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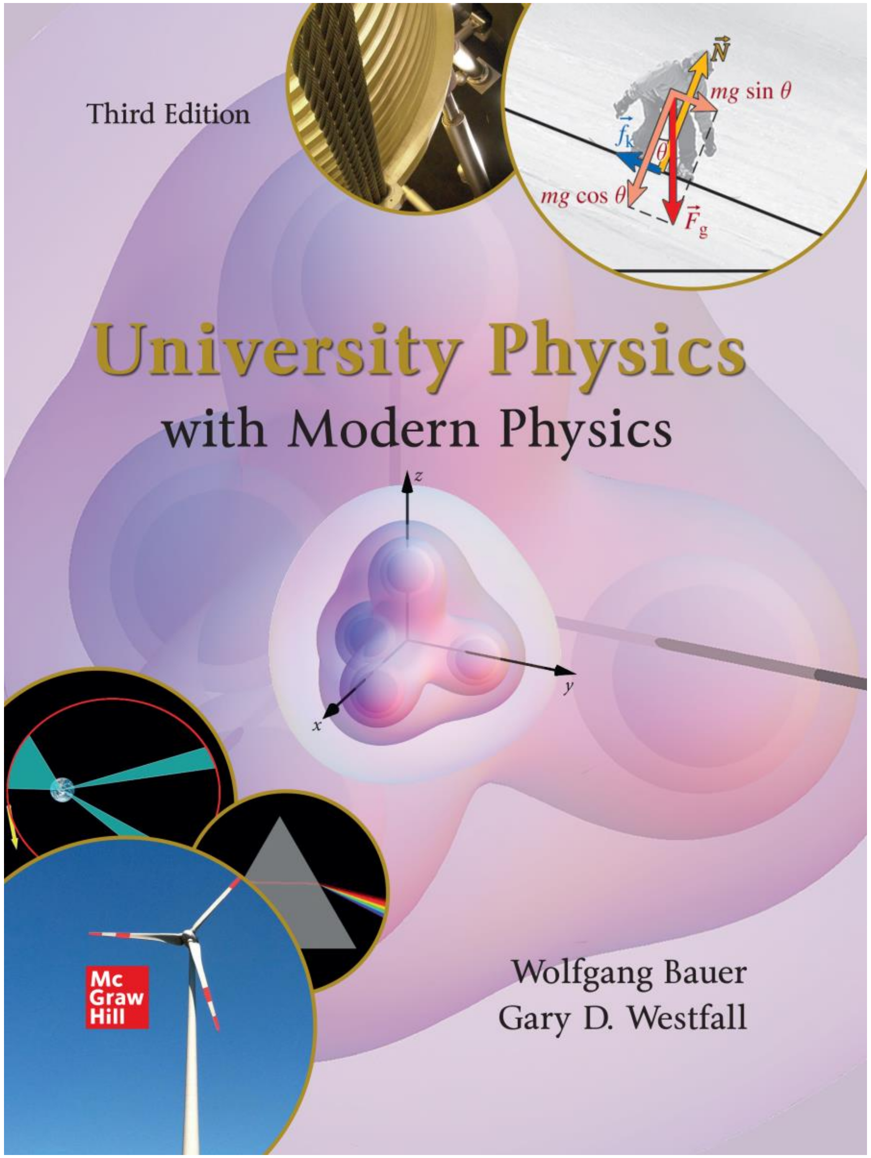
Chapter 19

Ideal Gases

University Physics with Modern Physics
Third Edition

Wolfgang Bauer Gary D. Westfall



Ideal Gases 1

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Ideal Gases 2

- In this chapter, we study the physics of gases.
- The results are based on an ideal gas, which doesn’t actually exist, but many real gases behave approximately like an ideal gas in many situations.
- We first examine the properties of gases based on observations, including laws first stated by pioneers of hot-air balloon navigation, who had a very practical interest in the behavior of gases at high altitudes.
- Then we gain additional insights from the kinetic theory of an ideal gas, which applies mathematical analysis to gas particles under several assumed conditions.

Empirical Gas Laws 1

- A gas consists of molecules that are spatially separated such that the intermolecular bonding, which is characteristic of liquids and solids, is absent.
- A gas expands to fill the container in which it is placed.
- The volume of a gas is the volume of its container.
- This chapter uses the term gas molecules to refer to the constituents of a gas, although a gas may consist of atoms or molecules or may be a combination of atoms and molecules.
- The temperature of a substance is defined in terms of its tendency to give off heat to its surroundings or to absorb heat from its surroundings.
- The pressure of a gas is defined as the force per unit area exerted by the gas molecules on the walls of a container.

Empirical Gas Laws 2

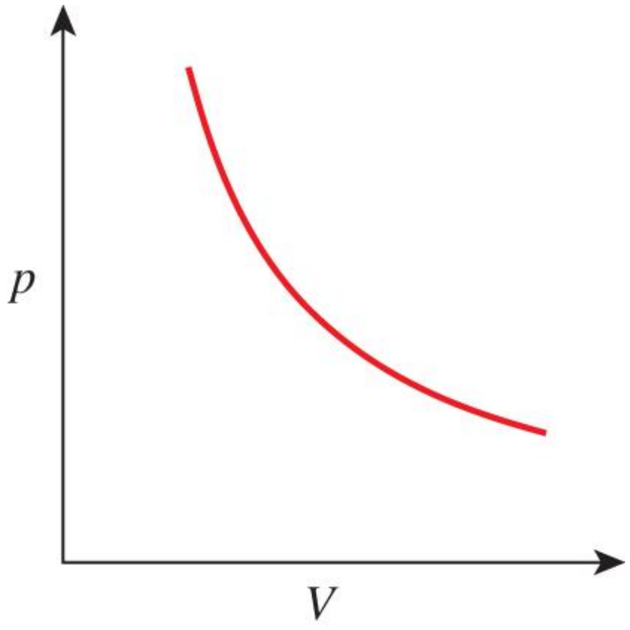
- For many applications, standard temperature and pressure (STP) is defined as 0 °C (273.15 K) and 100.000 kPa.
- Another characteristic of a gas, in addition to volume, temperature, and pressure, is the number of gas molecules in the volume of gas in a container.
- This number is expressed in terms of moles: 1 mole of a gas is defined to have $6.022 \cdot 10^{23}$ molecules.
- This number is known as Avogadro’s number.
- Several simple relationships exist among the four properties of a gas—pressure, volume, temperature, and number of molecules.
- This section covers four simple gas laws that relate these properties.

Empirical Gas Laws 3

- All these gas laws are named after their discoverers (Boyle, Charles, Gay-Lussac, Avogadro) and are empirical.
- In the next section, we'll combine these four laws to form the Ideal Gas Law, relating all the macroscopic characteristics of gases.
- If you understand the Ideal Gas Law, all the empirical gas laws follow immediately.
- Why not skip them?
- The answer is that these empirical gas laws form the basis from which the Ideal Gas Law is derived.

Boyle's Law 1

- The first empirical gas law is Boyle's Law, which is also known in Europe as Mariotte's Law.
- English scientist Robert Boyle published this law in 1662; French scientist Edme Mariotte published a similar result in 1676.
- Boyle's Law states that the product of a gas's pressure, p, and its volume, V, at constant temperature is a constant.
- Mathematically, Boyle's Law is expressed as pV = constant (at constant temperature).



Boyle’s Law 2

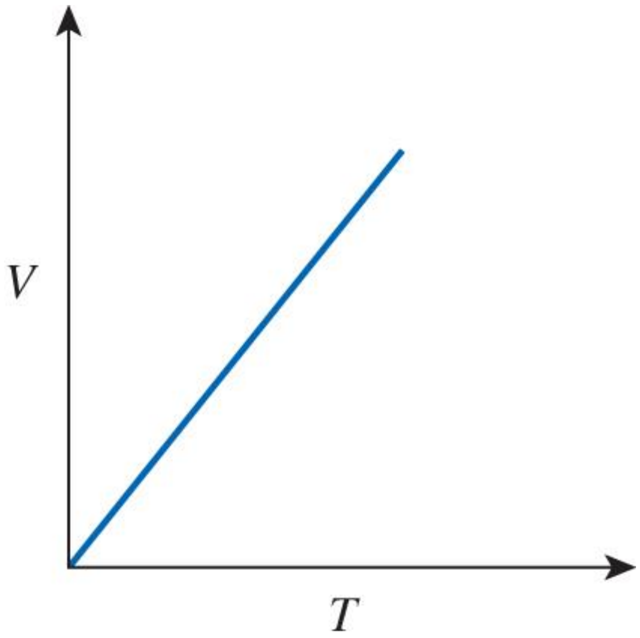
- Another way to express Boyle’s Law is to state that the product of the pressure, p_1, and volume, V_1, of a gas at time t_1 is equal to the product of the pressure, p_2, and the volume, V_2, of the same gas at the same temperature at another time, t_2:

  $p_1V_1 = p_2V_2$ (at constant temperature)

- An example of the application of Boyle’s Law is breathing.
- When you take in a breath, your diaphragm expands, and the expansion produces a larger volume in your chest cavity.
- According to Boyle’s Law, the air pressure in your lungs is reduced relative to the normal atmospheric pressure around you.
- The higher pressure outside your body then forces air into your lungs to equalize the pressure.

Charles's Law 1

- The second empirical gas law is **Charles's Law**, which states that for a gas kept at constant pressure, the volume of the gas, V, divided by its temperature, T, is constant.
- The French physicist Jacques Charles proposed this in 1787.
- Mathematically, Charles's Law is V/T = constant (at constant pressure).
- Another way to state Charles's Law is to state that the ratio of the temperature, T_1, and volume, V_1, of a gas at a given time, t_1, is equal to the ratio of the temperature, T_2, and the volume, V_2, of the same gas at the same pressure at another time, t_2.



Charles's Law 2

- This can be expressed as:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \quad \Rightarrow \quad \frac{V_1}{V_2} = \frac{T_1}{T_2}$$

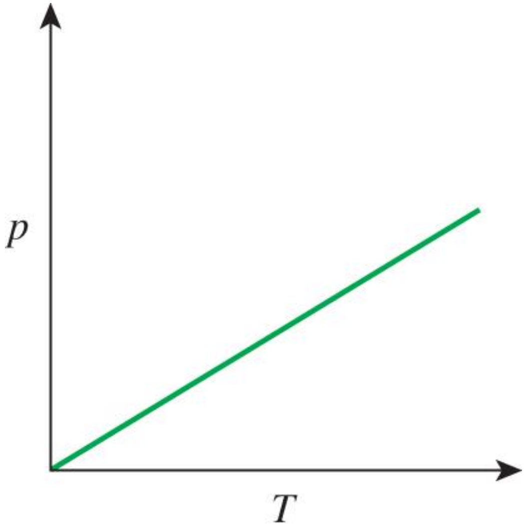
- The temperatures must be expressed in kelvins (K).
- Because the density, ρ, of a given mass, m, of gas is $\rho = m\,/V$, Charles's Law can also be written as ΔT = constant (at constant pressure).
- As a corollary to the equation above, we then have:

$$\rho_1 T_1 = \rho_2 T_2 \quad \Rightarrow \quad \frac{\rho_1}{\rho_2} = \frac{T_2}{T_1}$$

Gay-Lussac’s Law

- The third empirical gas law is **Gay-Lussac’s Law**, which states that ratio of the pressure, *p*, of a gas to its temperature, *T*, at the same volume is constant.
- This law was presented in 1802 by the French chemist Joseph Louis Gay-Lussac.
- Mathematically, Gay-Lussac’s Law is expressed as $p\,/T\ =$ constant (at constant volume).
- Another way to this law is to state that the ratio of the pressure of a gas, p_1 , and its temperature, T_1 , at a time, t_1, is equal to the ratio of the pressure, p_2, and the temperature, T_2, of the gas at the same volume at time, t_2:

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \quad \text{(at constant volume)}$$



Avogadro’s Law 1

- The 4th empirical gas law deals with the quantity of a gas.
- **Avogadro’s Law** states that the ratio of the volume of a gas, V, to the number of gas molecules, N, in that volume is constant if the pressure and temperature are held constant.
- This law was introduced in 1811 by the Italian physicist Amedeo Avogadro.
- Mathematically, Avogadro’s Law is expressed as V/N = constant (at constant pressure and temperature).
- Another way to express Avogadro’s Law is to state that the ratio of the volume, V_1, and the number of molecules, N_1, of a gas at a given time, t_1, is equal to the ratio of the volume, V_2, and the number of molecules, N_2, of the same gas at the same pressure and temperature at another time, t_2.

Avogadro's Law 2

- This can be expressed as:

$$\frac{V_1}{N_1} = \frac{V_2}{N_2} \quad \text{(at constant pressure and temperature)}$$

- It has been found that a volume of 22.4 L (1 L = 10^{-3} m^3) of a gas at standard temperature and pressure contains $6.022 \cdot 10^{23}$ molecules.
- This number of molecules is called Avogadro's number, N_A.
- The currently accepted value for Avogadro's number is:

$$N_\text{A} = (6.02214129 \pm 0.00000027) \cdot 10^{23}$$

- 1 mole of any gas will have Avogadro's number of molecules.

Avogadro's Law 3

- The number of moles is usually symbolized by *n*.
- Thus, the number of molecules, *N*, and the number of moles, *n*, of a gas are related by Avogadro's number:

  $N = nN_{\text{A}}$
- Therefore, the mass in grams of one mole of a gas is numerically equal to the atomic mass or molecular mass of the constituent particles in atomic mass units.
- For example, nitrogen gas consists of molecules composed of two nitrogen atoms.
- Each nitrogen atom has an atomic mass number of 14.
- Thus, the nitrogen molecule has a molecular mass number of 28, and a 22.4-L volume of nitrogen gas at standard temperature and pressure has a mass of 28 g.

Ideal Gas Law 1

- We can combine the empirical gas laws to obtain a more general law relating the properties of gases, called the **Ideal Gas Law**:

$$pV = nRT$$

- Here R is the **universal gas constant** given by:

$$R = (8.3144621 \pm 0.0000075)\ \text{J/(mol K)}$$

- The constant R can also be expressed in other units, which changes its numerical value, for example, R = 0.08205736 L atm/(mol K).
- The Ideal Gas Law was first stated by the French scientist Benoit Paul Émile Clapeyron in 1834.
- See Derivation 19.1 in the book.

Ideal Gas Law 2

- The Ideal Gas Law can also be written in terms of the number of gas molecules instead of the number of moles of gas:

$$pV = Nk_\text{B}T$$

- Here N is the number of atoms or molecules, and k_B is the Boltzmann constant, given by:

$$k_\text{B} = (1.3806488 \pm 0.0000013)\ \text{J/K}$$

- The Boltzmann constant is an important fundamental physical constant that often arises in relationships based on atomic or molecular behavior.
- It will be used again later in this chapter and again in discussions of solid-state electronics and quantum mechanics.

