7.2: Definition of Equation of State (EOS)

Assuming an equilibrium state, the three properties needed to completely define the state of a system are pressure (P), volume (V), and temperature (T). Hence, we should be able to formulate an equation relating these 3 variables, of the form \( f(P, T, V) = 0 \).

An equation of state (EOS) is a functional relationship between state variables — usually a complete set of such variables. Most EOS are written to express functional relationships between \( P, T \) and \( V \). It is also true that most EOS are still empirical or semi-empirical. Hence, the definition:

An Equation of State (EOS) is a semi-empirical functional relationship between pressure, volume and temperature of a pure substance. We can also apply an EOS to a mixture by invoking appropriate mixing rules.

There have been a number of attempts to derive a theoretically sound EOS; but, generally speaking, not much success has been achieved along that line. As a result, we use what are known as semi-empirical EOS. Most equations of state used today are semi-empirical in nature, this being so because they are fitted to data that are available. Additionally, equations of state are generally developed for pure substances. Their application to mixtures requires an additional variable (composition) and hence an appropriate mixing rule.

The functional form of an EOS can be expressed as:

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\text{Contact your instructor if you are unable to see or interpret this graphic. (7.4)}
\]

where \( a_k \) = EOS parameters.

As we stated earlier, most applicable EOS today are semi-empirical, in the sense that they have some theoretical basis.
but their parameters \((a_k)\) must be adjusted. The number of parameters \((n_p)\) determines the category/complexity of the EOS. For instance, 1-parameter EOS are those for which \(n_p = 1\), and 2-parameter EOS are those for which \(n_p = 2\). The higher \(n_p\) is, the more complex is the EOS. Also, in general terms, the more complex the EOS, the more accurate it is. However, this is not always the case; in some cases a rather simple EOS can do a very good job.

Since the time of the ideal gas law (ideal gas EOS), a great number of equations of state have been proposed to describe real gas behavior. However, many of those have not passed the test of time. Only few have persisted through the years, this because of their relative simplicity. In the petroleum business, the most common modern EOS are the Peng Robinson EOS (PR EOS) and Soave-Redlich-Kwong EOS (SRK EOS). Both of these are cubic EOS and hence derivations of the van der Waals EOS, which we will be discussing next. There are other more complex EOS, although they have not yet found widespread application in our field:

- Lee Kesler EOS (LK EOS)
- Benedict-Webb-Rubin EOS (BWR EOS)
- Benedict-Webb-Rubin-Starling EOS (BWRS EOS)

In the natural gas business, especially in the gas transmission industry, the standard EOS used is the AGA EOS; this is an ultra-accurate EOS for Z-factor calculations — a very sensitive variable for custody-transfer operations.

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