

## Chapter 2: Gases

Gases comprise a very important type of system that can be modeled using thermodynamics. This is true because gas samples can be described by very simple equations of state, such as the ideal gas law. In this chapter, both macroscopic and microscopic descriptions of gases will be used to demonstrate some of the important tools of thermodynamics.

### The Empirical Gas Laws

A number of important relationships describing the nature of gas samples have been derived completely empirically (meaning based solely on observation rather than making an attempt to define the theoretical reason these relationships may exist). These are the **empirical gas laws**.

#### Boyle's Law

One of the important relationships governing gas samples that can be modeled mathematically is the relationship between pressure and volume. Robert Boyle (1627 – 1691) (Hunter, 2004) did experiments to confirm the observations of Richard Towneley and Henry Powers to show that for a fixed sample of gas at a constant temperature, pressure and volume are inversely proportional.

$$pV = \text{const.} \quad \text{or} \quad p_1V_1 = p_2V_2$$

Boyle used a glass u-tube that was closed at one end and with the lower portion filled with mercury (trapping a sample of air in the closed end.) By adding mercury to the open end, he was able to observe and quantify the compression of the trapped air.

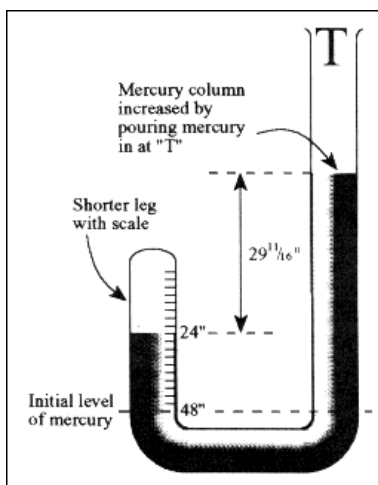


Figure 1. An apparatus similar to that used by Robert Boyle. (Image taken from (Fazio, 1992))



Figure 2. Robert Boyle (1627 - 1691)

## Charles' Law

Charles' Law states that the volume of a fixed sample of gas at constant pressure is proportional to the temperature. For this law to work, there must be an absolute minimum to the temperature scale since there is certainly an absolute minimum to the volume scale!

$$\frac{V}{T} = \text{const.} \quad \text{or} \quad \frac{V_1}{T_1} = \frac{V_2}{T_2}$$

The second law of thermodynamics also predicts an absolute minimum temperature, but that will be developed in a later chapter.

## Gay-Lussac's Law

Gay-Lussac's Law states that the pressure of a fixed sample of gas is proportional to the temperature. As with Charles' Law, this suggests the existence of an absolute minimum to the temperature scale since the pressure can never be negative.

$$\frac{p}{T} = \text{const.} \quad \text{or} \quad \frac{p_1}{T_1} = \frac{p_2}{T_2}$$

## Combined Gas Law

Boyle's, Charles', and Gay-Lussac's Laws can be combined into a single empirical formula that can be useful. For a given amount of gas, the following relationship must hold:

$$\frac{pV}{T} = \text{const.} \quad \text{or} \quad \frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2}$$

## Avogadro's Law



Amedeo Avogadro (1776-1856) (Encyclopedica, 2016) did extensive work with gases in his studies of matter. In the course of his work, he noted an important relationship between the number of moles in a gas sample. Avogadro's Law (Avogadro, 1811) states that at the same temperature and pressure, any sample of gas has the same number of molecules per unit volume.

$$\frac{n}{V} = \text{const.} \quad \text{or} \quad \frac{n_1}{V_1} = \frac{n_2}{V_2}$$

**Figure 3.** Amedeo Avogadro (1776 - 1856)

## The Ideal Gas Law

The **ideal gas law** combines the empirical laws into a single expression. It also predicts the existence of a single, universal gas constant, which turns out to be one of the most important fundamental constants in science.

$$pV = nRT$$

The ideal gas law constant is of fundamental importance and can be expressed in a number of different sets of units.

Value	Units
<b>0.08206</b>	atm L mol <sup>-1</sup> K <sup>-1</sup>
<b>8.314</b>	J mol <sup>-1</sup> K <sup>-1</sup>
<b>1.987</b>	cal mol <sup>-1</sup> K <sup>-1</sup>

The ideal gas law, as derived here, is based entirely on empirical data. It represents “limiting ideal behavior.” As such, deviations from the behavior suggested by the ideal gas law can be understood in terms of what conditions are required for ideal behavior to be followed (or at least approached.) As such, it would be nice if there was a theory of gases that would suggest the form of the ideal gas law and also the value of the gas law constant. As it turns out, the kinetic molecular theory of gases does just that!

## The Kinetic Molecular Theory of Gases

Theoretical models attempting to describe the nature of gases date back to the earliest scientific inquiries into the nature of matter and even earlier! In about 50 BC, Lucretius, a Roman philosopher, proposed that macroscopic bodies were composed of atoms that continually collide with one another and are in constant motion, despite the observable reality that the body itself is at rest. However, Lucretius’ ideas went largely ignored as they deviated from those of Aristotle, whose views were more widely accepted at the time.

In 1738, Daniel Bernoulli (Bernoulli, 1738) published a model that contains the basic framework for the modern Kinetic Molecular theory. Rudolf Clausius furthered the model in 1857 by (among other things) introducing the concept of mean free path (Clausius, 1857). These ideas were further developed by Maxwell (Maxwell, 1873). But, because atomic theory was not fully embraced in the early 20<sup>th</sup> century, it was not until Albert Einstein published one of his seminal works describing Brownian motion (Einstein, 1905) in which he modeled

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matter using a kinetic theory of molecules that the idea of an atomic (or molecular) picture really took hold in the scientific community.

In its modern form, the Kinetic Molecular Theory of gasses is based on five basic postulates.

1. Gas particles obey Newton's laws of motion and travel in straight lines unless they collide with other particles or the walls of the container.
2. Gas particles are very small compared to the averages of the distances between them.
3. Molecular collisions are perfectly elastic so that kinetic energy is conserved.
4. Gas particles do not interact with other particles except through collisions. There are no attractive or repulsive forces between particles.
5. The average kinetic energy of the particles in a sample of gas is proportional to the temperature.

Qualitatively, this model predicts the form of the ideal gas law.

1. More particles means more collisions with the wall ( $p \propto n$ )
2. Smaller volume means more frequent collisions with the wall ( $p \propto 1/V$ )
3. Higher molecular speeds means more frequent collisions with the walls ( $p \propto T$ )

Putting all of these together yields

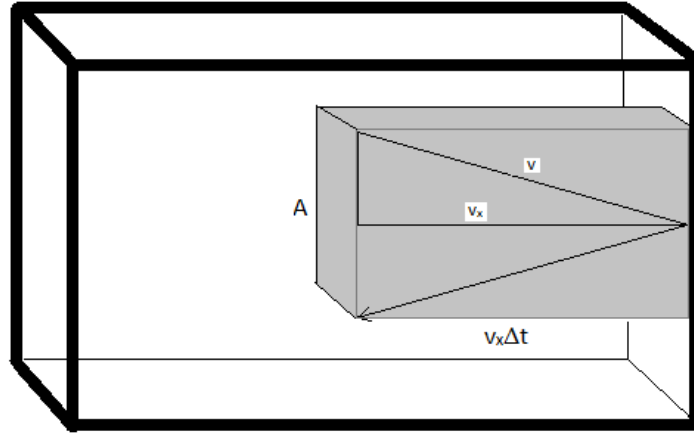
$$p = k \frac{nT}{V}$$

which is exactly the form of the ideal gas law! The remainder of the job is to derive a value for the constant of proportionality that is consistent with experimental observation.

For simplicity, imagine a collection of gas particles in a fixed-volume container with all of the particles traveling at the same velocity. What implications would the kinetic molecular theory have on such a sample? One approach to answering this question is to derive an expression for the pressure of the gas.