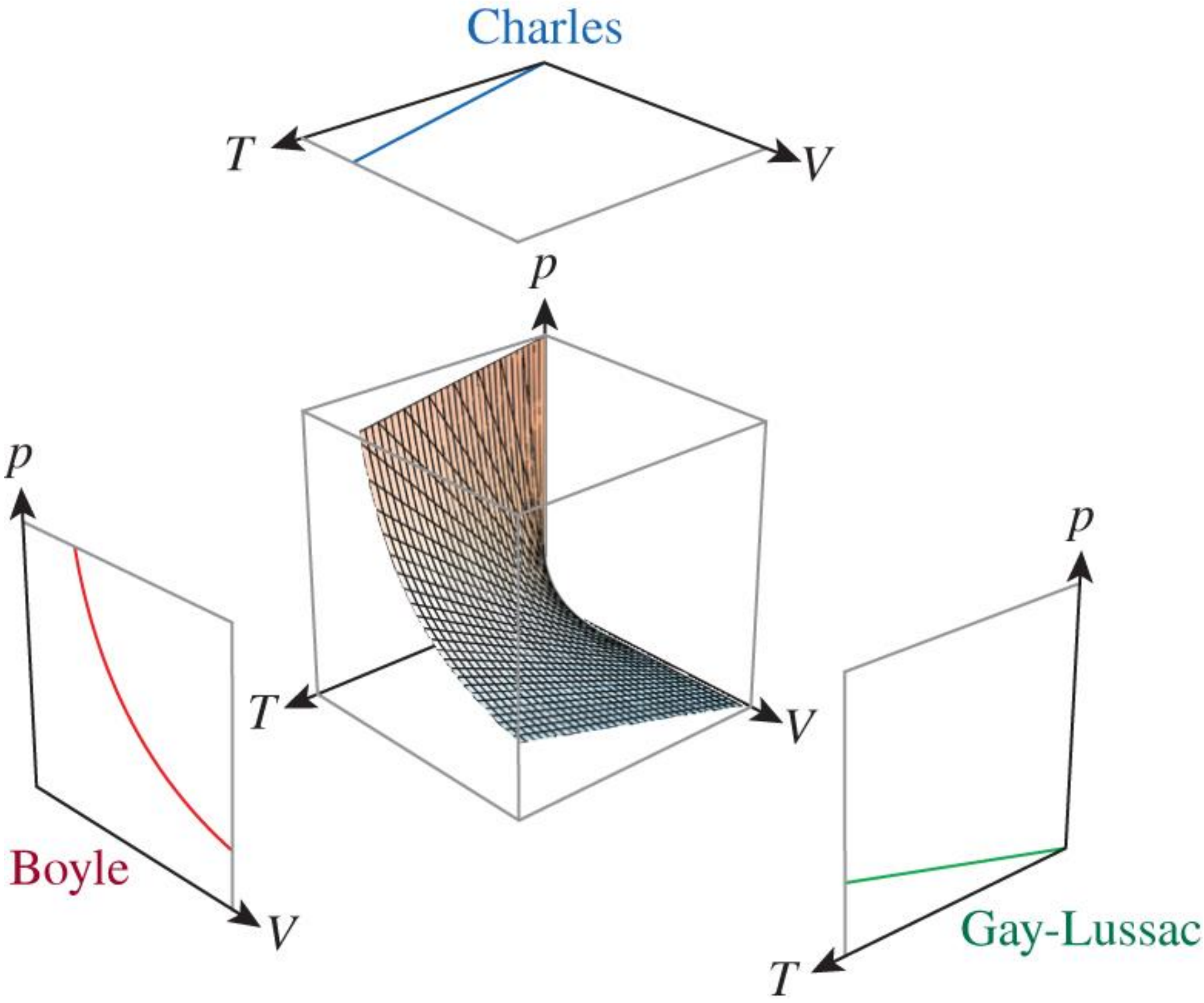
Ideal Gas Law 3

- Another way to express the Ideal Gas Law for a constant number of moles of gas is:

$$\frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2}$$

- The advantage of this formulation is that you do not have to know the numerical values of the universal gas constant or the Boltzmann constant to relate the pressures, volumes, and temperatures at two different times.
- It is straightforward to confirm that Boyle’s Law, Charles’s Law, and Gay-Lussac’s Law are embodied in the Ideal Gas Law.
- A three-dimensional surface can represent the relationship among the pressure, volume, and temperature of an ideal gas and we can look at various projections.

Ideal Gas Law 4



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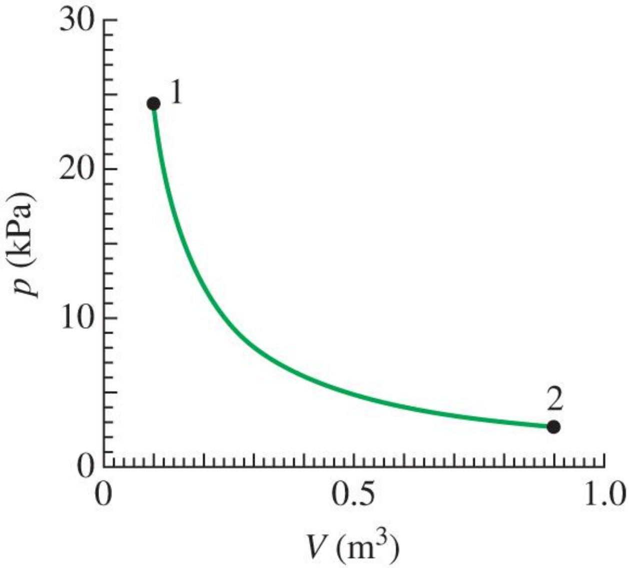
Gas in a Cylinder 1

- Consider a gas at a pressure of 24.9 kPa in a cylinder with a volume of 0.100 m^3 and a piston.
- This pressure and volume corresponds to point 1.
- The pressure of this gas must be decreased to allow a manufacturing process to work efficiently.
- The piston is designed to increase the volume of the cylinder from 0.100 m^3 to 0.900 m^3 while keeping the temperature constant.

PROBLEM:

- What is the pressure of the gas at a volume of 0.900 m^3?



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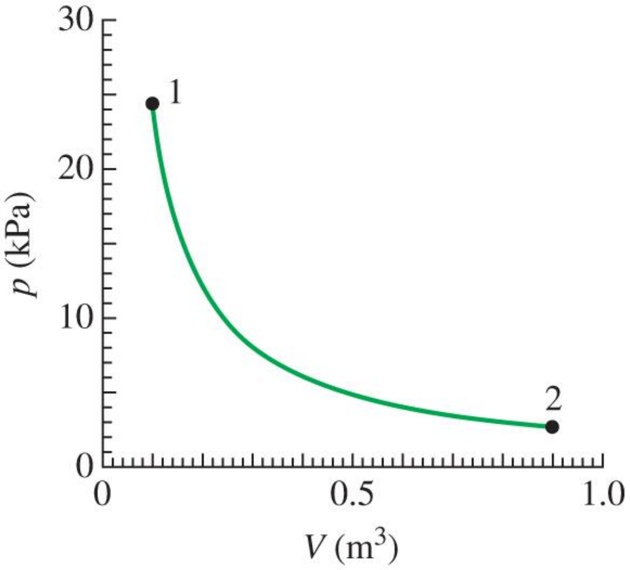
Gas in a Cylinder 2

SOLUTION:

- Point 2 represents the pressure at a volume of 0.900 m^3.
- You can see that the pressure decreases as the volume increases.
- Since the temperature is constant ($T_1 = T_2$) in this situation, the Ideal Gas Law reduces to $p_1V_1 = p_2V_2$, which we recognize as Boyle's Law.
- We can use this to calculate the new pressure:

$$p_2 = \frac{p_1V_1}{V_2} = \frac{(24.9\text{ kPa})(0.100\text{ m}^3)}{0.900\text{ m}^3}$$

$$p_2 = 2.77\text{ kPa}$$



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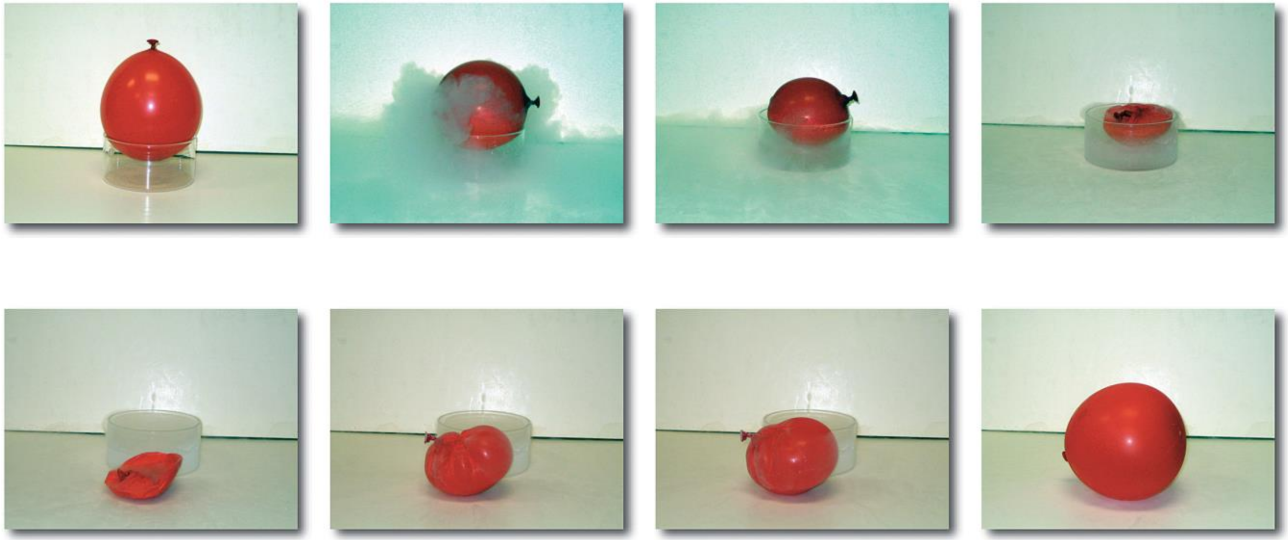
Cooling a Balloon 1

- A balloon is blown up at room temperature and then placed in liquid nitrogen.



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- The balloon is allowed to cool to liquid-nitrogen temperature, and it shrinks dramatically.

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Cooling a Balloon 2

- The cold balloon is then removed from the liquid nitrogen and allowed to warm back to room temperature.
- The balloon returns to its original volume.

PROBLEM:

- By what factor does the volume of the balloon decrease as the temperature of the air inside the balloon goes from room temperature to the temperature of liquid nitrogen?

SOLUTION:

- To a good approximation, the gas inside the balloon is kept at constant pressure ($p_1 = p_2$).
- The Ideal Gas Law becomes $V_1/T_1 = V_2/T_2$, which we recognize as Charles's Law.

Cooling a Balloon 3

- Assume room temperature is 22 °C, or T_1 = 295 K, and the temperature of liquid nitrogen is T_2 = 77.2 K.
- We can calculate the fractional change in volume of the balloon:

$$\frac{V_2}{V_1} = \frac{T_2}{T_1} = \frac{77.2\text{ K}}{295\text{ K}} = 0.262$$

DISCUSSION:

- The balloon in Figure 19.8 shrank more than we calculated.
- A ratio of cold volume to warm volume of 25% implies that the radius of the cold balloon should be 63% of the radius of the room-temperature balloon.
- At the temperature of liquid nitrogen, the water vapor freezes, and the oxygen liquefies, dramatically lowering the pressure inside the balloon beyond the ideal gas behavior.

Heat on the Golf Course 1

- The 2007 PGA Championship was played in August in Oklahoma at the Southern Hills Country Club, at the highest average temperature of any major golf championship in history, reaching approximately 101 °F (38.3 °C = 311.5 K).
- The air density was lower than at cooler temperatures, causing the golf balls to fly farther.
- The players had to correct for this effect, just as they must allow for longer flights when they play at higher elevations.

PROBLEM:

- The Southern Hills Country Club is 213 m (700 ft) above sea level.
- At what elevation would the Old Course at St. Andrews, Scotland, have to be located, if the air temperature was 48 °F (8.9 °C = 282.0 K), for the golf balls to have the same increase in flight length as at Southern Hills?

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Heat on the Golf Course 2

SOLUTION:

- First, we calculate how the temperature influences the air density.
- We can use the relationship between the density and temperature for constant pressure, $\rho_1/\rho_2 = T_2/T_1$.
- Putting in the known values (remember that we need to use kelvins for the air temperature), we obtain:

$$\frac{\rho_1}{\rho_2} = \frac{T_1}{T_2} = \frac{282.0\text{ K}}{311.5\text{ K}} = 0.9053$$

- The air at 101 °F has only 90.53% of the density of air at 48 °F, at the same pressure.

Heat on the Golf Course 3

- Now we must compute the altitude that corresponds to the same density ratio.
- The relation of the density to the altitude is:

$$\rho(h) = \rho_0 e^{-h\rho_0 g/p_0}$$

- The constants in this equation can be written as:

$$\frac{p_0}{\rho_0 g} = \frac{1.01 \cdot 10^5 \text{ Pa}}{(1.229 \text{ kg/m}^3)(9.81 \text{ m/s}^2)} = 8377 \text{ m}$$

- The air density at Southern Hills is:

$$\rho(h_1) = \rho_0 e^{-h_1/(8377)\text{m}}$$

- The air density at Old Course is:

$$\rho(h_2) = \rho_0 e^{-h_2/(8377)\text{m}}$$

Heat on the Golf Course 4

- Taking the ratio of the two air densities gives us:

$$\frac{\rho(h_2)}{\rho(h_1)} = \frac{\rho_0 e^{-h_2/(8377)\mathrm{m}}}{\rho_0 e^{-h_1/(8377)\mathrm{m}}} = e^{-(h_2-h_1)/(8377\ \mathrm{m})}$$

- Setting this ratio equal to the ratio of the densities from the temperature difference gives:

$$e^{-(h_2-h_1)/(8377\ \mathrm{m})} = 0.9053$$

- Taking the natural log of both sides gives:

$$-\big((h_2-h_1)\big)/\big((8377\ \mathrm{m})\big) = \ln(0.9053)$$

- Solving for h_2 gives:

$$h_2 = h_1 - (8377\ \mathrm{m})\ln(0.9053) = 213\ \mathrm{m} - (8377\ \mathrm{m})\ln(0.9053)$$

$$h_2 = 1046\ \mathrm{m}$$

Heat on the Golf Course 5

- Thus, at the temperature of 101 °F, the course at Southern Hills played as long as the Old Course would at an elevation of 1046 m (3432 ft) and a temperature of 48 °F.

