Key Points on Chapter 16: Temperature and the Kinetic Theory of Gases

- _____ is a form of energy that flows between two objects at different temperatures.

- Objects at the same temperature are in _____.

- Thermal _____ usually occurs when objects are heated.

- An ideal gas consists of identical _____ particles.

- The average _____ associated with each degree of freedom is $k_B T/2$.

- The pressure exerted by an ideal gas increases with the temperature and the _____.

- If you sample a population, you obtain a _____ of values.

- The _____ of an outcome is the number of ways of getting that outcome divided by the total number of outcomes.

- The Maxwell-Boltzmann distribution decays exponentially with _____ energy and velocity at a fixed temperature.

Lecture on Chapter 16: Temperature and the Kinetic Theory of Gases
Temperature

Thermodynamics is concerned with what happens when temperature is changed and energy (or heat) is transferred between a system and its environment. For example, when we cool water, it turns into ice. Thermodynamics helps us to understand how this happens. The study of thermodynamics began in the 18th and 19th centuries when people were trying to understand the basic principles of heat engines, i.e., how can heat be converted into useful work.

Key Point: _____ is a form of energy that flows between two objects at different temperatures. It has units of energy (Joules).

Key Point: Objects at the same temperature are in _____

One of the basic concepts is temperature with which you're all familiar. But actually when something feels how or cold to the touch, you are sensing the rate at which heat flows away from your hand rather than the actual temperature. For example, if you go outside to your car late at night, the metal on the outside of the car will feel much colder than the seat even though both are at the same temperature because metal conducts heat away from your hand faster than the seat. When two objects can exchange heat or energy, we say that they are in **thermal contact**. When there is no net exchange of energy between the objects because they are at the same temperature, we say that they are in **thermal equilibrium**. In fact we can think of temperature as the property that determines whether an object is in thermal equilibrium with other objects. The zeroth law of thermodynamics states that "if two objects are each in thermal equilibrium with a third object, then they are in thermal equilibrium with each other." Think of the third object as a thermometer. Of course if two objects are not in thermal equilibrium but are in thermal contact, then heat flows from the hotter object to the colder object.

Let us take a moment to talk about temperature scales. Here in the US we use the Fahrenheit scale, while in most other countries, the Celsius temperature scale is used. On the Celsius scale at 1 atmosphere of pressure the freezing point of water is 0^oC and the boiling point is 100^oC. On a mercury thermometer there are 100 evenly spaced marks between 0^oC and 100^oC. The thermometer works because the volume of the mercury is proportional to the temperature.

In physics we use the Kelvin temperature scale. On the Kelvin scale, 0^oC corresponds to 273.15 K. The boiling point of water at 1 atmosphere of pressure is 373.15 K. To convert between a temperature T_C in Celsius and the corresponding temperature T in Kelvin, use the equation

$$T_C = T - 273.15 \tag{1}$$

0 K = -273.15^oC is **absolute zero**. According to classical physics the kinetic energy of all molecules and atoms goes to zero at 0 K, but quantum mechanically, atoms and molecules can still vibrate. This vibration at 0 K is called zero point motion.

The boiling and freezing points of water depend on the ambient pressure which varies with altitude and other factors. Since the boiling and freezing points are not very good for calibrating thermometers, the standard points for calibrating thermometers are absolute

zero and the triple point of water since there is just one temperature and pressure at which water, water vapor, and ice coexist. The triple point of water is 273.16 K or 0.01^{o}C.

To convert between Fahrenheit and Celsius, use

$$T_F = \frac{9}{5}T_C + 32^o F \tag{2}$$

Water freezes at 32°F and boils at 212°F.

Thermal Expansion of Solids and Liquids

Key Point: Thermal _____ usually occurs when objects are heated.

