Chapter 5 – Single Phase Systems

Chemical engineering calculations rely heavily on the availability of physical properties of materials. There are three common methods used to find these properties. These include measuring them, looking them up in the available literature, and finally they can be estimated using physical models, that usually come in the form of equations.

1. Properties of Pure Ideal Components

Definitions

**Correlation:** This is a mathematical fit of experimental data (usually using statistical methods). These are used either in place of or in conjunction with physically based models.

**Equations of State (EOS):** These are correlation or physically based equations that relate Pressure, Volume, and Temperature that exist inside a material (typically gas). These three thermodynamic variables are easily measured and make up what is known as a PVT relationship.

**Incompressible:** This term is used to specify the assumption of constant density of a material. Incompressibility is closely followed by liquids and solids under many situations of interest.

Density of Liquids and Solids

**Solutions and Mixtures.** The density of a liquid or solid solution can be approximated by the following:

$$ \bar{\rho} = \sum_{i=1}^{n} x_i \rho_i $$

(1)

$$ \frac{1}{\bar{\rho}} = \sum_{i=1}^{n} x_i \rho_i $$

(2)
Here, $x_i$ is the mass fraction of component $i$. The density of the solution, $\rho$, is found by adding contributions from each pure component density $\rho_i$ according to its mass fraction. The more you have of $i$, the more it affects the total average density. Equation 2 assumes that the total volume is the sum of the individual volumes; although this additive volume concept may make sense intuitively it is not necessarily true. Volume additivity is relatively accurate for solutions of liquids with similar molecular structures. In general, the accuracy of equation 1 over equation 2 depends on the system considered.

Example. What is the average density of a hexane/octane mixture comprised of 10 kg of hexane and 30 kg of octane? The density of hexane is 0.66 and that of octane is 0.703.

### Density of Gases/Ideal Gas Equation

Gases are highly compressible, and therefore the incompressibility assumption does not apply. EOS’s then must include the pressure, temperature, and volume to account for the variation of the density of a gas. The simplest of these models is the ideal gas equation of state:

$$PV = nRT$$

where

- $P$ Absolute Pressure
- $V$ (V, $\dot{V}$) Volume (Volumetric Flow Rate, Specific molar volume [= volume of 1 mole of gas particles])
- $n$ ($\dot{n}$) Number of moles (molar flow rate)
- $R$ Ideal gas constant
- $T$ Absolute temperature
- $m$ Mass
- $M$ Molar mass (molecular weight)
- $\rho$ Density
Equation 3 can be rewritten in other forms. These alternate forms may be useful depending on the situation; they are given below:

\[ PV = \dot{n}RT \]  \quad (4) \quad \text{using} \quad \dot{V} = V / \Delta t; \, \dot{n} = n / \Delta t

\[ P\dot{V} = RT \]  \quad (5) \quad \text{using} \quad \dot{V} = V / n

\[ P = \frac{\rho RT}{M} \]  \quad (6) \quad \text{using} \quad n = m/M

The ideal gas EOS is based on the primary assumptions that

- There are no intermolecular forces between the gas particles.
- The volumes of molecules are negligible (i.e. the gas particles can be treated as “point” particles).

Understanding these assumptions helps to understand the utility and limitations of this EOS. For example the ideal gas assumption cannot be used at higher pressures because molecules will interact with each other. Also, at lower temperatures there can be substantial error associated with the ideal gas equation, because molecules do not have enough thermal energy to overcome the interactions between one another. Generally, the ideal gas EOS works well at pressures of 1 atm or less and temperatures greater than 0 °C (both conditions should be satisfied). The text describes further tests that can be applied to validate the applicability of ideal gas behavior.

**Standard Temperature and Pressure (STP)**. Most often (always for this course), STP conditions are defined as 0°C and 1 atm. *Standard cubic meters (SCM)* and *standard cubic feet (SCF)* refer to volumes of gas evaluated at STP conditions.

The volume of one mole of ideal gas at STP is 22.415 L = 0.022415 m³. The volume of 1 lb-mole of ideal gas at STP is 359.05 ft³.