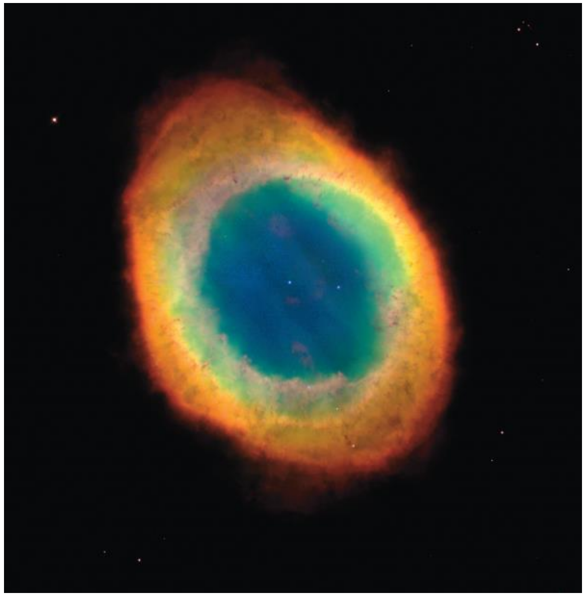
DISCUSSION:

- Our solution neglected the effect of the high humidity at Southern Hills, which reduced the air density by an additional 2% relative to the density of dry air, causing the course to play like one with dry air and a temperature of 48 °F at an altitude over 4000 ft above sea level.
- We will discuss the effect of water vapor in the air when we discuss Dalton’s Law.

Pressure of a Planetary Nebula 1

PROBLEM:

- A planetary nebula is a cloud of mainly hydrogen gas with a density, ρ, of $1.0 \cdot 10^3$ molecules per cubic centimeter (cm^3) and a temperature, T, of $1.0 \cdot 10^4$ K.
- An example of a planetary nebula is the Ring Nebula.
- What is the pressure of the gas in the nebula?



The Hubble Heritage Team (AURA/STScI/NASA)

SOLUTION:

Think

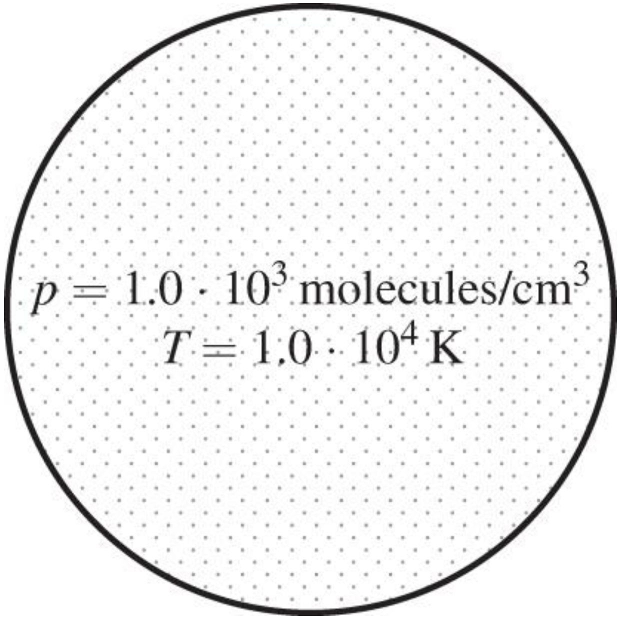
- Because of the very low density of the gas in a planetary nebula, it is a very good approximation to treat that gas as an ideal gas and apply the Ideal Gas Law.

Pressure of a Planetary Nebula 2

- We know the particle density, which is the number of gas molecules per unit volume, so we can replace the number of molecules in the Ideal Gas Law with the density times the volume of the nebula.
- The volume then cancels out, and we can solve for the pressure of the gas.

Sketch

- Here is a sketch of a planetary nebula:



Pressure of a Planetary Nebula 3

Research

- The Ideal Gas Law is:

$$pV = Nk_{\mathrm{B}}T$$

- The number of molecules is:

$$N = \rho V$$

Simplify

- Combining our equations gives us:

$$pV = \rho V k_{\mathrm{B}}T$$

- The pressure in the nebula is:

$$p = \rho k_{\mathrm{B}}T$$

Pressure of a Planetary Nebula 4

Calculate

- Putting in our numerical values gives:

$$p = \rho k_{\mathrm{B}} T$$

$$p = \left(\frac{1.0 \cdot 10^3 \text{ molecules}}{1 \text{ cm}^3}\right)\left(\frac{1 \text{ cm}^3}{10^{-6} \text{ m}^3}\right)(1.38 \cdot 10^{-23} \text{ J/K})(1.0 \cdot 10^4 \text{ K})$$

$$p = 1.381 \cdot 10^{-10} \text{ Pa}$$

Round

- We report our results to two significant figures:

$$p = 1.4 \cdot 10^{-10} \text{ Pa}$$

Double-check

- The units are good.

Pressure of a Planetary Nebula 5

- We need a reference for judging the order of magnitude.
- The pressure of the gas in the nebula must be very low, much lower than the pressure of Earth's atmosphere, because the density of the gas molecules in the nebula is so small.
- In fact, the pressure we calculated is astonishingly low; as a comparison, the pressure of a good vacuum in a lab on Earth is $p_{\text{lab}} = 10^{-7}$ Pa, which is about 1000 times higher than the pressure in the nebula.
- Note that although a gas generally expands to fill its container, in this case there is no container.
- The gas in a planetary nebula is held together by the gravitational interactions among its molecules.

Work Done by an Ideal Gas at Constant Temperature 1

- Suppose we have an ideal gas at a constant temperature in a closed container whose volume can be changed, such as a cylinder with a piston.
- This setup allows us to perform an isothermal process.
- For an isothermal process, the Ideal Gas Law says that the pressure is equal to a constant times the inverse of the volume: $p = nRT/V$.
- If the volume of the container is changed from an initial volume, V_i, to a final volume, V_f, the work done by the gas is given by:

$$W = \int_{V_\mathrm{i}}^{V_\mathrm{f}} p dV$$

Work Done by an Ideal Gas at Constant Temperature 2

- Substituting the expression for the pressure into this integral gives:

$$W = \int_{V_\mathrm{i}}^{V_\mathrm{f}} p\,dV = (nRT)\int_{V_\mathrm{i}}^{V_\mathrm{f}} \frac{dV}{V} = nRT\left[\ln V\right]_{V_\mathrm{i}}^{V_\mathrm{f}}$$

$$W = nRT \ln\left(\frac{V_\mathrm{f}}{V_\mathrm{i}}\right)$$

- We see that the work done by the gas if positive if $V_\mathrm{f} > V_\mathrm{i}$ and is negative if $V_\mathrm{f} < V_\mathrm{i}$.
- If the volume is held constant rather than the temperature, the gas can do no work: $W = 0$. If the pressure is held constant, the work done by the gas is:

$$W = \int_{V_\mathrm{i}}^{V_\mathrm{f}} p\,dV = p\int_{V_\mathrm{i}}^{V_\mathrm{f}} dV = p(V_\mathrm{f} - V_\mathrm{i}) = p\Delta V$$

Concept Check 1

- Consider a box filled with an ideal gas. The box undergoes a sudden free expansion from V_1 to V_2.
- Which of the following correctly describes this process?

A. Work done by the gas during the expansion is equal to $nRT \ln(V_2/V_1)$.

B. Heat is added to the box.

C. Final temperature equals initial temperature times (V_2/V_1).

D. The internal energy of the gas remains constant.

Solution Concept Check 1

- Consider a box filled with an ideal gas. The box undergoes a sudden free expansion from V_1 to V_2.
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B. Heat is added to the box.

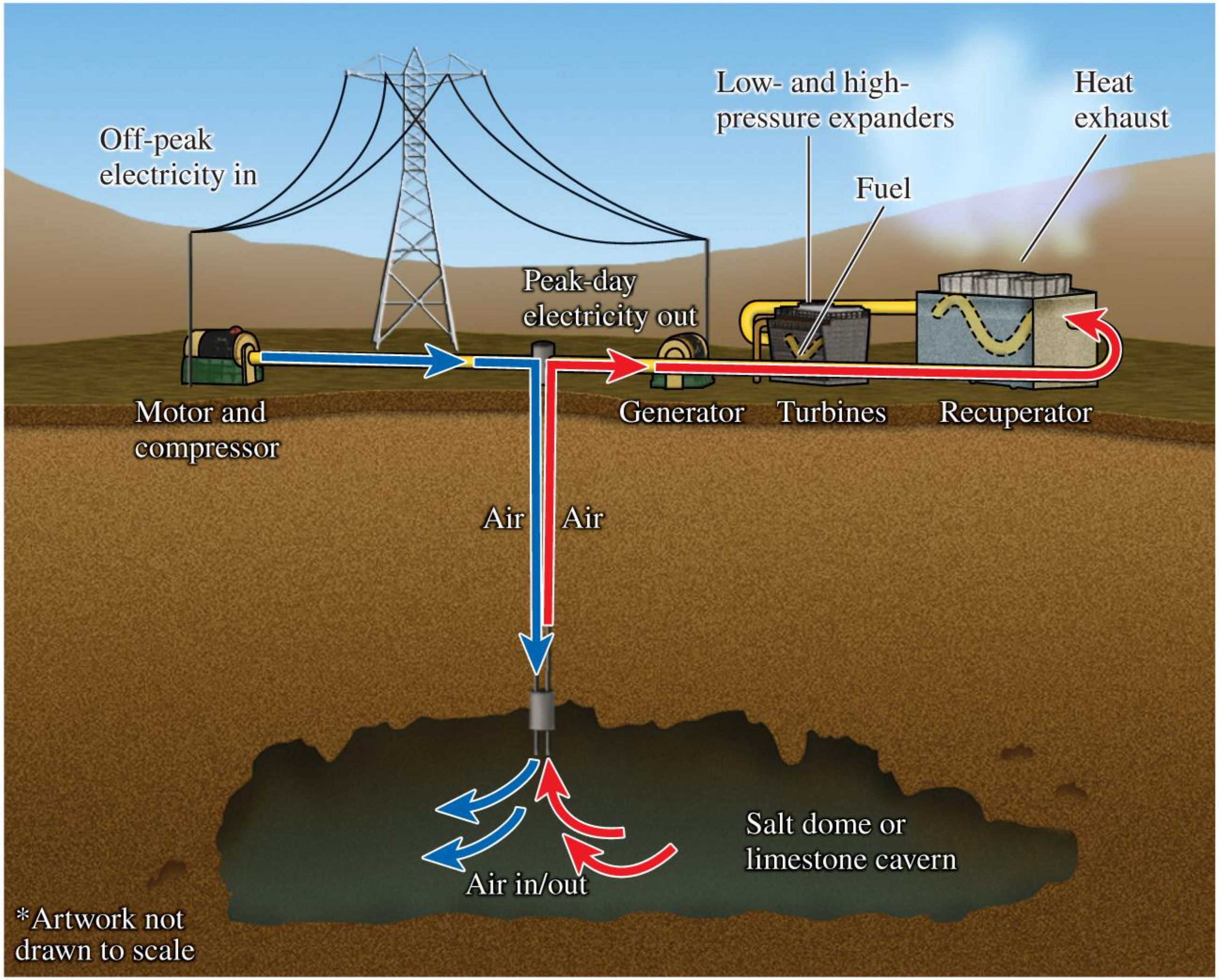
C. Final temperature equals initial temperature times (V_2/V_1).

D. The internal energy of the gas remains constant.

Compressed Air Energy Storage 1

- Compressed air can be used to store energy temporarily, which is necessary in situations where power production is intermittent; for example, with wind farms and solar power plants.
- The use of large-scale storage facilities can smooth the time profile of the produced power.
- Energy storage and retrieval by these facilities are not as efficient as they are with pump storage facilities that use water, but in geographical locations with very little altitude variation, they may be the only way to accomplish energy storage.
- The first compressed air storage facility was built in 1978 in Huntorf, Germany, and a 110-MW facility, built in 1991 in McIntosh, Alabama, was the first in the United States.

Compressed Air Energy Storage 2



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Home Energy Storage 1

- Homes located in areas with ample sunshine can harvest energy with solar panels.
- But in order to avoid buying electricity from the grid (or if a home is located off the grid, for example, in a rural area in a developing country), a homeowner needs some way to store the energy gathered by the solar cells for use during the times when the Sun isn't shining.

PROBLEM:

- Suppose a home's energy storage device is a 10.0-L tank and its solar panels deliver enough electricity to compress ambient air very slowly from atmospheric pressure to 23.1 Mpa.
- What is the total energy stored in the air in the tank?

Home Energy Storage 2

SOLUTION:

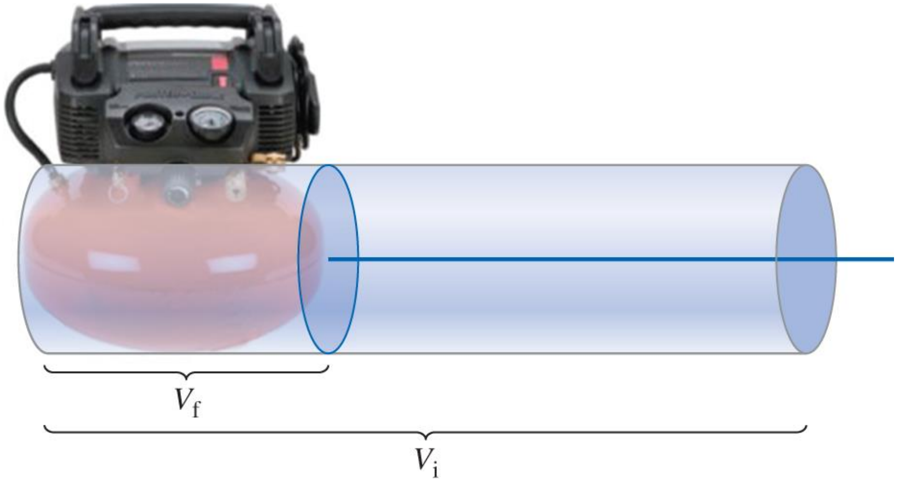
Think

- At first, it might seem that no energy can be stored by increasing the pressure of a gas inside a tank of fixed volume, because a constant volume implies that no work can be done.
- However, it is the volume of the gas that matters, not the volume of the container in the final state.
- If the air is compressed very slowly, then the assumption that it stays at constant temperature is fulfilled.
- Thus, we can use the concept of work done on an ideal gas at constant temperature, that is, work done by isothermal compression.

Home Energy Storage 3

Sketch

- The pump used in the air compressor acts like a piston that changes the volume of the gas from its initial value to its final value.



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- The final value is the volume of the tank, and the initial value is the volume that the same amount of air would occupy under normal atmospheric pressure.

