GENERAL CHEMISTRY

Chapter 10

Gases

Contents

10-1 Characteristics of Gases

- Unlike liquids and solids, gases
  - expand to fill their containers;
  - are highly compressible;
  - have extremely low densities.

- Vapors are substances that are normally liquids or solids at room temperature.

- The gaseous states of three halogens.

Cl_2	Br_2	I_2
greenish yellow	brownish red	violet

- Most common gases are colorless
  - H_2, O_2, N_2, CO and CO_2

TABLE 10.1 **Some Common Compounds That Are Gases at Room Temperature**

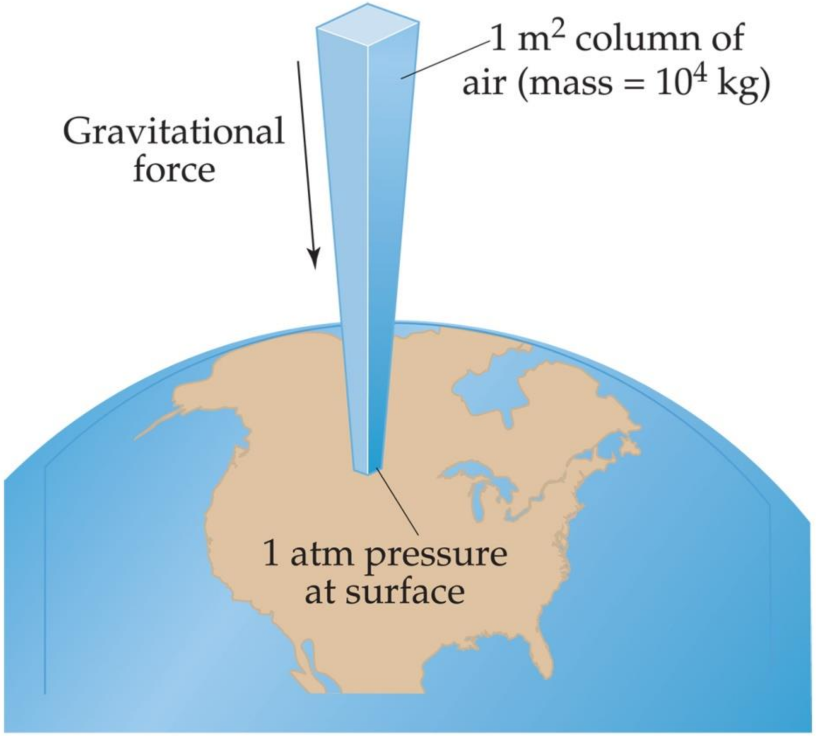
Formula	Name	Characteristics
HCN	Hydrogen cyanide	Very toxic, slight odor of bitter almonds
H_2S	Hydrogen sulfide	Very toxic, odor of rotten eggs
CO	Carbon monoxide	Toxic, colorless, odorless
CO_2	Carbon dioxide	Colorless, odorless
CH_4	Methane	Colorless, odorless, flammable
C_2H_4	Ethene (Ethylene)	Colorless, ripens fruit
C_3H_8	Propane	Colorless, odorless, bottled gas
N_2O	Nitrous oxide	Colorless, sweet odor, laughing gas
NO_2	Nitrogen dioxide	Toxic, red-brown, irritating odor
NH_3	Ammonia	Colorless, pungent odor
SO_2	Sulfur dioxide	Colorless, irritating odor

10-2 Pressure

- Pressure is the amount of force applied to an area.

$$\text{Presure (Pa)} = \frac{\text{Force (N)}}{\text{Area (m}^2\text{)}}$$

- Atmospheric pressure is the weight of air per unit of area.

