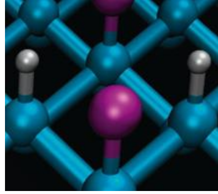




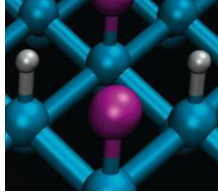
Chapter **5**

Gases

Properties of Gases

- Expand to fill the volume of any container
- Have much lower densities than solids or liquids
- Have highly variable densities, depending on conditions
- Mix with one another readily and thoroughly
- Change volume dramatically with changing temperature

Properties of Gases



- The ideal gas law is the quantitative relationship between pressure or *P*, volume *or V*, number of moles of gas present or *n,* and the absolute temperature or *T*
- *R* is the universal gas constant
  - $R = 0.08206\ \text{L atm mol}^{-1}\,\text{K}^{-1}$; used in most gas equations
  - $R = 8.314\ \text{J mol}^{-1}\,\text{K}^{-1}$; used in equations involving energy

$$PV = nRT$$

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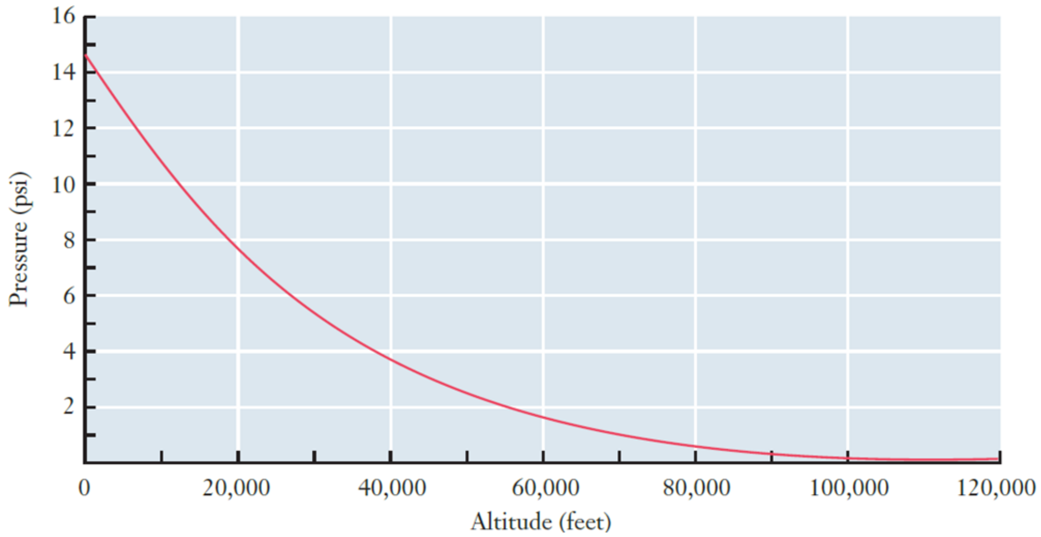
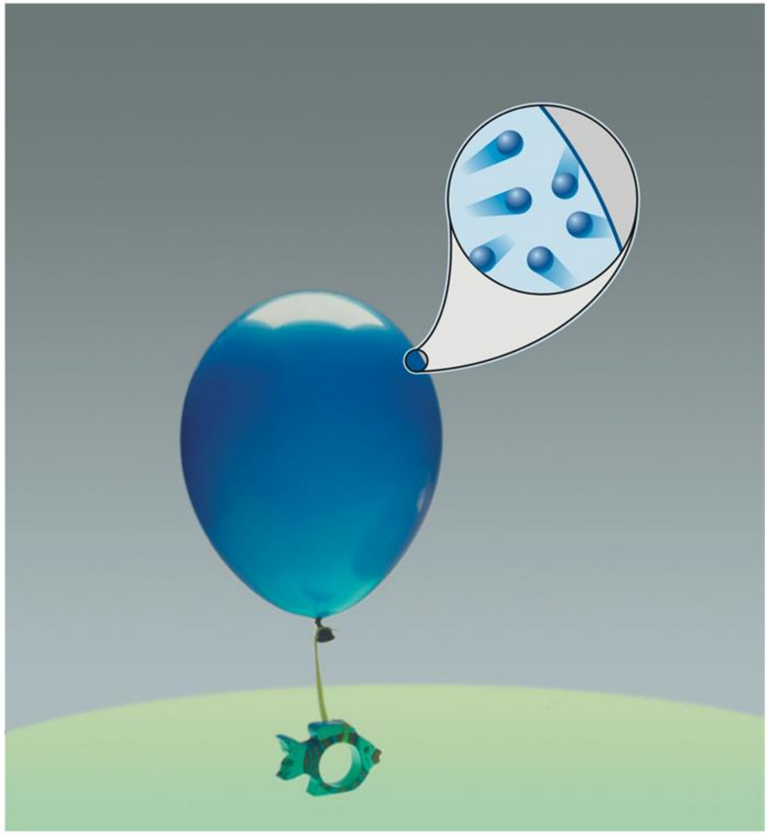
Pressure

