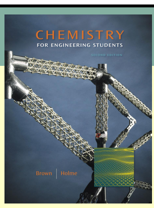


BROOKS/COLE CENGAGE Learning

Larry Brown
Tom Holme

www.cengage.com/chemistry/brown

Chapter 5
Gases

Jacqueline Bennett • SUNY Oneonta

Warning!!

- These slides contains visual aids for learning BUT they are NOT the actual lecture notes!
- Failure to attend to lectures most probably result in failing the lecture!
- So I strongly recommend that you attend to the classes. Take a pen, a notebook and WRITE!

2

Chapter Objectives

- Describe the physical properties of gases.
- Identify several gaseous compounds or classes of compounds that are important in urban air pollution.
- Use the ideal gas law for calculating changes in the conditions of gases.
- Use the concept of partial pressure to work with mixtures of gases.

3

Chapter Objectives

- Perform stoichiometric calculations for reactions involving gases as reactants or products.
- State the postulates of the kinetic theory of gases.
- Describe qualitatively how the postulates of the kinetic theory account for the observed behavior of gases.
- Describe the Maxwell-Boltzmann distribution of speeds and the effects of temperature and molar mass on molecular speed.

4

Chapter Objectives

- Identify conditions under which gases might not behave ideally.
- Use the van der Waals equation to perform calculations for gases under nonideal conditions.
- Describe the principles of operation for some pressure-measuring devices.

5

Air Pollution

Table 5.1

The composition of a one cubic meter sample of dry air at 25°C and normal atmospheric pressure

Gas	# Moles Present
N_2	31.929
O_2	8.567
Ar	0.382
CO_2	0.013
Other trace gases	0.002
Total	40.893

- Clean air is a mixture of several gases.
  - Nitrogen and oxygen are major components
  - Water vapor (humidity) varies with place, time, and temperature.
  - Dry air is a convenient reference point

6

Air Pollution

- Six Principal Criteria Pollutants
  - CO, NO_2, O_3, SO_2, Pb, and Particulate Matter (PM)
  - Commonly found throughout the country; cause a variety of negative effects on health, environment, and/or property.
- EPA established criteria for acceptable levels:
  - Primary standards intended to protect health.
    - Nonattainment area: region that exceeds primary standards
  - Secondary standards intended to protect environment and property.
  - Allowable levels usually less than one part per million (ppm).

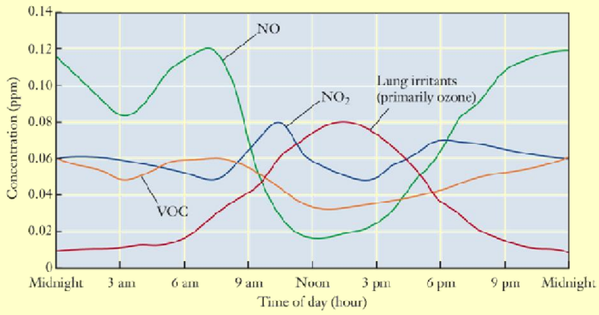
Air Pollution

- The criteria pollutant nitrogen dioxide, NO_2, is emitted by automobiles.
  - High temperatures inside car engines cause oxygen and nitrogen to react to produce a variety of nitrogen oxides, designated with the generic formula NO_x.
  - Brown color of smog due to NO_2; attacks lung membranes

Air Pollution

- Photochemical reactions, reactions initiated by light energy, can trigger formation of ozone, another criteria pollutant, at ground level from:
  - nitrogen oxides
  - volatile organic compounds (VOCs): hydrocarbons that readily evaporate
- Reactions between these two types of compounds produce a mixture a gases collectively referred to as smog.
  - Many components are lung irritants.
    - Ozone is the most significant lung irritant.

Air Pollution



- Pollutant levels vary with time of day and location.

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.

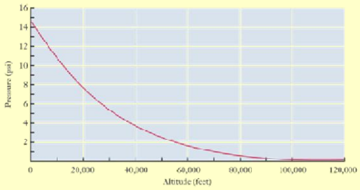
Properties of Gases

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

$$PV = nRT$$

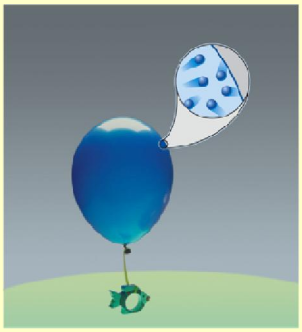
Pressure

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



13

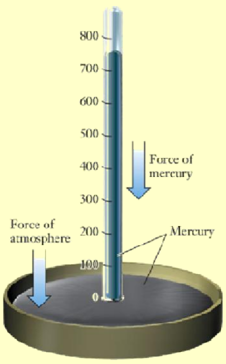
Pressure



- 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.

