Objectives

- Basic concepts in thermodynamics
- Discuss the usefulness of equations of state
1. What Is Thermodynamics and Why Is It Useful?
2. Basic Definitions Needed to Describe Thermodynamic Systems
3. Thermometry
4. Equations of State and the Ideal Gas Law
5. A Brief Introduction to Real Gases
1.1 What is Thermodynamics and Why Is It Useful?

- Thermodynamics describes a system of interest in terms of its bulk properties
1.2 Basic Definitions Needed to Describe Thermodynamic Systems

• A **system** consists of all the materials involved in the process under study.

• An **Open system** can exchange matter with the surroundings. If not, it is a **closed system**.

• **Isolated systems** exchange neither matter nor energy with the surroundings.

• The interface between the system and its surroundings is called the **boundary**.
1.2 Basic Definitions Needed to Describe Thermodynamic Systems

- **The zeroth law of thermodynamics states that two systems that are separately in thermal equilibrium with a third system are also in thermal equilibrium with one another.**
1.3 Thermometry

- **thermometer** is an instrument that can measure relative hotness or coldness.
- **Celsius scale** is determined by one fixed reference point at which ice, liquid water, and gaseous water are in equilibrium.
- Empirical temperature, \( t \), is linearly related to the value of the thermometric property, \( x \):

\[
t(x) = a + bx
\]
1.3 Thermometry

- At constant volume $V$, the thermometric property $P$ varies with temperature as

$$ P = c + dt $$

- The absolute temperature $T(K)$, is given by

$$ T(K) = \frac{27316}{P_{tp}} $$
1.4 Equations of State and the Ideal Gas Law

- **Ideal gas law** equation of state:
  
  \[ PV = NkT = nRT \]

  - \( k \) = Boltzmann constant
  - \( R \) = ideal gas constant
  - \( N \) = number of molecules
  - \( n \) = number of moles of the gas

- It can also be written in terms of intensive variables:
  
  \[ P = \rho RT \]

- For an ideal gas mixture
  
  \[ P = \sum_i \frac{n_i RT}{V} = \sum P_i = P_1 + P_2 + P_3 + \ldots \]
1.4 Equations of State and the Ideal Gas Law

- Pressure units related to Pascal as shown

<table>
<thead>
<tr>
<th>TABLE 1.1 UNITS OF PRESSURE AND CONVERSION FACTORS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unit of Pressure</td>
</tr>
<tr>
<td>------------------</td>
</tr>
<tr>
<td>Pascal</td>
</tr>
<tr>
<td>Atmosphere</td>
</tr>
<tr>
<td>Bar</td>
</tr>
<tr>
<td>Torr or millimeters of Hg</td>
</tr>
<tr>
<td>Pounds per square inch</td>
</tr>
</tbody>
</table>
1.4 Equations of State and the Ideal Gas Law

- Values of the constant $R$ with different combinations of units as shown

**TABLE 1.2  THE IDEAL GAS CONSTANT, $R$, IN VARIOUS UNITS**

- $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$
- $R = 8.314 \text{ Pa m}^3 \text{ K}^{-1} \text{ mol}^{-1}$
- $R = 8.314 \times 10^{-2} \text{ L bar K}^{-1} \text{ mol}^{-1}$
- $R = 8.206 \times 10^{-2} \text{ L atm K}^{-1} \text{ mol}^{-1}$
- $R = 62.36 \text{ L Torr K}^{-1} \text{ mol}^{-1}$
Example 1.1

Starting out on a trip into the mountains, you inflate the tires on your automobile to a recommended pressure of $3.21 \times 10^5$ Pa on a day when the temperature is $-5.00^\circ$ C. You drive to the beach, where the temperature is $28.0^\circ$ C. What is the final pressure in the tires?

b. Derive a formula for the final pressure assuming more realistically that the volume of the tire increases with increasing internal pressure as

$$V_f = V_i (1 + \gamma(P_f - P_i))$$
Solution

a. Because the number of moles is constant,

\[
\frac{PV_i}{T_i} = \frac{PV_i}{T_i} \quad ; \quad P_f = \frac{PVT_f}{V_f T_i} \quad ; \quad \text{at constant volume}
\]

\[
P_f = \frac{PVT_f}{T_i} = 3.21 \times 10^5 \times \frac{(273.15 + 28.0)}{(273.15 - 5.00)} = 3.60 \times 10^5 \text{ Pa}
\]

b. \[
\frac{PV_i}{T_i} = \frac{P_f V_i [1 + \gamma (P_f - P_i)]}{T_f}
\]

\[
P_f = \frac{-T_i (1 - P_i \gamma) \pm \sqrt{T_i^2 (1 - P_i \gamma)^2 + 4T_i T_f \gamma P_i}}{2T_i \gamma}
\]
Example 1.2

Consider the composite system, which is held at 298 K, shown in the following figure. Assuming ideal gas behavior, calculate the total pressure, and the partial pressure of each component if the barriers separating the compartments are removed. Assume that the volume of the barriers is negligible.
Solution