The pressure is going to be determined by considering the collisions of gas molecules with the wall of the container. Each collision will impart some force. So the greater the number of collisions, the greater the pressure will be. Also, the larger force imparted per collision, the greater the pressure will be. And finally, the larger the area over which collisions are spread, the smaller the pressure will be.

$$p \propto (\text{number of collisions}) \times (\text{force imparted per collision}) / \text{area}$$



**Figure 4.** The "collision volume" is the subset of the total volume that contains molecules that will actually collide with area  $A$  in the time interval  $\Delta t$ .

First off, the pressure that the gas exerts on the walls of the container would be due entirely to the force imparted each time a molecule collides with the interior surface of the container. This force will be scaled by the number of molecules that hit the area of the wall in a given time. For this reason, it is convenient to define a “collision volume”.

$$V_{col} = (v_x \cdot \Delta t) \cdot A$$

where  $v_x$  is the speed the molecules are traveling in the  $x$  direction,  $\Delta t$  is the time interval (the product of  $v_x \cdot \Delta t$  gives the length to the collision volume box) and  $A$  is the area of the wall with which the molecules will collide. Half of the molecules within this volume will collide with the wall since half will be traveling toward it and half will be traveling away from it. The number of molecules in this collision volume will be given by the total number of molecules in the sample and the fraction of the total volume that is the collision volume. And thus, the number of molecules that will collide with the wall is given by

$$N_{col} = \frac{1}{2} N_{tot} \frac{V_{col}}{V}$$

And thus the number of molecules colliding with the wall will be

$$N_{col} = \frac{1}{2} N_{tot} \frac{(v_x \Delta t) A}{V}$$

The magnitude of that force imparted per collision will be determined by the time-rate of change in momentum of each particle as it hits the surface. It can be calculated by determining the total momentum change and dividing by the total time required for the event. Since each colliding molecule will change its velocity from  $v_x$  to  $-v_x$ , the magnitude of the momentum change is  $2(mv_x)$ . Thus the force imparted per collision is given by

$$F = \frac{2(mv_x)}{\Delta t}$$

and the total force imparted is

$$\begin{aligned} F_{tot} &= N_{col} \frac{2(mv_x)}{\Delta t} \\ &= \frac{1}{2} N_{tot} \left[ \frac{(v_x \Delta t) A}{V} \right] \left[ \frac{2(mv_x)}{\Delta t} \right] \\ &= N_{tot} \left( \frac{mv_x^2}{V} \right) A \end{aligned}$$

Since the pressure is given as the total force exerted per unit area, the pressure is given by

$$p = \frac{F_{tot}}{A} = N_{tot} \left( \frac{mv_x^2}{V} \right) = \frac{N_{tot} m}{V} (v_x^2)$$

The question then becomes how to deal with the velocity term. Initially, it was assumed that all of the molecules had the same velocity, and so the magnitude of the velocity in the x-direction was merely a function of the trajectory. However, real samples of gases comprise molecules with an entire distribution of molecular speeds and trajectories. To deal with this distribution of values, we replace  $(v_x^2)$  with the squared average of velocity in the x direction  $\langle v_x \rangle^2$ .

$$p = \frac{N_{tot} m}{V} \langle v_x \rangle^2$$

The distribution function for velocities in the x direction, known as the **Maxwell-Boltzmann distribution**, is given by.

$$f(v_x) = \left( \frac{m}{2\pi k_B T} \right)^{\frac{1}{2}} e^{-\frac{mv_x^2}{2k_B T}}$$

This function has two parts: a **normalization constant**, and an exponential term. The normalization constant,  $\left( \frac{m}{2\pi k_B T} \right)^{\frac{1}{2}}$ , is derived by noting that

$$\int_{-\infty}^{\infty} f(v_x) dv_x = 1$$

### **Normalizing the distribution**

The Maxwell-Boltzmann distribution has to be normalized because it is a probability distribution. As such, the sum of the probabilities for all possible values of  $v_x$  must be unity. And since  $v_x$  can take any value between  $-\infty$  and  $\infty$ , the following must be true:

$$\int_{-\infty}^{\infty} f(v_x) dv_x = 1$$

So if the form of  $f(v_x)$  is assumed to be

$$f(v_x) = N e^{-\frac{mv_x^2}{2k_B T}}$$

the normalization constant  $N$  can be found from

$$\int_{-\infty}^{\infty} N e^{-\frac{mv_x^2}{2k_B T}} dv_x = 1$$

The expression can be simplified by letting  $\alpha = \frac{m}{2k_B T}$ . It is then more simply written

$$N \int_{-\infty}^{\infty} e^{-\alpha v_x^2} dv_x = 1$$

A table of definite integrals says that

$$\int_{-\infty}^{\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{a}}$$

So

$$N \sqrt{\frac{\pi}{\alpha}} = 1$$

$$N = \sqrt{\frac{\alpha}{\pi}} = \left( \frac{m}{2\pi k_B T} \right)^{\frac{1}{2}}$$

And thus the normalized distribution function is given by

$$f(v_x) = \left( \frac{m}{2\pi k_B T} \right)^{\frac{1}{2}} e^{-\frac{mv_x^2}{2k_B T}}$$

**Calculating an Average from a Probability Distribution**

Calculating an average for a finite set of data is fairly easy. The average is calculated by

$$\bar{x} = \frac{1}{N} \sum_{i=1}^N x_i$$

But how does one proceed when the set of data is infinite? Or how does one proceed when all one knows are the probabilities for each possible measured outcome? It turns out that that is fairly simple too!

$$\bar{x} = \sum_{i=1}^N x_i \cdot P_i$$

where  $P_i$  is the probability of measuring the value  $x_i$ . This can also be extended to problems where the measurable properties are not discrete (like the numbers that result from rolling a pair of dice) but rather come from a continuous parent population. In this case, if the probability of measuring a specific outcome, the average value can then be determined by

$$\bar{x} = \int x \cdot P(x) dx$$

where  $P(x)$  is the function describing the probability distribution, and with the integration taking place across all possible values that  $x$  can take.

**Calculating the average value of  $v_x$** 

A value that is useful (and will be used in further developments) is the average velocity in the  $x$  direction. This can be derived using the probability distribution, as shown in the mathematical development box above. The average value of  $v_x$  is given by

$$\langle v_x \rangle = \int_{-\infty}^{\infty} v_x f(v_x) dx$$

This integral will, by necessity, be zero. This must be the case as the distribution is symmetric, so that half of the molecules are traveling in the  $+x$  direction, and half in the  $-x$  direction. These motions will have to cancel. So, a more satisfying result will be given by considering the magnitude of  $v_x$ , which gives the speed in the  $x$  direction. Since this cannot be negative, and given the symmetry of the distribution, the problem becomes



$$\langle |v_x| \rangle = 2 \int_0^{\infty} v_x f(v_x) dx$$

In other words, we will consider only half of the distribution, and then double the result to account for the half we ignored.

For simplicity, we will write the distribution function as

$$f(v_x) = N e^{-\alpha v_x^2}$$

Where  $N = \left( \frac{m}{2\pi k_B T} \right)^{\frac{1}{2}}$  and  $\alpha = \frac{m}{2k_B T}$ .

A table of definite integrals shows

$$\int_0^{\infty} x e^{-ax^2} dx = \frac{1}{2a}$$

So

$$\langle v_x \rangle = 2N \left[ \frac{1}{2\alpha} \right] = \frac{N}{\alpha}$$

Substituting our definitions for N and  $\alpha$  produces

$$\langle v_x \rangle = \left( \frac{m}{2\pi k_B T} \right)^{\frac{1}{2}} \left( \frac{2k_B T}{m} \right) = \left( \frac{2k_B T}{\pi m} \right)^{\frac{1}{2}}$$

This expression indicates the average speed for motion of in one direction.