When you heat up solids and liquids they usually expand. This is called thermal expansion. It is important to allow for thermal expansion in constructing roads, railroad tracks, etc. If there isn't a little room for the pieces to expand on a hot day, the road or tracks will buckle. The amount by which solids and liquids expand is proportional to the amount of the temperature increase. But if I heat up a bar of copper and tell you that its length increased by 1 cm, is that a big increase or not? Well, it depends on what the initial length of the bar was. If the bar was initially 1 km long, then 1 cm is not that much. But if the bar was initially 1 cm long, then it doubled in length and that would be a big increase. So it is important to compare the increase ΔL in length with the initial length L_i. In other words we are interested in the ratio $\Delta L/L_i$ which is sometimes called the relative or fractional increase in length. It is this relative increase in length which is proportional to the temperature change ΔT. Thus we can write

$$\frac{\Delta L}{L_i} = \alpha \Delta T \tag{3}$$

where the constant of proportionality α is called the average coefficient of linear expansion. $\Delta L = L_f - L_i$ where L_f is the final length of the bar. This equation also works when the temperature is decreased. When objects are cooled, they tend to shrink. In this case ΔT is negative and ΔL is also negative.

Similar considerations apply when a block of material is heated. Typically the block's volume increases by an amount $\Delta V = V_f - V_i$ where V_f is the final volume and V_i is the initial volume. The fractional increase in volume $\Delta V/V_i$ is proportional to the increase ΔT in temperature:

$$\frac{\Delta V}{V_i} = \beta \Delta T \tag{4}$$

where the constant of proportionality β is called the average coefficient of volume expansion. Your book goes through the derivation showing that $\beta = 3\alpha$. Again this equation works when the temperature decreases ($\Delta T < 0$) and the object shrinks ($\Delta V < 0$).

Example: How much does a 1 meter long copper bar expand due to a 50°C increase in temperature?

According to table 16.1, the linear expansion expansion coefficient of copper is $\alpha = 17 \times 10^{-6}/^o C$. So the relative increase in length is $\Delta L/L_i = \alpha \Delta T = 17 \times 10^{-6}/^o C \times 50^o C =$

8.5×10^{-4}. Notice that the relative increase in length is dimensionless. It's always a good idea to check that the dimensions of your answer match your expectations. So the change in length of the bar is $\Delta L = (\Delta L/L_i) \times L_i = \Delta L = 8.5 \times 10^{-4} \times 1\text{m} = 8.5 \times 10^{-4}\text{m}$. So the final length of the bar is $L_f = L_i + \Delta L = 1\text{m} + 8.5 \times 10^{-4}\text{m} = 1.00085$ m. Notice that the final answer has the right units, namely meters.

Ideal Gas

Key Point: An ideal gas consists of identical _____ particles.

You are no doubt familiar with the concept of an ideal gas from chemistry. An ideal gas consists of identical point-like particles which move randomly and do not interact with one another. Your book says that the particles have short range interactions with each other, but this is not correct. To a physicist, an ideal gas consists of identical *noninteracting* particles. This means that the particles do not know about one another. They can go through each other. The particles only have kinetic energy and no potential energy. This makes an ideal gas a very simple system to deal with.

Suppose we put an ideal gas in a container of volume V. Then the ideal gas law states that

$$PV = nRT \tag{5}$$

where P is the pressure exerted by the gas on the container walls, T is the temperature in Kelvin, n is the number of moles, and R is the universal gas constant:

$$R = 8.315 \ \text{J/mol} - \text{K} \tag{6}$$

A mole is the amount of an element or compound that contains Avogadro's number of molecules or atoms. Avogadro's number $N_A = 6.022 \times 10^{23}$. (Your book incorrectly implies that a mole has units of mass. It doesn't; a mole has no dimensions.) A molar mass is the mass of a mole of a substance. From the ideal gas law, the volume occupied by 1 mole of an ideal gas at 1 atmosphere of pressure at 0^oC is 22.4 liters. Let N be the number of particles. Then we can rewrite the ideal gas law as follows.

$$PV = nRT = \frac{N}{N_A}RT = N\left(\frac{R}{N_A}\right)T = Nk_BT \tag{7}$$

where k_B is Boltzmann's constant and has the value

$$k_B = \frac{R}{N_A} = 1.38 \times 10^{-23} \ \text{J/K} \tag{8}$$

Equipartition Theorem

Key Point: The average _____ associated with each degree of freedom is $k_BT/2$.