**Example 5.2-4.**
The flow rate of a methane stream at 285 °F and 1.30 atm is stated to be 3.95 × 10⁵ SCFM. What are the molar flowrate and true volumetric flowrate of the stream?


**Ideal Gas Mixtures**

Imagine we have a gas mixture inside a container. We can then define:

**Partial Pressure:** This is the pressure, $P_i$, that the moles of gas $i$ in the gas mixture would exert if the moles of gas $i$ was all that was present in the container (at the same temperature $T$).

**Pure Component Volume:** This is the volume, $v_i$, that the moles of pure gas $i$ would occupy at the total pressure $P$ and temperature $T$ of the mixture.

In an ideal gas mixture, the various gas molecules do not interact. This means that the pressure exerted by each component $i$ is independent of the others; thus its partial pressure is given by

$$P_i V = n_i RT$$

Dividing the above by the ideal gas EOS as applied to the total mixture (which is assumed to behave ideally), we get

$$P_i V / (PV) = n_i RT / (nRT) \quad \text{or} \quad P_i = y_i P$$

(4)

Therefore, the partial pressure of gas $i$ in an ideal gas mixture can be calculated from the total pressure $P$ and its mole fraction $y_i$.

**Dalton’s Law** states that the sum of the partial pressures over all the gases present in a mixture equals the total pressure (this follows from equation (4) and the fact that $\sum_i y_i = 1$). For example, for a mixture of three gases $A$, $B$ and $C$:

$$p_A + p_B + p_C = (y_A P + y_B P + y_C P) = P$$

(5)

There is an analogous law - **Amagat’s Law** – for the pure component volumes $v_i$ of an ideal gas mixture. Amagat’s law states that the sum of the pure component volumes is equal to the total volume:

$$v_A + v_B + v_C = V$$

(6)
where \( v_i \) is given by

\[
v_i = y_i V
\]  

(7)

Note that the volume fraction of \( i \), that is the ratio between the pure component volume of \( i \) and the total volume, is also equal to the mole fraction, \( v_i/V = y_i \). Thus, in an ideal gas mixture, the mole fraction and volume fraction of \( i \) are numerically equivalent.

Example. Prove equation (6).
Non-ideal Gases

Definitions

**Critical Temperature:** This is the temperature, \( T_c \), above which a pure component can no longer coexist as a mixture of liquid and vapor phases.

**Critical Point (Critical State) of a Fluid:** The critical point for a fluid refers to the state when the fluid is at \( T_c \) and the corresponding critical pressure, \( P_c \). Such a fluid can still coexist, at \( T_c \) and \( P_c \), as a liquid and a vapor mixture. However, if the temperature increases past \( T_c \) then coexistence is not possible and the fluid is referred to as a supercritical fluid (for \( P > P_c \)) or as a gas (for \( P < P_c \)).

**Critical Pressure:** This is the pressure, \( P_c \), at the critical point.

**Reduced Pressure** (\( P_r \)): This is the actual pressure of a fluid divided by its critical pressure, \( P_r = P/P_c \).

**Reduced Temperature** (\( T_r \)): This is the actual temperature of a fluid divided by its critical temperature, \( T_r = T/T_c \).

**Law of Corresponding States:** This is an empirically based principle that states that all fluids deviate from ideality in a similar fashion, when compared at the same reduced temperature \( T/T_c \) and reduced pressure \( P/P_c \).

**Pitzer Accentric Factor:** This factor (symbol \( \omega \)), is a parameter used in non-ideal equations of state that takes into account the geometry and polarity of a molecule.