- Pressure is force per unit area $P = \dfrac{F}{A}$
- Atmospheric pressure is the force attributed to the weight of air molecules attracted to Earth by gravity
- As altitude increases, atmospheric pressure decreases



Pressure



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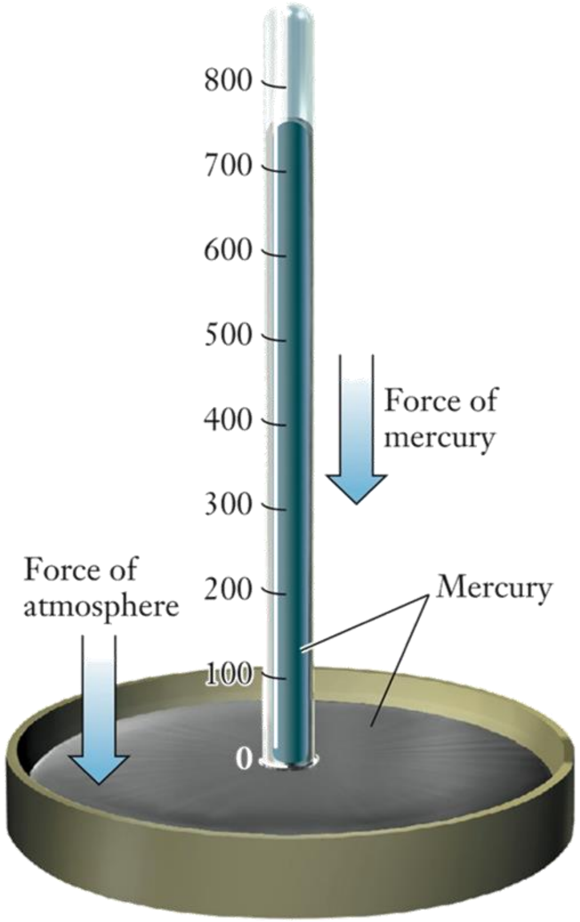
- Pressure results from molecular collisions between gas molecules and container walls
  - Each collision imparts a small amount of force
  - Summation of the forces of all molecular collisions produces the macroscopic property of pressure

Measuring Pressure



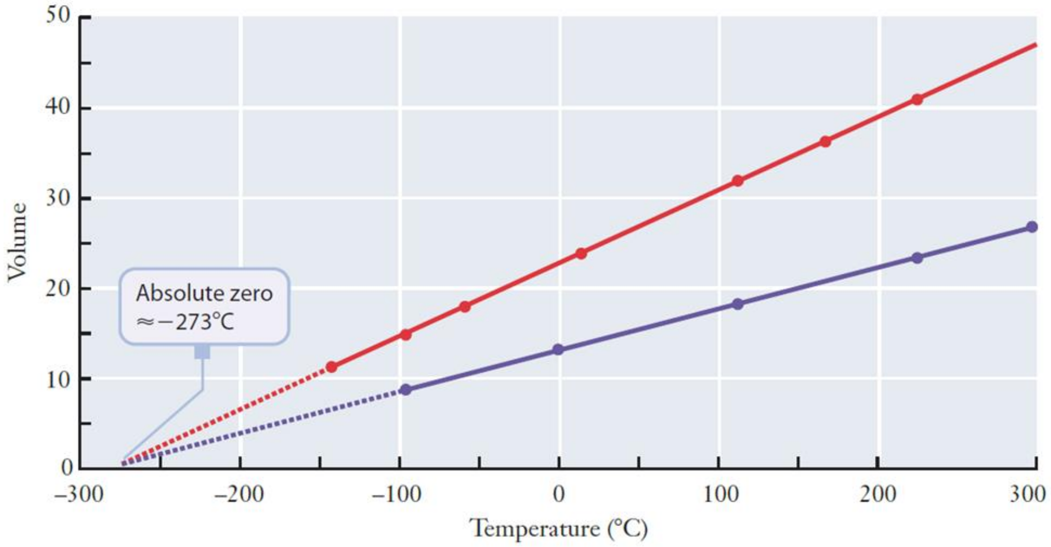
- A barometer is used to measure atmospheric pressure
  - Height of the mercury column is proportional to the applied pressure
- Units of pressure
  - 1 torr = 1 mm Hg
  - 1 atm = 760 torr (exactly)
  - 1 atm = 101,325 Pa (exactly)
  - 760 torr = 101,325 Pa (exactly)