When we say that a substance is hot, we mean that it has a high temperature. For an ideal gas, this high temperature means that the particles have a large average kinetic energy. In fact the average kinetic energy of each particle is proportional to the absolute temperature T measured in Kelvin:

$$\overline{\frac{1}{2}mv^2} \propto k_BT \tag{9}$$

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The bar or overline is a symbol that means average. Since the mass m is the same for each particle, we don't need to put a bar over the m. Only the velocity varies from particle to particle, so that's where we need the bar to indicate the average of the square of the velocity.

$$\frac{1}{2}m\overline{v^2} \propto k_B T \tag{10}$$

Now let's consider the constant of proportionality. In 3D each particle has 3 directions in which it can move: x, y, and z. That's why the velocity is a vector with 3 components: v_x, v_y, and v_z. We say that each particle has 3 degrees of freedom. According to the **equipartition theorem**, the average kinetic energy associated with each degree of freedom is $k_B T/2$. (Notice that $k_B T$ has units of energy just like mv^2.) In other words,

$$\begin{aligned}
\frac{1}{2}m\overline{v_x^2} &= \frac{1}{2}k_B T \\
\frac{1}{2}m\overline{v_y^2} &= \frac{1}{2}k_B T \\
\frac{1}{2}m\overline{v_z^2} &= \frac{1}{2}k_B T
\end{aligned} \tag{11}$$

So $\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2}$. Since $\overline{v^2} = \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2}$, $\overline{v^2} = 3\overline{v_x^2}$. Now we can figure out the constant of proportionality for eq. (10):

$$\begin{aligned}
\frac{1}{2}m\overline{v^2} &= \frac{1}{2}m\left(\overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2}\right) \\
&= \frac{1}{2}m\overline{v_x^2} + \frac{1}{2}m\overline{v_y^2} + \frac{1}{2}m\overline{v_z^2} \\
&= \frac{3}{2}k_B T
\end{aligned} \tag{12}$$

So the equipartition theorem says that for each degree of freedom, the average kinetic energy is $k_B T/2$. In 3D we have 3 degrees of freedom, so the average kinetic energy for one particle is $3k_B T/2$. If we have N particles in the gas, then the average total kinetic energy is $3N k_B T/2$. If we have n moles of an ideal gas, then $N = nN_A$, and we can write the total kinetic energy as $3nN_A k_B T/2 = 3nRT/2$. Note that the temperature T is the absolute temperature measured in Kelvin. This formula won't work if you use Celsius.

The equipartition theorem works for rotational and vibrational degrees of freedom as well. Suppose we have a diatomic molecule lying along the x axis. It can rotate about the y axis and about the z axis. So the average rotational kinetic energy from both these degrees of freedom is $2 \times k_B T/2$. We ignore rotations about the x axis because the moment of inertia is too small. We can also have vibrations along the axis of the molecule. Think of the 2 atoms as being connected by a spring. The average vibrational kinetic energy contributes $k_B T/2$ and the average vibrational potential energy also contributes $k_B T/2$.

Let's go back to the monoatomic ideal gas. We can use the equipartition theorem to deduce the root–mean–square (rms) speed of the particles:

$$v_{\text{rms}} = \sqrt{\overline{v^2}} = \sqrt{\frac{3k_BT}{m}} \tag{13}$$

Notice that the lighter the mass m, the bigger v_{rms} is. Also the higher the temperature, the bigger v_{rms} is. This is what we expect.

Example: What is the average kinetic energy of an ideal gas atom at 50^oC?
First we must convert Celsius to Kelvin: $50 + 273.15{=}323.15$ K. From the equipartition theorem, we know that the average kinetic energy of an ideal gas atom is $3k_BT/2 = 3(1.38 \times 10^{-23} \text{ J/K})(323.15 \text{ K})/2 = 6.69 \times 10^{-21}$ Joules. This seems like such a small number. I like to express it in multiples of k_B. So the average kinetic energy is $3(323 \text{ K})k_B/2 = 485 \text{ K } k_B$.

Pressure of an Ideal Gas

Key Point: The pressure exerted by an ideal gas increases with the temperature and the _____.