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Home Energy Storage 4

Research

- Since the process of isothermal compression of a gas applies here, $W = nRT \ln(V_f/V_i)$.
- We are given the final volume of the air (10.0 L) but not the initial volume and both the final pressure (23.1 MPa) and the initial pressure (atmospheric pressure = 101 kPa).
- According to Boyle's Law (the Ideal Gas Law for constant temperature), the initial and final pressures and volumes are related by $p_i V_i = p_f V_f$.

Simplify

- Solving Boyle's Law for the ratio of the volumes yields:

$$\frac{V_f}{V_i} = \frac{p_i}{p_f}$$

Home Energy Storage 5

- Putting this result into our expression for the work gives:

$$W = nRT \ln\left(\frac{p_\mathrm{i}}{p_\mathrm{f}}\right)$$

- Using the Ideal Gas Law $pV = nRT$ we get:

$$W = p_\mathrm{f}V_\mathrm{f} \ln\left(\frac{p_\mathrm{i}}{p_\mathrm{f}}\right)$$

Calculate

- Putting in our numerical values gives us:

$$W = (23.1 \cdot 10^6\ \mathrm{Pa})(10.0 \cdot 10^{-3}\ \mathrm{m}^3) \ln\left(\frac{101 \cdot 10^3\ \mathrm{Pa}}{23.1 \cdot 10^6\ \mathrm{Pa}}\right) = -1.2549 \cdot 10^6\ \mathrm{J}$$

Round

- We round our result to three significant figures:

$$W = -1.25 \cdot 10^6\ \mathrm{J} \quad \Rightarrow \quad E = +1.25 \cdot 10^6\ \mathrm{J}\ \text{stored in gas}$$

Home Energy Storage 6

Double-check

- Does the amount of stored energy we have calculated make sense?
- Since 1 kWh is 3.6 MJ, our result is approximately equal to 13 kWh.
- This would be enough to power a couple of 40-W light bulbs for about 5 h, assuming that we could convert all the stored energy into electricity.
- It seems plausible that a couple of light bulbs could be powered for a few hours with this relatively simple and cheap energy storage system.

Dalton's Law 1

- How do ideal gas considerations change, if there is more than one type of gas in each volume, as in the Earth's atmosphere?
- Dalton's Law states that the pressure of a gas composed of a homogeneous mixture of different gases is equal to the sum of the partial pressures of the component gases.
- Partial pressure is defined as the pressure each gas would exert if the other gases were not present.
- Dalton's Law means that each gas is unaffected by the presence of other gases, if there is no interaction between the gas molecules.
- The law is named for John Dalton, a British chemist, who published it in 1801.

Dalton's Law 2

- Dalton's Law gives the total pressure, p_{total}, exerted by a mixture of *m* gases, each with partial pressure p_{i}:

$$p_{\text{total}} = p_1 + p_2 + p_3 + \ \ldots + p_m = \sum_{i=1}^{m} p_i$$

- The total number of moles of gas, n_{total}, contained in a mixture of *m* gases is equal to the sum of the numbers of moles of each gas, n_i:

$$n_{\text{total}} = n_1 + n_2 + n_3 + \ \ldots + n_m = \sum_{i=1}^{m} n_i$$

- The mole fraction, r_i, for each gas is the number of moles of that gas divided by the total number of moles of gas:

$$r_i = \frac{n_i}{n_{\text{total}}}$$

Dalton’s Law 3

- The sum of the mole fractions is equal to 1:

$$\sum_{i=1}^{m} r_i = 1$$

- If the number of moles of gas increases, with the temperature and volume constant, the pressure must go up.
- We can then express each partial pressure as:

$$p_i = r_i p_{\text{total}}$$

- This means that the partial pressures in a mixture of gases are simply proportional to the mole fractions of the gases present in the mixture.

Earth's Atmosphere 1

- The atmosphere of the Earth has a mass of $5.2 \cdot 10^{18}$ kg.
- It is a mixture of several gases.

Table 19.1 Major Gases Making Up the Earth's Atmosphere

Gas	Percentage by Volume	Chemical Symbol	Molecular Mass
Nitrogen	78.08	N_2	28.0
Oxygen	20.95	O_2	32.0
Argon	0.93	Ar	39.9
Carbon dioxide	0.039	CO_2	44.0
Neon	0.0018	Ne	20.2
Helium	0.0005	He	4.00
Methane	0.0002	CH_4	16.0
Krypton	0.0001	Kr	83.8

- The table lists only the components of dry air.
- In addition, air also contains water vapor.

Earth’s Atmosphere 2

- Water vapor makes up approximately 0.25% of the entire atmosphere.
- This sounds like a small number but equals approximately 10^{16} kg of water, which is about four times the volume of water in all the Great Lakes!
- Near the Earth’s surface, the water content of air ranges from less than 1% to over 3%, depending mainly on the air temperature and the availability of liquid water in the vicinity.
- Water vapor in the air decreases the average density of the atmosphere, because the molecular mass of water is 18, which is smaller than the molecular or atomic mass of almost all the other atmospheric gases.

Concept Check 2

- What is the mass of 22.4 L of dry air at standard temperature and pressure?

A. 14.20 g

B. 28.00 g

C. 28.95 g

D. 32.22 g

E. 60.00 g

Solution Concept Check 2

- What is the mass of 22.4 L of dry air at standard temperature and pressure?

A. 14.20 g

B. 28.00 g

C. 28.95 g

D. 32.22 g

E. 60.00 g

78.08% N_2

20.95% O_2

0.93% Ar

…

$$0.78(28\text{ g}) + 0.21(32\text{ g}) + 0.0093(40\text{ g}) = 29.93\text{ g}$$

Concept Check 3

- What is the oxygen pressure in the Earth’s atmosphere at sea level?

A. 0

B. 0.21 atm

C. 1 atm

D. 4.8 atm

E. 20.9 atm

Solution Concept Check 3

- What is the oxygen pressure in the Earth’s atmosphere at sea level?

A. 0

[✓ B. 0.21 atm]

C. 1 atm

D. 4.8 atm

E. 20.9 atm

$$20.95\%\ \mathrm{O_2}$$

$$0.21(1\ \text{atm}) = 0.21\ \text{atm}$$

Density of Air at STP 1

PROBLEM:

- What is the density of air at standard temperature and pressure (STP)?

SOLUTION:

Think

- We know that a mole of any gas at STP occupies a volume of 22.4 L.
- We know the relative fractions of the gases that comprise the atmosphere.
- We can combine Dalton’s Law, Avogadro’s Law, and the fractions of gases in air to obtain the mass of air contained in 22.4 L.
- The density is the mass divided by the volume.

Density of Air at STP 2

Sketch

- Not necessary.

Research

- We consider only the four gases that constitute a significant fraction of the atmosphere: N_2, O_2, Ar, and CO_2.
- We know that 1 mole of any gas has a mass M (in grams) in a volume of 22.4 L at STP.
- We know that the mass of each gas in 22.4 L will be the fraction by volume times the molecular mass, so we have:

$$m_{\text{air}} = r_{\text{N}_2} M_{\text{N}_2} + r_{\text{O}_2} M_{\text{O}_2} + r_{\text{Ar}} M_{\text{Ar}} + r_{\text{CO}_2} M_{\text{CO}_2}$$

$$\rho_{\text{air}} = \frac{m_{\text{air}}}{V_{\text{air}}} = \frac{m_{\text{air}}}{22.4 \text{ L}}$$

Density of Air at STP 3

Simplify

- The density of air is:

$$\rho_{\text{air}} = \frac{r_{\text{N}_2} M_{\text{N}_2} + r_{\text{O}_2} M_{\text{O}_2} + r_{\text{Ar}} M_{\text{Ar}} + r_{\text{CO}_2} M_{\text{CO}_2}}{22.4\ \text{L}}$$

Calculate

- Carrying out the numerical calculations gives us:

$$\rho_{\text{air}} = \frac{0.7808(28\ \text{g}) + 0.2095(32\ \text{g}) + 0.0093(40\ \text{g}) + 0.00039(44\ \text{g})}{22.4 \cdot 10^{-3}\ \text{m}^3}$$

$$\rho_{\text{air}} = 1.29266\ \text{kg/m}^3$$

Round

- We report our results to three significant figures:

$$\rho_{\text{air}} = 1.29\ \text{kg/m}^3$$

Density of Air at STP 4

Double-check

- We can double-check our result by calculating the density of nitrogen gas alone at STP, since air is 78.08% nitrogen.
- The density of nitrogen at STP is:

$$\rho_{\mathrm{N_2}} = \frac{28.0\ \mathrm{g}}{22.4\ \mathrm{L}} = \frac{28.0 \cdot 10^{-3}\ \mathrm{kg}}{22.4 \cdot 10^{-3}\ \mathrm{m}^3} = 1.25\ \mathrm{kg/m}^2$$

- This result is close to and slightly lower than our result for the density of air; so, our result is reasonable.

Equipartition Theorem 1

- We have been discussing the macroscopic properties of gases, including volume, temperature, and pressure.
- To explain these properties in terms of the constituents of a gas, its molecules (or atoms), requires making several assumptions about the behavior of these molecules in a container.
- These assumptions, along with the results derived from them, are known as the **kinetic theory of an ideal gas**.
- Suppose we have a gas in a container of volume $V,$ and the gas fills this container evenly.
- We make several assumptions.

Equipartition Theorem 2

- The number of molecules, *N*, is large, but the molecules themselves are small, so the average distance between molecules is large compared to their size.
- All molecules are identical, and each has mass *m*.
- The molecules are in constant random motion on straight-line trajectories.
- They do not interact with one another and can be considered point particles.
- The molecules have elastic collisions with the walls of the container.
- The volume, *V*, of the container is large compared to the size of the molecules.
- The container walls are rigid and stationary.

Equipartition Theorem 3

- Kinetic theory explains how the microscopic properties of the gas molecules give rise to the macroscopic observables of pressure, volume, and temperature as related by the Ideal Gas Law.
- For now, we are mainly interested in what the average kinetic energy of the gas molecules is and how it relates to the temperature of the gas.
- This connection is called the **equipartition theorem**.
- First, we obtain the average kinetic energy of the ideal gas by averaging the kinetic energies of the individual gas molecules:

$$K_{\text{ave}} = \frac{1}{N}\sum_{i=1}^{N} K_i = \frac{1}{N}\sum_{i=1}^{N}\frac{1}{2}m{v_i}^2 = \frac{1}{2}m\left(\frac{1}{N}\sum_{i=1}^{N}{v_i}^2\right) = \frac{1}{2}m{v_{\text{rms}}}^2$$

Equipartition Theorem 4

- The **root-mean-square speed** of the gas molecules, v_{rms}, is defined as:

$$v_{\mathrm{rms}} = \sqrt{\frac{1}{N}\sum_{i=1}^{N} {v_i}^2}$$

- The root-mean-square speed is *not the same* as the average speed of the gas molecules.
- It is a suitable average because it immediately relates to the average kinetic energy.
- The temperature of an ideal gas is proportional to the average kinetic energy, with a proportionality constant 3/2 times the Boltzmann constant (Derivation 19.2) :

$$K_{\mathrm{ave}} = \frac{3}{2}k_{\mathrm{B}}T$$

Equipartition Theorem 5

- This is the *equipartition theorem*, which states that gas molecules in thermal equilibrium have the same average kinetic energy, equal to ½ $k_B T$, associated with each of their three independent degrees of freedom.
- Thus, when we measure the temperature of a gas, we are determining the average kinetic energy of the molecules of the gas.
- This relationship is one of the key insights of kinetic theory.
- We can relate the root-mean-square speed of the gas molecules to the temperature of the gas (Derivation 19.2):

$$v_{\mathrm{rms}} = \sqrt{\frac{3k_{\mathrm{B}}T}{m}}$$

Average Kinetic Energy of Air Molecules

- Suppose a roomful of air is at a temperature of 22.0 °C.

PROBLEM:

- What is the average kinetic energy of the molecules (and atoms) in the air?

SOLUTION:

- The average kinetic energy of the air molecules is given by:

$$K_{\text{ave}} = \frac{3}{2} k_{\text{B}} T = \frac{3}{2} (1.381 \cdot 10^{-23} \text{ J/K})(273.15 \text{ K} + 22.0 \text{ K}) = 6.11 \cdot 10^{-21} \text{ J}$$

- Often, the average kinetic energy of air molecules is given in electron-volts (eV) rather than joules:

$$K_{\text{ave}} = (6.11 \cdot 10^{-21} \text{ J}) \frac{1 \text{ eV}}{1.602 \cdot 10^{-19} \text{ J}} = 0.0382 \text{ eV} \approx \frac{1}{25} \text{ eV}$$

Concept Check 4

- The average kinetic energy of molecules of an ideal gas doubles if the ______ doubles.

A. temperature

B. pressure

C. mass of the gas molecules

D. volume of the container

E. none of the above

Solution Concept Check 4

- The average kinetic energy of molecules of an ideal gas doubles if the ______ doubles.

A. temperature

B. pressure

C. mass of the gas molecules

D. volume of the container

E. none of the above

$$K_{\mathrm{ave}} = \frac{3}{2} k_{\mathrm{B}} T$$

Specific Heat of an Ideal Gas 1

- Gases consist of atoms or molecules, and the internal energy of gases can be expressed in terms of their atomic and molecular properties.
- These relationships lead to the molar specific heats of ideal gases.
- Let’s begin with **monatomic gases**, which are gases in which atoms are not bound to other atoms.
- Monatomic gases include helium, neon, argon, krypton, and xenon (the noble gases).
- We assume that all the internal energy of a monatomic gas is in the form of translational kinetic energy.
- The average translational kinetic energy depends only on the temperature.

Specific Heat of an Ideal Gas 2

- The internal energy of a monatomic gas is the number of atoms, N, times the average translational kinetic energy of one atom in the gas:

$$E_{\text{int}} = NK_{\text{ave}} = N\left(\frac{3}{2}k_{\text{B}}T\right)$$

- The number of atoms of the gas is the number of moles, n, times Avogadro's number, N_{A}:

$$N = nN_{\text{A}}$$

- Since $N_{\text{A}}k_{\text{B}} = R$, we can express the internal energy as:

$$E_{\text{int}} = \frac{3}{2}nRT$$

Specific Heat at Constant Volume 1

- Suppose an ideal monatomic gas at temperature T is held at constant volume.
- If heat, Q, is added to the gas, it has been shown empirically that the temperature of the gas changes according to:

$$Q = nC_V \Delta T$$

- Here C_V is the molar specific heat at constant volume.
- The volume of the gas is constant, so it can do no work.
- We can use the First Law of Thermodynamics to write:

$$\Delta E_{\text{int}} = Q - W = nC_V \Delta T \text{ (at constant volume)}$$

- The internal energy of a monatomic gas depends only on its temperature, so the change in internal energy is:

$$\Delta E_{\text{int}} = \frac{3}{2} nR\Delta T$$

Specific Heat at Constant Volume 2

- Combining this result with $Q = nC_V \Delta T$ gives:

$$nC_V \Delta T = \frac{3}{2} nR\Delta T \quad \Rightarrow \quad C_V = \frac{3}{2}R = 12.5 \text{ J/(mol K)}$$

- This value for the molar specific heat of an ideal monatomic gas agrees well with measured values for monatomic gases. at standard temperature and pressure.

