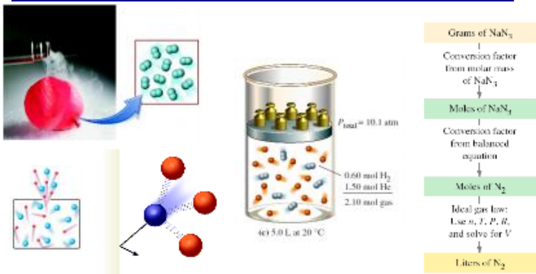
Chapter Five

Gases

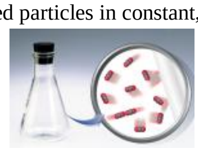


5.1 Gases: What Are They Like:

Gases: What Are They Like?

Composed of widely separated particles in constant, random motion.

Flow readily and occupy the entire volume of their container



Vapor is the term used to denote the gaseous state of a substance existing more commonly as a liquid e.g., **water is a vapor**, **oxygen is a gas**

Many low molar mass molecular compounds are gases – methane (CH_4), carbon monoxide (CO)

EOS

Table 5.1 Some Common Gases[a]

Substance	Formula	Typical Use(s)
Acetylene	C_2H_2	Fuel for welding metals
Ammonia	NH_3	Fertilizer, manufacture of plastics
Argon	Ar	Filling gas for specialized lightbulbs
Butane	C_4H_{10}	Fuel for heating (LPG)
Carbon dioxide	CO_2	Beverage carbonation
Carbon monoxide	CO	Reducing agent in metallurgy
Chlorine	Cl_2	Disinfectant, bleach
Ethylene	C_2H_4	Manufacture of plastics
Helium	He	Lifting gas for balloons
Hydrogen	H_2	Chemical reagent, fuel for fuel cells
Hydrogen sulfide	H_2S	Chemical reagent
Methane	CH_4	Fuel, manufacture of hydrogen
Nitrogen	N_2	Manufacture of ammonia
Nitrous oxide	N_2O	Anesthetic
Oxygen	O_2	Support of combustion, respiration
Propane	C_3H_8	Fuel for heating (LPG)
Sulfur dioxide	SO_2	Preservative, disinfectant, bleach

[a] All of these substances are gases at room temperature (about 25 °C) and at pressures comparable to atmospheric pressure, but they can be converted to liquids and solids by cooling or an increase in pressure.

5.2 An Introduction to the kinetic-Molecular Theory

An Introduction to Kinetic-Molecular Theory

- Provides a model for gases at the microscopic level.
- Molecules are in rapid, random motion.
- Movement of gases through three-dimensional space is called *translational motion*.

- ***Pressure***: collision of gas molecules with wall of container.
- ***Temperature***: related to average speed of gas molecules.

5.3 Gas Pressure

Gas Pressure

- ***Pressure*** is the force per unit area.
- In SI, force is expressed in *newtons* (*N*) and area in square meters (m^2).
- The unit of pressure in SI is the ***pascal*** (Pa) with the units N/m^2.
- **Kilopascals** (kPa) are often used instead since the pascal is such a small unit.
- The ***atmosphere*** and ***mmHg*** (***Torr***) are the most common scientific units for pressure.
- Converting from one unit to another simply requires the appropriate conversion factor(s).

Table 5.2 The Standard Atmosphere of Pressure in Different Units

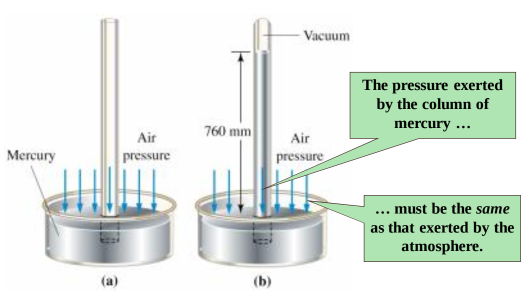
1 atm =	760 mmHg
	760 Torr
	1.01325 bar
	1013.25 mb
	14.696 $lb/in.^2$
	101,325 N/m^2
	101,325 Pa
	101.325 kPa

Barometers

- Used to measure atmospheric pressure.
- One ***atmosphere (atm)***: pressure exerted by a column of mercury exactly 760 mm high.
- One millimeter of mercury is called a **Torr**.