When we put an ideal gas in a box, the particles bounce off the walls of the box. Since they change their momentum when they bounce off the walls, they impart a force on the walls. This force produces pressure on the walls. Think of a gas filled balloon; the balloon puffs out due to the gas pressure inside. Pressure has units of force per unit area. Now let's do some dimensional analysis. When I use square brackets, that means the units or dimensions. So

$$
\begin{aligned}
[P] &= \frac{[\text{Force}]}{[\text{Area}]} \\
&= \frac{[\text{Force} \cdot \text{length}]}{[\text{Area} \cdot \text{length}]} \\
&= \frac{[\text{Energy}]}{[\text{Volume}]}
\end{aligned} \tag{14}
$$

So pressure has the same units as energy per unit volume or energy density.

We can calculate the pressure produced by an ideal gas on the walls of its container. Remember that the pressure is due to the collisions of the particles with the walls. If there are a lot of particles, there will be a lot of collisions and this will produce an average pressure P. The more kinetic energy the gas has, the higher the pressure. This means that the higher the temperature, the higher the pressure for a fixed volume. This is what the ideal gas law tells us: $PV = Nk_BT$. Let's solve this for the pressure:

$$P = \frac{Nk_BT}{V} \tag{15}$$

Now we know from the equipartition theorem that the average kinetic energy $(1/2)m\overline{v^2} = 3k_BT/2$ or

$$k_BT = \left(\frac{2}{3}\right)\left(\frac{1}{2}m\overline{v^2}\right) \tag{16}$$

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Plugging this into eq. (15) leads to

$$P = \frac{2}{3} \left(\frac{N}{V} \right) \left(\frac{1}{2} m \overline{v^2} \right) \tag{17}$$

We see that the pressure is proportional to the number of molecules per unit volume and to the average kinetic energy of the molecules. Notice also that the units on the right hand side are energy per volume which is correct.

Distributions and Probability

Key Point: If you sample a population, you obtain a _____ of values.

Key Point: The _____ of an outcome is the number of ways of getting that outcome divided by the total number of outcomes.

In an ideal gas the particles have a variety or distribution of energies and speeds. Often when you sample a population, you get a distribution of values. For example the grades on the midterm will have a distribution. The same goes for the heights of 2 year olds, or the concentration of an enzyme in different people's bloodstream. What determines if an enzyme level is abnormal or within normal limits? It's the distribution of enzyme levels. So distributions and probabilities are important. That is why I want to take a few moments to discuss them.

Hopefully you talked about probability in the discussion section. If we flip a coin, the chance of heads is 1/2 and the chance of tails is 1/2. The probability of an outcome is the number of ways of getting that outcome divided by the total number of outcomes. We often write $P(x_i)$ for the probability that an outcome is x_i. So if we flip 2 coins, then P(head,head)=1/4, and P(head,tail)=1/2 because there are a total of 4 possible outcomes and 2 ways of getting one coin heads and one coin tails. Notice that if we sum over all the probabilities, the sum is 1.

Normalization, Averages, Second Moment

Let $P(x_i)$ be the probability distribution for the probability that an outcome is x_i. If we sum over all possible outcomes, one of them is bound to happen, so

$$\sum_{x_i} P(x_i) = 1 \tag{18}$$

In other words, the probability distribution function $P(x_i)$ is normalized to one. One can also have a probability distribution function $P(x)$ of a continuous variable x. For example, suppose you leave a meter stick outside on the ground. $P(x)dx$ could be the probability that the first raindrop to hit the stick will strike between position x and $x + dx$. $P(x)$ is called the probability density. The normalization condition is

$$\int dx P(x) = 1 \tag{19}$$

The average of some quantity x is

$$< x >= \overline{x} = \frac{\int dx P(x) x}{\int dx P(x)} \tag{20}$$

Averages can be denoted by $<x>$ or $\overline{x}$. For a discrete quantity

$$\overline{x} = \frac{\sum_i P(x_i) x_i}{\sum_i P(x_i)} \tag{21}$$

If the probability is normalized, then the denominator is 1. For example, suppose $N(A_i)$ is the number of people with age A_i. Then the average age is

$$
\begin{aligned}
\overline{A} &= \frac{\sum_{A_i=0}^{\infty} N(A_i)\, A_i}{\sum_{A_i=0}^{\infty} N(A_i)} \\
&\rightarrow \frac{\int dA\, N(A)\, A}{\int dA\, N(A)}
\end{aligned} \tag{22}
$$

