CHAPTER 12
GASES AND KINETIC-MOLECULAR THEORY

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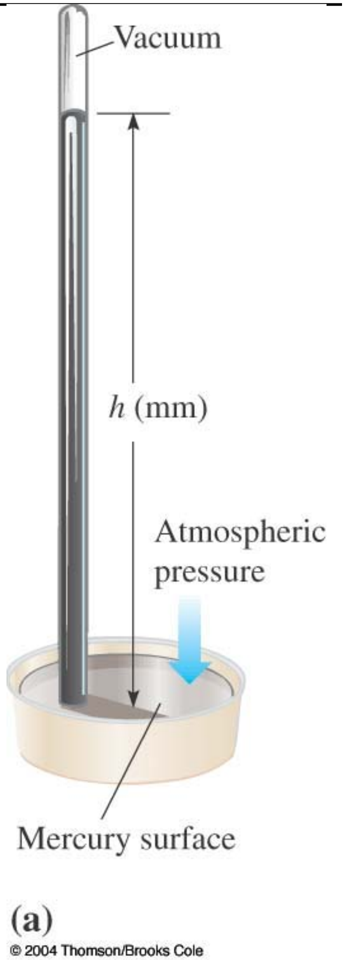
Pressure

- Pressure is force per unit area.
  - lb/in^2
  - N/m^2
- Gas pressure as most people think of it.
- Atmospheric pressure is measured using a barometer.
- Definitions of standard pressure
  - 76 cm Hg
  - 760 mm Hg
  - 760 torr
  - 1 atmosphere
  - 101.3 kPa



Hg density = 13.6 g/mL

Boyle's Law: The Volume-Pressure Relationship

- $V \propto 1/P$ or
- $V = k\,(1/P)$ or $PV = k$
- $P_1V_1 = k_1$ for one sample of a gas.
- $P_2V_2 = k_2$ for a second sample of a gas.
- $k_1 = k_2$ for the same sample of a gas at the same T.
- Thus we can write Boyle's Law mathematically as $P_1V_1 = P_2V_2$

Boyle's Law:
The Volume-Pressure Relationship

- At 25^{o}C a sample of He has a volume of 4.00 x 10^2 mL under a pressure of 7.60 x 10^2 torr. What volume would it occupy under a pressure of 2.00 atm at the same T?

