*}
\]

This is the critical volume. Now use either of the two conditions to obtain the critical temperature \(T_c\). If we use the first one, we find

\[
\begin{align*}
\frac{nRT_c}{(V_c - nb)^2} &= \frac{2an^2}{(3nb)^3} \\
\frac{nRT_c}{(3nb - nb)^3} &= \frac{2an^2}{27nb^3} \\
RT_c &= \frac{8a}{27b}
\end{align*}
\]

Finally, plugging the critical temperature and volume into the van der Waals equation, we obtain the critical pressure as
\[
\begin{align}
  P &= \frac{nRT_c}{V_c - nb} - \frac{an^2}{V_c^2} \\
  &= \frac{8an/27b}{3nb - nb} - \frac{an^2}{\left( 3nb \right)^2} \\
  &= \frac{a}{27b^2} 
\end{align}
\]

It comes as no surprise that cubic equations of state like the van der Waals (and Redlich-Kwong) equations yield three different roots for volume and compressibility factor. This is simply because they are algebraic equations, and any nth order algebraic equation will always yield “n” roots. However, those “n” roots are not required to be distinct, and that is not all: they are not required be real numbers, either. A quadratic expression (n = 2) may have zero real roots (e.g., \(x^2 + 1 = 0\)); this is because those roots are complex numbers. In the case of cubic expressions (n = 3), we will either have one or three real roots; this is because complex roots always show up in pairs (i.e., once you have a complex root, its conjugate must also be a solution). In our case, and because we are dealing with physical quantities (densities, volumes, compressibility factors), only real roots are of interest. More specifically, we look for real, positive roots such that \(\bar{V} > b\) in the case of molar volume and \(Z > Pb/RT\) in the case of compressibility factor.

In a cubic equation of state, the possibility of three real roots is restricted to the case of sub-critical conditions (\(T < T_c\)), because the S-shaped behavior, which represents the vapor-liquid transition, takes place only at temperatures below critical. This restriction is mathematically imposed by the criticality conditions. Anywhere else, beyond the S-shaped curve, we will only get one real root of the type \(\bar{V} > b\). Figure \(\PageIndex{3}\) illustrates this point.

**Figure \(\PageIndex{3}\):** *Multiple Roots in Cubic EOS*

Let us examine the three cases presented in Figure \(\PageIndex{3}\):

1. Supercritical isotherms (\(T > T_c\)): At temperatures beyond critical, the cubic equation will have only one real root (the other two are imaginary complex conjugates). In this case, there is no ambiguity in the assignment of the volume root since we have single-phase conditions. The occurrence of a unique real root remains valid at any pressure: any horizontal (isobaric) line cuts the supercritical isotherm just once in Figure \(\PageIndex{3}\).

2. Critical isotherm (\(T = T_c\)): At the critical point (\(P = P_c\)), vapor and liquid properties are the same. Consequently, the cubic equation predicts three real and equal roots at this special and particular point. However, for any other pressure along the critical isotherm (\(P < P_c\) or \(P > P_c\)) the cubic equation gives a unique real root with two complex conjugates.
3. Subcritical isotherm \((T < T_c)\): Predictions for pressures within the pressure range for metastability \((P_A' < P < P_B')\) or for the saturation condition \((P = P^{sat})\) will always yield three real, different roots. In fact, this is the only region in Figure 10.1 where an isobar cuts the same isotherm more than once. The smallest root is taken as the specific volume of the liquid phase; the largest is the specific volume of the vapor phase; the intermediate root is not computed as it is physically meaningless. However, do not get carried away. Subcritical conditions will not always yield three real roots of the type \(\overline{\nu} > b\). If the pressure is higher than the maximum of the S-shaped curve, \((P_B')\), we will only have one (liquid) real root that satisfies \(\overline{\nu} > b\). By the same token, pressures between \((0 < P < P_A')\) yield only one (vapor) root. In the case of \((P_A')\) being a negative number, three real roots are to be found even for very low pressures when the ideal gas law applies. This can be seen in Figure 10.1 as well. The largest root is always the correct choice for the gas phase molar volume of pure components.

Most of these considerations apply to the cubic equation of state in \(Z\) (compressibility factor). The most common graphical representation of compressibility factor is the well-known chart of Standing and Katz, where \(Z\) is plotted against pressure (Figure \(\PageIndex{4}\)). Standing and Katz presented their chart for the compressibility factor \((Z)\) of sweet natural gases in 1942. This chart was based on experimental data. Graphical determination of properties was widespread until the advent of computers, and thus the Standing and Katz \(Z\)-chart became very popular in the natural gas industry. Typical Standing and Katz charts are given for high temperature conditions \((T > T_c)\) or \((T_r > 1)\). Figure \(\PageIndex{2}\), using a cubic equation of state for a pure gas, presents the qualitative behavior of the solution of \(Z\) versus pressure. Isotherms \((T > T_c)\) show the typical qualitative behavior we are accustomed to seeing in the Standing and Katz chart.

\[\text{Figure } \PageIndex{4}: \text{Compressibility Factor versus Pressure}\]

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