Table 19.2 Some Typical Molar Specific Heats Obtained for Different Types of Gases

Gas	C_V **[J/(mol K)]**	C_p **[J/(mol K)]**	$\gamma = C_p/C_V$
Helium (He)	12.5	20.8	1.66
Neon (Ne)	12.5	20.8	1.66
Argon (Ar)	12.5	20.8	1.66
Krypton (Kr)	12.5	20.8	1.66
Hydrogen (H_2)	20.4	28.8	1.41
Nireogen (N_2)	20.7	29.1	1.41
Oxygen (O_2)	21.0	29.4	1.41
Carbon Dioxide (CO_2)	28.2	36.6	1.29
Methane (CH_4)	27.5	35.9	1.30

Specific Heat at Constant Volume 3

- We can now write:

  $E_{\text{int}} = nC_V T$

- This equation applies to all gases if the appropriate molar specific heat is used.
- According to this equation, the change in internal energy of an ideal gas depends only on n, C_V, and ΔT.
- The change in internal energy does not depend on any corresponding pressure or volume change.
- Now let's see what happens if we hold the pressure constant rather than the volume.

Specific Heat at Constant Pressure 1

- Consider the situation in which the temperature of an ideal gas is increased while the pressure of the gas is held constant.
- The added heat, Q, has been shown empirically to be related to the change in temperature as follows:

  $$Q = nC_p\Delta T$$

- Here C_p is the molar specific heat at constant pressure.
- The molar specific heat at constant pressure is greater than the molar specific heat at constant volume because energy must be supplied to do work as well as to increase the temperature.
- To relate the molar specific heat at constant volume to the molar specific heat at constant pressure, we start with the First Law of Thermodynamics:

  $$\Delta E_{\text{int}} = Q - W$$

Specific Heat at Constant Pressure 2

- We just showed that $\Delta E_{\text{int}} = nC_V\Delta T$.
- This includes constant pressure.
- We can rewrite the First Law of Thermodynamics as:

$$E_{\text{int}} = Q - W$$

$$\left.\begin{aligned}\Delta E_{\text{int}} &= nC_V\Delta T\\ Q &= nC_p\Delta T\\ W &= p\Delta V\end{aligned}\right\} nC_V\Delta T = nC_p\Delta T - p\Delta V$$

- If the pressure is held constant, we can use the Ideal Gas Law to write:

$$p\Delta V = nR\Delta T$$

- We can now write:

$$nC_V\Delta T = nC_p\Delta T - nR\Delta T \quad \Rightarrow \quad C_p = C_V + R$$

Degrees of Freedom 1

- The relationship $C_V = (3/2)R$ holds for monatomic gases but not for diatomic and polyatomic gases.
- This failure can be explained in terms of the possible degrees of freedom of motion for various types of molecules.
- In general, a degree of freedom is a direction in which something can move.
- For a point particle in three-dimensional space, there are three orthogonal directions, which are independent of each other.
- For a collection of N point particles, there are $3N$ degrees of freedom for translational motion in three-dimensional space.

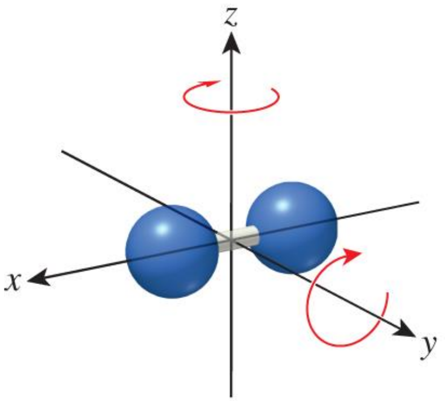
Degrees of Freedom 2

- If the point particles are arranged in a solid object, they cannot move independently of each other, and the number of degrees of freedom is reduced to the translational degrees of freedom of the center of mass of the object (three), plus independent rotations of the object around the center of mass.
- In general, there are three possible independent rotations, giving a total of six degrees of freedom, three translational and three rotational.
- Let’s consider three different kinds of gases.

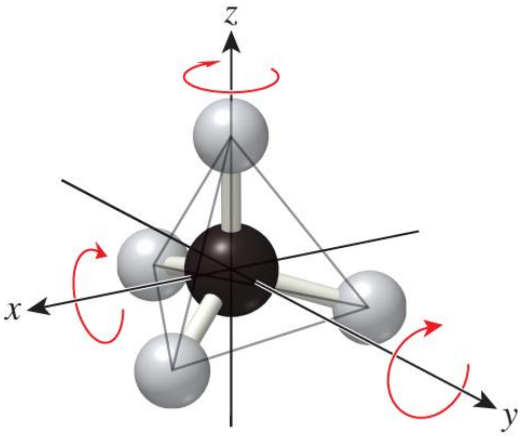
Degrees of Freedom 3

- The first is a monatomic gas, helium (He).
- The second is a diatomic gas, represented by nitrogen (N_2).
- The third is a polyatomic molecule, for example, methane (CH_4).
- The molecule of the polyatomic gas can rotate around all three coordinate axes and thus has three rotational degrees of freedom.
- The diatomic molecule is shown aligned with the *x*-axis, and rotation about this axis will not yield a different configuration.
- Therefore, this molecule has only two rotational degrees of freedom.

He



N_2



CH_4

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Degrees of Freedom 4

- The various ways in which the internal energy of an ideal gas can be allocated are specified by the principle of **equipartition of energy**, which states that gas molecules in thermal equilibrium have the same average energy associated with each independent degree of freedom of their motion.
- The average energy per degree of freedom is given by ½ $k_B T$ for each gas molecule.
- The equipartition theorem for gas molecules' average kinetic energy associated with temperature, $K_{\text{ave}} = (3/2)\,k_B T$, is consistent with the equipartition of the molecules' translational kinetic energy among three directions (or three degrees of freedom), x, y, and z.

Degrees of Freedom 5

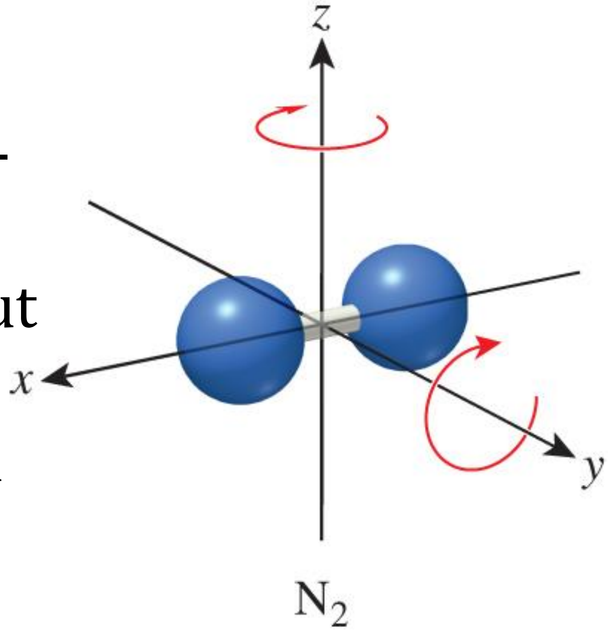
- The molar specific heat at constant volume from kinetic theory for monatomic gases assuming three degrees of freedom for translational motion is consistent with reality.
- The observed molar specific heats at constant volume are higher for diatomic and polyatomic gases.

Table 19.2 Some Typical Molar Specific Heats Obtained for Different Types of Gases

Gas	C_V (J/(mol K))	C_p (J/(mol K))	$\gamma = C_p/C_V$
Helium (He)	12.5	20.8	1.66
Neon (Ne)	12.5	20.8	1.66
Argon (Ar)	12.5	20.8	1.66
Krypton (Kr)	12.5	20.8	1.66
Hydrogen (H_2)	20.4	28.8	1.41
Nitrogen (N_2)	20.7	29.1	1.41
Oxygen (O_2)	21.0	29.4	1.41
Carbon dioxide (CO_2)	28.2	36.6	1.29
Methane (CH_4)	27.5	35.9	1.30

Specific Heat at Constant Volume for a Diatomic Gas 1

- The nitrogen molecule is lined up along the *x*-axis in the drawing.
- If we look along the *x*-axis at the molecule, we see a point and thus are not able to discern any rotation around the *x*-axis.
- However, if we look along the *y*-axis or the *z*-axis, we can see that the nitrogen molecule can have appreciable rotational motion about either of those axes.
- Therefore, there are two degrees of freedom for rotational kinetic energy of the nitrogen molecule and all diatomic molecules.
- Therefore, the average kinetic energy per diatomic molecule is $(3+2)\left(\frac{1}{2}k_{\mathrm{B}}T\right)=\frac{5}{2}k_{\mathrm{B}}T$.



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Specific Heat at Constant Volume for a Diatomic Gas 2

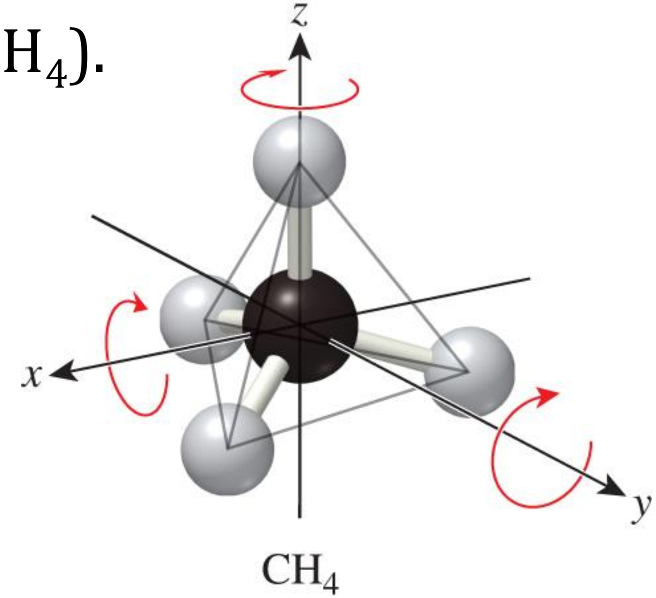
- This implies that calculation of the molar specific heat at constant volume for a diatomic gas should be like that for a monatomic gas, but with two additional degrees of freedom for the average energy.
- The specific heat at constant volume for a diatomic gas is:

$$C_V = \frac{3+2}{2}R = \frac{5}{2}R = \frac{5}{2}\big(8.31\ \mathrm{J/(mol\ K)}\big) = 20.8\ \mathrm{J/(mol\ K)}$$

Table 19.2 Some Typical Molar Specific Heats Obtained for Different Types of Gases

Gas	C_V (**J/(mol K)**)	C_p (**J/(mol K)**)	$\gamma = C_p/C_V$
Helium (He)	12.5	20.8	1.66
Neon (Ne)	12.5	20.8	1.66
Argon (Ar)	12.5	20.8	1.66
Krypton (Kr)	12.5	20.8	1.66
Hydrogen (H_2)	20.4	28.8	1.41
Nitrogen (N_2)	20.7	29.1	1.41
Oxygen (O_2)	21.0	29.4	1.41
Carbon dioxide (CO_2)	28.2	36.6	1.29
Methane (CH_4)	27.5	35.9	1.30

Specific Heat at Constant Volume for a Polyatomic Gas 1



- Consider the polyatomic gas, methane (CH_4).
- The methane molecule is composed of four hydrogen atoms arranged in a tetrahedron, bonded to a carbon atom at the center.
- Looking along any of the three axes, we can discern rotation of this molecule.
- This molecule and all polyatomic molecules have three degrees of freedom related to rotational kinetic energy.
- Thus, calculation of the molar specific heat at constant volume for a polyatomic gas should be like that for a monatomic gas, but with three additional degrees of freedom for the average energy.

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Specific Heat at Constant Volume for a Polyatomic Gas 2

- The specific heat at constant volume for a diatomic gas is:

$$C_V = \frac{3+3}{2}R = \frac{6}{2}R = 3\big(8.31\ \mathrm{J/(mol\ K)}\big) = 24.9\ \mathrm{J/(mol\ K)}$$

- Comparing this value to the actual measured molar specific heat at constant volume for the polyatomic gases methane and CO_2, we see that the value predicted by kinetic theory is close to, but somewhat lower than, the measured value.

Table 19.2 Some Typical Molar Specific Heats Obtained for Different Types of Gases

Gas	C_V **(J/(mol K))**	C_p **(J/(mol K))**	$\gamma = C_p/C_V$
Helium (He)	12.5	20.8	1.66
Neon (Ne)	12.5	20.8	1.66
Argon (Ar)	12.5	20.8	1.66
Krypton (Kr)	12.5	20.8	1.66
Hydrogen (H_2)	20.4	28.8	1.41
Nitrogen (N_2)	20.7	29.1	1.41
Oxygen (O_2)	21.0	29.4	1.41
Carbon dioxide (CO_2)	28.2	36.6	1.29
Methane (CH_4)	27.5	35.9	1.30

Specific Heat at Constant Volume for a Polyatomic Gas 3

- What accounts for the differences between predicted and actual values of the molar specific heats for diatomic and polyatomic molecules is the fact that these molecules can have internal degrees of freedom, in addition to translational and rotational degrees of freedom.
- The atoms of these molecules can oscillate with respect to one another. For example, imagine that the two oxygen atoms and one carbon atom of a carbon dioxide molecule are connected by springs.
- The three atoms could oscillate back and forth with respect to each other, which corresponds to extra degrees of freedom.
- The molar specific heat at constant volume is thus larger than the 24.9 J/(mol K) predicted for a polyatomic gas.