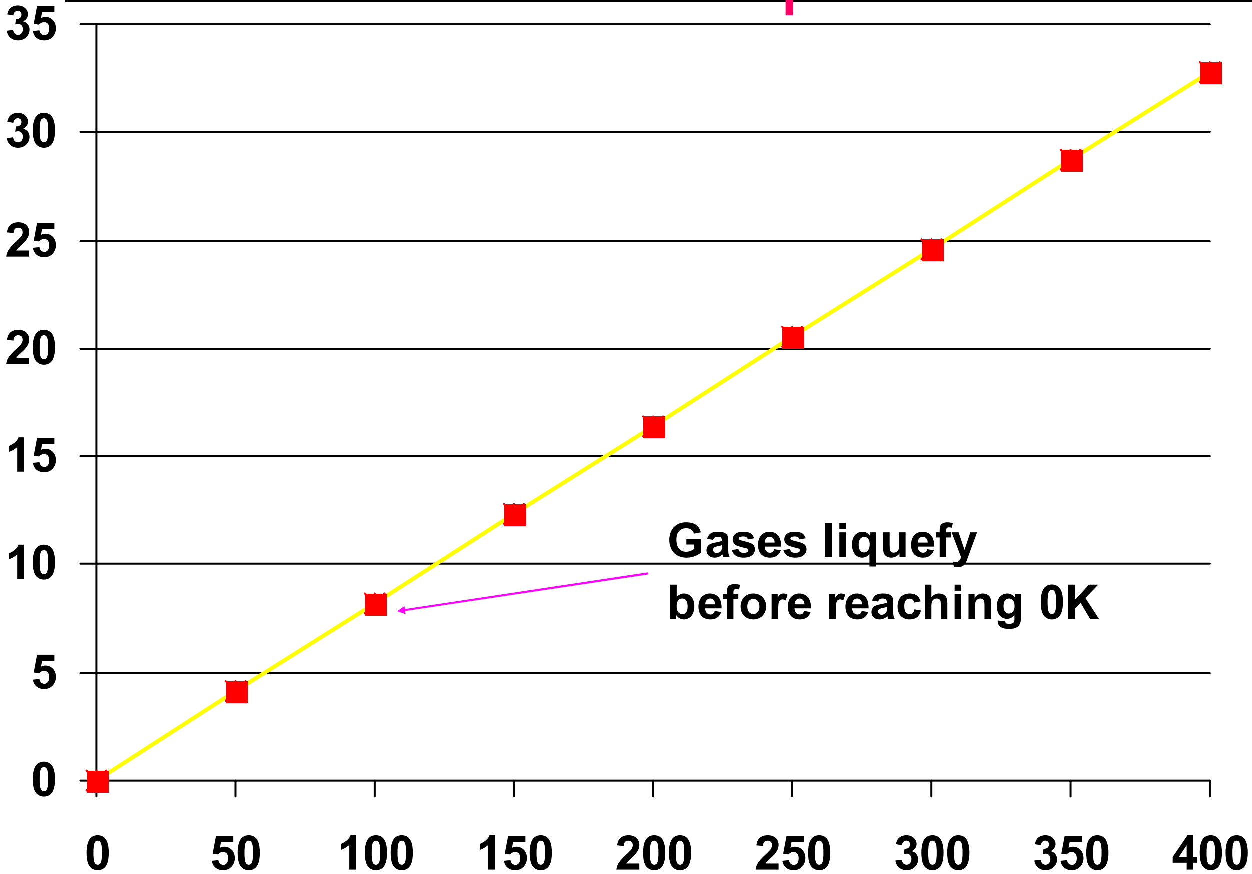
$$P_1 V_1 = P_2 V_2$$

$$V_2 = \frac{P_1 V_1}{P_2}$$

$$= \frac{(760 \text{ torr})(400 \text{ mL})}{1520 \text{ torr}}$$

$$= 2.00 \times 10^2 \text{ mL}$$

Charles' Law:
The Volume-Temperature Relationship;
The Absolute Temperature Scale



Volume (L)
vs.
Temperature (K)

absolute zero = -273.15 ^{0}C

Charles' Law: The Volume-Temperature Relationship; The Absolute Temperature Scale

- Charles's law states that the volume of a gas is directly proportional to the absolute temperature at constant pressure.
  - Gas laws must use the Kelvin scale to be correct.
- Relationship between Kelvin and centigrade.

$$K = {}^{o}C + 273$$

Charles' Law:
The Volume-Temperature Relationship; The Absolute Temperature Scale

- Mathematical form of Charles' law.

$$V \propto T \quad \text{or} \quad V = kT \quad \text{or} \quad \frac{V}{T} = k$$

$$\frac{V_1}{T_1} = k \quad \text{and} \quad \frac{V_2}{T_2} = k \text{ however the k's are equal so}$$

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \text{ in the most useful form}$$

Charles' Law: The Volume-Temperature Relationship; The Absolute Temperature Scale

- A sample of hydrogen, H_2, occupies 1.00×10^2 mL at 25.0°C and 1.00 atm. What volume would it occupy at 50.0°C under the same pressure?

$$T_1 = 25 + 273 = 298$$
$$T_2 = 50 + 273 = 323$$

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

$$V_2 = \frac{1.00 \times 10^2 \text{ mL} \times 323 \text{ K}}{298 \text{ K}}$$
$$= 108 \text{ mL}$$

Standard Temperature and Pressure

- Standard temperature and pressure is given the symbol STP.

- Standard P $\equiv$ 1.00000 atm or 101.3 kPa
- Standard T $\equiv$ 273.15 K or 0.00^{o}C

The Combined Gas Law Equation

- Boyle's and Charles' Laws combined into one statement is called the combined gas law equation.
  - Useful when the V, T, and P of a gas are changing.

Boyle's Law

$$P_1 V_1 = P_2 V_2$$

Charles' Law

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

For a given sample of gas:

$$\frac{P\,V}{T} = k$$

The combined gas law is:

$$\frac{P_1\,V_1}{T_1} = \frac{P_2\,V_2}{T_2}$$

The Combined Gas Law Equation

- A sample of nitrogen gas, N_2, occupies 7.50 x 10^2 mL at 75.0^{0}C under a pressure of 8.10 x 10^2 torr. What volume would it occupy at STP?