However, real gas samples have molecules not only with a distribution of molecular speeds and but also a random distribution of directions. Using normal vector magnitude properties (or simply using the Pythagorean Theorem), it can be seen that

$$\langle v \rangle^2 = \langle v_x \rangle^2 + \langle v_y \rangle^2 + \langle v_z \rangle^2$$

Since the direction of travel is random, the velocity can have any component in x, y, or z directions with equal probability. As such, the average value of the x, y, or z components of velocity should be the same. And so

$$\langle v \rangle^2 = 3\langle v_x \rangle^2$$

Substituting this into the expression for pressure yields

$$p = \frac{N_{tot}m}{3V} \langle v \rangle^2$$

All that remains is to determine the form of the distribution of velocity magnitudes the gas molecules can take. One of the first people to address this distribution was James Clerk Maxwell (1831-1879). In his 1860 paper (Maxwell, Illustrations of the dynamical theory of gases. Part 1. On the motions and collisions of perfectly elastic spheres, 1860), proposed a form for this distribution of speeds which proved to be consistent with observed properties of gases (such as their viscosities). He derived this expression based on a transformation of coordinate system from Cartesian coordinates ( $x, y, z$ ) to spherical polar coordinates ( $v, \theta, \phi$ ). In this new coordinate system,  $v$  represents the magnitude of the velocity (or the speed) and all of the directional data is carried in the angles  $\theta$  and  $\phi$ . The infinitesimal volume unit becomes

$$dx dy dz = v^2 \sin(\theta) dv d\theta d\phi$$

Applying this transformation of coordinates, and ignoring the angular part (since he was interested only in the speed) **Maxwell's distribution** took the following form

$$f(v) = N v^2 \exp \left\{ -\frac{mv^2}{2k_B T} \right\}$$

This function has three basic parts to it: **a normalization constant** ( $N$ ), a velocity dependence ( $v^2$ ), and an exponential term that contains the kinetic energy ( $\frac{1}{2}mv^2$ ). Since the function represents the fraction of molecules with the speed  $v$ , the sum of the fractions for all possible velocities must be unity. This sum can be calculated as an integral. The normalization constant insures that

$$\int_0^{\infty} f(v) dv = 1$$

Choosing the normalization constant as  $N = 4\pi \sqrt{\left(\frac{m}{2\pi k_B T}\right)^3}$  yields the final form of the Maxwell distribution of molecular speeds.

$$f(v) = 4\pi \sqrt{\left(\frac{m}{2\pi k_B T}\right)^3} v^2 e^{-\frac{mv^2}{2k_B T}}$$

At low velocities, the  $v^2$  term causes the function to increase with increasing  $v$ , but then at larger values of  $v$ , the exponential term causes it to drop back down asymptotically to zero.

The distribution will spread over a larger range of speed at higher temperatures, but collapse to a smaller range of values at lower temperatures.

### **Calculating the Average Speed**

Using the Maxwell distribution as a distribution of probabilities, the average molecular speed in a sample of gas molecules can be determined.

$$\begin{aligned}\langle v \rangle &= \int_0^\infty v \cdot 4\pi \sqrt{\left(\frac{m}{2\pi k_B T}\right)^3} v^2 e^{-\frac{mv^2}{2k_B T}} dv \\ &= 4\pi \sqrt{\left(\frac{m}{2\pi k_B T}\right)^3} \int_0^\infty v^3 e^{-\frac{mv^2}{2k_B T}} dv\end{aligned}$$

The following can be found in a table of integrals:

$$\int_0^\infty x^{2n+1} e^{-ax^2} dx = \frac{n!}{2a^{n+1}}$$

So

$$\langle v \rangle = 4\pi \sqrt{\left(\frac{m}{2\pi k_B T}\right)^3} \left[ \frac{1}{2 \left(\frac{m}{2k_B T}\right)^2} \right]$$

Which simplifies to

$$\langle v \rangle = \left( \frac{8k_B T}{\pi m} \right)^{\frac{1}{2}}$$

Note: the value of  $\langle v \rangle$  is twice that of  $\langle v_x \rangle$  which was derived in an earlier example!

$$\langle v \rangle = 2\langle v_x \rangle$$

### **Example:**

What is the average value of the squared speed according to the Maxwell distribution law?

### **Solution:**

$$\langle v^2 \rangle = \int_0^\infty v^2 f(v) dv$$

So

$$\begin{aligned}\langle v^2 \rangle &= \int_0^\infty v^2 \cdot 4\pi \sqrt{\left(\frac{m}{2\pi k_B T}\right)^3} v^2 e^{-\frac{mv^2}{2k_B T}} dv \\ &= 4\pi \sqrt{\left(\frac{m}{2\pi k_B T}\right)^3} \int_0^\infty v^4 e^{-\frac{mv^2}{2k_B T}} dv\end{aligned}$$

A table of integrals indicates that

$$\int_0^\infty x^{2n} e^{-ax^2} dx = \frac{1 \cdot 3 \cdot 5 \cdots (2n-1)}{2^{n+1} a^n} \sqrt{\frac{\pi}{a}}$$

Substitution (noting that  $n = 2$ ) yields

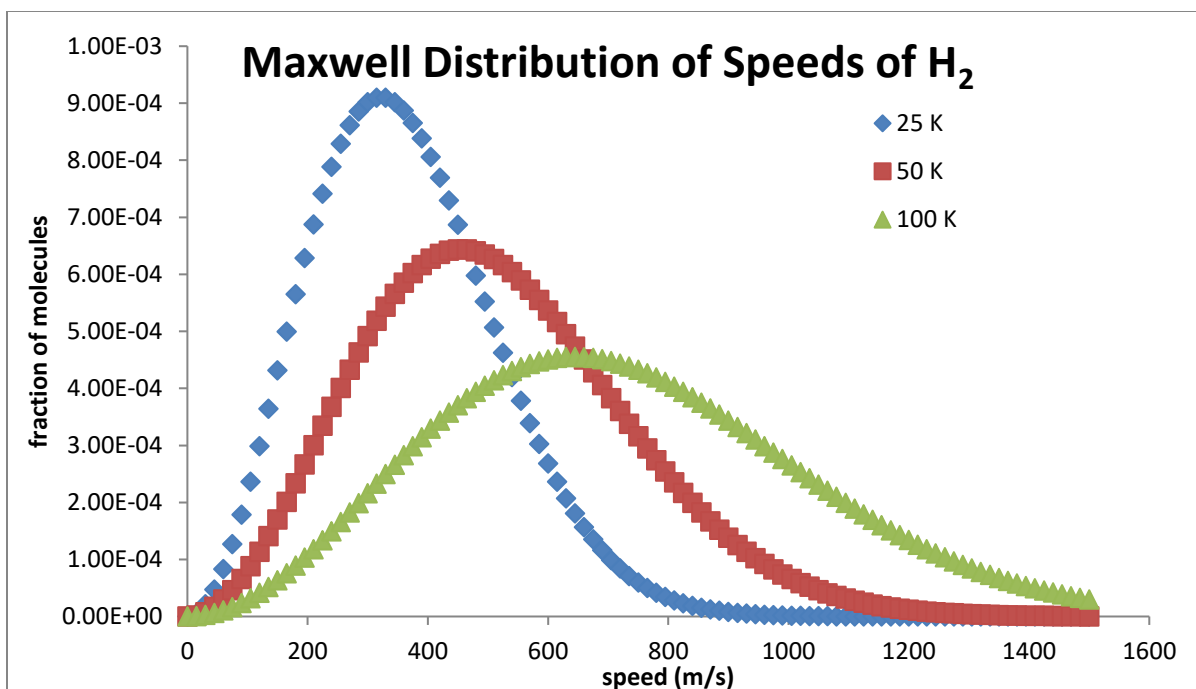
$$\langle v^2 \rangle = 4\pi \sqrt{\left(\frac{m}{2\pi k_B T}\right)^3} \left[ \frac{1 \cdot 3}{2^3 \left(\frac{m}{2k_B T}\right)^2} \sqrt{\frac{\pi}{\left(\frac{m}{2k_B T}\right)}} \right]$$

which simplifies to

$$\langle v^2 \rangle = \frac{3k_B T}{m}$$

*Note:* The square root of this average squared speed is called the **root mean square** (RMS) speed, and has the value

$$v_{RMS} = \left(\frac{3k_B T}{m}\right)^{\frac{1}{2}}$$



The entire distribution is also affected by molecular mass. For lighter molecules, the distribution is spread across a broader range of speeds at a given temperature, but collapses to a smaller range for heavier molecules.

