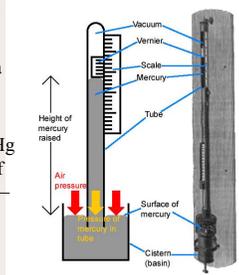


## Pressure

- Pressure is defined as force per unit area.
- Pressure is measured with a device called a barometer.
- A mercury barometer uses the weight of a column of Hg to determine the pressure of gas pushing on a reservoir—atmospheric pressure corresponds to a column height of 760 mm.



## Pressure Units

- Pressure may be measured in a number of different units:
  - atmosphere (atm): barometric pressure at sea level
  - Torr: mm of Hg—comes from use of Hg barometers
  - psi: pounds per square inch
  - Pascal (Pa): official SI units for pressure—1 pascal =  $1 \text{ N m}^{-2}$

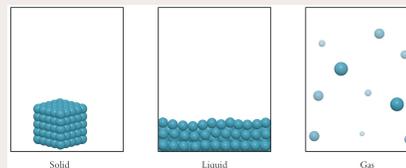
## Pressure Units

Pressure conversion factors:

- 760 Torr = 1 atm
- 760 mm Hg = 1 atm
- 14.7 psi = 1 atm
- 101,325 Pa = 1 atm

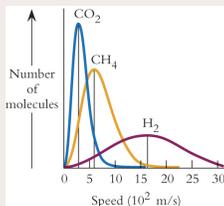
## Behavior of Gases

- Gas-phase molecules and atoms are free to move about their container—they fill the entire volume of the container unlike a liquid or a solid.



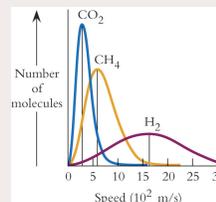
## Molecular Speed and Energy

- Gas molecules travel at a range of speeds—some molecules move much faster than others.
- The average speed of a gas depends on its molar mass—the lighter the mass, the faster the average speed.



## Molecular Speed and Energy

- Average speed can be defined several ways for molecules:
- The most probable speed corresponds to the speed at the maximum in a plot of molecules vs speed—if we could measure the speed of individual gas molecules, more of them would have this value than any other value.



## Molecular Speed and Energy

Kinetic energy is given by

$$E_T = \frac{1}{2}mu^2$$

m = mass      u = velocity (speed)

$$m_{H_2} = (2.0158 \text{ g mol}^{-1}) / (6.022 \times 10^{23} \text{ H}_2 \text{ mol}^{-1}) \\ = 3.347 \times 10^{-24} \text{ g} = 3.347 \times 10^{-27} \text{ kg}$$

$$u_{mp} = 1.57 \times 10^3 \text{ m s}^{-1}$$

$$E_T = \frac{1}{2}(3.347 \times 10^{-27} \text{ kg})(1.57 \times 10^3 \text{ m s}^{-1})^2 \\ = 4.13 \times 10^{-21} \text{ kg m}^2 \text{ s}^{-2} = 4.13 \times 10^{-21} \text{ J}$$

## Molecular Speed and Energy

$$u_{mp}(\text{CH}_4) = 557 \text{ m s}^{-1}$$

$$E_T(\text{CH}_4) = \frac{1}{2}(2.664 \times 10^{-26} \text{ kg})(557 \text{ m s}^{-1})^2 \\ = 4.13 \times 10^{-21} \text{ J}$$

$$u_{mp}(\text{CO}_2) = 337 \text{ m s}^{-1}$$

$$E_T(\text{CO}_2) = \frac{1}{2}(7.308 \times 10^{-26} \text{ kg})(337 \text{ m s}^{-1})^2 \\ = 4.15 \times 10^{-21} \text{ J}$$

- Even though the three gases ( $\text{H}_2$ ,  $\text{CH}_4$ , and  $\text{CO}_2$ ) have different speeds, they all possess the same amount of kinetic energy.

## Molecular Speed and Energy

- The average kinetic energy of a gas is determined by its temperature:

$$E_T(T) = \frac{3}{2} RT/N_A$$

R is the *gas constant*

$$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1} = .08206 \text{ L atm mol}^{-1} \text{ K}^{-1}$$

- The kinetic energy of the gas depends only on its temperature, not the identity of the gas.