$$V_1 = 750 \text{ mL} \qquad V_2 = ?$$

$$T_1 = 348 \text{ K} \qquad T_2 = 273 \text{ K}$$

$$P_1 = 810 \text{ torr} \qquad P_2 = 760 \text{ torr}$$

$$\text{Solve for } V_2 = \frac{P_1 V_1 T_2}{P_2 T_1}$$

$$= \frac{(810 \text{ torr})(750 \text{ mL})(273 \text{ K})}{(760 \text{ torr})(348 \text{ K})}$$

$$= 627 \text{ mL}$$

The Combined Gas Law Equation

- A sample of methane, CH_4, occupies 2.60 x 10^2 mL at 32°C under a pressure of 0.500 atm. At what temperature would it occupy 5.00 x 10^2 mL under a pressure of 1.20 x 10^3 torr?

$$V_1 = 260 \text{ mL} \qquad V_2 = 500 \text{ mL}$$

$$P_1 = 0.500 \text{ atm} \qquad P_2 = 1200 \text{ torr}$$

$$= 380 \text{ torr}$$

$$T_1 = 305 \text{ K} \qquad T_2 = ?$$

$$T_2 = \frac{T_1 P_2 V_2}{P_1 V_1} = \frac{(305 \text{ K})(1200 \text{ torr})(500 \text{ mL})}{(380 \text{ torr})(260 \text{ mL})}$$

$$= 1852 \text{ K} \approx 1580 \ {}^{\circ}\text{C}$$

Avogadro's Law and the Standard Molar Volume

- Avogadro's Law states that at the same temperature and pressure, equal volumes of two gases contain the same number of molecules (or moles) of gas.
- If we set the temperature and pressure for any gas to be STP, then one mole of that gas has a volume called the **standard molar volume**.
- The standard molar volume is 22.4 L at STP.
  - This is another way to measure moles.
  - For ***gases***, the volume is proportional to the number of moles.

Summary of Gas Laws: The Ideal Gas Law

- Boyle's Law - $V \propto 1/P$ (at constant T & n)
- Charles' Law – $V \propto T$ (at constant P & n)
- Avogadro's Law – $V \propto n$ (at constant T & P)
- Combine these three laws into one statement

$$V \propto nT/P$$

- Convert the proportionality into an equality.

$$V = nRT/P$$

- This provides the Ideal Gas Law.

$$\mathbf{PV = nRT}$$

- R is a proportionality constant called the universal gas constant.

Summary of Gas Laws: The Ideal Gas Law

- We must determine the value of R.
  - Recognize that for one mole of a gas at 1.00 atm, and 273 K (STP), the volume is 22.4 L.
  - Use these values in the ideal gas law.

$$R = \frac{PV}{nT} = \frac{(1.00\ \text{atm})(22.4\ \text{L})}{(1.00\ \text{mol})(273\ \text{K})}$$

$$= 0.0821 \frac{\text{L atm}}{\text{mol K}}$$

Summary of Gas Laws: The Ideal Gas Law

- R has other values if the units are changed.
- $R = 8.314$ J/mol K
  - Use this value in thermodynamics.
- $R = 8.314$ kg m^2/s^2 K mol
  - Use this later in this chapter for gas velocities.
- $R = 8.314$ dm^3 kPa/K mol
  - This is R in all metric units.
- $R = 1.987$ cal/K mol
  - This the value of R in calories rather than J.

Summary of Gas Laws: The Ideal Gas Law

- What volume would 50.0 g of ethane, C_2H_6, occupy at 1.40×10^2 ^oC under a pressure of 1.82×10^3 torr?

1. T = 140 + 273 = 413 K
2. P = 1820 torr (1 atm/760 torr) = 2.39 atm
3. 50 g (1 mol/30 g) = 1.67 mol

$$V = \frac{n\,R\,T}{P}$$

$$= \frac{(1.67\,\text{mol})\left(0.0821\frac{\text{L atm}}{\text{mol K}}\right)(413\,\text{K})}{2.39\,\text{atm}}$$

$$= 23.6\,\text{L}$$

Summary of Gas Laws: The Ideal Gas Law

- Calculate the number of moles in, and the mass of, an 8.96 L sample of methane, CH_4, measured at standard conditions.

$$n = \frac{PV}{RT} = \frac{(1.00\ \text{atm})(8.96\ \text{L})}{\left(0.0821\frac{\text{L atm}}{\text{mol K}}\right)(273\ \text{K})} = 0.400\ \text{mol CH}_4$$

$$?\ \text{g CH}_4 = 0.400\ \text{mol} \times \frac{16.0\ \text{g}}{\text{mol}} = 6.40\ \text{g}$$