The probability distribution function can also be used to derive an expression for the most probable speed ( $v_{mp}$ ), the average ( $v_{ave}$ ), and the root-mean-square ( $v_{rms}$ ) speeds as a function of the temperature and masses of the molecules in the sample. The most probable speed is the one with the **maximum probability**. That will be the speed that yields the maximum value of  $f(v)$ . It is found by solving the expression

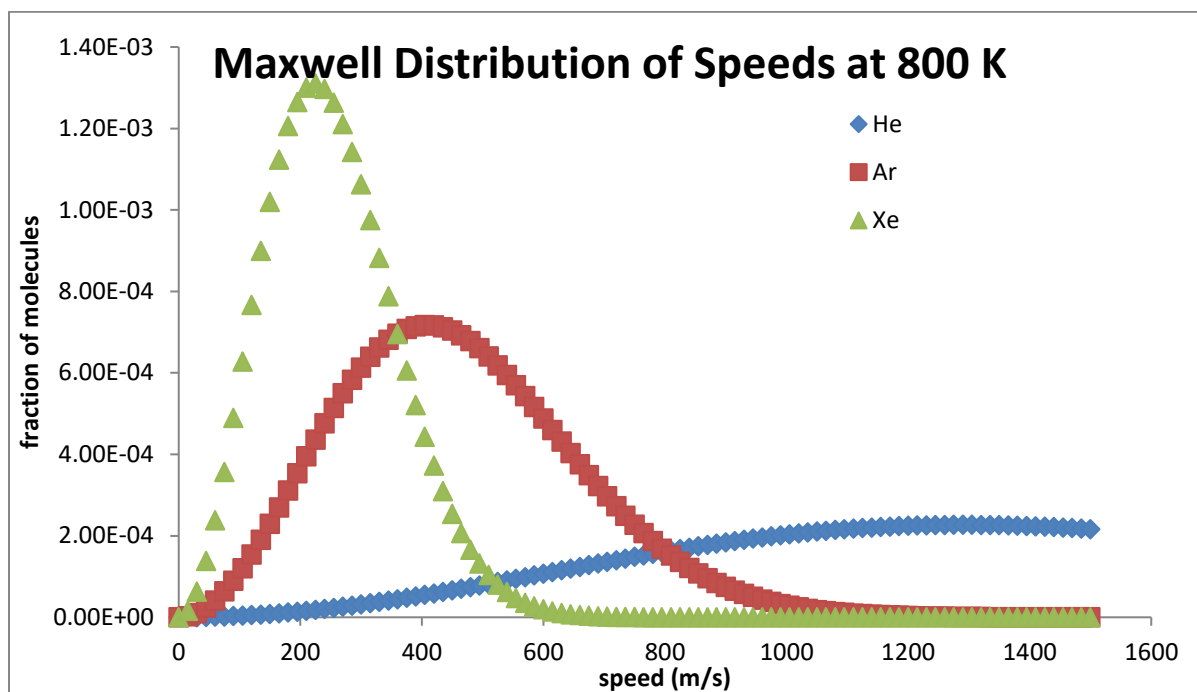
$$\frac{d}{dv} f(v) = 0$$

for the value of  $v$  that makes it true. This will be the value that gives the maximum value of  $f(v)$  for the given temperature. Similarly, the average value can be found using the distribution in the following fashion

$$v_{avg} = \langle v \rangle = \int_0^{\infty} v \cdot f(v) dv$$

and the **root-mean-square** (RMS) speed by finding the square root of the average value of  $v^2$

$$v_{rms} = \sqrt{\langle v^2 \rangle} = \sqrt{\int_0^{\infty} v^2 f(v) dv}$$



## Kinetic Energy

Using expressions for  $v_{mp}$ ,  $v_{ave}$ , or  $v_{rms}$ , it is fairly simple to derive expressions for kinetic energy from the expression

$$E_{kin} = \frac{1}{2}mv^2$$

It is important to remember that there will be a full distribution of molecular speeds in a thermalized sample of gas. Some molecules will be traveling faster and some more slowly. It is also important to recognize that the most probable, average, and RMS kinetic energy terms that can be derived from the Kinetic Molecular Theory do not depend on the mass of the molecules. As such, it can be concluded that the average kinetic energy of the molecules in a thermalized sample of gas depends only on the temperature. However, the average speed depends on the molecular mass. So, for a given temperature, light molecules will travel faster on average than heavier molecules.

Property	Speed	Kinetic Energy
Most probable	$\left(\frac{2k_B T}{m}\right)^{\frac{1}{2}}$	$k_B T$
Average	$\left(\frac{8k_B T}{\pi m}\right)^{\frac{1}{2}}$	$\frac{4k_B T}{\pi}$
Root-mean-square	$\left(\frac{3k_B T}{m}\right)^{\frac{1}{2}}$	$\frac{3}{2} k_B T$

## The Ideal Gas Law

The expression for the root-mean-square molecular speed can be used to show that the Kinetic Molecular model of gases is consistent with the ideal gas law. Consider the expression for pressure

$$p = \frac{N_{tot} m}{3V} \langle v \rangle^2$$

Replacing  $\langle v \rangle^2$  with the square of the RMS speed expression yields

$$p = \frac{N_{tot} m}{3V} \left( \frac{3k_B T}{m} \right)$$

which simplifies to

$$p = \frac{N_{tot} k_B T}{V}$$

Noting that  $N_{tot} = n \cdot N_A$ , where  $n$  is the number of moles and  $N_A$  is Avogadro's number

$$p = \frac{n N_A k_B T}{V}$$

Or

$$pV = n N_A k_B T$$

Finally, noting that  $N_A \cdot k_B = R$

$$pV = nRT$$

That's kind of cool, no? The only assumptions (beyond the postulates of the Kinetic Molecular Theory) is that the distribution of velocities for a thermalized sample of gas is described by the Maxwell-Boltzmann distribution law.

The next development will be to use the Kinetic Molecular Theory to describe molecular collisions (which are essential events in many chemical reactions.)