14

Measuring Pressure



- A barometer is used to measure atmospheric pressure.
  - The height of the mercury column is proportional to atmospheric 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)

15

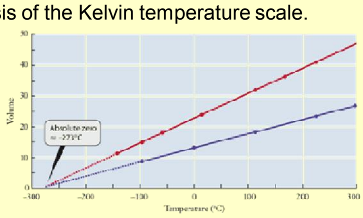
History and Application of the Gas Law

- Gases change significantly when the conditions in which they are found are altered.
- These 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
- The empirical gas laws led to the ideal gas law

16

Charles's Law

- Jacques Charles studied 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.



17

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:

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

18

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:

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

19

Avogadro's Law

- Avogadro's Law states that for fixed pressure and temperature, the volume and moles of a gas are directly proportional.

$$V \propto n$$

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

20

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?

21

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?

22

Units and the Ideal Gas Law

- *Temperature must be expressed in Kelvin for all gas calculations!*
  - Negative temperatures would result in negative pressures, volumes, and moles.
  - 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 J mol^{-1} K^{-1}
  - R = 0.08206 L atm mol^{-1} K^{-1}
  - R = 62.37 L torr mol^{-1} K^{-1}

23

Example Problem 5.3

- A sample of CO_2 gas has a volume of 575 cm^3 at 752 torr and 72˚F. What is the mass of carbon dioxide in this sample?

24

Partial Pressure

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

25

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).

$$P = \sum_i P_i$$

- Daltons 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 gas present.
  - The partial pressure of each gas is related to its mole fraction.

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

26

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.

27

Example Problem 5.5

- A mixture has the mole fractions given in the following table:

Gas	N_2	O_2	H_2O	SO_2
Mole Fraction	0.751	0.149	0.080	0.020

- If the desired pressure is 750. torr, what should the partial pressures be for each gas?
- If the gas is to be in a 15.0 L vessel held at 30° C, how many moles of each substance are needed?

28

Stoichiometry of Reactions Involving Gases

- For reactions involving gases, the ideal gas law is used to determine moles of gas involved in the reaction.
  - Use mole ratios (stoichiometry)
  - Connect number of moles of a gas to its temperature, pressure, or volume with ideal gas law

$$PV = nRT$$

29

Example Problem 5.6

- When an experiment required a source of carbon dioxide, a student combined 1.4 g of sodium bicarbonate ($NaHCO_3$) with excess hydrochloric acid (HCl). If the CO_2 produced is collected at 722 torr and 17˚C, what volume will the gas occupy?

30

STP Conditions

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

31

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?

32

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 temperature.
  - Nonideal gas behavior can be explained using 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.

33

Postulates of the Model

- Gases are made up of large collections of particles, which are in constant, random motion.
- Gas particles are infinitely small and occupy negligible volume.
- Gas particles move in straight lines except when they collide with other particles or with the container walls. These collisions are elastic, so kinetic energy of particles is conserved.
- Particles interact with each other only when collisions occur.

34

Postulates of the Model

- The average kinetic energy of a gas is proportional to the absolute temperature of the gas but does not depend upon the identity of the gas

$$\mathrm{KE}_{\mathrm{avg}} = \frac{1}{2} m \upsilon_{\mathrm{rms}}^2$$

  - As temperature increases, average speed for gas molecules increases.
  - Faster moving molecules collide more often and with greater force, exerting a higher pressure.

35

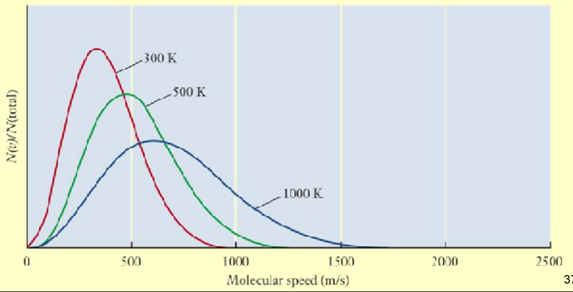
Postulates of the Model

- 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.

36

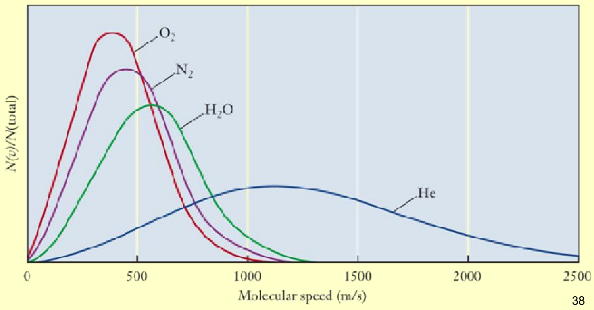
Postulates of the Model

- As temperature increases, <u>average</u> speed increases.
  - As temperature increases, the <u>fraction</u> of molecules moving at higher speeds increases.



Postulates of the Model

- For a fixed temperature, as the molecular weight increases, the average speed for the gas molecules decreases.