## Molecular Speed and Energy

- We can equate the two expressions for kinetic energy:

$$E_{T,avg} = \frac{1}{2} m u_{avg}^2 = \frac{3}{2} RT/N_A$$

$$\frac{1}{2} u_{avg}^2 = \frac{3}{2} RT/mN_A$$

$$u_{avg}^2 = 3 RT/mN_A$$

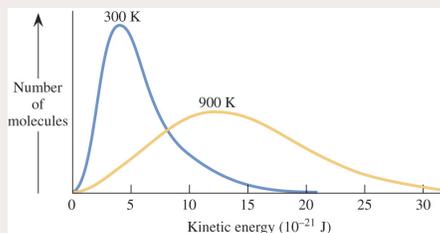
$$u_{avg} = [3 RT/mN_A]^{1/2}$$

$$mN_A = M \text{ (molecular weight)}$$

$$u_{avg} = [3 RT/M]^{1/2} \quad \text{root-mean-square speed}$$

## Molecular Speed and Energy

- The average speed of a gas increases with increasing temperature:



## Molecular Speed and Energy

The average speed of a gas is important because it determines a number of properties of a gas:

- pressure exerted by a gas—pressure depends on the rate of collision with the walls of a vessel and the force of those collisions.
- collision rate—how frequently gas molecules collide, and for reactive collisions, have the opportunity to undergo reaction.
- rate of diffusion—how fast one gas mixes with another

## Ideal Gases

An *Ideal Gas* has two unique properties that distinguish it from real gases

1. An ideal gas particle has no volume—it is simply a point moving through space.
2. An ideal gas has no intermolecular attractive forces—collisions with other ideal gas molecules or the walls of a container are perfectly elastic—no energy is lost in collisions.

## Ideal Gas Equation

- The properties of an ideal gas lead to an equation that relates the temperature, pressure, and volume of the gas:

$$PV = nRT \quad (\text{pivnert})$$

P = pressure (atm)

V = volume (L)

n = number of moles of gas

T = temperature (K)

R = 0.08206 L atm mol<sup>-1</sup> K<sup>-1</sup>

## Ideal Gas Equation

What volume would 2.00 mol of an ideal gas with a pressure of 1000 Torr and a temperature of -25.0 °C occupy?

$$(1000 \text{ Torr}) (1 \text{ atm}/760 \text{ Torr}) = 1.32 \text{ atm}$$

$$-25.0 \text{ }^\circ\text{C} + 273.2 \text{ }^\circ\text{C} = 248.2 \text{ K}$$

$$V = nRT/P$$

$$= \frac{(2.00 \text{ mol})(0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1})(248.2 \text{ K})}{(1.32 \text{ atm})}$$

$$V = 30.9 \text{ L}$$

## Variations of the Ideal Gas Law

- If the system is closed (no input or removal of gas from the container), the number of moles of gas cannot change—n is fixed.
- At constant temperature:

$$nRT = \text{a constant}$$

$$\therefore P_1V_1 = P_2V_2 \quad \text{Boyle's Law}$$

If the pressure [volume] is increased, the volume [pressure] will decrease.

If the pressure [volume] is decreased, the volume [pressure] will increase.

## Variations of the Ideal Gas Law

- At constant volume:

$$nR/V = \text{a constant}$$

$$\therefore P_1/T_1 = P_2/T_2$$

If the pressure [temperature] is increased, the temperature [pressure] will increase.

If the pressure [temperature] is decreased, the temperature [pressure] will decrease.

## Variations of the Ideal Gas Law

- At constant pressure:

$$nR/P = \text{a constant}$$

$$\therefore V_1/T_1 = V_2/T_2 \quad \text{Charles' Law}$$

If the volume [temperature] is increased, the temperature [volume] will increase.

If the volume [temperature] is decreased, the temperature [volume] will decrease.

## Variations of the Ideal Gas Law

- At constant temperature and pressure:

$$V/n = \text{a constant}$$

$$\therefore V_1/n_1 = V_2/n_2 \quad \text{Avagadro's Law}$$

If the volume of a gas at constant T and P is increased, the amount of gas must increase.