The probability that a person is A old is

$$P(A) = \frac{N(A)}{\int dA\, N(A)} \tag{23}$$

Notice that this satisfies the normalization condition. More generally, if $f(x)$ is a function of x, then the average value of $f(x)$ is

$$\overline{f(x)} = \frac{\int dx P(x) f(x)}{\int dx P(x)} \tag{24}$$

One of the more useful functions concerns the deviation of x from the mean $\overline{x}$:

$$\Delta x = x - \overline{x} \tag{25}$$

Then

$$
\begin{aligned}
\overline{\Delta x} &= \overline{x - \overline{x}} \\
&= \overline{x} - \overline{x} \\
&= 0
\end{aligned} \tag{26}
$$

A more useful quantity is the square of the deviation from the mean

$$
\begin{aligned}
\overline{(\Delta x)^2} &= \overline{(x - \overline{x})^2} \\
&= \overline{(x^2 - 2x\overline{x} + \overline{x}^2)} \\
&= \overline{x^2} - 2\overline{x}\,\overline{x} + \overline{x}^2 \\
&= \overline{x^2} - \overline{x}^2
\end{aligned} \tag{27}
$$

This is known as the second moment of x about its mean. The first moment is just $\overline{x}$.

Gaussian Distribution

One of most useful distributions is the Gaussian distribution. This is sometimes called the bell curve which is well known as the ideal grade distribution.
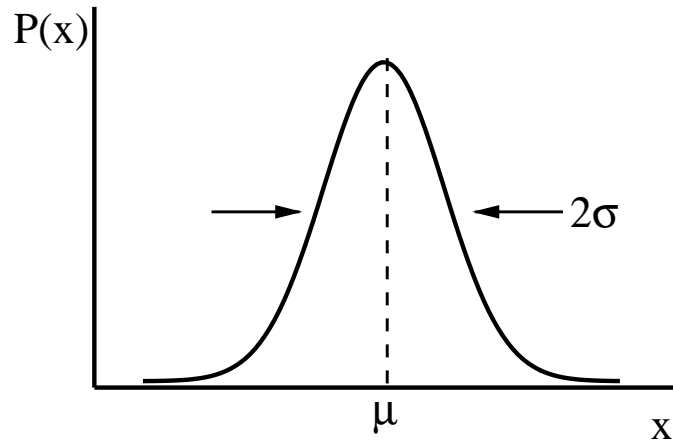
The formula for a Gaussian distribution is

$$P(x)dx = \frac{1}{\sqrt{2\pi}\sigma}e^{-(x-\mu)^2/2\sigma^2}dx \tag{28}$$

where $\mu = \overline{x}$ is the mean. The coefficient is set so that the normalization condition is satisfied. $\sigma^2 = \overline{(\Delta x)^2} = \overline{(x - \overline{x})^2}$. 2σ is the width of the distribution. There is a 68% chance that $-\sigma \leq x \leq \sigma$. One obtains this by integrating $P(x)$ from $-\sigma$ to $+\sigma$. σ is sometimes called the root–mean–square (rms) deviation or the standard deviation.

As an example of a distribution, let me explain roughly how I plan to curve the grades for this course. (This is not absolute, but only a rough guide of how the grades are curved.) First I combine the quiz scores, midterm, and final for each student into a single number between 1 and 100 using the weighting in the syllabus. Now let's suppose the histogram or distribution of the grades obeys a gaussian distribution. I use the mean or average value $\overline{x}$ as the dividing point between B's and C's. Scores within one standard deviation above the mean ($\overline{x} < x < \overline{x} + \sigma$) will be some type of B (i.e., B+, B, or B-). Scores within one standard deviation below the mean ($\overline{x} - \sigma < x < \overline{x}$) will be some kind of C. Some type of A goes to those with a grade $x > \overline{x} + \sigma$. Some type of D or F is assigned to those with $x < \overline{x} - \sigma$.

## Maxwell–Boltzmann Distribution

Key Point: The Maxwell-Boltzmann distribution decays exponentially with _____ energy and velocity at a fixed temperature.