Postulates of the Model

- The equation for the Maxwell-Boltzmann distribution describes *N(υ)*, which is the number of molecules moving with speeds close to *υ*.

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

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

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

Postulates of the Model

- The Maxwell-Boltzmann distribution can be described in terms of the average speed or root-mean-square speed.
  - Average speed, υ_{avg}, is 1.128 times υ_{mp}.
    - The existence of the "tail" on the distribution curve at high speeds will pull the average to a speed higher than the most probable value.
  - υ_{rms} = 1.085 times υ_{avg}.
    - The root-mean-square speed is useful because the average kinetic energy is given by $\text{KE}_{\text{avg}} = \frac{1}{2}m\upsilon_{\text{rms}}^2$

Real Gases and Limitations of the Kinetic Theory

- Kinetic molecular theory implies that the volume of a gas molecule is insignificant compared to the "empty space" volume for a gas sample.
  - Mean free path used to test validity of assumption.
    - Average distance a particle travels between collisions with other particles.
    - The mean free path for air at room temperature and atmospheric pressure is 70 nm.
      - This value is 200 times larger than the typical radius of a small molecule like N_2 or O_2.
    - Volume of empty space in a gas is 1 million times that of gas particle volume.

Real Gases and Limitations of the Kinetic Theory

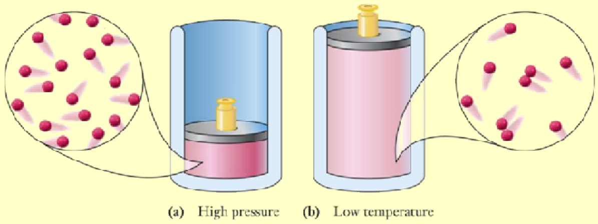
- The volume of a gas particle is significant compared to the "empty space" volume under high pressure conditions.
  - Mean free path decreases as pressure increases.
  - Gas molecules are very close together.
  - Therefore, volume of the gas particles becomes significant.

Real Gases and Limitations of the Kinetic Theory

- Kinetic molecular theory asserts that gas molecules move in straight lines and interact only through perfectly elastic collisions.
  - Gas molecules neither attract nor repel.
  - Strength of attractive forces small compared to kinetic energy of gas molecules.
- Attractive and repulsive forces are significant under conditions of low temperature.
  - Kinetic energy decreases with temperature.
  - Gas molecules experience “sticky” collisions.
  - Collision rate decreases, decreasing the pressure.

43

Real Gases and Limitations of the Kinetic Theory



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

44

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.

45

Correcting the Ideal Gas Equation

Table 5.2

Van der Waals constants for several common gases

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.

46

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?

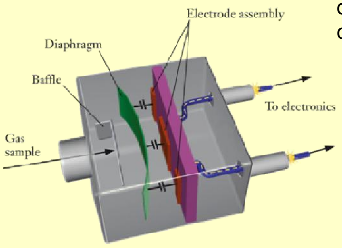
47

Gas Sensors

- The concentration of air pollutants is monitored by the EPA.
  - The concentration of a gas is proportional to the partial pressure of the gas.
- Gas pressure sensors are used to monitor changes in partial pressure or concentration of gases.

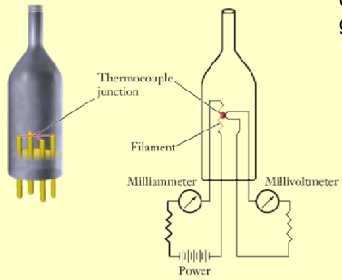
48

Capacitance Manometer



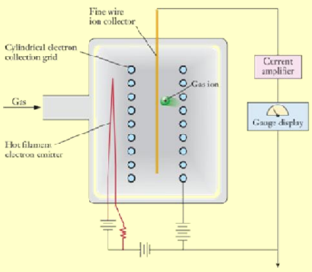
- Changes in pressure cause deflections in the diaphragm, changing the capacitance.
- Used to measure pressures from 0.001 - 1000 torr

Thermocouple Gauge



- Measures pressure by the cooling effect of colliding gas molecules.
- Higher pressure, more collisions with heated filament, lowers filament temperature.
- Used to measure pressures from 0.01 to 1.0 torr

Ionization Gauge



- Pressure measured by producing gaseous caions with the electrons emitted from a hot filament.
- Higher pressure, more gas cations, more current collected at the grid.
- Used to measure pressures as low as 10^{-11} torr.

Gas Sensors

- A thermocouple gauge, a capacitance manometer, and an ionization gauge.

Mass Spectrometers

- Mass spectrometers can be used to measure partial pressures for gas mixtures.
  - Mass spectrometers ionize gas like an ionization gauge, but can select the mass of the gas being analyzed with the use of a magnetic field.
  - Several masses can be scanned simultaneously allowing for multiple gas analyses.
  - Current generated can be used to determine the partial pressure of gas.