If the volume of a gas at constant T and P is decreased, the amount of gas must decrease.

## Variations of the Ideal Gas Law

Determination of molar mass:

$$n = m/M \quad M = \text{molecular weight}$$

Substituting into the Ideal Gas Law:

$$PV = mRT/M$$

Rearranging gives:

$$M = mRT/PV$$

## Determination of Molecular Weight

A sample of hydrocarbon with  $m = 1.65 \text{ g}$  exerts a pressure of  $1.50 \text{ atm}$  in a  $945 \text{ mL}$  container at  $21.5 \text{ }^\circ\text{C}$ . What is the chemical formula of the hydrocarbon?

$$T = 21.5 \text{ }^\circ\text{C} + 273.2 \text{ }^\circ\text{C} = 294.7 \text{ K}$$

$$M = \frac{(1.65 \text{ g}) (.0821 \text{ L atm mol}^{-1} \text{ K}^{-1}) (294.7 \text{ K})}{(1.50 \text{ atm}) (.945 \text{ L})}$$

$$= 28.1 \text{ g mol}^{-1}$$

formula:  $\text{C}_2\text{H}_4$  (ethylene— $M = 28.1 \text{ g mol}^{-1}$ )

## Dalton's Law of Partial Pressures

- When a container is filled with a mixture of gases, Dalton hypothesized that each individual gas behaved as if it were in a vacuum, *i.e.*, there is no interaction between different types of gas molecules that would affect the resulting pressure within the container.
- Each gas in the mixture exerts a pressure equal to the pressure it would exert if no other gases were in the container
- Partial pressure* is the pressure exerted by a gas in a mixture as if it were in a vacuum.

## Dalton's Law of Partial Pressures

- The total pressure of a gas mixture is given by:

$$P_{\text{tot}} = n_{\text{tot}}RT/V$$

$n_{\text{tot}}$  = total number of moles of all gases in container

Also

$$P_{\text{tot}} = P_A + P_B + P_C + \dots$$

Dalton's Law of Partial Pressures

$$P_A = n_A RT/V \quad \text{partial pressure of A}$$

$$P_B = n_B RT/V \quad \text{partial pressure of B}$$

$$P_C = n_C RT/V \quad \text{partial pressure of C}$$

## Partial Pressure and Mole Fraction

- The mole fraction of a mixture component is defined as the number of moles of that component divided by the total number of moles:

$$X_A = n_A/n_{\text{tot}}$$

- For a gas mixture:

$$\frac{P_A}{P_{\text{tot}}} = \frac{\frac{n_A RT}{V}}{\frac{n_{\text{tot}} RT}{V}} = \frac{n_A}{n_{\text{tot}}} = X_A$$

## Real Gases vs Ideal Gases

- We made the following assumptions in defining an ideal gas:
  - no volume—gas behaves as a point
  - perfectly elastic collisions
- Real gases do not follow these rules—they occupy a volume of space, and there are intermolecular forces attracting colliding gas molecules

## The van der Waals' Equation

- To better describe real gases, we can use a different equation of state to predict their behavior:

$$P = \frac{nRT}{V - nb} - \frac{a n^2}{V^2} \quad \text{Van der Waals' Equation}$$

where a and b are measured constants

The vdw b constant is a measure of the volume of the gas molecules

The vdw a constant is a measure of the internuclear attractive forces

## The van der Waals' Equation

Example: Compare the pressure of oxygen determined by the ideal gas law and the van der Waals' equation under the following conditions:

$$n = 25.0 \text{ mol} \quad T = 375 \text{ K} \quad V = 20.0 \text{ L}$$

$$a(\text{O}_2) = 1.36 \text{ L}^2\text{atm mol}^{-2} \quad b(\text{O}_2) = .0318 \text{ L mol}^{-1}$$

Ideal gas:  $P = 38.5 \text{ atm}$

Van der Waals':  $P = 29.7 \text{ atm}$

## Real Gases vs Ideal Gases

- Gases tend to behave ideally under low pressure conditions
  - The time between collisions is much longer so there is less relative time for attractive forces to affect pressure (minimizes effect of a constant)
  - The volume occupied by the gas molecules is much smaller than the total volume of the container (minimizes effect of b constant)