In an ideal gas the particles have a variety or distribution of energies and speeds. In general the probability $P(E)$ that a particle will have an energy between E and $E + dE$ is

$$P(E)dE = Ce^{-E/k_BT}dE \tag{29}$$

where C is a normalization constant. This exponential distribution is called the Boltzmann distribution. It holds for any particle or system in equilibrium, not just ideal gases. We see from this expression that zero energy or $E = 0$ has the highest probability. (I am assuming that there are no negative energies $E < 0$.) The higher the energy E, the lower

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the probability that the particle will have energy E. If $E \lesssim k_B T$, then there is a good chance we can find a particle with this energy. But if $E \gg k_B T$, then $\exp(-E/k_B T)$ is very small and there is a very small chance that a particle will have this energy. This makes sense; we don't expect to find particles with energies a whole lot higher than the ambient temperature.

Boltzmann Distribution vs. Energy E

$P(E) = \exp(-E/T)$
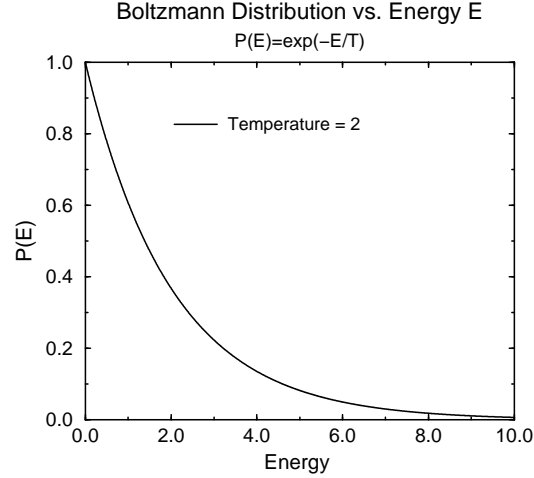
In an ideal gas, a particle with velocity $\vec{v}$ has energy $E = (1/2)mv^2$. Plugging this into eq. (29) yields the probability $P(v)d^3v$ that a particle will have velocity between $\vec{v}$ and $\vec{v} + d\vec{v}$:

$$P(\vec{v})d^3v = Ce^{-mv^2/2k_B T}d^3v \tag{30}$$

Notice that the exponent is quadratic in the speed v. This means the distribution is Gaussian and will produce a bell shaped curve. The most probable velocity is $\vec{v} = 0$. Particles are as likely to be moving forward as they are backward; the gas as a whole has no net velocity. It's not going anywhere. Since the system is isotropic, i.e., there is no net preference for the x, y, or z directions, we can use spherical coordinates and write $d^3v = 4\pi v^2 dv$. So the probability that a particle has speed between v and $v + dv$ is

$$
\begin{aligned}
P(v)dv &= P(\vec{v})d^3v \\
&= 4\pi v^2 P(\vec{v})dv \\
&= 4\pi C v^2 e^{-mv^2/2k_B T}dv
\end{aligned}
\tag{31}
$$

It is customary to normalize the curve, i.e., to set C so that the area under the curve is 1. This yields

$$P(v)dv = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} v^2 e^{-mv^2/2k_B T}dv \tag{32}$$

The probability that a particle has speed v is equal to the number N_v of particles with speed v divided by the total number of particles N, i.e., $P(v) = N_v/N$ or $N_v = NP(v)$. So we can write

$$N_v = 4\pi N \left(\frac{m}{2\pi k_B T} \right)^{3/2} v^2 e^{-mv^2/2k_B T} \tag{33}$$

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In your book there is a plot of N_v vs v. It is a slightly asymmetric bell shaped curve. Notice that there are no negative values of v; $|v| = v \geq 0$. The peak of this curve occurs at the v_{mp}, the most probable value of v.

The median value of the velocity marks where you would put a vertical dividing line such that half the area under the curve is to the right of the line and half the area is to the left. Often the median value and the average value are very close to one another but this is not always the case. For example, suppose you want the average price of houses in Bill Gates' neighborhood. If his house costs a billion dollars, then the average price will be high even if he lives in a slum. But the median house price is the one such that half the houses cost more and half the houses cost less.