CHAPTER 16
A MACROSCOPIC DESCRIPTION OF MATTER

This brief chapter provides an introduction to thermodynamics. The goal is to use phenomenological descriptions of the microscopic details of matter in order to form conclusions about how the matter behaves on macroscopic scales. Much of it is a review from previous chemistry courses.
16.1 Solids, Liquids, and Gases

Virtually every chemical compound (and all chemical elements) can exist as a solid, liquid, or gas – these are the three common **phases of matter**. More exotic phases exist, such as plasmas, Bose-Einstein condensates, etc., but we won’t worry about them in PHYS 212.
16.1 Solids, Liquids, and Gases

State Variables
Parameters used to describe a macroscopic system are known as state variables. In the last chapter (and in PHYS 211) you learned several of these: volume, pressure, mass, mass density, thermal energy. These are properties of a “large chunk” of a material, but they ultimately are determined by its microscopic nature. In this chapter, we will introduce a few more state variables: moles, number density, and temperature. Three of the state variables that you already know are related to each other: \( \rho = \frac{M}{V} \) (the text uses \( M \) as the mass of a macroscopic object or system of objects, and \( m \) as the mass of an atom).

Changing any of the state variables represents a change in the state of the system.
To prepare for some upcoming problems, we must describe the relation among atoms and moles, atomic mass and atomic mass number, moles and molar mass. Those of you who took introductory chemistry should have no trouble with this section.

According to the textbook, “a typical macroscopic system contains $N \sim 10^{25}$ atoms”. Of course, this depends quite a bit on the physical size of the system (is the system contained within a $1 \text{ m}^3$ box, or a small test tube?) as well as the phase of matter (is it a low-pressure gas, or a solid or liquid?). However, the figure $N \sim 10^{25}$ atoms does serve as a reminder that macroscopic systems have substantially more than “thousands” or “billions” of atoms.
16.2 Atoms and Moles

The **number density** is a state variable that indicates how densely-packed the atoms are in their container. If there are $N$ atoms in a container of volume $V$, then the number density is simply $N / V$. Note that it has SI units of m$^{-3}$, since $N$ is dimensionless. In a solid, the number density is $\sim 10^{29}$ m$^{-3}$. This value doesn’t change very much among different solids, since the inter-atomic spacing of atoms is fixed within a small range of values. Try not to confuse number density with the mass density $\rho$.

The **atomic mass number** $A$ of an atom is the # of protons plus the # of neutrons in its nucleus (as a “count”, $A$ must be an integer). For example, the most common isotope of carbon is $^{12}$C, which has 6 protons and 6 neutrons, such that $A = 12$. The $^{14}$C isotope – used for carbon dating – has 2 additional neutrons, such that $A = 14$. 
16.2 Atoms and Moles

The **atomic mass** is based on the *atomic mass unit*, u:

\[ 1 \text{ u} = 1.661 \times 10^{-27} \text{ kg} \]

By definition, one atom of carbon-12 has an atomic mass of *exactly* 12 u. The atomic mass of all other atoms are expressed relative to \(^{12}\text{C}\). They are not exactly integer multiples of 1 u – for instance, the atomic mass of \(^{16}\text{O}\) (the most common isotope of oxygen) is about 15.995 u. In PHYS 212, this level of precision is not necessary, and therefore we can assume that the atomic mass of any isotope is equal to its atomic number, multiplied by 1 u.

The **molecular mass** of a molecule is simply the sum of the atomic masses of each atom in the molecule. For example, the molecular mass of \(\text{CO}_2\) is 12 u \(+(16 \text{ u} \times 2) = 44 \text{ u}\).
Moles and Molar Mass

By definition, one mole of any substance contains as many “particles” of that substance as there are atoms in 12 grams of $^{12}$C. A more useful description is

$$1 \text{ mol} = 6.02 \times 10^{23} \text{ particles}$$

The photo shows one mole of helium, sulfur, copper, and mercury.
16.2 Atoms and Moles

Despite its apparent simplicity, the mole is actually considered to be an SI base unit (on par with the meter, kilogram, second, etc.) The number of particles per mole is called **Avogadro’s number:**

\[ N_A = 6.02 \times 10^{23} \text{ mol}^{-1} \]

Thus, the number of moles in a substance containing \( N \) particles is

\[ n = \frac{N}{N_A} \]

Finally, the **molar mass** \( M_{\text{mol}} \) of a substance is the mass of 1 mole of the substance (expressed in units of kg / mol). That is, the number of moles in a system of mass \( M \) and molar mass \( M_{\text{mol}} \) is

\[ n = \frac{M}{M_{\text{mol}}} \]
Problem #1: Laughing Gas

Nitrous oxide (aka laughing gas) has the chemical formula $\text{N}_2\text{O}$. \textbf{What is the mass (in grams) of 0.5 mol of N}_2\text{O?} The atomic mass numbers of nitrogen and oxygen are 14 and 16, respectively.

