

## 1.1: Thermodynamic Variables and Equations of State

Based on "Thermodynamic Variables and Equations of State" by Serge L. Smirnov and James McCarty, LibreTexts is licensed under CC BY-NC-SA

Classical thermodynamics provides a conceptual framework from which we can understand the behavior of molecular systems at a quantitative level. This chapter introduces some of the concepts relating to properties of a system and its surroundings that we will need to study classical thermodynamics. In this chapter, we will focus on how the macroscopic properties of a system are related to and depend on the properties of the constituent atoms and molecules. As an example we will discuss the ideal-gas equation, its range of validity, and how it can be extended to real gases or fluids of interacting molecules.

### Learning Objectives

- Build a precise vocabulary of thermodynamic definitions before applying them to biochemical systems.
- Understand state variables and how they are mathematically related in an equation of state.
- Be able to manipulate the ideal gas equation of state.
- Understand how real gases deviate from ideality and how real gases can be modeled by the virial equation of state, which is an expression for the pressure of a gas as a polynomial in the density.

### 1.1.1: Basic Definitions

We begin our discussion of thermodynamics with some definitions that will allow us to make general statements about how energy is exchanged and converted into various forms.

A **system** is any part of the universe that is of interest to us. This might be the Sun-Earth-Moon system, a human lung, fruit fly, a single bacteria cell, or a container on a bench top. Some example systems are shown in figure 1.1.1.



Figure 1.1.1: Some systems of varying complexity include the sun-earth-moon system, a human lung, a fruit fly, a single bacteria cell, or a Erlenmeyer flask.

Everything else in the universe that is not part of the system is called the **surroundings**. The system + the surroundings constitutes the **universe**.

We can classify systems into 3 types: open systems, closed systems, or isolated systems. An **open system** is able to exchange both matter and heat with the surroundings. A **closed system** cannot exchange matter with the surroundings but *can* exchange heat with the surroundings. An **isolated system** cannot exchange any heat or any matter with surroundings. These three types of systems are depicted in figure 1.1.2:

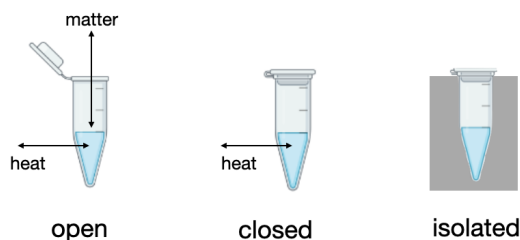


Figure 1.1.2: An open system can exchange both matter and heat with the surroundings. A closed system cannot exchange matter with the surroundings but can exchange heat. An isolated system cannot exchange heat or matter with the surroundings.

The branch of science called **thermodynamics** is interested in the relationships between properties of a system and how properties change as the system changes state. A **property** is any mathematically quantifiable parameter of the system. Some properties could include the pressure, the temperature, the density, the index of refraction, etc ....

We can distinguish between two types of properties: intensive and extensive. **Intensive** properties are *independent* of the quantity (amount of matter) being measured. Some intensive properties include the density, pressure, and temperature. On the other hand,

**Extensive** properties *depend* on the quantity (amount) being measured. Some extensive properties are the mass, the volume, and the number of moles.

Intensive properties can be constructed as the ratio between two extensive properties. For example the **density** is

$$\text{density} = \frac{\text{mass}}{\text{volume}} \quad (1.1.1)$$

Notice that both **mass** and **volume** are extensive (depend on the amount), but the density (the ratio of the mass over volume) is intensive.

Similarly, the **pressure** is defined as

$$\text{pressure} = \frac{\text{force}}{\text{area}} \quad (1.1.2)$$

The SI units of pressure is the Pascal (Pa) and  $1 \text{ Pa} = 1 \text{ N} \cdot \text{m}^{-2} = 1 \text{ kg} \cdot \text{m}^{-1} \cdot \text{s}^{-2} = 1 \text{ J} \cdot \text{m}^{-3}$ . Table 1.1.1 relates some common units of pressure.

**Table 1.1.1:** Some common units of pressure

1 Pa = 1 N m <sup>-2</sup>
1 bar = 100 kPa (10 <sup>5</sup> Pa)
1 atm = 101.32 kPa
1 torr (mm Hg) = 1/760 atm

**Note:** **Energy** by itself (measured in Joules or calories) is an *extensive* property. Often, we report energies as a molar ratio in units of J/mol or cal/mol which is an *intensive* property.

A common way to define an intensive property is to define the **molar** quantity by dividing some extensive variable by the number of moles. For example, the **molar volume** is defined as:

$$\bar{V} = \frac{V}{n} \quad (1.1.3)$$

Here **n** is the number of moles and  $\bar{V}$  is called the molar volume and is an intensive quantity.