1 atm = 760 mmHg
= 760 Torr
= 101.325 kPa

A Mercury Barometer



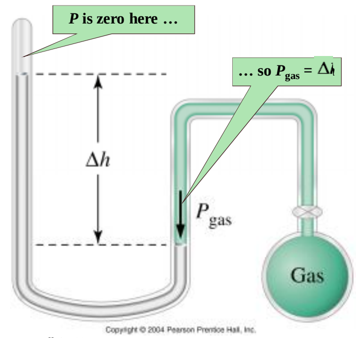
Example 5.1

A Canadian weather report gives the atmospheric pressure as 100.2 kPa. What is the pressure expressed in the unit Torr?

Manometers

- A manometer is used to measure the pressure of a sample of gas.
- Pressure is measured using the ***difference*** in the heights of mercury (or other liquid) in the two arms of the manometer.

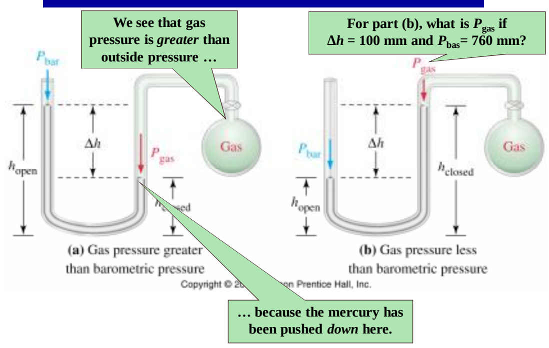
A Closed-End Manometer



- If the liquid is mercury, Δh can be expressed directly in mmHg.
- For other liquids, the pressure exerted by a liquid column is:

$$P = g \cdot d \cdot h$$

An Open-End Manometer



Example 5.2

Calculate the height of a column of water (d = 1.00 g/cm^3) that exerts the same pressure as a column of mercury (d = 13.6 g/cm^3) 760 mm high.

Example 5.3: A Conceptual Example

Without doing calculations, arrange the drawings in Figure 5.5 so that the pressures denoted in red are in increasing order.

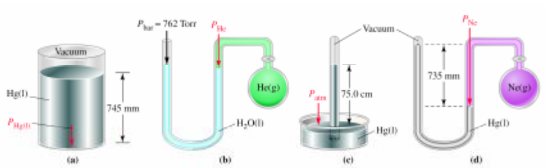


FIGURE 5.5 Example 5.3 illustrated

5.4 Bolye's Law: The Pressure-Volume Relationship

Boyle's Law: Pressure-Volume Relationship

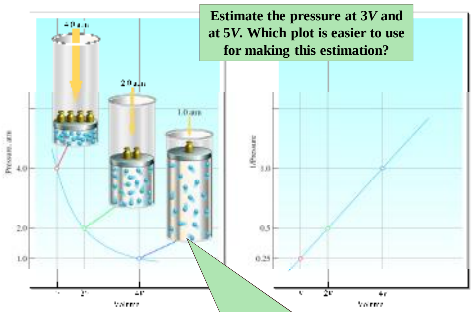
- For a fixed amount of a gas at constant temperature, the volume of the gas varies *inversely* with its pressure.
- For a fixed amount of a gas at constant temperature, the product of pressure and volume is a constant.

$$PV = constant \quad or \quad P_{\text{initial}}V_{\text{initial}} = P_{\text{final}}V_{\text{final}}$$

$$P_1V_1 = P_2V_2$$

Graphical Representation of Boyle's Law

Estimate the pressure at 3*V* and at 5*V*. Which plot is easier to use for making this estimation?



When volume is increased there is more area for the molecules to "hit"; less force *per* area.

Example 5.4

A helium-filled party balloon has a volume of 4.50 L at sea level, where the atmospheric pressure is 748 Torr. Assuming that the temperature remains constant, what will be the volume of the balloon when it is taken to a mountain resort at an altitude of 2500 m, where the atmospheric pressure is 557 Torr?