### Collisions with the Wall

In the derivation of an expression for the pressure of a gas, it is useful to consider the frequency with which gas molecules collide with the walls of the container. To derive this expression, consider the expression for the "collision volume".

$$V_{col} = v_x \Delta t \cdot A$$

All of the molecules within this volume, and with a velocity such that the x-component exceeds  $v_x$  (and is positive) will collide with the wall. That fraction of molecules is given by

$$N_{col} = \frac{N \langle v_x \rangle \Delta t \cdot A}{V \cdot 2}$$

and the frequency of collisions with the wall per unit area per unit time is given by

$$Z_w = \frac{N \langle v_x \rangle}{V \cdot 2}$$

In order to expand this model into a more useful form, one must consider motion in all three dimensions. Considering that

$$\langle v \rangle = \sqrt{\langle v_x \rangle^2 + \langle v_y \rangle^2 + \langle v_z \rangle^2}$$

and that

$$\langle v_x \rangle = \langle v_y \rangle = \langle v_z \rangle$$

it can be shown that

$$\langle v \rangle = \sqrt{3} \langle v_x \rangle$$

or



$$\langle v_x \rangle = \frac{1}{2} \langle v \rangle$$

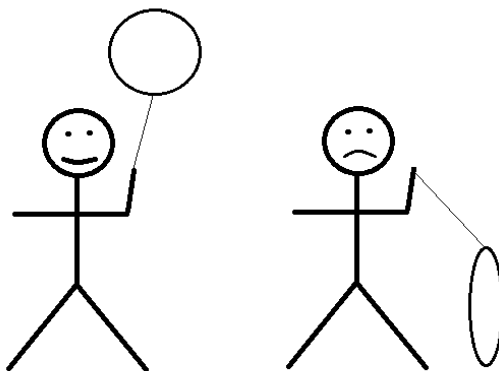
and so

$$Z_w = \frac{1}{4} \frac{N}{V} \langle v \rangle$$

The factor of  $N/V$  is often referred to as the “number density” as it gives the number of molecules per unit volume. At 1 atm pressure and 298 K, the number density for an ideal gas is approximately  $2.5 \times 10^{19}$  molecule/cm<sup>3</sup>. (This value is easily calculated using the ideal gas law.) By comparison, the average number density for the universe is approximately 1 molecule/cm<sup>3</sup>.

### *Graham's Law of Effusion*

An important consequence of the kinetic molecular theory is what it predicts in terms of effusion and diffusion effects. Effusion is defined as a loss of material across a boundary. A common example of effusion is the loss of gas inside of a balloon over time.



The rate at which gases will effuse from a balloon is affected by a number of factors. But one of the most important is the frequency with which molecules collide with the interior surface of the balloon. Since this is a function of the average molecular speed, it has an inverse dependence on the square root of the molecular weight.

$$\text{Rate of effusion} \propto 1/(\text{MW})^{1/2}$$

This can be used to compare the relative rates of effusion for gases of different molar masses.

**Example:** Consider two identical balloons, filled to the same volume, at the same pressure and temperature. One balloon (A) is filled with SO<sub>2</sub> (MW: 48.06 g/mol) and the other (B) with N<sub>2</sub> (MW: 28.01 g/mol). After a certain amount of time, the volume of balloon A decreases by 0.100 L. By how much is the volume of balloon B expected to decrease in the same time?

**Solution:** Since the diffusion rate is inversely proportional to the square-root of the molar mass

$$rate \propto 1/\sqrt{MW}$$

the ratio of the rates of diffusion will be given by

$$\frac{rate_A}{rate_B} = \sqrt{\frac{MW_B}{MW_A}}$$

and the *rate* can be taken as the ratio of the change in volume divided by the time the gas is allowed to diffuse. Since the time is the same for both balloons, it will cancel out in the ratio. So

$$\frac{0.100\text{ L}}{x} = \sqrt{\frac{28.01 \frac{\text{g}}{\text{mol}}}{48.06 \frac{\text{g}}{\text{mol}}}}$$

or

$$x = 0.131\text{ L}$$

### *The Knudsen Cell Experiment*

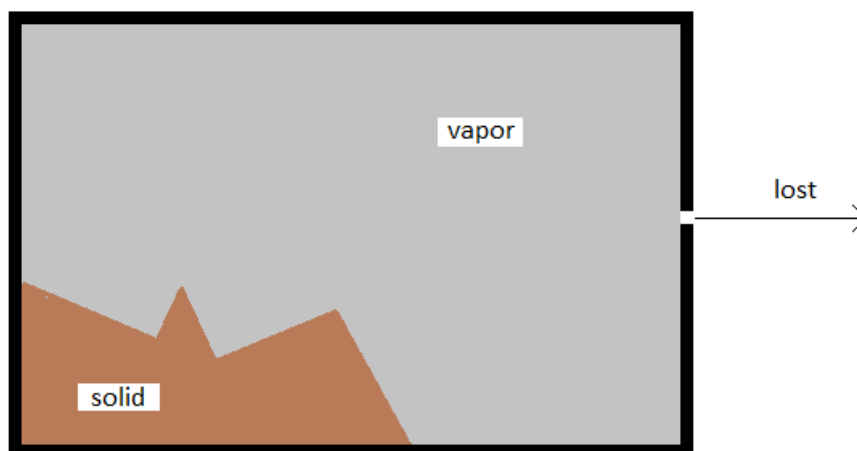
A Knudsen cell is a chamber in which a thermalized sample of gas is kept, but allowed to effuse through a small orifice in the wall. The gas sample can be modeled using the Kinetic Molecular Theory model as a collection of particles traveling throughout the cell, colliding with one another and also with the wall. If a small orifice is present, any molecules that would collide with that portion of the wall will be lost through the orifice.

This makes a convenient arrangement to measure the vapor pressure of the material inside the cell, as the total mass lost by effusion through the orifice will be proportional to the vapor pressure of the substance. The vapor pressure can be related to the mass lost by the expression

$$p = \frac{g}{A\Delta t} \sqrt{\frac{2\pi RT}{MW}}$$

where *g* is the mass lost, *A* is the area of the orifice,  $\Delta t$  is the time the effusion is allowed to proceed, *T* is the temperature and *MW* is the molar mass of the compound in the vapor phase.

The pressure is then given by  $p$ . A schematic of what a Knudsen cell might look like is given below.



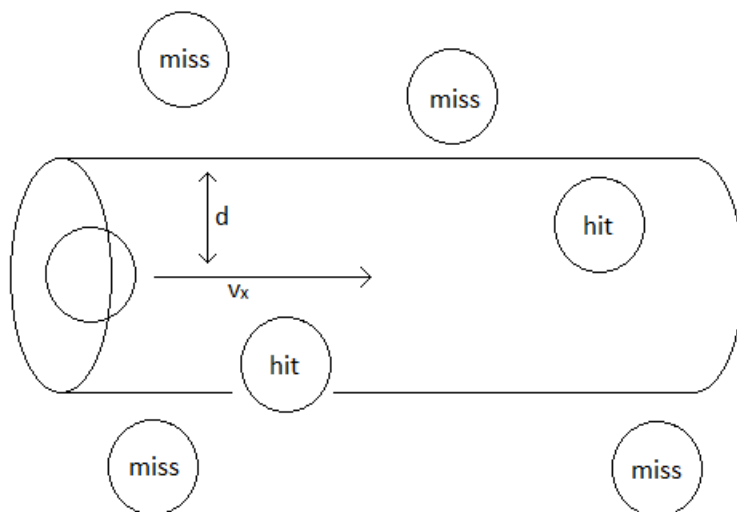
**Example:** Knudsen Cell Example

**Solution:**

### Collisions with Other Molecules

A major concern in the design of many experiments is collisions of gas molecules with other molecules in the gas phase. For example, molecular beam experiments are often dependent on a lack of molecular collisions in the beam that could degrade the nature of the molecules in the beam through chemical reactions or simply being knocked out of the beam.

In order to predict the frequency of molecular collisions, it is useful to first define the conditions under which collisions will occur. For convenience, consider all of the molecules to be spherical and in fixed in position except for one which is allowed to move through a “sea” of other molecules. A molecular collision will occur every time the center of the moving molecule comes within one molecular diameter of the center of another molecule.