Temperature is another important thermodynamic parameter that will be defined in several ways throughout this text. For now, we will define the **temperature** as the measure of the motion of the atoms within the system. This definition of temperature implies that the “thermodynamic” temperature is measured in Kelvin, because the Kelvin scale is the absolute temperature scale. In the limit that  $T=0 \text{ K}$  (absolute zero), the motion of the atoms approaches zero. We can convert between temperature in Kelvin and Celsius scales using the relation:

$$T(\text{in Kelvins}) = T(\text{in } ^\circ\text{C}) + 273.15 \quad (1.1.4)$$



#### Caution

**Note:** Absolute temperatures (in K) must be used in thermodynamic calculations.

See Practice Problems 1.1.1 and 1.1.2

### 1.1.2: Thermodynamic Equations of State

An **equation of state** is a mathematical expression that fully describes the thermodynamic state of the system in terms of a set of physical properties. The most familiar example is the ideal gas law:

$$PV = nRT \quad (1.1.5)$$

or, introducing the molar volume (Equation 1.1.3):

$$P\bar{V} = RT \quad (1.1.6)$$

where **P** is the pressure, **V** is the volume, **n** is the number of moles, **T** is the temperature. **R** is the gas constant given in table 1.1.2. Equation 1.1.5 is known as the **ideal gas equation of state**. The ideal gas equation of state ( $PV=nRT$ ) allows us to see how the properties of an ideal gas are related.

**Table 1.1.2:** Common units for the ideal gas constant R.

$R = 8.314462618 \text{ J K}^{-1} \text{ mol}^{-1} = 0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1}$	$\text{L atm} = 101.325 \text{ J}$
---	------------------------------------

The ideal gas equation of state will be a useful model for us to work with as we derive thermodynamic relationships because it is intuitive and algebraically easy to manipulate. At this point, it is worthwhile to make some comments concerning the ideal gas equation of state:

1. The ideal gas equation of state can be derived from first principles (kinetic theory of gases).
2. At sufficiently *high* temperature and *low* pressure, all gases fit the ideal gas law.
3. Assumptions made in the ideal gas law:
  - The gas molecules themselves occupy no volume.
  - There are no attractive or repulsive forces between gas molecules.
  - All collisions are perfectly elastic.

See Practice Problems 1.1.3 and 1.1.4

Because of these assumptions, we expect all **real gases** to deviate from ideal behavior. To quantify this we define the **compressibility factor, Z**, as

$$Z = \frac{P\bar{V}}{RT} \quad (1.1.7)$$

Notice from Equation 1.1.5 that for an ideal gas,  $Z = 1$ . All real gases will deviate from this ideal behavior. Figure 1.1.3 shows the compressibility factor  $Z$  as a function of pressure for  $\text{N}_2$  gas at different temperatures. A perfect ideal gas would have  $Z = 1$  for all pressures and temperatures. For  $\text{N}_2$  gas we see that at sufficiently low pressure  $Z \rightarrow 1$  and that at higher temperature (purple curve), the gas behaves more like an ideal gas (dotted line).

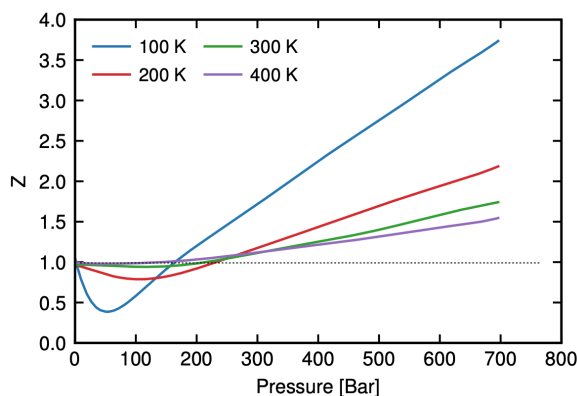


Figure 1.1.3: Compressibility factor of nitrogen gas as a function of pressure for different temperatures. The ideal gas limit is shown by the dotted line at  $Z=1$ .

In order to derive an equation of state for a non-ideal gas, we can consider a series expansion of the compressibility factor, **Z**, in powers of the inverse molar volume,  $1/\bar{V}$ :

$$Z = 1 + \frac{B_2}{\bar{V}} + \frac{B_3}{\bar{V}^2} + \frac{B_4}{\bar{V}^3} + \dots \quad (1.1.8)$$

Equation 1.1.8 is called the **virial equation of state**, and **B<sub>2</sub>** is called the **second virial coefficient**, **B<sub>3</sub>** is called the third virial coefficient, etc.... The virial coefficients ( $B_2, B_3, \dots$ ) are typically fit to experimental data and are temperature dependent. Notice that for a perfect ideal gas, the second and higher virial coefficients are all zero. The virial equation of state works well to describe any gas, but has the drawback of needing the virial coefficients from fitting to experimental data.