Example 5.5: An Estimation Example

A gas is enclosed in a cylinder fitted with a piston. The volume of the gas is 2.00 L at 398 Torr. The piston is moved to increase the gas pressure to 5.15 atm. Which of the following is a reasonable value for the volume of the gas at the greater pressure?

0.20 L 0.40 L 1.00 L 16.0 L

5.5 Charles's Law: The Temperature-Volume Relationship

Charles's Law: Temperature-Volume Relationship

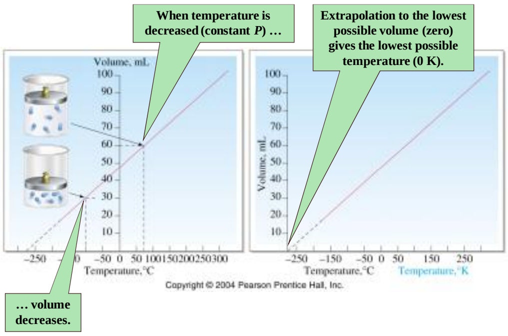
- The volume of a fixed amount of a gas at constant pressure is directly proportional to its ***Kelvin*** (absolute) temperature.
- $V \propto T$ or $V = bT$
- ***Absolute zero(絕對零度)*** is the temperature obtained by extrapolation to zero volume.
- Absolute zero on the Kelvin scale = –273.15 °C

Charles's Law: Temperature-Volume Relationship

- $V \propto T$ or $V = bT$

$$\frac{V_{initial}}{T_{initial}} = \frac{V_{final}}{T_{final}} \quad or \quad \frac{V_1}{T_1} = \frac{V_2}{T_2}$$

Graphical Representation of Charles's Law



Example 5.6

A balloon indoors, where the temperature is 27 ℃, has a volume of 2.00 L. What will its volume be outdoors, where the temperature is –23 ℃? (Assume no change in the gas pressure.)

Example 5.7: An Estimation Example

A sample of nitrogen gas occupies a volume of 2.50 L at –120 ℃ and 1.00 atm pressure. To which of the following approximate temperatures should the gas be heated in order to double its volume while maintaining a constant pressure?

30 ℃ –12 ℃ –60 ℃ –240 ℃

5.6 Avogadro's Law: The Mole-Volume Reationship

Avogadro's Law: Mole-Volume Relationship

- At a fixed temperature and pressure, the volume of a gas is directly proportional to the amount of gas in moles (n) or to the number of molecules of gas.

  $V \propto n \quad \Rightarrow \quad V = cn \quad \Rightarrow \quad V/n = c$
- ***Standard temperature and pressure*** (***STP***) is equal to 0 ℃ and 1 atm.
- The ***molar volume*** of a gas is the volume occupied by one mole of the gas.
- ***At STP***, molar volume of an ideal gas is 22.4 liters.

Example 5.8

Calculate the volume occupied by 4.11 kg of methane gas, $CH_4(g)$, at STP.

5.7 The Combined Gas Law

The Combined Gas Law

$V = \dfrac{a}{P}$ $\qquad V = bT \qquad V = cn$

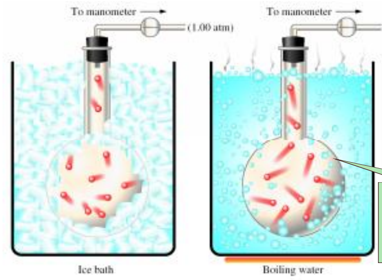
Therefore $\quad V \propto \dfrac{nT}{P}$

We can cancel any term (*P, V, n, T*) that is the same on both sides.

and $\dfrac{PV}{nT}$ = a constant OR $\dfrac{P_1V_1}{n_1T_1} = \dfrac{P_2V_2}{n_2T_2}$

Example 5.9

The flasks pictured in Figure 5.11 contain O_2(g), the one on the left at STP and the one on the right at 100 ˚C. What is the pressure at 100 ˚C?



What pressure would be exerted if the vessel were transferred to an oil bath at 200 ˚C?