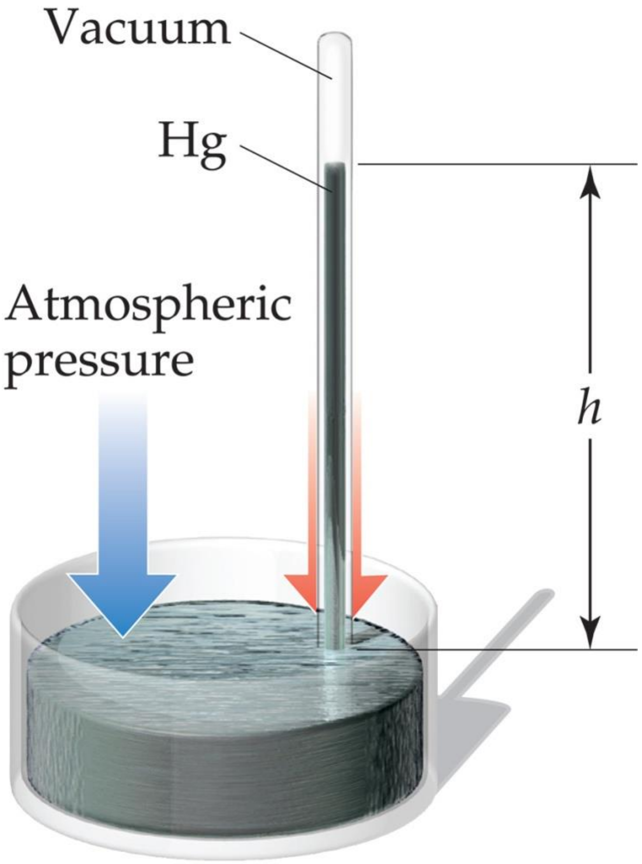


Units of Pressure

- Pascals
  - 1 Pa = 1 N/m^2
- Bar
  - 1 bar = 10^5 Pa = 100 kPa

- mm Hg or torr
  - These units are literally the difference in the heights measured in mm (*h*) of two connected columns of mercury.

- Atmosphere
  - 1.00 atm = 760 torr



Liquid Pressure

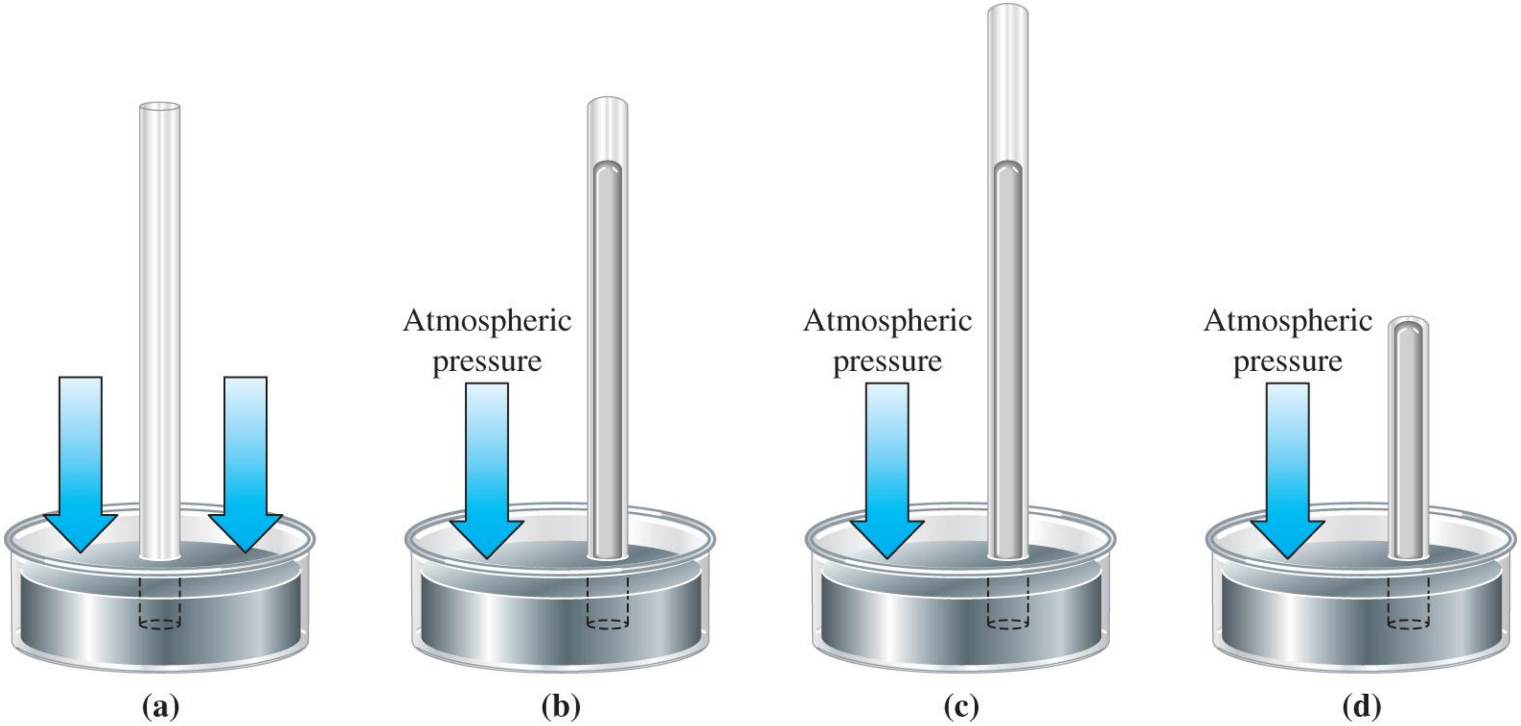
- The pressure exerted by a liquid depends on:
    - The height of the column of liquid.
    - The density of the column of liquid.