History and Application of the Gas Law

- Gases change significantly when the conditions in which they are found are altered
- Changes are determined empirically using gas laws
  - Charles's law: Relationship between T and V
  - Boyle's law: Relationship between P and V
  - Avogadro's law: Relationship between n and V
- Empirical observations led to the ideal gas law

Charles's Law

- Jacques Charles studied the relationship between volume and temperature
  - Plots of V versus T for different gas samples converged to the same temperature at zero volume
    - Basis of the Kelvin temperature scale



Charles's Law

- For fixed pressure and fixed number of moles of gas, the volume and the absolute temperature of a gas are directly proportional

$$V \propto T$$

- All of the fixed variables can be factored out of the ideal gas law as a new constant that can be used to relate two sets of conditions

$$\frac{V_1}{T_1} = \frac{nR}{P} = \text{constant} = \frac{V_2}{T_2}$$

Boyle's Law

- Pressure and volume are inversely proportional

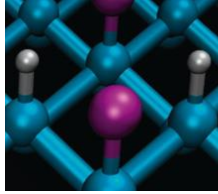
$$V \propto \frac{1}{P}$$

- All of the fixed variables can be factored out as a new constant that can be used to relate two sets of conditions

$$P_1V_1 = nRT = \text{constant} = P_2V_2$$

- R is a universal constant

Avogadro's Law



- For fixed pressure and temperature, the volume and moles of a gas are directly proportional

$$V \propto n$$

$$\frac{V_1}{n_1} = \frac{RT}{P} = \text{constant} = \frac{V_2}{n_2}$$

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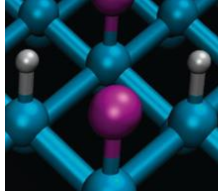


Example Problem 5.1

- A common laboratory cylinder of methane has a volume of 49.0 L and is filled to a pressure of 154 atm. Suppose that all of the CH_4 from this cylinder is released and expands until its pressure falls to 1.00 atm.
  - What volume would the CH_4 occupy?

$$PV = nRT$$

$$V_2 = \frac{P_1 V_2}{P_2} = \frac{49 \times 154}{1} = 7546$$

Example Problem 5.2

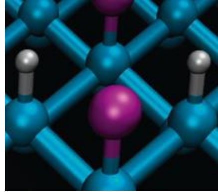
- A balloon is filled with helium and its volume is 2.2 L at 298 K. The balloon is then dunked into a thermos bottle containing liquid nitrogen.
  - When the helium in the balloon has cooled to the temperature of the liquid nitrogen (77 K), what will the volume of the balloon be?

$$V_2 = \frac{V_1}{T_1}\cdot T_2 = \frac{2.2\times 77}{298} = 0.568\,L$$

0.57 L

两位有效数字

~~Still~~ By the way, we don't know the phase of helium ~~of~~ at 77K,



Units and the Ideal Gas Law

- Temperature must be expressed on an absolute scale for all gas calculations
  - In some engineering fields, the Rankine temperature scale is used, which is another absolute temperature scale
    - 0° R = 0 K
    - 1° R = 1.8 K
- The unit for moles is always mol
- The units for measuring pressure and volume can vary
  - In gas calculations, these units must agree with those of the gas constant
    - $R = 8.314 \text{ J mol}^{-1}\text{K}^{-1}$
    - $R = 0.08206 \text{ L atm mol}^{-1}\text{K}^{-1}$
    - $R = 62.37 \text{ L torr mol}^{-1}\text{K}^{-1}$

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Example Problem 5.3

- A sample of C_2H_6 gas has a volume of $575\,cm^3$ at 752 torr and 72°F
  - What is the mass of ethane in this sample?