Ratio of Specific Heats

- Finally, it is convenient to take the ratio of the specific heat at constant pressure to that at constant volume:

$$\gamma \equiv \frac{C_p}{C_V}$$

- Inserting the predicted values for the specific heats of ideal gases with different degrees of freedom gives:

$$\gamma = \frac{C_p}{C_V} = \left(\left(\frac{5}{2}R\right)\right)\Big/\left(\left(\frac{3}{2}R\right)\right) = \frac{5}{3} = 1.67 \text{ for monatomic gases}$$

$$\gamma = \frac{C_p}{C_V} = \left(\left(\frac{7}{2}R\right)\right)\Big/\left(\left(\frac{5}{2}R\right)\right) = \frac{7}{5} = 1.40 \text{ for diatomic gases}$$

$$\gamma = \frac{C_p}{C_V} = \left(\left(\frac{8}{2}R\right)\right)\Big/\left(\left(\frac{6}{2}R\right)\right) = \frac{4}{3} = 1.33 \text{ for polyatomic gases}$$

Examples: He $\gamma = 1.66$; N_2 $\gamma = 1.41$; CH_2 $\gamma = 1.30$

Concept Check 5

- The ratio of specific heat at constant pressure to specific heat at constant volume, C_p/C_V, for an ideal gas

A. is always equal to 1.

B. is always smaller than 1.

C. is always larger than 1.

D. can be smaller or larger than 1, depending on the degrees of freedom of the gas molecules.

Solution Concept Check 5

- The ratio of specific heat at constant pressure to specific heat at constant volume, C_p/C_V, for an ideal gas

A. is always equal to 1.

B. is always smaller than 1.

[✓ C. is always larger than 1.]

D. can be smaller or larger than 1, depending on the degrees of freedom of the gas molecules.

Adiabatic Processes for an Ideal Gas 1

- An adiabatic process is one in which the state of a system changes and no exchange of heat with the surroundings takes place during the change.
- An adiabatic process can occur when the system change occurs quickly.
- $Q = 0$ for an adiabatic process.
- From the First Law of Thermodynamics, we then have $\Delta E_{\text{int}} = -W$.
- Let's explore how the change in volume is related to the change in pressure for an ideal gas undergoing an adiabatic process, that is, a process in the absence of heat transfer.

Adiabatic Processes for an Ideal Gas 2

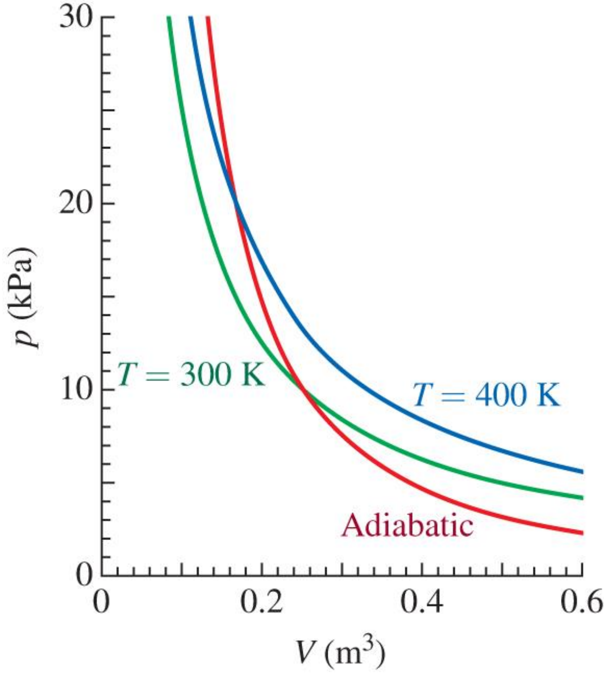
- The relationship is given by:

  $pV^{\gamma} = \text{constant}$

- See Derivation 19.3 in the book.
- Another way of stating the relationship between pressure and volume for an adiabatic process for an ideal gas is:

  $p_{\mathrm{f}} V_{\mathrm{f}}{}^{\gamma} = p_{\mathrm{i}} V_{\mathrm{i}}{}^{\gamma}$ (for an adiabatic process)

- We can compare an adiabatic process, and two isothermal processes at different temperatures.
- The adiabatic process shows a steeper decreases in pressure as a function of volume.



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Adiabatic Processes for an Ideal Gas 3

- We can combine the the relationship between pressure and volume for an adiabatic process with the Ideal Gas Law:

$$pV^{\gamma} = \left(\frac{nRT}{V}\right)V^{\gamma} = (nR)TV^{\gamma-1}$$

- Assume the gas is in a closed container so *n* is constant.
- We can rewrite this relationship as $TV^{\gamma-1}$ = constant (for an adiabatic process), or:

$$T_{\mathrm{f}}V_{\mathrm{f}}^{\gamma-1} = T_{\mathrm{i}}V_{\mathrm{i}}^{\gamma-1}$$

- An adiabatic expansion like this occurs when you open a container that holds a cold, carbonated beverage.
- The carbon dioxide from the carbonation and the water vapor make up a gas with a pressure above atmospheric pressure.

Adiabatic Processes for an Ideal Gas 4

- When this gas expands and some comes out of the container’s opening, the system must do work.
- Because the process happens very quickly, no heat can be transferred to the gas; thus, the process is adiabatic, and the product of the temperature and the volume raised to the power $\gamma - 1$ remains constant.
- The volume of the gas increases, and the temperature must decrease.
- Thus, condensation occurs around the opening of the container.

Concept Check 6

- A monatomic ideal gas occupies a volume V_i, which is then decreased to $(1/2)V_\mathrm{i}$ via an adiabatic process.
- Which relationship is correct for the pressures of this gas?

A. $p_\mathrm{f} = 2p_\mathrm{i}$
B. $p_\mathrm{f} = (1/2)p_\mathrm{i}$
C. $p_\mathrm{f} = 2^{5/3}p_\mathrm{i}$
D. $p_\mathrm{f} = (1/2)^{5/3}p_\mathrm{i}$

Solution Concept Check 6

- A monatomic ideal gas occupies a volume V_i, which is then decreased to $(1/2)V_i$ via an adiabatic process.
- Which relationship is correct for the pressures of this gas?

A. $p_f = 2p_i$
B. $p_f = (1/2)p_i$
C. $p_f = 2^{5/3}p_i$
D. $p_f = (1/2)^{5/3}p_i$

$$p_f(V_i/2)^{5/3} = p_i V_i^{5/3}$$

$$p_f(1/2)^{5/3} = p_i$$

$$p_f = 2^{5/3}p_i$$

Concept Check 7

- A monatomic ideal gas occupies a volume V_i, which is then decreased to $(1/2)V_i$ via an adiabatic process.
- Which relationship is correct for the temperatures of this gas?

A. $T_f = 2^{2/3}T_i$
B. $T_f = 2^{5/3}T_i$
C. $T_f = (1/2)^{2/3}T_i$
D. $T_f = (1/2)^{5/3}T_i$

Solution Concept Check 7

- A monatomic ideal gas occupies a volume V_i, which is then decreased to $(1/2)V_i$ via an adiabatic process.
- Which relationship is correct for the temperatures of this gas?

$\boxed{\text{A.}\quad T_f = 2^{2/3}T_i}$

B. $T_f = 2^{5/3}T_i$

C. $T_f = (1/2)^{2/3}T_i$

D. $T_f = (1/2)^{5/3}T_i$

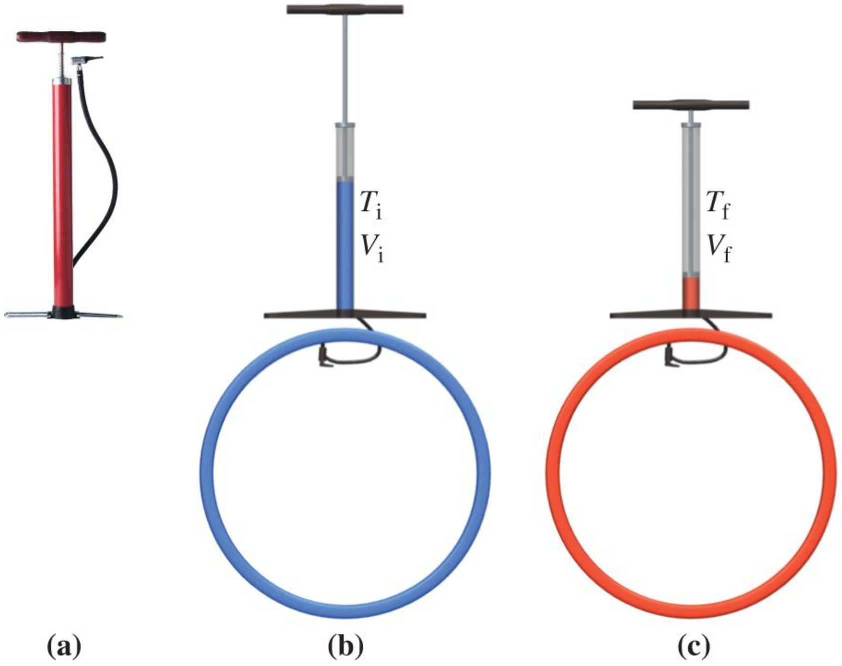
$$T_f\left(\frac{1}{2}V_i\right)^{\frac{5}{3}-1} = T_i V_i^{\frac{5}{3}-1}$$

$$T_f\left(\frac{1}{2}\right)^{\frac{2}{3}} = T_i$$

$$T_f = 2^{2/3}T_i$$

Bicycle Tire Pump 1

- A hand-operated tire pump is used to inflate a bicycle tire.
- The tire pump consists of a cylinder with a piston.
- The tire pump is connected to the tire with a small hose.
- There is a valve between the pump and the tire that allows air to enter the tire, but not to exit.



- In addition, there is a valve that allows air to enter the pump after the compression stroke is complete and the piston is retracted to its original position.

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Bicycle Tire Pump 2

- The inner radius of the cylinder of the pump is $r_p = 1.00$ cm, the height of the active volume before the compression stroke is $h_i = 60.0$ cm, and the height of the active volume after the compression stroke is $h_f = 10.0$ cm.
- The tire is a cylindrical ring with inner radius $r_1 = 66.0$ cm, outer radius $r_2 = 67.5$ cm, and thickness $t = 1.50$ cm.
- The temperature of the air in the pump and tire before the compression stroke is $T_i = 295$ K.

PROBLEM:

- What is the temperature, T_f, of the air after one compression stroke?

Bicycle Tire Pump 3

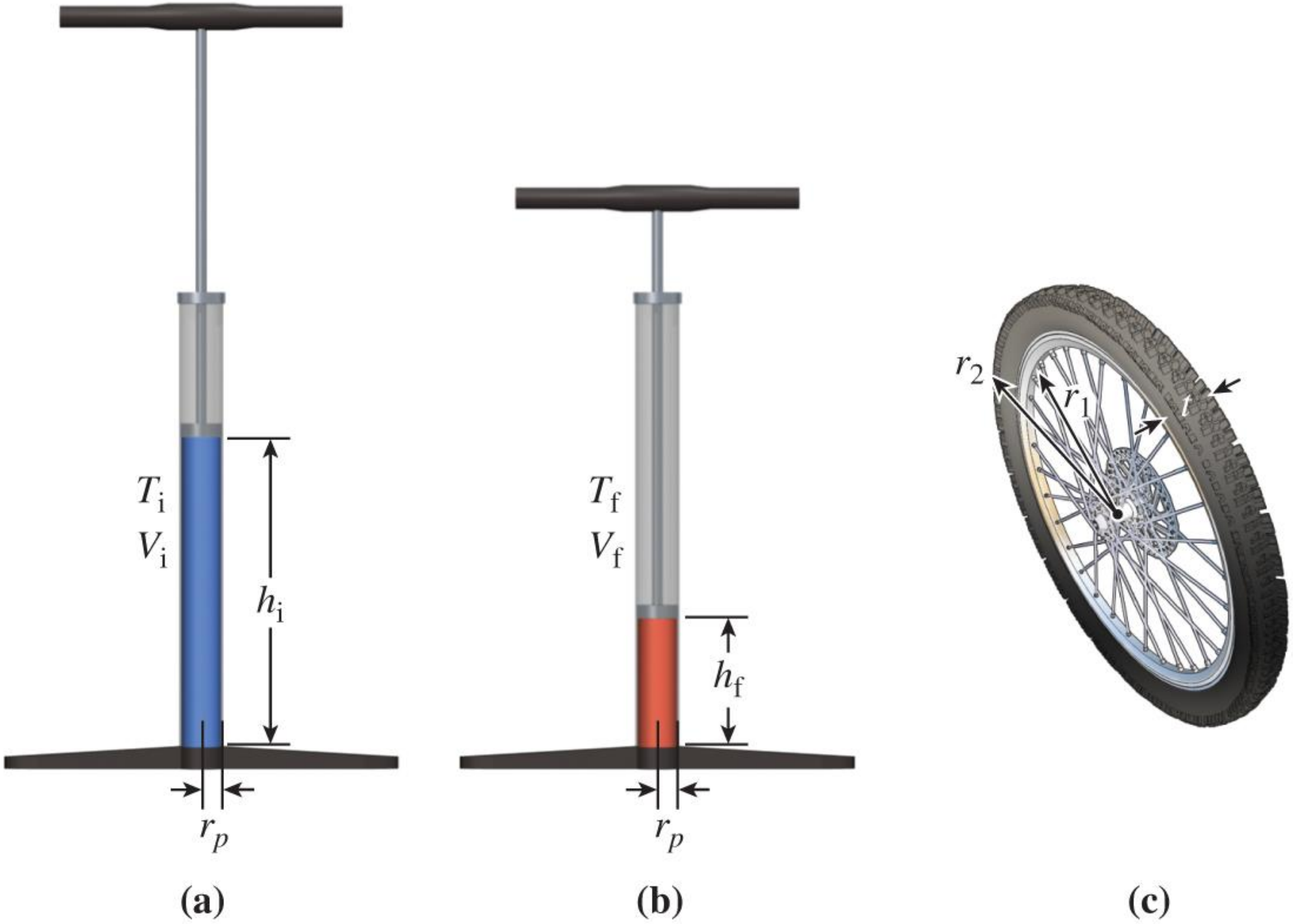
SOLUTION:

Think

- The volume and temperature of the air before the compression stroke are V_i and T_i, respectively, and the volume and temperature of the air after the compression stroke are V_f and T_f, respectively.
- The compression stroke takes place quickly, so no heat can be transferred into or out of the system, and this process can be treated as an adiabatic process.
- The volume of air in the pump decreases when the pump handle is pushed down while the volume of air in the tire remains constant.

Bicycle Tire Pump 4

Sketch



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Bicycle Tire Pump 5

Research

- The volume of air in the tire is:

$$V_{\text{tire}} = t(\pi {r_2}^2 - \pi {r_1}^2)$$

- The volume of air in the pump before the compression stroke is:

$$V_{\text{pump,i}} = \pi {r_\text{p}}^2 h_\text{i}$$

- The volume of air in the pump after the compression stroke is:

$$V_{\text{pump,f}} = \pi {r_\text{p}}^2 h_\text{f}$$

- The initial volume of air in the pump-tire system is $V_\text{i} = V_{\text{pump,i}} + V_{\text{tire}}$, and the final volume of air in the pump-tire system is $V_\text{f} = V_{\text{pump,f}} + V_{\text{tire}}$.