For gases that exhibit small deviations from ideal gas behavior, we can truncate Equation 1.1.8 to include just the second virial coefficient:

$$Z \approx 1 + \frac{B_2}{V} \quad (1.1.9)$$

The second virial coefficient,  $B_2$  is related to the interactions between atoms described by a potential energy function  $U(r)$ , where  $r$  is the distance between atom pairs. For a dilute system of non-polar molecules, the relationship between the second virial coefficient and the potential energy is

$$B_2 = N_A \frac{1}{2} \int_0^\infty \left[ 1 - e^{-U(r)/k_B T} \right] 4\pi r^2 dr \quad (1.1.10)$$

where  $N_A$  is Avogadro's number,  $k_B$  is Boltzmann's constant, and  $T$  is the temperature. In most cases, we cannot analytically solve the integral in Equation 1.1.10. Note that in the absence of interactions,  $U(r) = 0$ , then from Equation 1.1.10,  $B_2 = 0$  and the gas behaves like an ideal gas as we would expect for non-interacting gas molecules.

See Practice Problems 1.1.5 — 1.1.7.

### 1.1.3: Examples

#### ✓ Example 1.1.1

Classify each of the following systems as either open, closed, or isolated. (a) A red blood cell, (b) a gas in a piston without valves, (c) boiling water in a kettle on the stove, (d) A closed Thermos flask of hot coffee (approximately).

##### Solution

(a) open; (b) closed; (c) open; (d) isolated

#### ✓ Example 1.1.2

Classify each of the following properties as intensive or extensive: (a) molar mass, (b) pressure, (c) temperature, (d) mass

##### Solution

(a) intensive; (b) intensive; (c) intensive; (d) extensive

#### ✓ Example 1.1.3

A Bellingham homebrewer collects the amount of gas evolved during the fermentation process. Later, the brewer measures the volume of gas to be 0.64 L at a cold temperature of 12.3 °C and 1 atm. Assuming ideal gas behavior, what was the volume of the gas at the fermentation temperature of 37.0 °C and 1 atm.

##### Solution

We use the ideal gas equation:  $PV=nRT$  to set up a ratio between the low temperature and high temperature system:

$$\frac{V_1}{V_2} = \frac{T_1}{T_2} \quad (1.1.11)$$

$$\frac{0.64 \text{ L}}{V_2} = \frac{285.45 \text{ K}}{310.15 \text{ K}} \quad (1.1.12)$$

$$V_2 = 0.695 \text{ L} \quad (1.1.13)$$

### 1.1.4: Practice problems

**Problem 1.1.1.** Classify each of the following systems as either open, closed, or isolated. (a) perfectly insulated water heater, (b) a glass thermometer (c) the universe (d) soup cooking on a stove (e) the earth (f) automobile (g) a sealed reaction flask

**Problem 1.1.2.** Classify each of the following properties as intensive or extensive: (a) density, (b) force, (c) molar volume, (d) heat.

**Problem 1.1.3.** Under which of the following sets of conditions would you expect a real gas to be adequately described by the ideal gas model (a) low pressure and low temperature; (b) low pressure and high temperature, (c) high pressure and high temperature, and (d) high pressure and low temperature.

**Problem 1.1.4.** An ideal gas in a piston is originally at a pressure of 118.0 atm and 85 °C. When the piston expands, its final volume, pressure, and temperature were 3.5 L, 1.0 atm, and 45 °C, respectively. What was the initial volume of the gas?

**Problem 1.1.5.** At 300 K, the second virial coefficient ( $B_2$ ) of  $\text{CO}_2$  gas is  $-120.5 \text{ cm}^3 \text{ mol}^{-1}$ , for methane gas,  $\text{CH}_4$ , the second virial coefficient is  $-41.9 \text{ cm}^3 \text{ mol}^{-1}$ , and for  $\text{N}_2$  gas the second virial coefficient is  $-4.2 \text{ cm}^3 \text{ mol}^{-1}$ . Rank these gases from most ideal gas to least ideal gas at this temperature? Explain your reasoning.

**Problem 1.1.6.** Calculate the pressure of methane at 398.15 K if the molar volume is  $0.2 \text{ L mol}^{-1}$ , given that the second virial coefficient ( $B_2$ ) of methane is  $-0.0163 \text{ L mol}^{-1}$ . Compare your results with that obtained using the ideal gas equation. Is methane more or less compressible than an ideal gas at this temperature? (Assume that all other higher order virial coefficients can be neglected).

**Problem 1.1.7.** The **Boyle temperature** is the temperature at which the coefficient  $B_2$  is zero. Therefore, a real gas behaves like an ideal gas at this temperature. **(a)** give a physical interpretation of this behavior. **(b)** Calculate the Boyle temperature for a gas whose second virial coefficient has the following form:  $B_2 = a - \frac{b}{T}$  with the experimentally determined second virial coefficient measured at the following temperatures:

Second virial coefficient ( $B_2$ ) ( $\text{L mol}^{-1}$ )	Temperature (K)
-0.0237	292.95
-0.0231	296.15
-0.0228	298.15
-0.0218	303.15
-0.0201	313.15
-0.0185	323.15
-0.0117	373.15
-0.0065	423.15

1.1: Thermodynamic Variables and Equations of State is shared under a [CC BY-NC-SA 4.0](#) license and was authored, remixed, and/or curated by LibreTexts.

- 1.1: Thermodynamic Variables and Equations of State by Serge L. Smirnov and James McCarty is licensed [CC BY-NC-SA 4.0](#).