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

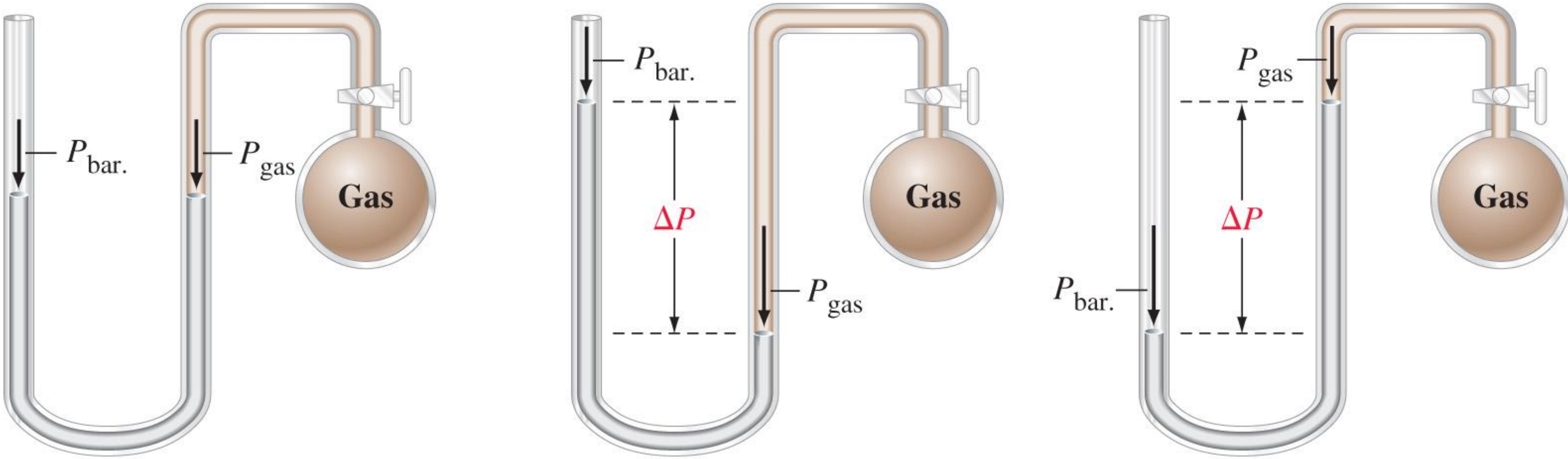
Barometric Pressure

Standard Atmospheric Pressure

1.00 atm, 760 mm Hg, 760 torr, 101.325 kPa, 1.01325 bar



Manometers



$P_{gas} = P_{bar.}$

(a) Gas pressure equal to barometric pressure

$P_{gas} = P_{bar.} + \Delta P$
$(\Delta P > 0)$

(b) Gas pressure greater than barometric pressure

