

Chapter 5

PVT CORRELATIONS

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1. Ideal Gas

To solve most problems that involve gases, an expression is needed that relates specific volume to temperature and pressure so that if any two of three properties are known, the third can be calculated. An equation that relates the quantities (mass or moles) and volume of a gas to its pressure and temperature is call **Equation of State**. The simplest and most widely used equation of state is the **ideal gas law** which is adequate for many engineering calculations over a wide range of conditions. At high pressures and low temperatures, however, all gases deviate from ideal behavior and more complex equations of state are needed to describe PVT relations.

1.1. Ideal Gas Law

The ideal gas law can be derived from the kinetic theory of gases by assuming that gas molecules have negligible volume, exert no force on one another and collide elastically with walls of their container. This law can be expressed as:

$$PV = nRT \quad (1)$$

where,

- P = Absolute pressure of the gas
- V = Volume of the gas
- n = Number of moles of the gas
- R = The gas constant
- T = Absolute temperature of the gas

The above equation can be written for one mole of the gas, as

$$Pv = RT \quad (2)$$

The gas constant, R, has the units of (Pressure)(volume)/(mole)(temperature). Since the product of pressure and volume has units of energy, R may also be expressed as (energy)/(mole)(temperature). The units of R are listed on the last page of Felder and Rousseau in various system of units.

1.2. Standard Conditions

The reference temperature of 0°C (273 K, 492 R) and a pressure of one atmosphere (1 atm) are commonly referred to as standard temperature and pressure. The gas law gives,

$$P_s V_s = n_s R T_s \quad (3)$$

or,

$$R = \left(\frac{P_s}{T_s} \right) \left(\frac{V_s}{n_s} \right) \quad (4)$$

however,

$$\left(\frac{V_s}{n_s} \right) = 22.4 \frac{\text{liters}}{\text{mol}} (STP) = 359 \frac{\text{ft}^3}{\text{lbmol}} (STP)$$

The value of gas constant R can therefore be calculated from equation (4).

1.3. Ideal Gas Mixtures

Let us consider a mixture of ideal gases and assume that the mixture itself can be considered an ideal gas. Let us further assume that the mixture consists of components A and B and that initially the components are separated and exist at temperature and pressure of the mixture as shown schematically in the figure below.

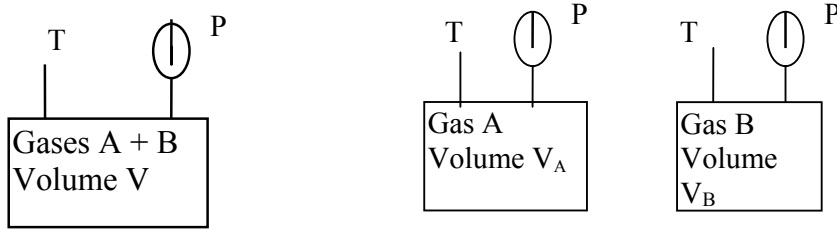


Figure 3. The Amagat's rule

We can then write the equation of state for the individual component on a molal basis as follows:

$$PV_A = n_A RT \quad (5)$$

$$PV_B = n_B RT \quad (6)$$

At the same temperature and pressure, if the components are mixed together in one container, then

$$PV = n RT \quad (1)$$

It therefore follows that

$$\frac{V_A}{V} = \frac{n_A}{n} = y_A \quad (7)$$

This equation simply means that volume fraction (V_A/V) is equation to mole fraction.

Further,

$$n = n_A + n_B \quad (8)$$

or

$$\frac{PV}{RT} = \frac{PV_A}{RT_A} + \frac{PV_B}{RT_B} \quad (9)$$

i.e.
$$V = V_A + V_B \quad (10)$$

This leads to the Amagat's rule of additive volumes which states that the volume of the mixture is equal to the sum of the volumes of individual constituents at the temperature and pressure of the mixture.

An alternate approach in the analysis of ideal gas mixture is to consider that each component occupies the entire volume. The pressure of the component under these conditions is referred to as partial pressure. This is shown schematically in Figure 4.

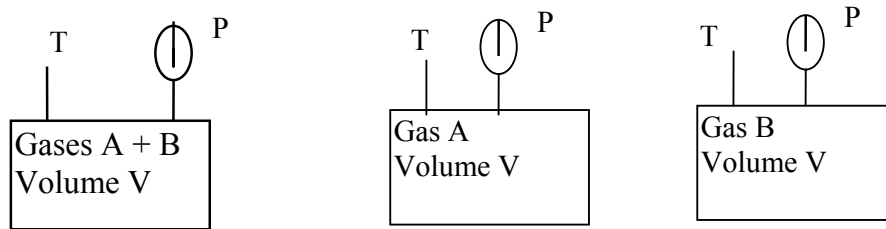


Figure 4. The Dalton's model

The equation of state of each component of the mixture:

$$P_A V = n_A R T \quad (11)$$

$$P_B V = n_B R T \quad (12)$$

$$P V = n R T \quad (1)$$

$$\frac{P_A}{P} = \frac{n_A}{n} = y_A \quad (13)$$

Therefore, the ratio of partial pressure of the component to the total pressure is equal to the mole fraction.

Further,

$$n = n_A + n_B \quad (8)$$

$$\frac{PV}{RT} = \frac{P_A V}{RT} + \frac{P_B V}{RT} \quad (14)$$

i.e. $P = P_A + P_B \quad (15)$

where each partial pressure is evaluated at the temperature and volume of the mixture. The above equation is called **Dalton's law of Partial Pressure**.

2. Real Gas

As the temperature of the gas decreases and the pressure increases, the ideal gas law discussed earlier provides increasingly poor description of the gas behavior. It becomes essential to turn to other equations of state which may satisfactorily represent the PVT behavior.