Bicycle Tire Pump 6

- We ignore the volume of air in the hose between the pump and the tire.
- This process is adiabatic, so we can write:

  $$T_\mathrm{f} {V_\mathrm{f}}^{\gamma-1} = T_\mathrm{i} {V_\mathrm{i}}^{\gamma-1}$$

  Simplify
- We can solve this equation for the final temperature:

  $$T_\mathrm{f} = T_\mathrm{i} \frac{{V_\mathrm{i}}^{\gamma-1}}{{V_\mathrm{f}}^{\gamma-1}} = T_\mathrm{i} \left(\frac{V_\mathrm{i}}{V_\mathrm{f}} \right)^{\gamma-1}$$

- We can then insert the expressions for the initial volume and the final volume:

  $$T_\mathrm{f} = T_\mathrm{i} \left(\frac{\pi {r_\mathrm{p}}^2 h_\mathrm{i} + t(\pi {r_2}^2 - \pi {r_1}^2)}{\pi {r_\mathrm{p}}^2 h_\mathrm{f} + t(\pi {r_2}^2 - \pi {r_1}^2)} \right)^{\gamma-1} = T_\mathrm{i} \left(\frac{{r_\mathrm{p}}^2 h_\mathrm{i} + t({r_2}^2 - {r_1}^2)}{{r_\mathrm{p}}^2 h_\mathrm{f} + t({r_2}^2 - {r_1}^2)} \right)^{\gamma-1}$$

Bicycle Tire Pump 7

Calculate

- Air is mostly diatomic gases, so we take $\gamma = 7/5$:

$$T_\text{f} = T_\text{i}\left(\frac{(0.0100\text{ m})^2(0.600\text{ m}) + (0.015\text{ m})\left((0.675\text{ m})^2 - (0.660\text{ m})^2\right)}{(0.0100\text{ m})^2(0.100\text{ m}) + (0.015\text{ m})\left((0.675\text{ m})^2 - (0.660\text{ m})^2\right)}\right)^{\frac{7}{5}-1}$$

$$T_\text{f} = 313.162\text{ K}$$

Round

- We report our results to two significant figures:

$$T_\text{f} = 313\text{ K}$$

Double-check

- The units are good.

Bicycle Tire Pump 8

- The ratio of the initial volume of air to the final volume is:

  $V_\mathrm{i}/V_\mathrm{f} = 1.16$
- During the compression stroke, the temperature increases from 295 K to 313 K, so the ratio of final to initial temperature is:

  $T_\mathrm{f}/T_\mathrm{i} = \left((313\text{ K})\right)/\left((295\text{ K})\right) = 1.06$
- This seems reasonable because the final temperature should be equal to the initial temperature times the ratio of the initial and final volume raised to the power $\gamma - 1$:
  $(1.16)^{\gamma-1} = 1.16^{0.4} = 1.06$.
- If you depress the piston many times in a short period of time, each compression stroke will increase the temperature of the air in the tire by about 6%.
- Thus, the air in the tire and in the pump gets warmer as the tire is inflated.

Work Done by an Ideal Gas in an Adiabatic Process 1

- We can also find the work done by a gas undergoing an adiabatic process from an initial state to a final state.
- In general, the work is given by:

$$W = \int_{\mathrm{i}}^{\mathrm{f}} p dV$$

- For an adiabatic process, we can write $p = cV^{-\gamma}$ and the integral determining the work becomes:

$$W = \int_{\mathrm{i}}^{\mathrm{f}} cV^{-\gamma} dV = c\int_{\mathrm{i}}^{\mathrm{f}} V^{-\gamma} dV = c\left[\frac{V^{1-\gamma}}{1-\gamma}\right]_{V_{\mathrm{i}}}^{V_{\mathrm{f}}} = \frac{c}{1-\gamma}\left({V_{\mathrm{f}}}^{1-\gamma} - {V_{\mathrm{i}}}^{1-\gamma}\right)$$

- The constant c has the value $c = pV^{\gamma}$.

Work Done by an Ideal Gas in an Adiabatic Process 2

- Using the Ideal Gas Law in the form $p = nRT/V$, we have:

$$c = \left(\frac{nRT}{V}\right)V^{\gamma} = nRTV^{\gamma-1}$$

- Now we insert this constant into the expression for the work and use the relationship between pressure and volume for an adiabatic process.
- We finally find the work done by a gas undergoing an adiabatic process:

$$W = \frac{nR}{1-\gamma}\left(T_{\mathrm{f}} - T_{\mathrm{i}}\right)$$

Kinetic Theory of Gases 1

- The root-mean-square speed of gas molecules at a given temperature is:

$$v_{\text{rms}} = \sqrt{\frac{3k_{\text{B}}T}{m}}$$

- What is the distribution of speeds?
- What is the probability that a gas molecule has some given speed between *v* and *v* + *dv*?
- The speed distribution, called the Maxwell speed distribution, or sometimes the Maxwell-Boltzmann speed distribution, is given by:

$$f(v) = 4\pi\left(\frac{m}{2\pi k_{\text{B}}T}\right)^{3/2} v^2 e^{-\frac{mv^2}{2k_{\text{B}}T}}$$

Kinetic Theory of Gases 2

- The units of the Maxwell speed distribution are $(\mathrm{m/s})^{-1}$.
- As required for a probability distribution, integration of this distribution with respect to *dv* yields 1:

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

- A very important feature of probability distributions for observable quantities is that all kinds of physically meaningful averages can be calculated from them by simply multiplying the quantity to be averaged by the probability distribution and integrating over the entire range.
- For example, we can obtain the average speed for the Maxwell speed distribution by multiplying the speed, v, by the probability distribution, $f(v)$, and integrating this product, $vf(v)$, over all possible values of the speed from zero to infinity.

Kinetic Theory of Gases 3

- The average speed is then given by:

$$v_{\text{ave}} = \int_0^\infty v f(v)\,dv = \sqrt{\frac{8k_{\text{B}}T}{\pi m}}$$

- To find the root-mean-square speed for the Maxwell speed distribution, we first find the average speed squared:

$$(v^2)_{\text{ave}} = \int_0^\infty v^2 f(v)\,dv = \frac{3k_{\text{B}}T}{m}$$

- We then take the square root:

$$v_{\text{rms}} = \sqrt{(v^2)_{\text{ave}}} = \sqrt{\frac{3k_{\text{B}}T}{m}}$$

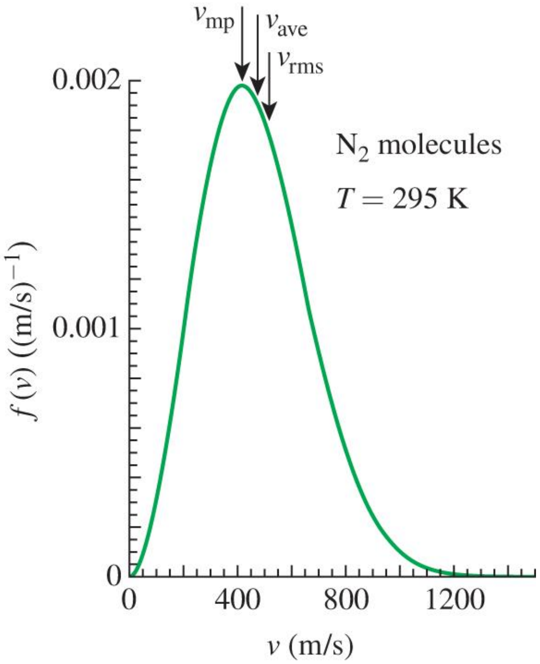
- This agrees with the speed of gas molecules in an ideal gas.

Kinetic Theory of Gases 4

- The most probable speed for the Maxwell speed distribution—that is, the value at which *f*(*v*) has a maximum—is calculated by taking the derivative of *f*(*v*) with respect to *v*, setting that derivative equal to zero, and solving for *v*, which gives:

$$v_{\mathrm{mp}} = \sqrt{\frac{2k_{\mathrm{B}}T}{m}}$$

- Here is the Maxwell speed distribution for N_2 molecules in air at a temperature of 295 K, with the most probable speed, the average speed, and the root-mean-square speed.



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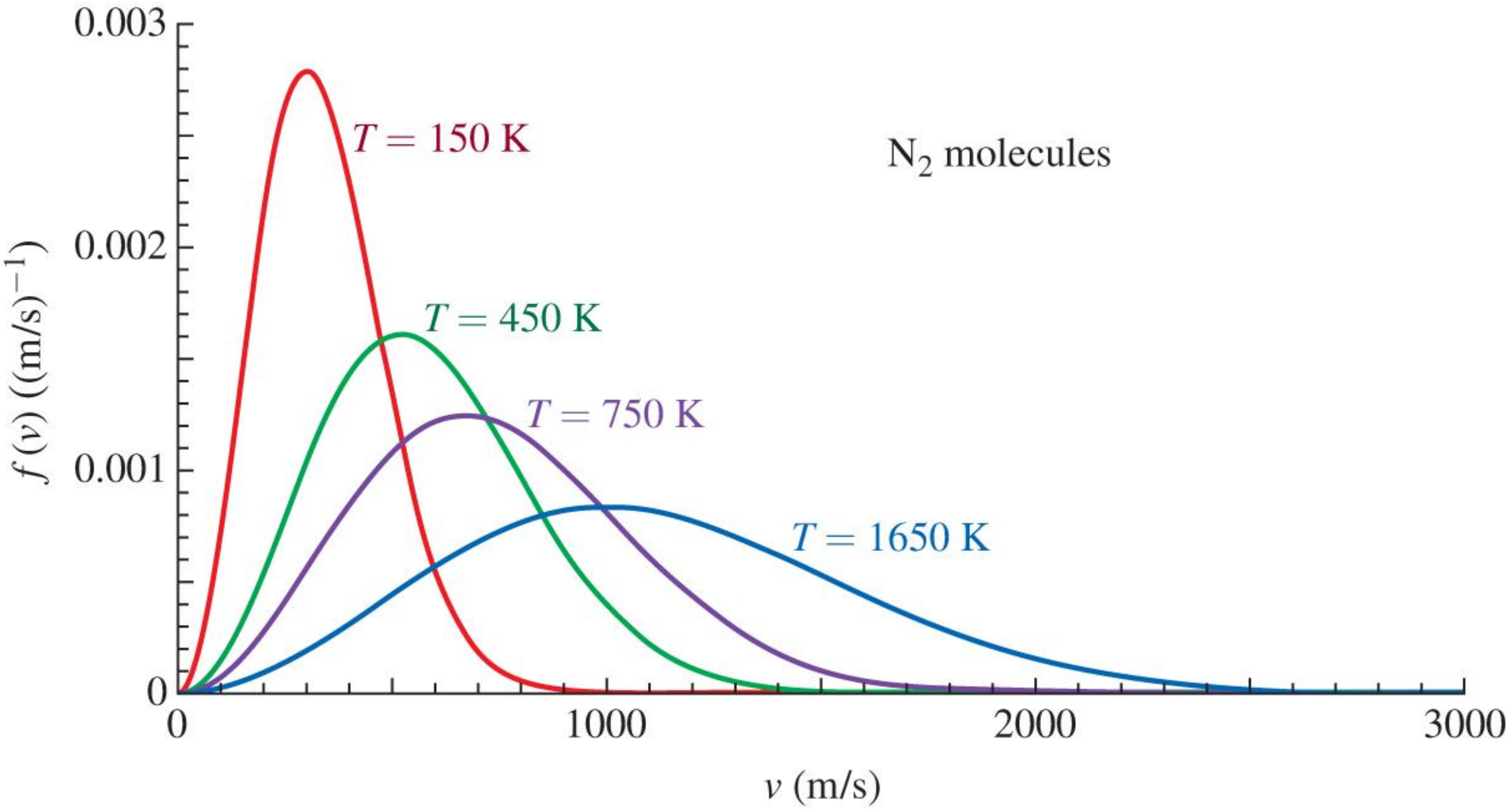
Kinetic Theory of Gases 5

- Here we show the Maxwell speed distribution for nitrogen molecules at four different temperatures.



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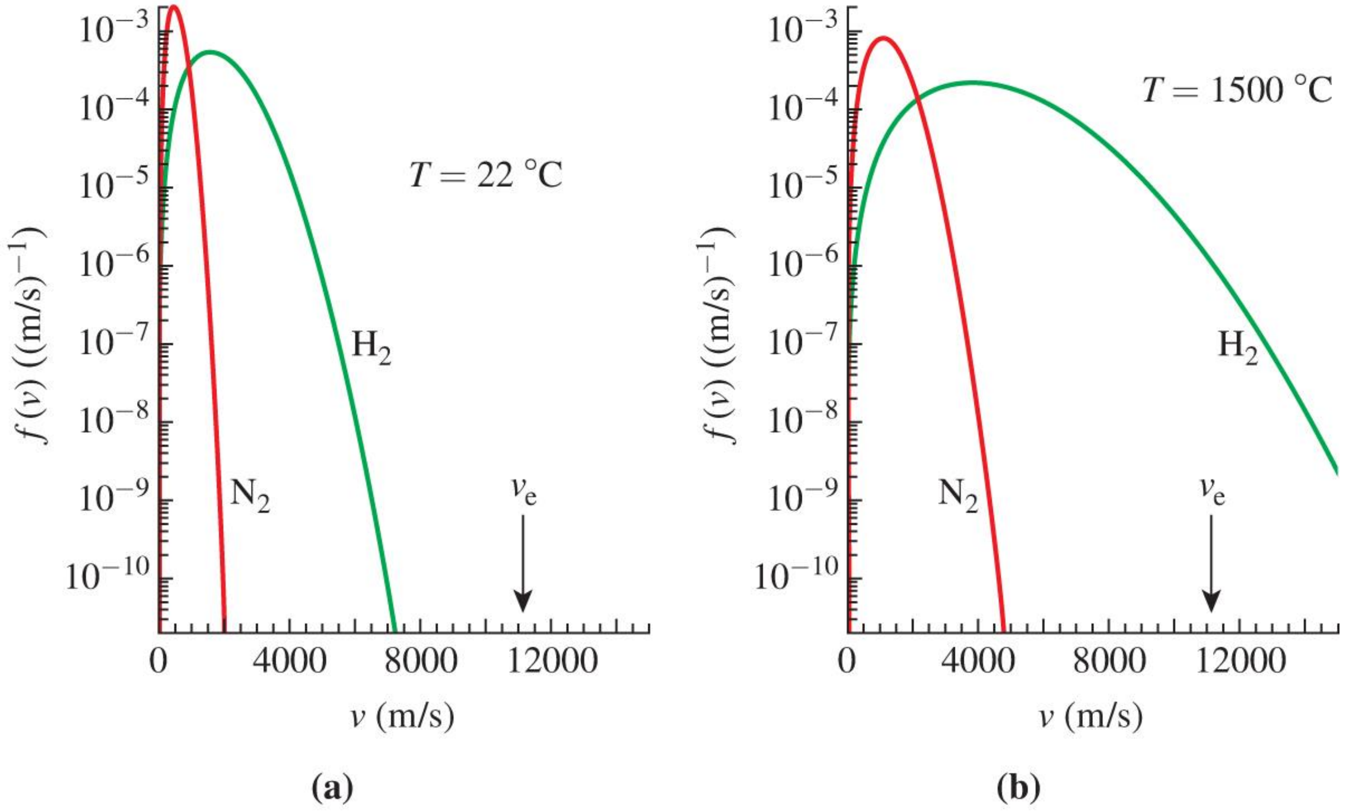
Kinetic Theory of Gases 6

- Here we show the Maxwell speed distribution for hydrogen and nitrogen molecules at two different temperatures.