5.8 The Ideal Gas Law and Its Applications

The Ideal Gas Law

$\dfrac{PV}{nT}$ = constant = R

***R* = 0.08206 (L·atm)/(mol·K)**
The *ideal gas constant*

$PV = nRT$ ← **The *ideal gas law***

- P in atm, V in L, n in moles, T in kelvins.
- If any other units are used for these variables, a different value for R must be used …

Table 5.3 Units for the Gas Constant, *R*

R has the value	When
0.082058 L atm mol^{-1} K^{-1}	P is in atm
62.364 L Torr mol^{-1} K^{-1}	P is in torr
8.3145 J mol^{-1} K^{-1}	P is in Pa; V is in m^3

Example 5.10

What is the pressure exerted by 0.508 mol O_2 in a 15.0-L container at 303 K?

Example 5.11

What is the volume occupied by 16.0 g ethane gas (C_2H_6) at 720 Torr and 18 ˚C?

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Applications of the Ideal Gas Law: Molecular Mass Determination

Mw = molar mass and m = mass in grams

$$Mw = \frac{m \text{ (grams)}}{n \text{ (moles)}} \quad \text{so} \quad n = \frac{m}{Mw}$$

The ideal gas equation rearranges to: $n = \dfrac{PV}{RT}$

Setting the equations equal to one another: $\dfrac{m}{Mw} = \dfrac{PV}{RT}$

… and solving for M: $\mathbf{Mw = \dfrac{mRT}{PV}}$

Alternative to equation: (A) find *n* using the ideal gas equation; (B) Divide *m* (grams) by *n* (moles) to get grams/mol.

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Example 5.12

If 0.550 g of a gas occupies 0.200 L at 0.968 atm and 289 K, what is the molecular mass of the gas?

Example 5.13

Calculate the molecular mass of a liquid that, when vaporized at 100 ℃ and 755 Torr, yields 185 mL of vapor that has a mass of 0.523 g.

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Applications of the Ideal Gas Law: Gas Densities

- Gases are much less dense than liquids and solids, so gas densities are usually reported in g/L.

$$Mw = \frac{mRT}{PV} \quad \text{rearranges to} \quad \frac{m}{V} = \frac{MwP}{RT}$$

$$\text{and density} = \frac{m}{V} \quad \text{so} \quad \mathbf{d = \frac{MwP}{RT}}$$

Alternative: find volume of one mole (*n* = 1) or other fixed quantity of gas. Divide mass of that quantity by volume to find g/L.

Density of a gas is *directly* proportional to its molar mass and pressure, and is *inversely* proportional to Kelvin temperature.

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Example 5.14

Calculate the density of methane gas, CH_4, in grams per liter at 25 ℃ and 0.978 atm.

Example 5.15

Under what pressure must O_2(g) be maintained at 25 ℃ to have a density of 1.50 g/L?

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5.9 Gases in Reaction Stiochiometry

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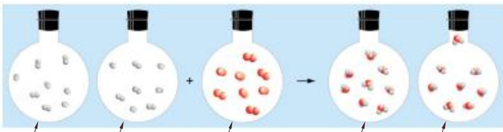
Gases in Reaction Stoichiometry: The Law of Combining Volumes

- *When gases measured at the same temperature and pressure are allowed to react, the volumes of gaseous reactants and products are in small whole-number ratios.*
- Example: At a given temperature and pressure, 2.00 L of H_2 will react with 1.00 L of O_2 (Why 2:1? Balance the equation …)
- Example: At a given temperature and pressure, 6.00 L of H_2 of will react with 2.00 L of N_2 to form 4.00 L of NH_3 (Why 6:2:4? Balance the equation …)
- We don't need to know *actual* conditions for the reaction … as long as the *same* conditions apply to all the gases.

Avogadro's Explanation of Gay-Lussac's Law of Combining Volumes

At a fixed temperature and pressure …



… each of the identical flasks contains the same number of molecules.

Therefore, the ratio of *volumes* is the same as the *mole* ratio from the balanced equation:
$2\ H_2 + O_2 \rightarrow 2\ H_2O$

Example 5.16

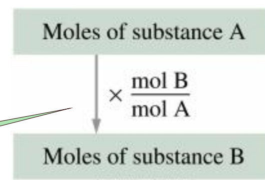
How many liters of O_2(g) are consumed for every 10.0 L of CO_2(g) produced in the combustion of liquid pentane, C_5H_{12}, if all volumes are measured at STP?