$72°F = (72-32)\frac{5}{9} + 273 = 295\,K$

$PV = nRT$

$n = \frac{PV}{RT} = \frac{752 \times 575 \times 10^{-3}}{62.37 \times 295} = 0.235$

$m = 0.705$

Partial Pressure

- Air is a mixture of gases
  - Gas laws do not depend on identity of gases
  - Pressure due to total moles of gas present
- The pressure exerted by a component of a gas mixture is called the partial pressure of the component gas

Partial Pressure

- Dalton's law of partial pressures: The total pressure (*P*) of a mixture of gases is the sum of the partial pressures of the component gases (P_i)

$$P = \sum_i P_i$$

- Dalton's law can be expressed in terms of mole fraction
  - Mole fraction (X_i) for a gas in a gas mixture is the moles of the gas (n_i) divided by the total moles of gas present
  - The partial pressure of each gas is related to its mole fraction

$$X_i = \frac{n_i}{n_{\text{total}}} \quad \Rightarrow \quad P_i = X_i P$$

Example Problem 5.4

- A scientist tries to generate a mixture of gases similar to a volcano by introducing 15.0 g of water vapor, 3.5 g of SO_2, and 1.0 g of CO_2 into a 40.0-L vessel held at 120.0°C
  - Calculate the partial pressure of each gas and the total pressure

$120^\circ C = 120 + 273.15 = 393.15 K$

$P = \frac{nRT}{V} = \frac{0.082 \times 393.15}{40} n = 0.81 n$

$P_{water} = \frac{15}{18} \times 0.81 = 0.68$

$P_{SO_2} = \frac{3.5}{64} \times 0.81 = 0.044$

$P_{CO_2} = \frac{1}{44} \times 0.81 = 0.018$

$P_{total} = 1.158$

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Stoichiometry of Reactions Involving Gases

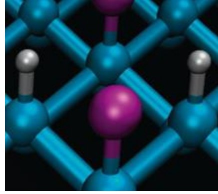
- For reactions involving gases, the ideal gas law is used to determine moles of gas involved in the reactions
  - Number of moles of a gas is connected to its temperature, pressure, or volume with the ideal gas law

$$PV = nRT$$

STP Conditions

- Standard temperature and pressure, STP, for a gas is 0°C or 273.15 K and 1 atm
  - For one mole of gas at STP, the standard molar volume is 22.41 L
    - Calculated using the ideal gas law
  - This number provides a conversion factor for stoichiometric problems that include gases, provided the STP conditions are maintained

Example Problem 5.7



- Carbon dioxide can be removed from a stream of gas by reacting it with calcium oxide to form calcium carbonate
- If we react 5.50 L of CO_2 at STP with excess CaO, what mass of calcium carbonate will form?

$$m = \frac{V_{CO_2}}{V_{mc}} \cdot \frac{n_{CO_2}}{n_{CaCO_3}} \cdot 100$$

$$= \frac{5.50}{22.4} \times 100 = 24.6$$

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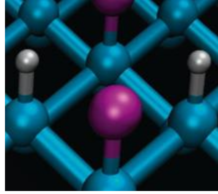
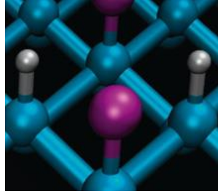


Kinetic–Molecular Theory and Ideal versus Real Gases

- In many important practical settings, gases do not always behave ideally, especially at very high pressure and or very low temperatures
    - Nonideal gas behavior can be explained using kinetic–molecular theory
        - Kinetic–molecular theory provides connections between observed macroscopic properties of gases, the gas law equation, and the behavior of gas molecules on a microscopic scale

Postulates of the Model



- At a given temperature, gas molecules in a sample can be characterized by an average speed
  - Some gas molecules move faster than average, some move slower than average
  - The distribution function that describes the speeds of a collection of gas particles is known as the Maxwell-Boltzmann distribution of speeds

Postulates of the Model (6 of 7)