\textit{Solution: in class}
Problem #2: Aluminum and Mercury

RDK Ex. 16.9

What volume of aluminum has the same number of atoms as 10 cm$^3$ of mercury?

Relevant data: $\rho_{Hg} = 13,600$ kg/m$^3$, $\rho_{Al} = 2700$ kg/m$^3$

$M_{mol,Hg} = 201$ g/mol, $M_{mol,Al} = 27$ g/mol

Solution: in class
16.3 Temperature

Temperature is still a bit difficult to define at this point, and will be clarified in chapter 18. For now, it suffices to say that it is related to the quantity of thermal energy in a system. There are three primary scales with which we measure temperature. The first has units of degrees Celcius (°C) – this scale is based on the freezing and boiling points of water (0 and 100 °C, respectively). The second – used extensively in the United States, but not in the rest of the world – has units of degrees Fahrenheit (°F). Converting between these units is done as follows:

\[ T_F = \frac{9}{5} T_C + 32 \]
\[ T_C = \frac{5}{9} (T_F - 32) \]
16.3 Temperature

The third scale is in units of Kelvins (K, not “degrees Kelvin”). This scale is closely related to the °C scale, but with a constant offset:

\[ T_K = T_C + 273.15 \]

That is, the freezing and boiling points of water are 273.15 K and 373.15 K, respectively.
16.3 Temperature

In class, we will discuss the Kelvin scale, and the concept of **absolute zero**.
In future PHYS 212 work, remember that you **should always work in Kelvins**. Even problems that request answers in other temperature scales usually must be solved first in Kelvins.
In the last chapter, we defined an **ideal fluid** in order to simplify problems in fluid dynamics. Here, we will define an **ideal gas**. This situation arises when:

1. The density of the gas is low (such that the atoms occupy a total volume much less than that of their container)
2. The temperature is well above the **condensation point**. This simply indicates that the gas will remain a gas even if we perform experiments in which its temperature is lowered or its pressure is raised. For more info, see section 16.4 of the text (note that you will receive no assignment or exam problems from section 16.4).

Essentially, these conditions ensure that the complex attractive forces that exist between molecules are negligible.
16.5 Ideal Gases

For an ideal gas in a container, the state variables are the volume $V$ of the container, the pressure $p$ that the gas exerts on the container walls, the number of moles present $n$, and the temperature $T$ of the gas and its container.

Suppose that you alter any of the state variables (by heating, compressing, etc.), and then measure $V$, $p$, $n$, and $T$. Then, you plot the product of $p$ and $V$ vs. the product of $n$ and $T$. You will find that the plot is a straight line, with slope $R = 8.31$ J/mol·K (and a zero intercept). Furthermore, you will get this same result independently of what type of gas you use!

The graph of $pV$ versus $nT$ is a straight line with slope $R = 8.31$ J/mol·K.
16.5 Ideal Gases

This result defines the **ideal-gas law**, an explicit relationship among the four state variables that describe a gas:

\[ pV = nRT, \quad R = 8.31 \text{ J/mol} \cdot \text{K} \]

Here, \( R \) is known as the **universal gas constant**.

In PHYS 212, we will always consider “sealed” containers. This simply means that the number of moles remains constant. Then, \( \frac{pV}{T} = nR = \text{constant} \). In other words, an ideal gas that transitions from an initial state \( i \) to a final state \( f \) must obey

\[ \frac{p_i V_i}{T_i} = \frac{p_f V_f}{T_f} \]
16.5 Ideal Gases

Moles to Molecules
Instead of referring to the number of moles $n$, we are often more interested in the number of molecules $N$. Since $n = \frac{N}{N_A}$, we can write

$$pV = nRT = \frac{N}{N_A}RT = N \frac{R}{N_A}T$$

Numerically, the ratio $\frac{R}{N_A}$ is $1.38 \times 10^{-23}$ J/K. This value is known as Boltzmann’s Constant, $k_B$. This constant appears in thermodynamics, statistical mechanics, solid-state physics (i.e. the theory behind electronic devices), among other areas. It can be thought of as the gas constant per molecule, rather than per mole. Using Boltzmann’s constant, the ideal-gas law can be written as

$$pV = Nk_B T$$
Problem #3: Equal Volumes of Gas

You have two containers of equal volume. One is full of helium gas. The other holds an equal mass of nitrogen gas. Both gases have the same pressure. How does the temperature of the helium compare to that of the nitrogen?