One can easily determine the number of molecules the moving molecule will “hit” by determining the number of molecules that lie within the “collision cylinder”. Because we fixed the positions of all but one of the molecules, we must use the relative speed of the moving molecule, which will be given by

$$v_{rel} = \sqrt{2} \cdot v$$

The volume of the collision cylinder is given by

$$\begin{aligned} V_{col} &= \sqrt{2} \cdot v \Delta t \cdot A \\ &= \sqrt{2} \cdot v \Delta t \cdot (\pi d^2) \end{aligned}$$

The **collisional cross section**, which determined by the size of the molecule is given by

$$\sigma = \pi d^2$$

Some values of  $\sigma$  are given in the table below:

Molecule	$\sigma$ (nm <sup>2</sup> )
<b>He</b>	0.21
<b>Ne</b>	0.24
<b>N<sub>2</sub></b>	0.43
<b>CO<sub>2</sub></b>	0.52
<b>C<sub>2</sub>H<sub>4</sub></b>	0.64

Since the number of molecules within the collision cylinder is given by

$$N_{col} = \frac{N}{V} V_{col}$$

and since the number density ( $N/V$ ) is given by

$$\frac{N}{V} = \frac{p}{k_B T}$$

the number of collisions is given by

$$N_{col} = \frac{p}{k_B T} (\sqrt{2} \cdot v \Delta t \cdot \sigma)$$

The frequency of collisions (number of collisions per unit time) is then given by

$$Z = \frac{\sqrt{2} p \sigma}{k_B T} \langle v \rangle$$

Perhaps a more useful value is the **mean free path**, which is the distance a molecule can travel on average before it collides with another molecule. This is easily derived from the collision frequency. How far something can travel between collisions is given by the ratio of how fast it is traveling and how often it hits other molecules:

$$\lambda = \frac{\langle v \rangle}{Z}$$

Thus, the mean free path is given by

$$\lambda = \frac{k_B T}{\sqrt{2} p \sigma}$$

The mere fact that molecules undergo collisions represents a deviation from the kinetic molecular theory. For example, if molecules were infinitesimally small ( $\sigma \approx 0$ ) then the mean free path would be infinitely long! The finite size of molecules represents one significant deviation from ideality. Another important deviation stems from the fact that molecules do exhibit attractive and repulsive forces between one another. These forces depend on a number of parameters, such as the distance between molecules and the temperature (or average kinetic energy of the molecules.)

## Real Gases

While the ideal gas law is sufficient for the prediction of large numbers of properties and behaviors for gases, there are a number of times that deviations from ideality are extremely important.

### The van der Waals Equation

Several equations of state have been suggested to account for the deviations from ideality. One simple, but useful, expression is that proposed by Johannes Diderik van der Waals (1837 – 1923) (Johannes Diderik van der Waals - Biographical, 2014)



**Figure 5.** Johannes van der Waals (1837 – 1923)

van der Waals' equation introduced corrections to the pressure and volume terms of the ideal gas law in order to account for intermolecular interactions and molecular size respectively.

$$\left(p + \frac{a}{V_m^2}\right)(V_m - b) = RT$$

or

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

In this expression, a and b are variables of a given substance which can be measured and tabulated. In general, molecules with large intermolecular forces will have large values of a, and large molecules will have large values of b. Some van der Waals constants are given in the following table:

Gas	a (atm L <sup>2</sup> mol <sup>-2</sup> )	b (L/mol)
<b>He</b>	0.0341	0.0238
<b>N<sub>2</sub></b>	1.352	0.0387
<b>CO<sub>2</sub></b>	3.610	0.0429
<b>C<sub>2</sub>H<sub>4</sub></b>	4.552	0.0305

The van der Waals model is useful because it makes it so simple to interpret the parameters in terms of molecular size and intermolecular forces. But it does have limitations as well (as is the case of every scientific model!) Some other useful two-parameter and three-parameter (or more) equations of state include the Redlich-Kwong, Dieterici, and Clasius

models. These have the advantage that they allow for temperature dependence on some of the parameters, which as will be seen later, is necessary to model certain behaviors of real gases.

Model	Equation
Ideal	$p = \frac{RT}{V_m}$
van der Waals (van der Waals J. D., 1967)	$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$
Redlich-Kwong (Redlich & Kwong, 1949)	$p = \frac{RT}{V_m - b} - \frac{a}{\sqrt{T}V_m(V_m + b)}$
Dieterici (Dieterici, 1899)	$p = \frac{RT}{V_m - b} \exp\left\{-\frac{a}{V_m RT}\right\}$
Clausius	$p = \frac{RT}{V_m - b} - \frac{a}{T(V_m + c)^2}$
Virial Equations	$p = \frac{RT}{V_m} \left(1 + \frac{B(T)}{V_m} + \frac{C(T)}{V_m^2} + \dots\right)$ $p = \frac{RT}{V_m} (1 + B' p + C' p^2 + \dots)$

## The Virial Equation

A very handy expression that allows for deviations from ideal behavior is the **Virial Equation** of state. This is a simple power series expansion in which the higher-order terms contain all of the deviations from the ideal gas law.

$$p = \frac{RT}{V_m} \left(1 + \frac{B(T)}{V_m} + \frac{C(T)}{V_m^2} + \dots\right)$$

In the limit that  $B(T)$  (the **Second Virial Coefficient**) and  $C(T)$  are zero, the equation becomes the ideal gas law. Also, the molar volume of gases are small, the contributions from the third, fourth, etc. terms decrease in magnitude, allowing one to truncate the series at a convenient point. The second virial coefficient can be predicted from a theoretical intermolecular potential function by

$$B(T) = N_A \int_{r=0}^{\infty} \left[1 - e^{\frac{U(r)}{k_B T}}\right] 2\pi r^2 dr$$

The quality of an intermolecular potential can be determined (partially) by the potential's ability to predict the value of the second virial coefficient,  $B$ .

### The Leonard-Jones Potential

An intermolecular potential function is used to describe the interactions between molecules. These interactions will have to include attractive forces, which will draw molecules together, and repulsive forces which will push them apart. If the molecules are hard spheres, lacking any attractive interactions, the potential function is fairly simple.

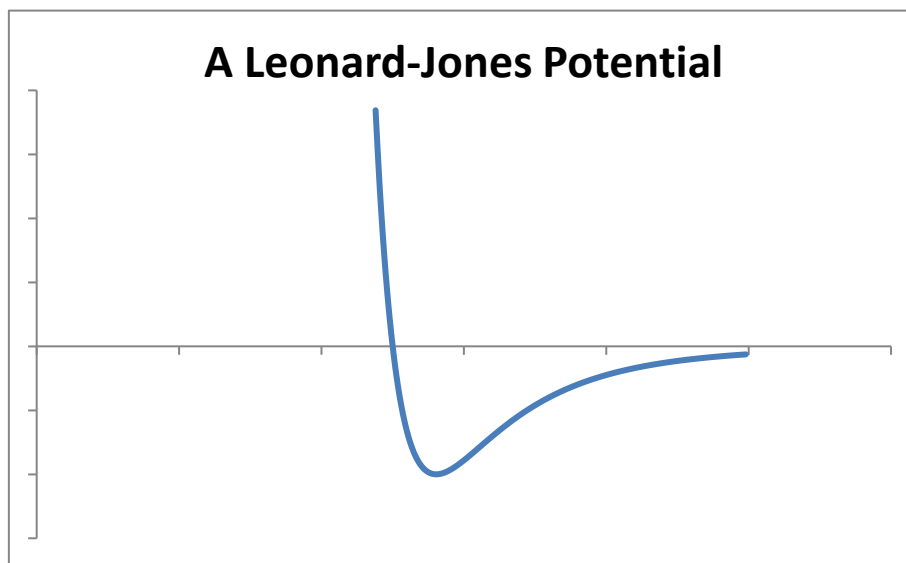
$$U(r) = \begin{cases} 0, & r > \sigma \\ \infty, & r \leq \sigma \end{cases}$$

In this function,  $\sigma$  is determined by the size of the molecules. If two molecules come within a distance  $r$  of one another, they collide, bouncing off in a perfectly elastic collision. Real molecules, however, will have a range of intermolecular separations through which they will experience attractive forces (the so-called “soft wall” of the potential surface.) And then at very small separations, the repulsive forces will dominate, pushing the molecules apart (the so-called “hard wall” of the potential surface.)

