10.3: Redlich-Kwong EOS (1949)

The vdW cubic equation of state had to wait almost 100 years before a real, successful improvement was introduced to it. As we stated before, this progress occurred once researchers committed themselves to finding the empirical temperature dependency of the attraction parameter \(a\) proposed by van der Waals. In contrast, very little attention has been paid to modifying the parameter \(b\) for co-volume. It makes a lot of sense that \(b\) would not be modified by temperature, because it represents the volume of the molecules, which should not be affected by their kinetic energy (measured in terms of temperature).

The very first noteworthy successful modification to the attraction parameter came with the publication of the equation of state of Redlich-Kwong in 1949. Redlich and Kwong revised van der Waals EOS and proposed the following expression:

\[
\left(P+\frac{a}{T^{0.5} v(v+b)}\right)(v-b)=R T \label{10.1}
\]

Notice that the fundamental change they introduced was to the functional form of \(\delta P_{\text{attraction}}\) (equation 7.8). Additionally, they introduced the co-volume “b” into the denominator of this functional form.

The important concept here is that the attraction parameter “a” of van der Waals needed to be made a function of temperature before any cubic EOS was able to do a better job of quantitatively matching experimental data. This was a realization that vdW himself had suggested, but no actual functional dependency had been introduced until the Redlich-Kwong EOS.

We know what follows at this point. To come up with an expression for “a” and “b” of Equation \ref{10.1}, we apply the criticality conditions to this EOS. As we recall, imposing the criticality conditions allows us to relate the coefficients “a” and “b” to the critical properties \((P_c, T_c)\) of the substance. Once we have done that, we obtain the definition of “a” and “b” for the Redlich-Kwong EOS,
\[a=0.427480 \frac{R^2 T_c^{2.5}}{P_c} \label{10.2a}\]
\[b=0.086640 \frac{RT_c}{P_c} \label{10.2b}\]

This EOS radically improved, in a quantitative sense, the predictions of vdW EOS. We now recall that vdW-type equations are cubic because they are cubic polynomials in molar volume and compressibility factor. It comes as no surprise then, that we can transform Equation \ref{10.1} into:
\[\tilde{v}^3 - \left(\frac{RT}{P}\right)\bar{v}^2 + \frac{1}{P}\left(\frac{a}{T^{0.5}} - b RT - pb^2\right)\bar{v} - \frac{ab}{T^{0.5}} = 0 \label{10.3}\]

and, by defining the following parameters,
\[A=\frac{a P}{R^2 T^{2.5}} \label{10.3a}\]
\[B=\frac{b P}{RT} \label{10.3b}\]

and introducing the compressibility factor definition (\(Z=\frac{P \tilde{v}}{RT}\)), we get:
\[Z^3 - Z^2 + \left(A-B-B^2\right)Z - AB = 0 \label{10.4}\]

We may also verify the two-parameter corresponding state theory by introducing Equations \ref{10.2a}, \ref{10.2b}, and \ref{10.3} into Equation \ref{10.4},
\[Z^3 - Z^2 + \frac{P_r}{T_r}\left(\frac{0.42748}{T_r^{1.5}} - 0.08664 - 0.007506 \frac{P_r}{T_r}\right)Z - 0.03704 \frac{P_r^2}{T_r^{3.5}} = 0 \label{10.5}\]

In Equation \ref{10.5} we can observe the same thing that we saw with vdW EOS: gases at corresponding states have the same properties. Equation \ref{10.5} is particularly clear about it: any two different gases at the same \(P_r, T_r\) condition **have the same compressibility factor**.

Just as any other cubic equation of state, Equations \ref{10.1}-\ref{10.5}, as they stand, are to be applied to pure substances. For mixtures, however, we apply the same equation, but we impose certain mixing rules to obtain “a” and “b”, which are functions of the properties of the pure components. Strictly speaking, we create a new “pseudo” pure substance that has the average properties of the mixture. Redlich-Kwong preserved the same mixing rules that vdW proposed for his EOS:
\[a_{(m)}=\sum_{(i)} \sum_{(j)} y_{(i)} y_{(j)} a_{(i j)} \label{10.6a1}\]
\[a_{(i j)}=\sqrt{a_{(i)} a_{(j)}} \label{10.6a2}\]
\[b_{(m)}=\sum_{(i)} y_{(i)} b_{(i)} \label{10.6b}\]

Naturally, Redlich and Kwong did not have the last word on possible improvements to the vdW EOS. The Redlich-Kwong EOS, as shown here, is no longer used in practical applications. Research continued and brought with it new attempts to improve the RK EOS. After more than two decades, a modified RK EOS with very good potential was developed. The **Soave-RK EOS** was born.
Contributors and Attributions

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