One approach to represent the PVT behavior of real gases is to use equations of state that contain number of constants whose value differ for different gases. Another approach is to correct the deviation from ideal behavior by including a term called the **compressibility factor** in the ideal gas law. The resulting equation is called the compressibility factor equation of state.

2.1. Compressibility Factor Equation of State

An equation of state that retains the simplicity of ideal gas law but describes the PVT behavior of real gases over a much wider range of conditions is of the following form:

$$PV = Z n R T \quad (16)$$

$$P v = Z R T \quad (17)$$

The coefficient Z is called the compressibility factor and the equation is called the compressibility equation of state. A value of $Z = 1$ corresponds to ideal gas behavior.

The compressibility factor depends on the gas temperature and pressure and differs for different gases at a given T and P .

2.2. Estimation of Compressibility Factors

2.2.1 Law of Corresponding States

It is possible to construct a single universal chart for the estimation of compressibility factors for all gases if independent variables other than P and T are used. Figure 5 (Figure 5.4 in Felder and Rousseau) shows such a plot called generalized compressibility chart. The variables P and T are replaced by $P_r = (P/P_c)$, and $T_r = (T/T_c)$ where P_c and T_c are critical pressure and temperature respectively of the gas. The basis for the generalized compressibility chart is the experimentally observed fact that the value of certain physical properties of gases, such as compressibility depend on a greater extent on how near the gas is to its critical state. This suggests that a plot of Z versus reduced temperature (T_r) and reduced pressure (P_r) should be approximately be the same for all substances which indeed is the case. This assertion is known as **law of corresponding states**.

2.3. Real Gas Mixtures

The techniques that is both simple and reasonably accurate is Kay's Rule which uses the compressibility factor equation of state:

$$PV = Z_m n R T \quad (18)$$

$$P v = Z_m R T \quad (19)$$

with Z_m as the mean compressibility factor.

In order to determine Z_m for the mixture of gases, A, B, C with the composition of mole fraction y_A, y_B, y_C the pseudocritical constants of the mixture as average values of critical constants of the mixture components are calculated as follows:

Pseudocritical Temperature

$$T'_c = y_A T_{cA} + y_B T_{cB} + y_C T_{cC} + \dots \quad (20)$$

Pseudocritical pressure

$$P'_c = y_A P_{cA} + y_B P_{cB} + y_C P_{cC} + \dots \quad (21)$$

If the temperature and pressure of the mixture are known, pseudo reduced temperature

$T'_r = \frac{T}{T'_c}$ and pseudo reduced pressure $P'_r = \frac{P}{P'_c}$ are calculated and used to obtain

the value of Z_m for the mixture using the generalized compressibility charts. This value of Z_m can be used to calculate V or v as desired from Eq. (18) or (19).

4. Selected Instruments For Process Variable Measurement

4.1. Fluid Pressure Measurement

Several mechanical devices are used for the measurement of fluid pressure. The most common of these devices is a *Bourdon Gauge* which is a hollow tube closed at one end and bent into a C configuration. The open end of the tube is exposed to the fluid whose pressure is to be measured. As the pressure increases, the tube tends to straighten, causing a pointer attached to the tube to rotate. The position of the pointer on the calibrated dial gives the gauge pressure of the fluid. Figure 6 shows the schematic diagram of the Bourdon gauge.

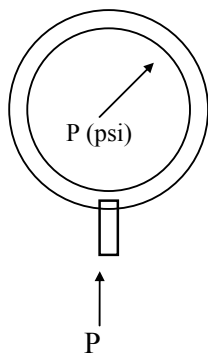


Figure 6. Bourdon Gauge

A manometer is a U-shaped tube partially filled with a liquid of known density. When the ends of the tube are exposed to different pressures the fluid levels drop in the high pressure arm and rise in the low pressure arm. The difference between the pressures can be calculated from the measured difference between the liquid level in each arm. Manometers are used in different ways as shown in Figure 7 (Figure 3.4-4 in Felder and Rousseau). In each arm P_1 and greater than P_2 .

Figure 7a shows an open ended manometer. One end is exposed to the fluid whose pressure is to be measured and the other end to the atmosphere. Figure 7b shows a differential manometer, used to measure the pressure difference between two points in a process line. Figure 7c shows a sealed end manometer which has a vacuum enclosed at one end. If the open end of the sealed-end manometer is exposed to the atmosphere ($P_1 = P_{\text{atm}}$) the device functions like a barometer.

4.2. Temperature Measurement

The temperature of a substance in a particular state of aggregation (solid, liquid or gas) is a measure of the average kinetic energy possessed by the substance molecules. Since the energy cannot be measured directly, the temperature must be determined indirectly by measuring some physical property of the substance whose value depends on the temperature in a known manner. Such properties and the temperature measuring devices based on them include electrical resistance of the conductor (*Resistance Thermometer*) voltage at the junction of two dissimilar metals (*Thermocouple*), spectra of emitted radiation (*Pyrometer*), and volume of fixed mass of fluid (*Thermometer*).

4.3. Flow Rate Measurement

A flow meter is a device mounted in a process line that provides a continuous reading of flow rate in the line. Two commonly used flow meters - The *Rotameter* and the *Orifice meter* are shown in Figure 8 (Figure 3.2-1 in Felder and Rousseau).

The rotameter is a tapered vertical tube containing float, the larger the flow rate, the higher the float rises in the tube. The orifice meter is an obstruction in flow channel with a narrow opening through which the fluid passes. The fluid pressure drops from the upstream side of the orifice to the downstream side. The pressure drop varies with the flow rate; the greater the flow rate the larger is the pressure drop.