The Ideal Gas Equation in Reaction Stoichiometry

- We can use the law of combining volumes for stoichiometry *only* for gases and *only* if the gases are at the same temperature and pressure.
- Otherwise, we must use stoichiometric methods from Chapter 3 – combined with the ideal gas equation.

The Ideal Gas Equation in Reaction Stoichiometry

- As in other stoichiometry calculations, the problem centers around the mole ratio:



Remember this? From Chapter 3, Stoichiometry?

- If ***A*** is a gas, we find moles of ***A*** first by using the ideal gas equation and *P, V,* and *T*.
- If ***B*** is a gas, we solve for moles of ***B*** (*n*), then use the ideal gas equation to find *P, V,* or *T*.

Example 5.17

In the chemical reaction used in automotive air-bag safety systems, N_2(g) is produced by the decomposition of sodium azide, NaN_3(s), at a somewhat elevated temperature:

$$2\ NaN_3(s) \rightarrow 2\ Na(l) + 3\ N_2(g)$$

What volume of N_2(g), measured at 25 °C and 0.980 atm, is produced by the decomposition of 62.5 g NaN_3?

5.10 Mixtures of Gases: Dalton's Law of Partial Pressures

Mixtures of Gases: Dalton's Law of Partial Pressures

- **Dalton's law of partial pressures** is used in dealing with mixtures of gases.
- The total pressure exerted by a mixture of gases is equal to the sum of the ***partial pressures*** exerted by the separate gases:

$$P_{total} = P_1 + P_2 + P_3 + \cdots$$

Partial pressure: the pressure a gas would exert if it were alone in the container.

$$P_1 = \frac{n_1RT}{V} \qquad P_2 = \frac{n_2RT}{V} \qquad P_3 = \frac{n_3RT}{V} \cdots$$

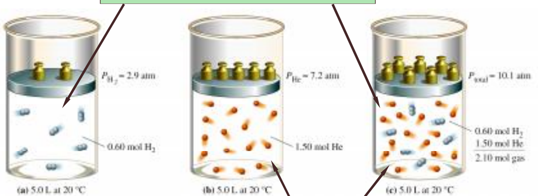
Example 5.18

A 1.00-L sample of dry air at 25 ℃ contains 0.0319 mol N_2, 0.00856 mol O_2, 0.000381 mol Ar, and 0.00002 mol CO_2. Calculate the partial pressure of $N_2(g)$ in the mixture.

Partial Pressures Illustrated

What would be the total pressure if 0.90 mol of N_2 were added to the gas mixture in (c)?

Partial pressure of H_2 is 2.9 atm.



Partial pressure of He is 7.2 atm.

Hmm … partial pressure appears to be related to the number of moles of gas …

Mole Fraction(莫耳分率)

- The ***mole fraction*** (x) of a gas is the fraction of all the molecules in a mixture that are of a given type.

$$x_1 = \frac{n_1}{n_{total}}$$

We can find the partial pressure of a gas from its mole fraction and the total pressure.

- Since pressure (at constant T and V) is directly proportional to number of moles:

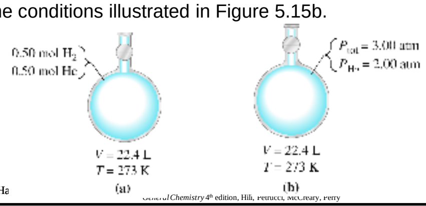
$$x_1 = \frac{P_1}{P_{total}} \quad \text{or} \quad P_1 = x_1 P_{total}$$

Example 5.19

The main components of dry air, by volume, are N_2, 78.08%; O_2, 20.95%; Ar, 0.93%; and CO_2, 0.04%. What is the partial pressure of each gas in a sample of air at 1.000 atm?