The number of moles of He, Ne, and Xe is given by

\[ n_{He} = \frac{P_{He}V_{He}}{RT} = \frac{1.50 \times 2.00}{8.314 \times 10^{-2} \times 298} = 0.121 \text{mol} \]

\[ n_{Ne} = \frac{P_{Ne}V_{Ne}}{RT} = \frac{2.50 \times 3.00}{8.314 \times 10^{-2} \times 298} = 0.303 \text{mol} \]

\[ n_{Xe} = \frac{P_{Xe}V_{Xe}}{RT} = \frac{1.00 \times 1.00}{8.314 \times 10^{-2} \times 298} = 0.0403 \text{mol} \]

\[ n = n_{He} + n_{Ne} + n_{Xe} = 0.464 \]
Solution

The mole fractions are

\[ x_{He} = \frac{n_{He}}{n} = \frac{0.121}{0.464} = 0.261 \]

\[ x_{Ne} = \frac{n_{Ne}}{n} = \frac{0.303}{0.464} = 0.653 \]

\[ x_{Xe} = \frac{n_{Xe}}{n} = \frac{0.0403}{0.464} = 0.0860 \]
Solution

The total pressure is given by

\[ P = \frac{(n_{He} + n_{Ne} + n_{Xe})RT}{V} = \frac{0.464 \times 8.3145 \times 10^{-2} \times 298}{6.00} = 1.29 \text{bar} \]

The partial pressures are given by

\[ P_{He} = x_{He} P = 0.261 \times 1.92 = 0.501 \text{bar} \]
\[ P_{Ne} = x_{Ne} P = 0.653 \times 1.92 = 1.25 \text{bar} \]
\[ P_{Xe} = x_{Xe} P = 0.0860 \times 1.92 = 0.165 \text{bar} \]
1.5 A Brief Introduction to Real Gases

- Two assumptions for ideal gas:
  a) Atoms or molecules of an ideal gas do not interact with one another,
  b) Atoms or molecules can be treated as point masses.

- Van der Waals equation of state

\[ P = \frac{nRT}{V - nb} - \frac{n^2a}{V^2} \]
Example 1.3

Van der Waals parameters are generally tabulated with either of two sets of units:

\( a \): Pa m\(^6\) mol\(^{-2}\) or bar dm\(^6\) mol\(^{-2}\)

\( b \): m\(^3\) mol\(^{-1}\) or dm\(^3\) mol\(^{-1}\)

Determine the conversion factor to convert one system of units to the other. Note that 1 dm\(^3\) = 10\(^{-3}\) m\(^3\) = 1 L.
Solution

Thus we have

\[ \text{Pa m}^6 \text{ mol}^{-2} \times \frac{\text{bar}}{10^5 \text{ Pa}} \times \frac{10^6 \text{ dm}^6}{\text{m}^6} = 10 \text{ bar dm}^6 \text{ mol}^{-2} \]

\[ \text{m}^3 \text{ mol}^{-1} \times \frac{10^3 \text{ dm}^3}{\text{m}^3} = 10^3 \text{ dm}^3 \text{ mol}^{-1} \]
Example 1.4

a. Calculate the pressure exerted by \( \text{N}_2 \) at 300 K for molar volumes of \( V_1 = 250 \text{ L} \) and \( V_2 = 0.100 \text{ L} \) using the ideal gas and the van der Waals equations of state. The values of parameters \( a \) and \( b \) for \( \text{N}_2 \) are 1.370 bar dm\(^6\) mol\(^{-2}\) and 0.0387 dm\(^3\) mol\(^{-1}\), respectively.
Example 1.4

b. Compare the results of your calculations at the two pressures. If $P$ calculated using the van der Waals equation of state is greater than those calculated with the ideal gas law, we can conclude that the repulsive interaction of the $N_2$ molecules outweighs the attractive interaction for the calculated value of the density. A similar statement can be made regarding the attractive interaction. Is the attractive or repulsive interaction greater for $N_2$ at 300 K and $V_m = 0.100$ L?
Solution

a. The pressures calculated from the ideal gas equation of state are

\[ P_1 = \frac{nRT}{V_1} = \frac{1 \times 8.314 \times 10^{-2} \times 300}{250} = 9.98 \times 10^{-2} \text{ bar} \]

\[ P_2 = \frac{nRT}{V_2} = \frac{1 \times 8.314 \times 10^{-2} \times 300}{0.100} = 249 \text{ bar} \]
Solution

The pressures calculated from the van der Waals equation of state are

\[ P_1 = \frac{nRT}{V_1 - nb} - \frac{n^2a}{V_1^2} \]

\[ = \frac{1 \times 8.314 \times 10^{-2} \times 300}{250 - 0.0387 \times 1} - \frac{(1)^2 \times 1.370}{(250)^2} = 9.98 \times 10^{-2} \text{ bar} \]

\[ P_2 = \frac{nRT}{V_2 - nb} - \frac{n^2a}{V_2^2} \]

\[ = \frac{1 \times 8.314 \times 10^{-2} \times 300}{0.100 - 0.0387 \times 1} - \frac{(1)^2 \times 1.370}{(0.100)^2} = 270 \text{ bar} \]
Solution

b. Note that the result is identical with that for the ideal gas law for \( V_m = 250 \text{ L} \), and that the result calculated for \( V_m = 0.100 \text{ L} \) deviates from the ideal gas law result. Because \( P_{\text{real}} > P_{\text{ideal}} \), we conclude that the repulsive interaction is more important than the attractive interaction for this specific value of molar volume and temperature.