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Kinetic Theory of Gases 7

- At an altitude of 100 km above the surface, the Earth's atmosphere starts to become very warm and can reach temperatures of 1500 °C.
- This layer of the atmosphere is called the *thermosphere*.
- We can calculate the fraction of hydrogen molecules that will have a speed higher than the escape speed by evaluating the integral for the Maxwell speed distribution from the escape speed to infinity:

$$\text{Fraction H}_2\text{ escaping} = \int_{v=11.2\text{ km/s}}^{\infty} f(v)dv = 7 \cdot 10^{-4} = 0.07\%$$

- Only a small fraction of the hydrogen molecules in the thermosphere have speeds above the escape speed.

Kinetic Theory of Gases 8

- The hydrogen molecules remaining behind have the same temperature as the rest of the thermosphere, and the speed distribution will reflect this temperature.
- Thus, over time on the geologic scale, most hydrogen molecules in the Earth’s atmosphere rise to the thermosphere and eventually leave the Earth.
- Essentially no nitrogen molecules have speeds above the escape speed.
- The ratio of the value of the Maxwell speed distribution at the escape speed for nitrogen relative to that for hydrogen is:

$$\left(f_{\mathrm{N}_2}\left(11.2\,\frac{\mathrm{km}}{\mathrm{s}}\right)\right)\Big/\left(f_{\mathrm{H}_2}\left(11.2\,\frac{\mathrm{km}}{\mathrm{s}}\right)\right) = 3\cdot 10^{-48}$$

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Maxwell Kinetic Energy Distribution 1

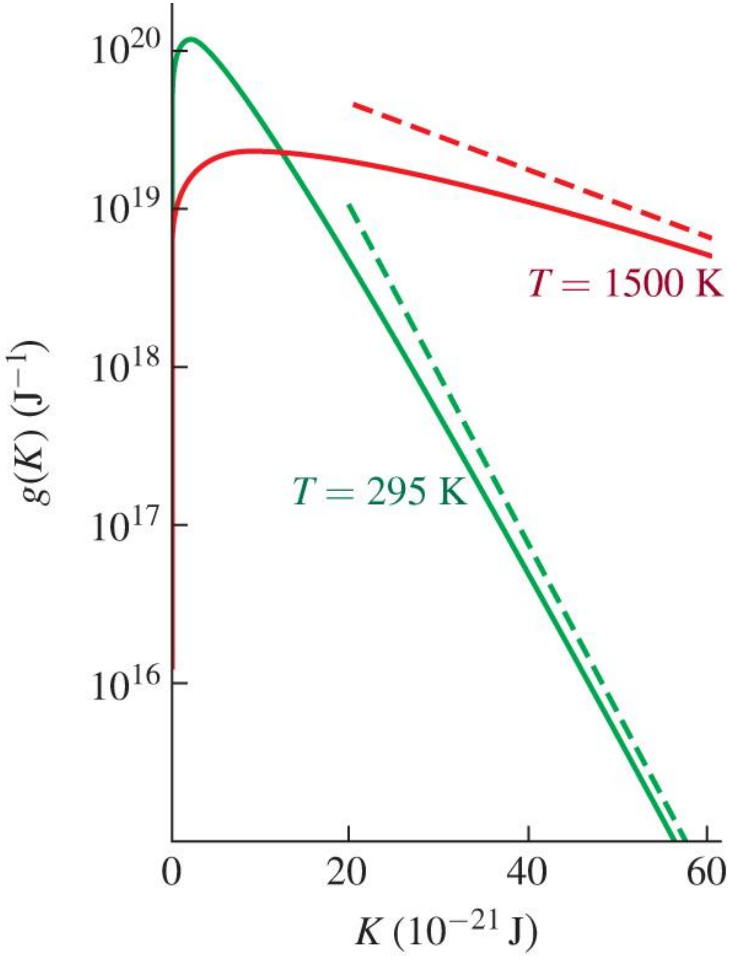
- Just as gas molecules have a distribution of speeds, they also have a distribution of kinetic energies.
- The Maxwell kinetic energy distribution (sometimes called the Maxwell-Boltzmann kinetic energy distribution) describes the energy spectra of gas molecules and is given by:

$$g(K) = \frac{2}{\sqrt{\pi}}\left(\frac{1}{k_{\mathrm{B}}T}\right)^{3/2}\sqrt{K}e^{-\frac{K}{k_{\mathrm{B}}T}}$$

- The Maxwell kinetic energy distribution times dK gives the probability of observing a gas molecule with a kinetic energy between K and $K + dK$.
- Integration of this distribution with respect to dK yields 1.

Maxwell Kinetic Energy Distribution 2

- We show the Maxwell energy distribution for nitrogen molecules at two different temperatures.
- The distribution for the higher temperature is much flatter.
- At high kinetic energies, the distributions approach a simple exponential with a slope of $-1/(k_B T)$ as shown by the dashed lines.



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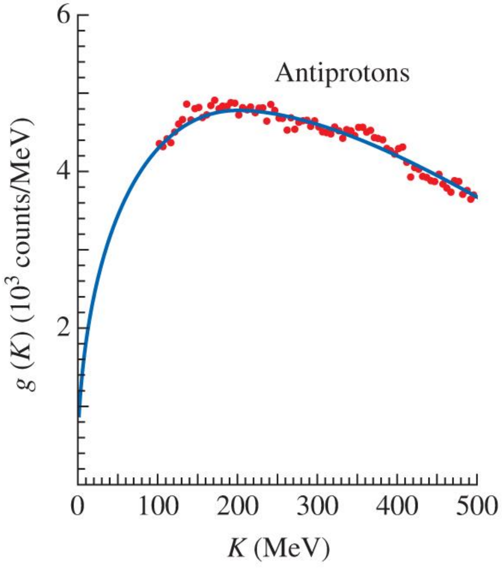
Temperature of the Quark Gluon Plasma 1

- Measuring the kinetic energy distribution of the constituents of a gas can reveal the temperature of the gas.
- This technique is used in many applications, including the study of gases consisting of elementary particles and nuclei.
- On the next slide is the kinetic energy distributions of antiprotons and pions produced in relativistic heavy ion collisions of gold nuclei.
- The data were produced by the STAR collaboration at the Relativistic Heavy Ion Collider at Brookhaven National Laboratory.

Temperature of the Quark Gluon Plasma 2



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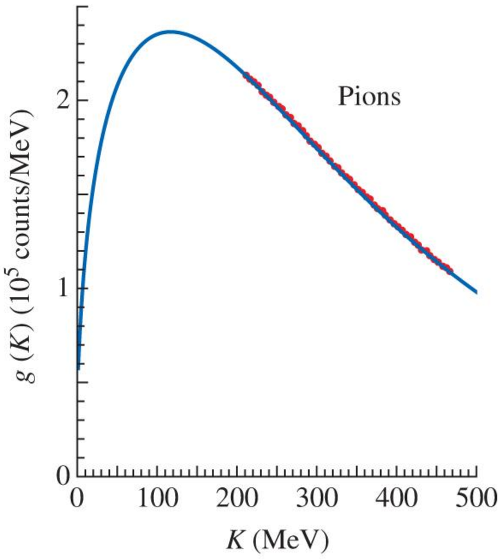

(c)

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Temperature of the Quark Gluon Plasma 3

- The blue lines represent fits to the data, using the Maxwell kinetic energy distribution with the best-fit value for the temperature, *T*.
- Values of $k_B T = 6.71 \cdot 10^{-11}$ J = 419 MeV for the antiprotons and $k_B T = 3.83 \cdot 10^{-11}$ J = 239 MeV for the pions were extracted, meaning that the temperatures of the antiprotons and pions are $4.86 \cdot 10^{12}$ K and $2.77 \cdot 10^{12}$ K, respectively.
- These temperatures are several hundred million times higher than the temperature at the surface of the Sun!
- These observations and others enable researchers to infer that a quark-gluon plasma with a temperature of $2 \cdot 10^{12}$ K is created for a very short time of approximately 10^{-22} s in these collisions.

Fusion in the Sun

- Nuclear fusion in the center of the Sun is the source of energy that causes all the Sun's radiation and enables life on Earth.
- The temperature at the center of the Sun is $1.5 \cdot 10^7$ K.
- The average kinetic energy of the hydrogen ions in the Sun's center is $(3/2)k_\text{B}T = 3.1 \cdot 10^{-16}$ J = 1.9 keV.
- For two hydrogen atoms to fuse, they must come close enough to each other to overcome their electrostatic repulsion.
- The minimum energy required to overcome the electrostatic repulsion is on the order of 1 MeV, or a few hundred times higher than the average kinetic energy of the hydrogen ions in the Sun's center.
- Thus, only hydrogen ions on the extreme tail of the Maxwell distribution have sufficient energy to participate in fusion reactions.

Mean Free Path 1

- One of the assumptions about an ideal gas is that the gas molecules are point particles and do not interact with each other.
- Real gas molecules do have (very small, but nonzero) sizes and so have a chance of colliding with each other.
- Collisions of gas molecules with each other produce a scattering effect that causes the motion to be random and the distribution of their speeds to become the Maxwell distribution speed very quickly, independently of any initial speed distribution.
- How far do real gas molecules travel before they encounter another molecule?
- This distance is the mean free path, λ, of molecules in a gas.

Mean Free Path 2

- The mean free path is inversely proportional to the cross-sectional area and the density of molecules:

$$\lambda = \frac{1}{(4\pi r^2)n_V}$$

- For an ideal gas we have (See Derivation 19.4):

$$\lambda = \frac{k_\mathrm{B}T}{\sqrt{2}(4\pi r^2)p}$$

- Let's look at the most important gas, the Earth's atmosphere.
- An ideal gas has an "infinitely" long mean free path relative to the spacing between molecules in the gas.
- Let's see how close Earth's atmosphere is to being an ideal gas.

Concept Check 8

- The mean free path of a gas molecule doubles if the ______.

A. density of molecules goes down by a factor of 2

B. density of molecules doubles

C. diameter of the gas molecules doubles

D. diameter of the gas molecules goes down by a factor of 2

E. none of the above

Solution Concept Check 8

- The mean free path of a gas molecule doubles if the ______.

A. density of molecules goes down by a factor of 2

B. density of molecules doubles

C. diameter of the gas molecules doubles

D. diameter of the gas molecules goes down by a factor of 2

E. none of the above

$$\lambda = \frac{1}{(4\pi r^2)n_V}$$

Mean Free Path of Air Molecules 1

PROBLEM:

- What is the mean free path of a gas molecule in air at normal atmospheric pressure of 101.3 kPa and a temperature of 20.0 °C?
- Since air is 78.1% nitrogen, we’ll assume for the sake of simplicity that air is 100% nitrogen.
- The radius of a nitrogen molecule is about 0.150 nm.
- Compare the mean free path to the radius of a nitrogen molecule and to the average spacing between the nitrogen molecules.

Mean Free Path of Air Molecules 2

SOLUTION:

- The mean free path is:

$$\lambda = \frac{(1.381 \cdot 10^{23}\ \mathrm{J/K})(293.15\ \mathrm{K})}{\sqrt{2}(4\pi(0.150 \cdot 10^{-9}\ \mathrm{m})^2)(101.3 \cdot 10^3\ \mathrm{Pa})} = 9.99 \cdot 10^{-8}\ \mathrm{m}$$

- The ratio of the mean free path to the molecular radius is:

$$\frac{\lambda}{r} = \frac{9.99 \cdot 10^{-8}\ \mathrm{m}}{0.150 \cdot 10^{-9}\ \mathrm{m}} = 666$$

- The volume per particle in an ideal gas is:

$$\frac{V}{N} = \frac{k_{\mathrm{B}}T}{p}$$

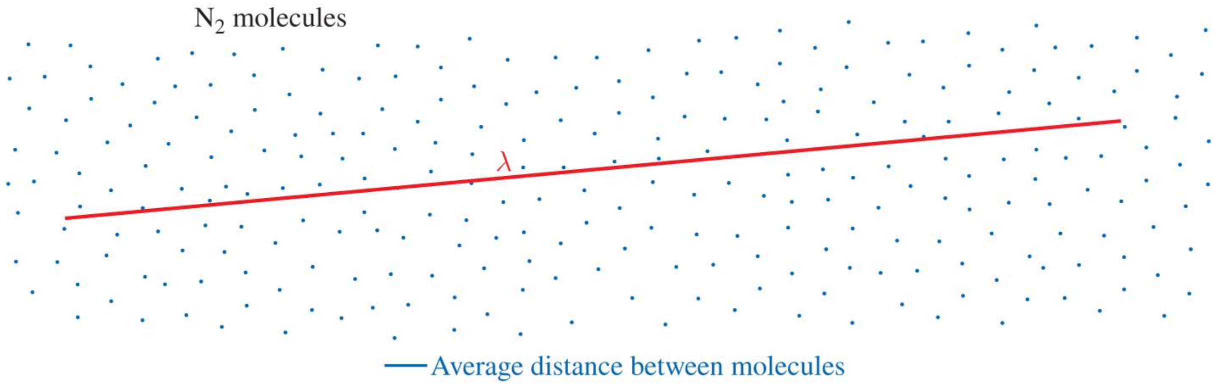
Mean Free Path of Air Molecules 3

- The average spacing between molecules is then the average volume to the 1/3 power:

$$\left(\frac{V}{N}\right)^{1/3} = \left(\frac{k_\mathrm{B}T}{p}\right)^{1/3} = \left(\frac{(1.381 \cdot 10^{-23}\ \mathrm{J/K})(293.15\ \mathrm{K})}{101.3 \cdot 10^{3}\ \mathrm{Pa}}\right)^{1/3} = 3.42 \cdot 10^{-9}\ \mathrm{m}$$

- Thus, the ratio between the mean free path and the average spacing between molecules is:

$$\frac{9.99 \cdot 10^{-8}\ \mathrm{m}}{3.42 \cdot 10^{-9}\ \mathrm{m}} = 29.2$$



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