Example 5.20: A Conceptual Example

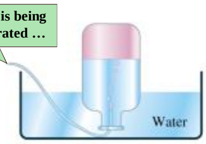
Describe what must be done to change the gaseous mixture of hydrogen and helium shown in Figure 5.15a to the conditions illustrated in Figure 5.15b.



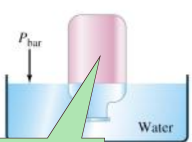
Collection of Gases over Water

- As (essentially insoluble) gas is bubbled into the container for collection, the water is displaced.
- The gas collected is usually saturated with water vapor.

If O_2 is being generated …



Assuming the gas is saturated with water vapor, the partial pressure of the water vapor is the ***vapor pressure*** of the water.



$$P_{gas} = P_{total} - P_{H_2O(g)} = P_{bar} - P_{H_2O(g)}$$

… what TWO gases are present here?

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Example 5.21

Hydrogen produced in the following reaction is collected over water at 23 °C when the barometric pressure is 742 Torr:

$$2\ Al(s) + 6\ HCl(aq) \rightarrow 2\ AlCl_3(aq) + 3\ H_2(g)$$

What volume of the "wet" gas will be collected in the reaction of 1.50 g Al(s) with excess HCl(aq)?

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5.11 The Kinetic-Molecular Theory: Some Quantitative Aspects

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The Kinetic-Molecular Theory: Some Quantitative Aspects

The principal assumptions of kinetic-molecular theory are:

– A gas is made up of molecules that are in constant, random, straight-line motion.
– Molecules of a gas are far apart; a gas is mostly empty space.
– There are no forces between molecules except during the instant of collision.
– Individual molecules may gain or lose energy as a result of collisions; however, the *total energy remains constant*.

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The Kinetic-Molecular Theory: Some Quantitative Aspects (2)

Using the assumptions of kinetic-molecular theory, we can show that:

$$P = \frac{1}{3} \cdot \frac{N}{V} \cdot m \cdot \overline{u^2}$$

where

P = pressure
N = number of molecules
V = volume
m = mass of each molecule
u^2 = average of the squares of the speeds of the molecules.

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The Kinetic-Molecular Theory and Temperature

From the previous equation we can derive the following:

$$\boldsymbol{e_k = \frac{3}{2} \cdot \frac{R}{N_A} \cdot T}$$

where

R = ideal gas constant (a constant)
N_A = Avogadro's number (a constant), therefore:

$$\boldsymbol{e_k = (\text{constant}) \cdot T}$$

The average translational kinetic energy of the molecules of a gas is directly proportional to the Kelvin temperature.

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Molecular Speeds

- Gas molecules do not all move at the same speed, they have a wide distribution of speeds.
- The root-mean-square speed, u_{rms}, is the square root of the average of the squares of the molecular speeds.

$$u_{rms} = \sqrt{\overline{u^2}} = \sqrt{\frac{3RT}{M}}$$

- Typical speeds are quite high, on the order of 1000 m/s.
- At a fixed temperature, molecules of higher mass (M) move *more slowly* than molecules of lower mass.

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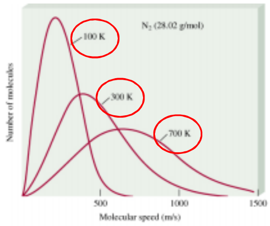
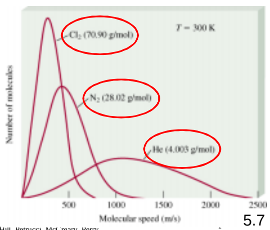


The distribution of speeds for nitrogen gas molecules at three different temperatures

$$u_{rms} = \sqrt{\frac{3RT}{\mathcal{M}}}$$

The distribution of speeds of three different gases at the same temperature



Example 5.22: A Conceptual Example

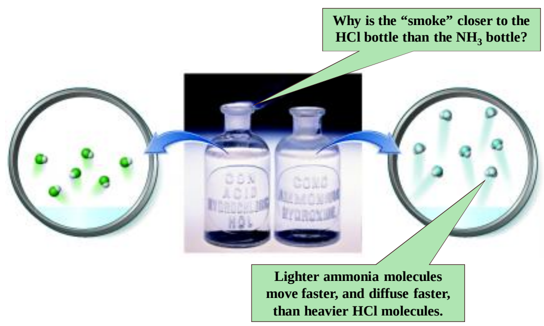
Without doing detailed calculations, determine which of the following is a likely value for u_{rms} of O_2 molecules at 0 ℃, if u_{rms} of H_2 at 0 ℃ is 1838 m/s.