- A $T_{He} > T_{N_2}$
- B $T_{He} = T_{N_2}$
- C $T_{He} < T_{N_2}$
Problem #4: Cylinder of Neon Gas

RDK Ex. 16.21

A 10-cm-diameter cylinder of neon gas is 30 cm long and has a temperature of 30°C. A pressure gauge on the cylinder reads 120 psi (this is gauge pressure, not absolute pressure!)

**What is the mass density of the gas?**

**Conversion factor:** 1 psi = 6.895 kPa

Molar mass of Helium = 20 g/mol

*Solution: in class*
Problem #5: Exploding Gas Cylinders

One of the many dangers in a lab fire is that the intense heat can cause the pressure within gas cylinders to increase to a point where the cylinder explodes. Suppose that a particular cylinder of compressed air has been filled to an absolute pressure of 25 atm at a temperature of 20 °C. The cylinder will fail (explosively) if the pressure reaches 100 atm. At what temperature (in °C) will the cylinder fail?

Conversion factor: 1 atm = 101.3 kPa

Solution: in class
16.6 Ideal-Gas Processes

Having learned the ideal-gas law (the connection among the state variables - pressure, volume, and temperature - of a gas), we are now in a position to describe **ideal-gas processes**, in which the gas changes from one state to another. This is best accomplished through the use of a $pV$ diagram – a plot that shows the pressure and volume of the gas. Assuming that the number of moles $n$ is known, having information on $p$ and $V$ also allows us to calculate $T$.

When an ideal gas undergoes a process by which one or more state variables are changed, this can be indicated by a “trajectory” on the $pV$ diagram, as shown in the bottom figure.
16.6 Ideal-Gas Processes

In PHYS 212, we will assume that all processes are quasi-static. Essentially, this means that the changes in the state variables occur “very slowly” (that’s intentionally vague...the question of how slowly is very slowly is not the subject of this course). We also assume that all processes are reversible. That is, any trajectory on a $pV$ diagram can be followed forward or backward.

The remainder of this chapter will describe particular processes in which one of the state variables $p, V, \text{ or } T$ remains constant. We will assume that the number of moles is also constant (a “sealed container”). Thus, keeping one of $p, V, \text{ or } T$ constant requires that either the other two state variables must change or none of them change (although the latter case makes for a rather boring problem).
Consider a process in which the volume of gas remains constant: $V_f = V_i$. This is called a constant-volume or isochoric process. Such a process is shown below. Since $V$ is constant, an isochoric process appears as a vertical line on a $pV$ diagram.
A constant-pressure or isobaric process is on for which $p_f = p_i$. It is indicated by a horizontal line on a $pV$ diagram.

Since the volume of gas must change during an isobaric process, we can have either an isobaric expansion or isobaric compression. In the former, the volume increases, while in the latter, the volume decreases. What can we say about the temperature in these two cases?
16.6 Ideal-Gas Processes

The third process is, unsurprisingly, called a constant-temperature or isothermal process: $T_f = T_i$. Since temperature is not explicitly shown on either axis of a $pV$ diagram, an isothermal process does not appear as a straight line. However, we do know that $pV = nRT$. Since $R$ is a constant and we are assuming that $n$ is constant, an isothermal process must be one for which the product $pV$ does not change; the trajectory is a hyperbola.

Since volume must change in an isothermal process, we can define isothermal expansion and isothermal compression, in a manner similar to that on the previous slide.
Problem #6: \( pV \) Diagram Analysis

What is the ratio \( \frac{T_f}{T_i} \) for this process?
Assume that \( n \) is constant.

A \( \frac{1}{2} \)

B \( 1 \) (no change)

C 2

D There is not enough information to answer this question
Problem #7: Cooling a Rigid Container

RDK EX 16.25

A rigid container holds hydrogen gas at an absolute pressure of 3.0 atm and a temperature of 20 °C. What will the pressure be (in atmospheres) if the temperature is lowered to -20 °C?

Solution: in class

To note: what type of ideal-gas process is this? Does it matter that the gas is hydrogen?
A gas with an initial temperature (point 1) of 900 °C undergoes the process shown in the figure.

a) What type of process is this?
b) What is the final temperature in °C?
c) How many moles of gas are there?

Solution: in class

Recall: \( R = 8.31 \text{ J/mol·K} \)