A commonly used intermolecular potential,  $U(r)$ , is the **Leonard-Jones potential**. This function has the form

$$U(r) = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right]$$

where  $\sigma$  governs the width of the potential well, and  $\varepsilon$  governs the depth. The distance between molecules is given by  $r$ . The repulsive interactions between molecules are contained in the  $\left( \frac{\sigma}{r} \right)^{12}$  terms and the attractive interactions are found in the  $\left( \frac{\sigma}{r} \right)^6$  term.



### Taylor Series Expansion

A commonly used method of creating a power series based on another equation is the **Taylor Series Expansion**. This is an expansion of a function about a useful reference point



where each of the terms is generated by differentiating the original function.

For a function  $f(x)$ , the Taylor series  $F(x)$  can be generated from the expression

$$F(x) = f(a) + \left. \frac{d}{dx} f(x) \right|_{x=a} (x-a) + \frac{1}{2!} \left. \frac{d^2}{dx^2} f(x) \right|_{x=a} (x-a)^2 + \dots$$

This can be applied to any equation of state to derive an expression for the virial coefficients in terms of the parameters of the equation of state.

### **Application to the van der Waals equation:**

The van der Waals equation can be written in terms of molar volume as

$$p = \frac{RT}{V-b} - \frac{a}{V^2}$$

Multiplying the right hand side by  $\frac{u}{u}$  (where  $u = \frac{1}{V}$ ) yields:

$$p = \frac{RTu}{1-bu} - au^2$$

This expression can be expanded about  $u = 0$  (which corresponds to an infinite molar volume.) The coefficient terms that are needed for the expansion are

$$p(u=0) = 0$$

$$\left. \frac{dp}{du} \right|_{u=0} = \left[ \frac{RT}{1-bu} + \frac{bRTu}{(1-bu)^2} - 2au \right]_{u=0} = RT$$

$$\left. \frac{1}{2!} \frac{d^2p}{du^2} \right|_{u=0} = \frac{1}{2} \left[ \frac{bRT}{(1-bu)^2} + \frac{bRT}{(1-bu)^2} + \frac{2b^2RTu}{(1-bu)^3} - 2a \right]_{u=0} = bRT - a$$

$$\left. \frac{1}{3!} \frac{d^3p}{du^3} \right|_{u=0} = RTb^2$$

And the virial equation can then be expressed in terms of the van der Waals parameters as

$$p = 0 + RT(u) + (bRT - a)(u)^2 + RTb^2(u)^3 + \dots$$

Substituting  $u = 1/V$  and simplifying gives the desired result:

$$p = RT \left[ \frac{1}{V} + \frac{\left(b - \frac{a}{RT}\right)}{V^2} + \frac{b^2}{V^3} + \dots \right]$$

And the second virial coefficient is given by

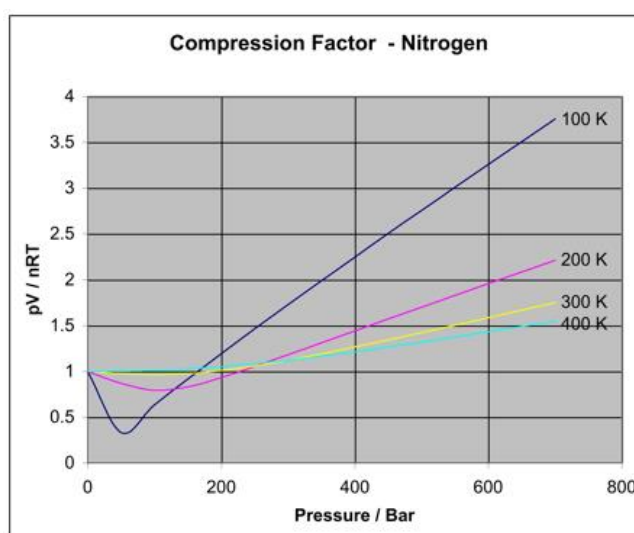
$$B(T) = b - \frac{a}{RT}$$

## The Boyle Temperature

A useful way in which deviations from ideality can be expressed is by defining the **compression factor** ( $Z$ ).  $Z$  is given by

$$Z = \frac{pV_m}{RT}$$

where  $V_m$  is the molar volume. For an ideal gas,  $Z = 1$  under all combinations of  $P$ ,  $V_m$ , and  $T$ . However, real gases will show some deviation (although all gases approach ideal behavior at low  $p$ , high  $V_m$ , and high  $T$ .) The compression factor for nitrogen at several temperatures is shown below over a range of pressures.



As can be seen, the gas behaves closer to ideally over a longer range of pressure at the higher temperatures. In general, there is one temperature, the **Boyle temperature**, at which a gas will approach ideal behavior as the pressure goes to zero asymptotically, and thus behave ideally over a broad range of lower pressures. The Boyle temperature is found by solving

$$\lim_{p \rightarrow 0} \left( \frac{\partial Z}{\partial p} \right) = 0$$

or

$$\lim_{1/V_m \rightarrow 0} \left( \frac{\partial Z}{\partial \left( \frac{1}{V_m} \right)} \right) = 0$$

Using the virial equation of state, The Boyle temperature can be expressed in terms of the virial coefficients. Starting with the compression factor

$$Z = 1 + \frac{B}{V_m} + \dots$$

and then differentiating with respect to  $1/V_m$  yields

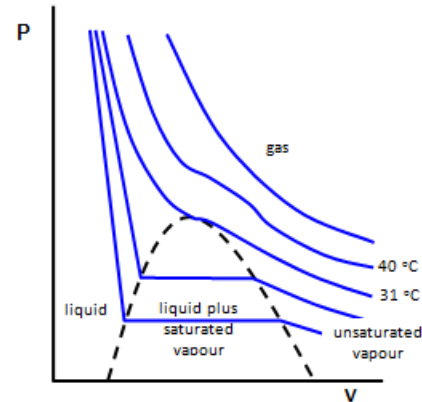
$$\left( \frac{\partial Z}{\partial \left( \frac{1}{V_m} \right)} \right) = B$$

So it can be concluded that at the Boyle temperature, the second virial coefficient  $B$  is equal to zero. This should make some sense given that the first virial coefficient provides most of the deviation from the ideal gas law, and so it must vanish as the gas behaves more ideally.

## Critical Behavior

The isotherms (lines of constant temperature) of  $\text{CO}_2$  reveal a very large deviation from ideal behavior.

At high temperatures,  $\text{CO}_2$  behaves according to Boyle's Law. However, at lower temperatures, the gas begins to condense to form a liquid at high pressures. At one specific temperature, the **critical temperature**, the isotherm begins to display this critical behavior. The temperature, pressure, and molar volume ( $p_c$ ,  $T_c$ , and  $V_c$ ) at this point define the **critical point**. In order to solve for expressions for the critical constants, one requires three equations. The equation of state provides one relationship. The second can be generated by recognizing that the slope of the isotherm at the critical point is zero. And finally, the third expression is derived by recognizing that the isotherm passes through an inflection point at the critical point. Using the van der Waals equation as an example, these three equations can be generated as follows:



$$p = \frac{RT}{V - b} - \frac{a}{V^2}$$

$$\left( \frac{\partial p}{\partial V} \right) = -\frac{RT}{(V - b)^2} + \frac{2a}{V^3} = 0$$

$$\left( \frac{\partial^2 p}{\partial V^2} \right) = \frac{2RT}{(V - b)^3} - \frac{6a}{V^4} = 0$$

Solving these expressions for  $p_c$ ,  $T_c$ , and  $V_c$  yields

$$p_c = \frac{a}{27b^2} \qquad T_c = \frac{8a}{27bR} \qquad V_c = 3b$$

The critical variables can be used in this fashion to determine the values of the molecular parameters used in an equation of state (such as the van der Waals equation) for a given substance.