**Nonideal gases:** Because in reality molecules of a gas do interact, all real gases are nonideal. Even though the ideal gas EOS may be a very good approximation at low pressures and high temperatures, at higher pressures and/or lower temperatures the impact of intermolecular interactions on gas behavior increases. Then, methods for nonideal gases must be used to account for the effect of these interactions on the relationship between \( P, V, \) and \( T \) (and related properties such as density) of a gas. Below, the following five methods will be introduced:
A. Virial Equation of State
B. Van der Waals Equation of State
C. Soave-Redlich-Kwong (SRK) Equation of State
D. Compressibility Factor Equation of State
E. Kay’s Rule (for nonideal gas mixtures)

Virial Equation of State

The virial equation of state is an infinite power series in the inverse of the specific molar volume:

\[
\frac{P\hat{V}}{RT} = 1 + \frac{B}{\hat{V}} + \frac{C}{\hat{V}^2} + \frac{D}{\hat{V}^3} + \cdots
\]  

(8)

Equation 8 has a rigorous theoretical basis. With \(B\) and all higher virial coefficients set to 0, it reduces to the ideal gas EOS. Most often, the virial EOS is truncated after the second term to simplify to:

\[
\frac{P\hat{V}}{RT} = 1 + \frac{B}{\hat{V}} \quad \text{or} \quad \frac{P}{RT} \hat{V}^2 - \hat{V} = B
\]  

(9)

\(B\) is called the second virial coefficient. If \(P\) is the unknown, equation 8 or 9 is easily solved. If the specific molar volume is the unknown, the truncated equation 9 can be solved using the quadratic formula. Note, however, that equation 9 loses accuracy for polar molecules.

\(B\) can be estimated from the following corresponding states correlations:

\[
B_0 = 0.083 - \frac{0.422}{T_r^{1.6}}
\]  

(10)

\[
B_1 = 0.139 - \frac{0.172}{T_r^{4.2}}
\]  

(11)

\[
B = \frac{RT_c}{P_c} \left( B_0 + \omega B_1 \right)
\]  

(12)

Our text lists values for the Pitzer accentric factor in table 5.3-1 and for the critical pressure and temperature in Appendix B (table B.1).
Van der Waals Equation of State

Starting with the ideal EOS,

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

two modifications can be made to account for non-ideal behavior:

\[ P = \frac{RT}{\hat{V} - b} - \frac{a}{\hat{V}^2} \]  \hspace{1cm} (13)

The “−b” in the denominator accounts for the fact that real gas molecules do possess a volume; thus reducing the total volume available to the gas (what would happen if a Van der Waals gas is progressively compressed?). The second term on the right, involving \( a \), accounts for molecular interactions. A positive \( a \) implies that the gas molecules attract one another. The effect of this attraction is to reduce the tendency (and thus the pressure) of the gas to expand. The parameters \( a \) and \( b \) change from one gas to another but are independent of temperature. They can be expressed as functions of the critical temperature and pressure:

\[ a = \frac{27R^2T_c^2}{64P_c} \quad b = \frac{RT_c}{8P_c} \]  \hspace{1cm} (14)

The Van der Waals EOS allows solution for \( P \) if \( T \) and \( \hat{V} \), and the critical state, are known. If the equation were instead to be solved for \( \hat{V} \), a cubic equation would result which can be solved by trial and error. Alternately, a rather lengthy analytical formula exists for the roots of a cubic equation that could also be used. Thus, the Van der Waals EOS is an example of a cubic equation of state.

Soave-Redlich-Kwong (SRK) Equation of State

A more accurate cubic EOS is the empirical SRK equation:
\[ P = \frac{RT}{\hat{V} - b} - \frac{\alpha a}{\hat{V}(\hat{V} + b)} \quad (15) \]

The parameters of the SRK EOS are calculated from the following:

\[ a = 0.42747 \frac{R^2T_c^2}{P_c} \quad (16) \]
\[ b = 0.08664 \frac{RT_c}{P_c} \quad (17) \]
\[ \alpha = \left[ 1 + m (1 - \sqrt{T_r}) \right]^2 \quad (18) \]
\[ m = 0.48508 + 1.55171\omega - 0.1561\omega^2 \quad (19) \]

*Example 5.3-3.* A stream of propane flows at 100.0 kmol/h, at temperature 423 °K and pressure \( P \). Using the SRK EOS, estimate the volumetric flowrate of the stream for \( P = 0.7 \) atm and \( P = 70 \) atm. Also, calculate the percentage difference in the volumetric flowrate between the values obtained from the SRK EOS and the ideal gas EOS.
Compressibility Factor Equation of State

The compressibility factor $Z$ for a gas is defined as $Z = \frac{P\hat{V}}{RT}$. $Z$ serves as a measure of deviation from ideal behavior. If the gas is ideal, then $Z = 1$; otherwise, it has a value other than unity.