Summary of Gas Laws: The Ideal Gas Law

- Calculate the pressure exerted by 50.0 g of ethane, C_2H_6, in a 25.0 L container at 25.0°C.

$$n = 1.67 \text{ mol and } T = 298 \text{ K}$$

$$P = \frac{nRT}{V}$$

$$P = \frac{(1.67 \text{ mol})\left(0.0821 \frac{\text{L atm}}{\text{mol K}}\right)(298 \text{ K})}{25.0 \text{ L}}$$

$$P = 1.63 \text{ atm}$$

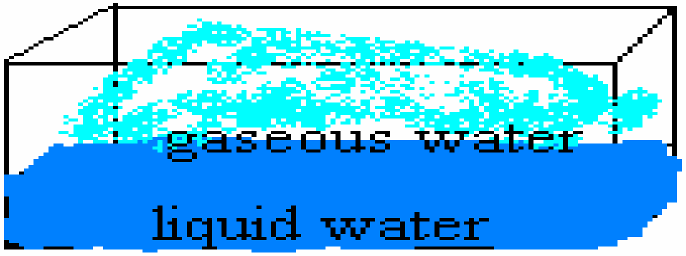
Dalton's Law of Partial Pressures

- Dalton's law states that the pressure exerted by a mixture of gases is the sum of the partial pressures of the individual gases.

$$P_{total} = P_A + P_B + P_C + \ldots..$$

Dalton’s Law of Partial Pressures

- Vapor Pressure is the pressure exerted by a substance’s vapor over the substance’s liquid at equilibrium.



The Kinetic-Molecular Theory

- The basic assumptions of kinetic-molecular theory are:
- Postulate 1
  - Gases consist of discrete molecules that are relatively far apart.
  - Gases have few intermolecular attractions.
  - The volume of individual molecules is very small compared to the gas's volume.
- Proof - Gases are easily compressible.

The Kinetic-Molecular Theory

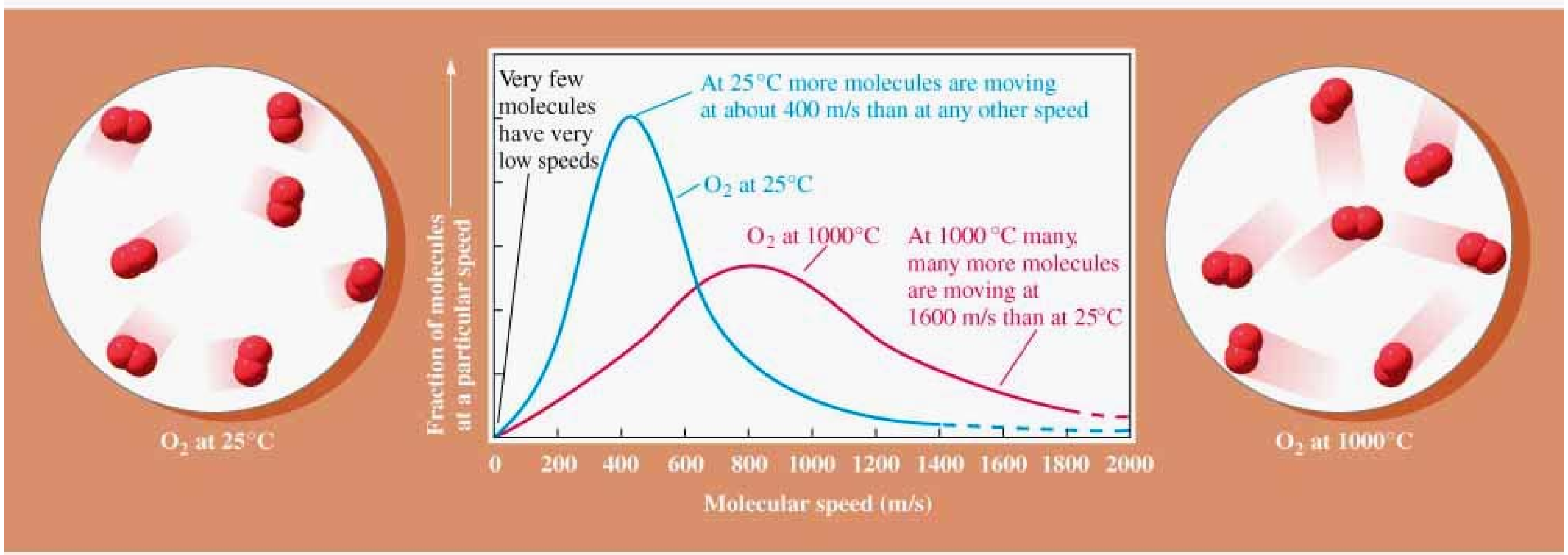
- Postulate 2
  - Gas molecules are in constant, random, straight line motion with varying velocities.
- Proof - Brownian motion displays molecular motion.
- Postulate 3
  - Gas molecules have elastic collisions with themselves and the container.
  - Total energy is conserved during a collision.
- Proof - A sealed, confined gas exhibits no pressure drop over time.