### The Principle of Corresponding States

The **principle of corresponding states** was proposed by van der Waals in 1913 (van der Waals J. D., 1913). He noted that the compression factor at the critical point

$$Z_c = \frac{p_c V_c}{RT_c}$$

is very nearly the same for any substance. This is consistent with what is predicted by the van der Waals equation, which predicts  $Z_c = 0.375$  irrespective of substance.

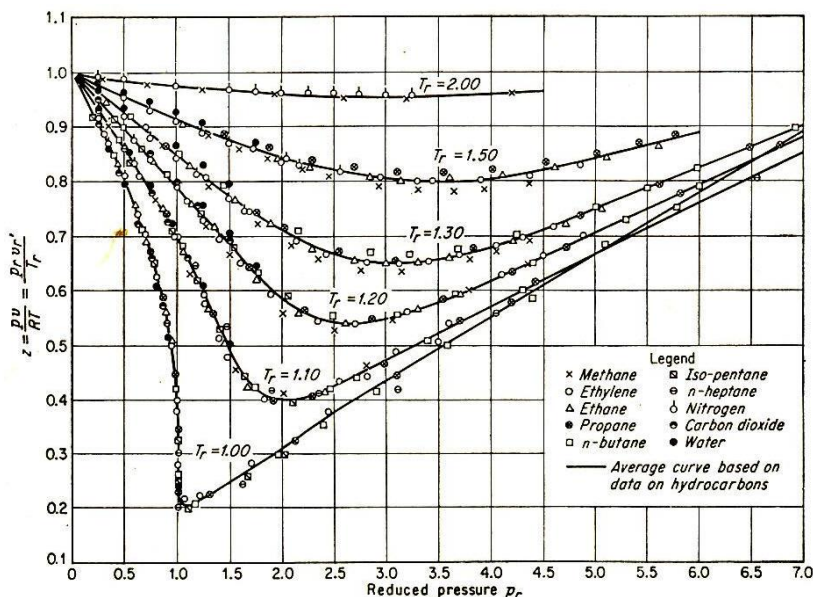
Further, it can be noted that based on **reduced variables** defined by

$$p_r = \frac{p}{p_c} \qquad V_r = \frac{V}{V_c} \qquad T_r = \frac{T}{T_c}$$

several physical properties are found to be comparable for real substances. For example (Guggenheim, 1945), for argon, krypton, nitrogen, oxygen, carbon dioxide and methane the reduced compressibility is

$$\frac{p_c V_c}{RT_c} \approx 0.292$$

Also, the reduced compression factor can be plotted as a function of reduced pressure for several substances at several reduced isotherms with surprising consistency irrespective of the substance:



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## Chapter 2 - Gases

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### Learning Objectives

After mastering the material covered in this chapter, one will be able to:

1. Understand the relationships demonstrated by and perform calculations using the empirical gas laws (Boyle's Law, Charles' Law, Gay-Lussac's Law, and Avogadro's Law, as well as the combined gas law.)
2. Understand and be able to utilize the ideal gas law in applications important in chemistry.
3. State the postulates of the Kinetic Molecular theory of gases.
4. Utilize the Maxwell and Maxwell-Boltzmann distributions to describe the relationship between temperature and the distribution of molecular speeds.
5. Derive an expression for pressure based on the predictions of the kinetic molecular theory for the collisions of gas molecules with the walls of a container.
6. Derive and utilize an expression for the frequency with which molecules in a gas sample collide with other molecules.
7. Derive and utilize an expression for the mean-free-path of molecules based on temperature, pressure, and collisional cross section.

- Explain how the van der Waals (and other) model(s) allow for deviations from ideal behavior of gas samples.
- Derive an expression for the Boyle temperature and interpret the results based on how a gas's behavior approaches that of an ideal gas.
- Explain and utilize the Principle of Corresponding States.

## Problems

- Assuming the form of the Maxwell distribution allowing for motion in three directions to be

$$f(v) = Nv^2 e^{-\frac{mv^2}{2k_B T}}$$

derive the correct expression for N such that the distribution is normalized. Hint: a table of definite integrals indicates

$$\int_0^\infty x^2 e^{-ax^2} dx = \frac{1}{4} \frac{\sqrt{\pi}}{a^{3/2}}$$

- Dry ice (solid CO<sub>2</sub>) has a density of 1.6 g/cm<sup>3</sup>. Assuming spherical molecules, estimate the collisional cross section for CO<sub>2</sub>. How does it compare to the value listed in the text?
- Calculate the pressure exerted by 1.00 mol of Ar, N<sub>2</sub>, and CO<sub>2</sub> as an ideal gas, a van der Waals gas, and a Redlich-Kwong gas, at 25 °C and 24.4 L.
- The compression factor Z for CO<sub>2</sub> at 0 °C and 100 atm is 0.2007. Calculate the volume of a 2.50 mole sample of CO<sub>2</sub> at 0 °C and 100 atm.
- Calculate the pressure exerted by 1.00 mol of each gas at 273 K if the sample of gas occupies 22.4 L

	Ar	N <sub>2</sub>	CO <sub>2</sub>
<b>ideal</b>			
<b>van der Waals</b>			
<b>Redlich-Kwong</b>			

- What is the maximum pressure that will afford a N<sub>2</sub> molecule a mean-free-path of at least 1.00 m at 25 °C?
- In a Knudsen cell, the effusion orifice is measured to be 0.50 mm<sup>2</sup>. If a sample of naphthalene is allowed to effuse for 1.0 hr at a temperature of 40.3 °C, the cell loses 0.0236 g. From this data, calculate the vapor pressure of naphthalene at this temperature.

8. The vapor pressure of scandium was determined using a Knudsen cell [Kirkorian, *J. Phys. Chem.*, **67**, 1586 (1963)]. The data from the experiment are given below.

Vapor Pressure of Scandium	
Temperature	1555.4 K
Time	110.5 min
Mass loss	9.57 mg
Diameter of orifice	0.2965 cm

From this data, find the vapor pressure of scandium at 1555.4 K.

9. A thermalized sample of gas is one that has a distribution of molecular speeds given by the Maxwell-Boltzmann distribution. Considering a sample of  $N_2$  at 25 °C what fraction of the molecules have a speed less than
- the most probably speed
  - the average speed
  - the RMS speed?
  - The RMS speed of helium atoms under the same conditions?
10. Assume that a person has a body surface area of 2.0 m<sup>2</sup>. Calculate the number of collisions per second with the total surface area of this person at 25 °C and 1.00 atm. (For convenience, assume air is 100%  $N_2$ )
11. Two identical balloons are inflated to a volume of 1.00 L with a particular gas. After 12 hours, the volume of one balloon has decreased by 0.200 L. In the same time, the volume of the other balloon has decreased by 0.0603 L. If the lighter of the two gases was helium, what is the molar mass of the heavier gas?
12. Assuming it is a van der Waals gas, calculate the critical temperature, pressure and volume for  $CO_2$ .
13. Find an expression in terms of van der Waals coefficients for the Boyle temperature. (*Hint*: use the virial expansion of the van der Waals equation to find an expression for the second virial coefficient!)
14. Consider a gas that follows the equation of state

$$p = \frac{RT}{V_m - b}$$

Using a virial expansion, find an expression for the second virial coefficient.

15. Consider a gas that obeys the equation of state



$$p = \frac{nRT}{V - nb} - \frac{an}{V}$$

where  $a$  and  $b$  are non-zero constants. Does this gas exhibit critical behavior? If so, find expressions for  $p_c$ ,  $V_c$ , and  $T_c$  in terms of the constants  $a$ ,  $b$ , and  $R$ .

16. Consider a gas that obeys the equation of state

$$pV = nRT + anpT + nbp$$

- a. Find an expression for the Boyle temperature in terms of the constant  $a$ ,  $b$ , and  $R$ .
- b. Does this gas exhibit critical behavior? If so, find expressions for  $p_c$ ,  $V_c$ , and  $T_c$  in terms of the constants  $a$ ,  $b$ , and  $R$ .