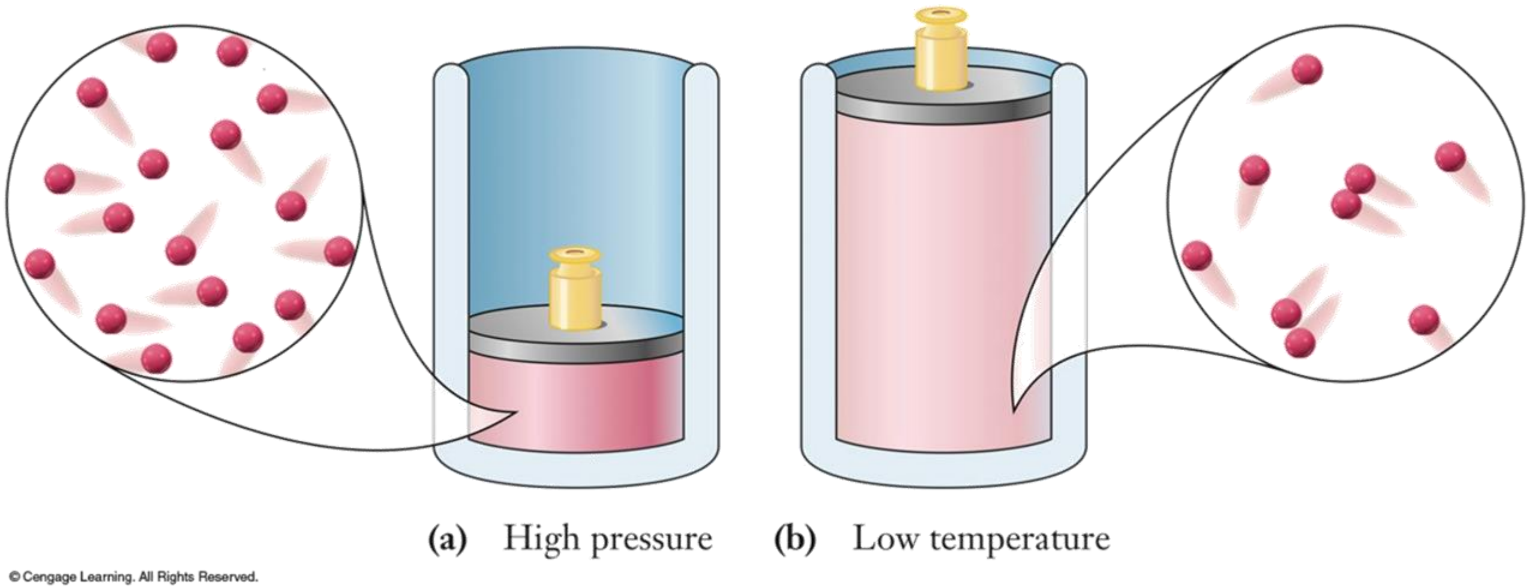
- The equation for the Maxwell-Boltzmann distribution describes $N(\upsilon)$, which is the number of molecules moving with speeds between υ and $\Delta\upsilon$

$$\frac{N(\upsilon)}{N_{\text{total}}} = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2}\upsilon^2 e^{-M\upsilon^2/2RT}$$

- Most gas molecules move at the most probable speed, which is the peak of the curve in the Maxwell-Boltzmann plot

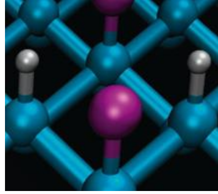
$$\upsilon_{\text{mp}} = \sqrt{\frac{2RT}{M}}$$

Real Gases and Limitations of the Kinetic Theory



- The ideal gas model breaks down at high pressures and low temperatures
  - High pressure: The volume of particles is no longer negligible
  - Low temperature: Particles move slowly enough to interact

Correcting the Ideal Gas Equation



- Van der Waals equation is commonly used to describe the behavior of real gases

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

- *a* corrects for attractive forces
  - Molecules with stronger attractive forces have larger a values
- *b* corrects for the volume occupied by gas molecules
  - Large molecules have larger *b* values

Correcting the Ideal Gas Equation

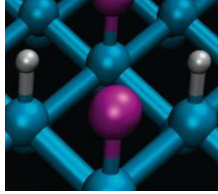
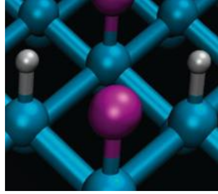


Table 5.2 Van der waals constant

Gas	a (atm L^2 mol^{-2})	b (L mol^{-1})
Ammonia, NH_3	4.170	0.03707
Argon, Ar	1.345	0.03219
Carbon dioxide, CO_2	3.592	0.04267
Helium, He	0.034	0.0237
Hydrogen, H_2	0.2444	0.02661
Hydrogen fluoride, HF	9.433	0.0739
Methane, CH_4	2.253	0.04278
Nitrogen, N_2	1.390	0.03913
Oxygen, O_2	1.360	0.03183
Sulfur dioxide, SO_2	6.714	0.05636
Water, H_2O	5.464	0.03049

- The van der Waals constants *a* and *b* are compound specific
  - Both are zero in gases behaving ideally

Example Problem 5.8



- An empty 49.0 L methane storage tank has an empty mass of 55.85 kg and, when filled, has a mass of 62.07 kg
  - Calculate the pressure of CH_4 in the tank at 21°C using both the ideal gas equation and the van der Waals equation
  - What is the percentage correction achieved by using the more realistic van der Waals equation?

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