The Kinetic-Molecular Theory

- Postulate 4
  - The kinetic energy of the molecules is proportional to the absolute temperature.
  - The average kinetic energies of molecules of different gases are equal at a given temperature.
- Proof - Brownian motion increases as temperature increases.

The Kinetic-Molecular Theory

- The kinetic energy of the molecules is proportional to the absolute temperature. The kinetic energy of the molecules is proportional to the absolute temperature.
  - Displayed in a Maxwellian distribution.

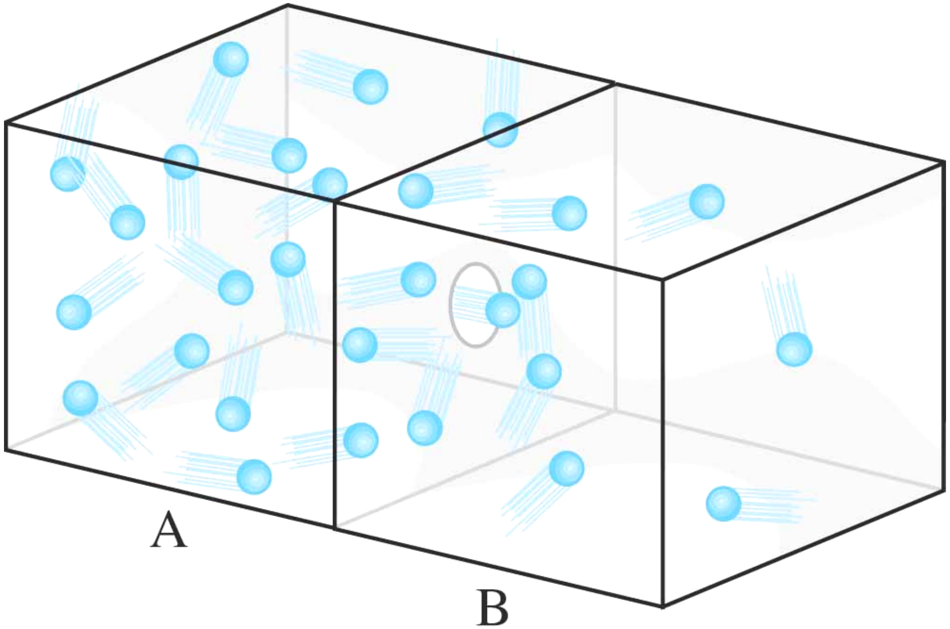


The Kinetic-Molecular Theory

- Boyle's Law
  - $P \propto 1/V$
  - As the V increases the molecular collisions with container walls decrease and the P decreases.
- Dalton's Law
  - $P_{total} = P_A + P_B + P_C + ...$
  - Because gases have few intermolecular attractions, their pressures are independent of other gases in the container.
- Charles' Law
  - $V \propto T$
  - An increase in temperature raises the molecular velocities, thus the V increases to keep the P constant.

Diffusion and Effusion of Gases

- Diffusion is the intermingling of gases.
- Effusion is the escape of gases through tiny holes.



Diffusion and Effusion of Gases

- The rate of effusion is inversely proportional to the square roots of the molecular weights or densities.

$$\frac{R_1}{R_2} = \sqrt{\frac{M_2}{M_1}}$$

or

$$\frac{R_1}{R_2} = \sqrt{\frac{D_2}{D_1}}$$

Real Gases: Deviations from Ideality

- Real gases behave ideally at ordinary temperatures and pressures.
- At low temperatures and high pressures real gases do not behave ideally.
- The reasons for the deviations from ideality are:
  1. The molecules are very close to one another, thus their volume is important.
  2. The molecular interactions also become important.

Real Gases:
Deviations from Ideality

- van der Waals' equation accounts for the behavior of real gases at low T and high P.

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

- The van der Waals constants a and b take into account two things:
  1. a accounts for intermolecular attraction
  2. b accounts for volume of gas molecules

Chemistry is fun!