(a) 115 m/s **(b)** 460 m/s **(c)** 1838 m/s **(d)** 7352 m/s **(e)** 29,400 m/s

Diffusion(擴散)

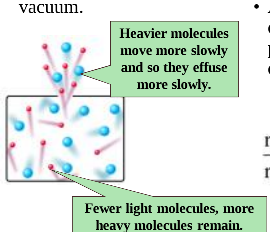
- ***Diffusion*** is the process by which one substance mixes with one or more other substances as a result of the translational motion of molecules.
- Diffusion of gases is much slower than would be predicted by molecular speeds due to the frequent collisions of molecules.
- The average distance a molecule travels between collisions is called its *mean free path*.

Diffusion of Gases



Effusion(逸散)

- ***Effusion*** is the process in which a gas escapes from its container through a tiny hole, or orifice, into a vacuum.



- Effusion is (mathematically) simpler than diffusion since effusion does not involve molecular collisions.
- At a fixed T, the rates of effusion of gas molecules are *inversely* proportional to the square roots of their molar masses:

$$\frac{\text{rate}_1}{\text{rate}_2} = \frac{\sqrt{\frac{\cancel{3RT}}{M_1}}}{\sqrt{\frac{\cancel{3RT}}{M_2}}} = \sqrt{\frac{M_2}{M_1}}$$

Example 5.23

If compared under the same conditions, how much faster than helium does hydrogen effuse through a tiny hole?

Example 5.24

One percent of a measured amount of Ar(g) escapes through a tiny hole in 77.3 s. One percent of the same amount of an unknown gas escapes under the same conditions in 97.6 s. Calculate the molar mass of the unknown gas.

5.12 Real Gases

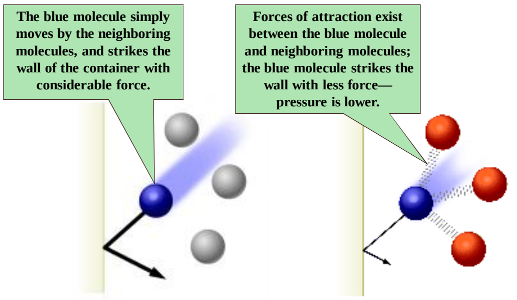
Real Gases

Under some conditions, *real* gases do not follow the ideal gas law.

1. Intermolecular forces of attraction cause the measured pressure of a real gas to be ***less*** than expected.
2. When molecules are close together, the volume of the ***molecules*** themselves becomes a significant fraction of the total volume of a gas.

Under what conditions of temperature and pressure will #1 and #2 become important?

Intermolecular Forces of Attraction



Real Gases

- Ideal gas equation (ideal gases):

  $[P \quad\quad\quad]\ (V \quad)\ = nRT$

- van der Waals equation (real gases):

  $[P + \{(n^2a)/V^2\}]\ (V - nb)\ = nRT$

- a – term is related to intermolecular force strength.
- b – term is related to volume of the gas molecules (in liters per mole).
- Both a and b are *empirical* constants, determined by experiment.

Table 5.5 van der Waals Constants for Selected Gases

Substance	a (L^2 atm mol^{-2})	b (L mol^{-1})
He	0.0341	0.02370
Ar	1.34	0.0322
H_2	0.244	0.0266
O_2	1.36	0.0318
CO_2	3.59	0.0427
CCl_4	20.4	0.1383

Cumulative Example

Two cylinders of gas are used in welding. One cylinder is 1.2 m high and 18 cm in diameter, containing oxygen gas at 2550 psi and 19 °C. The other is 0.76 m high and 28 cm in diameter, containing acetylene gas (C_2H_2) at 320 psi and 19 °C. Assuming complete combustion, which tank will be emptied, leaving unreacted gas in the other?