If $Z$ is known, it can be used to calculate $P$ from $T$ and $\hat{V}$, or $\hat{V}$ from $P$ and $T$, etc., just as we did for an ideal gas using:

$$P\hat{V} = ZRT \quad \text{or} \quad P\hat{V} = Z\hat{v}RT \quad (20)$$

Where can $Z$ values be found? One can appeal to the law of corresponding states. In particular, we will assume that the compressibility factor $Z$, for an arbitrary gas, depends predominantly on the proximity to its critical state as captured in the reduced temperature $T_r$ and reduced pressure $P_r$. Then, a generalized compressibility chart can be constructed which gives values of $Z$ as a function of $T_r$ and $P_r$ (e.g. see Fig. 5.4-1 in the text). If we take a look at such a chart, we’ll notice that as a fluid approaches its critical state it markedly deviates from ideal gas behavior. Strong deviations are also observed at low temperatures and high pressures.

The procedure for using the generalized compressibility chart is as follows:

1. Find the critical pressure and the critical temperature for the fluid of interest (note: if the fluid is hydrogen or helium these critical values must be corrected – see text).
2. Calculate the reduced pressure and temperature (note: all temperatures used must be absolute!).
3. Use the compressibility chart to determine $Z$.

In some problems, the pressure or the temperature may be unknown, and instead the molar volume $\hat{V}$ is given. In that case, you can instead calculate an “ideal” reduced volume as follows:

$$\hat{V}_{r,\text{ideal}} = \frac{P_r\hat{V}}{RT_r} \quad (21)$$
and use a generalized compressibility chart that is expressed in terms of $\hat{V}_r^{\text{ideal}}$ instead of the unknown pressure or temperature (see Fig. 5.4-4 in the text).

**Kay’s Rule – Nonideal Gas Mixtures**

Above, we considered several methods for accounting for the nonideal behavior of real, but pure, gases. What about mixtures of nonideal gases? In general, this is a difficult problem. Kay’s Rule is a relatively simple method that works best for mixtures of nonpolar gases whose critical temperatures and pressures are within about a factor of 2 of one another.

Kay’s Rule is an empirical mixing rule that uses data from generalized compressibility charts. The procedure for using Kay’s Rule is as follows:

1. Calculate the **pseudocritical pressure** $P_c^*$ and the **pseudocritical temperature** $T_c^*$ for the mixture, using (with corrections for H$_2$ and He if needed):
   
   \[ P_c^* = y_A P_{cA} + y_B P_{cB} + y_C P_{cC} + \cdots \]  
   \[ T_c^* = y_A T_{cA} + y_B T_{cB} + y_C T_{cC} + \cdots \]  

2. Calculate the **pseudoreduced pressure** and the **pseudoreduced temperature**, using:
   
   \[ P_r^* = P/P_c^* \]  
   \[ T_r^* = T/T_c^* \]  

   If $\hat{V}$ for the mixture is known instead of $T$ or $P$, you can calculate a pseudoreduced ideal volume, $V_r^{\text{ideal}} = P_c^* \hat{V}/RT_c^*$, instead of the pseudoreduced temperature or pseudoreduced pressure.

3. Use the generalized compressibility charts to determine $Z_m$, the compressibility factor for the mixture, making use of the pseudoreduced values just as you would of the reduced values in the case of a pure fluid.

The compressibility factor EOS for a nonideal mixture is defined as for a pure fluid:

\[ P\hat{V} = Z_m RT \]  

\[ \text{(26)} \]
**Final remark:** All equations of state discussed above have inherent approximations, and like the ideal gas equation have ranges of validity and errors associated with them.