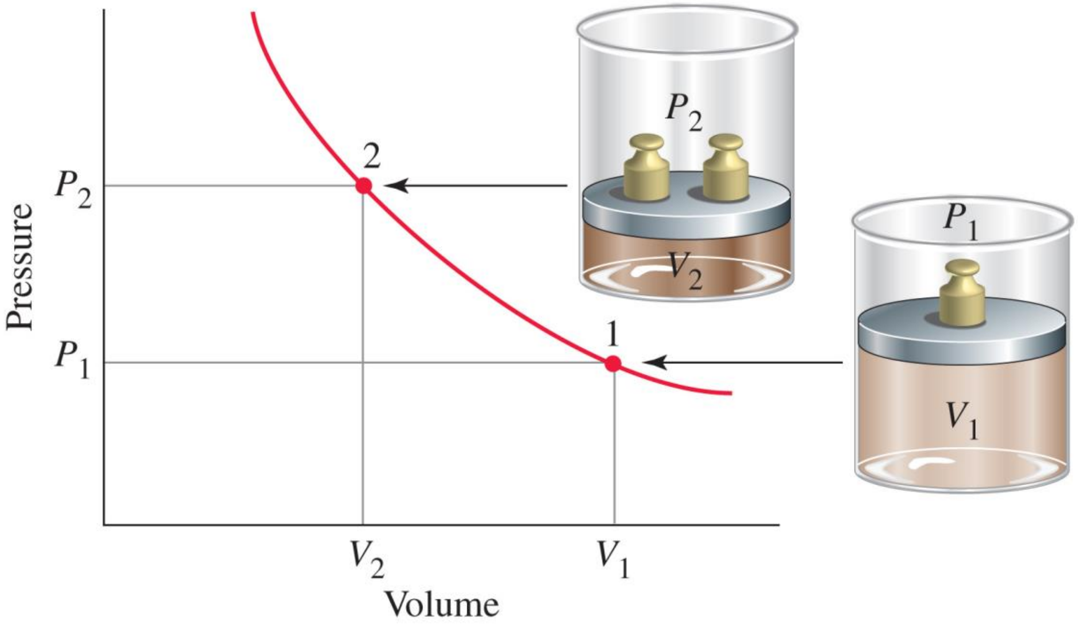
$P_{gas} = P_{bar.} + \Delta P$
$(\Delta P < 0)$

(c) Gas pressure less than barometric pressure

This device is used to measure the difference in pressure between atmospheric pressure and that of a gas in a vessel.

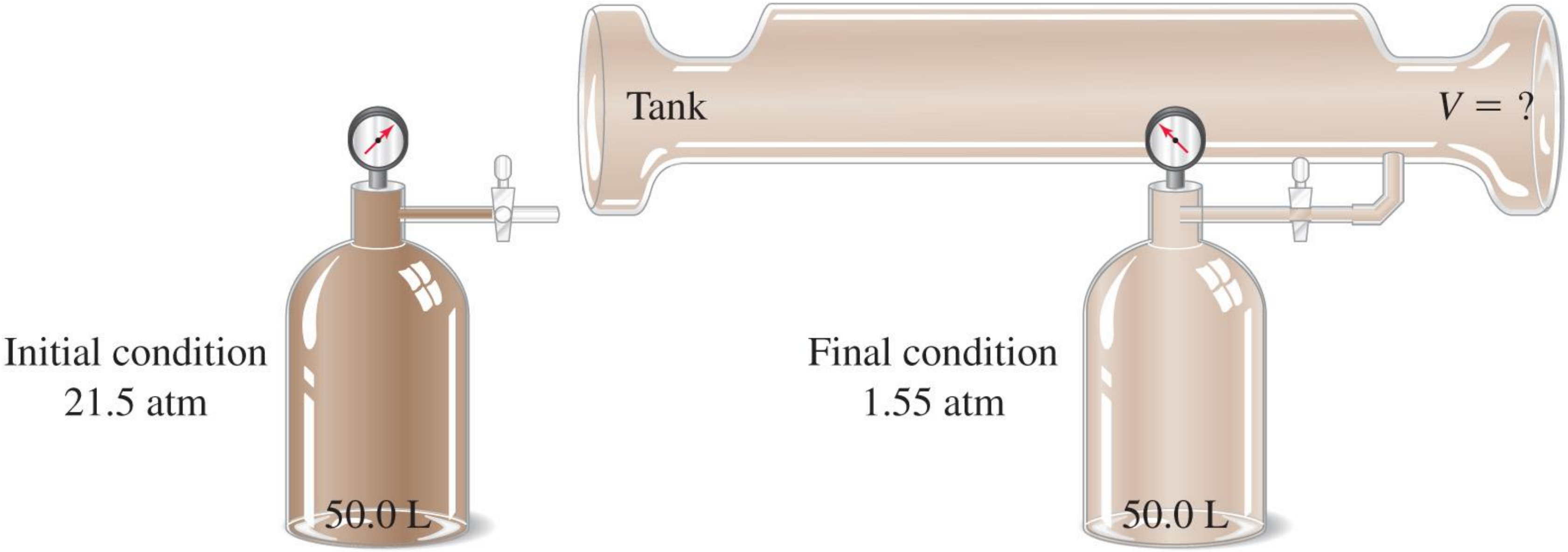
10-3 The Gas Laws

- Boyle 1662 $P \propto \frac{1}{V}$ PV = constant

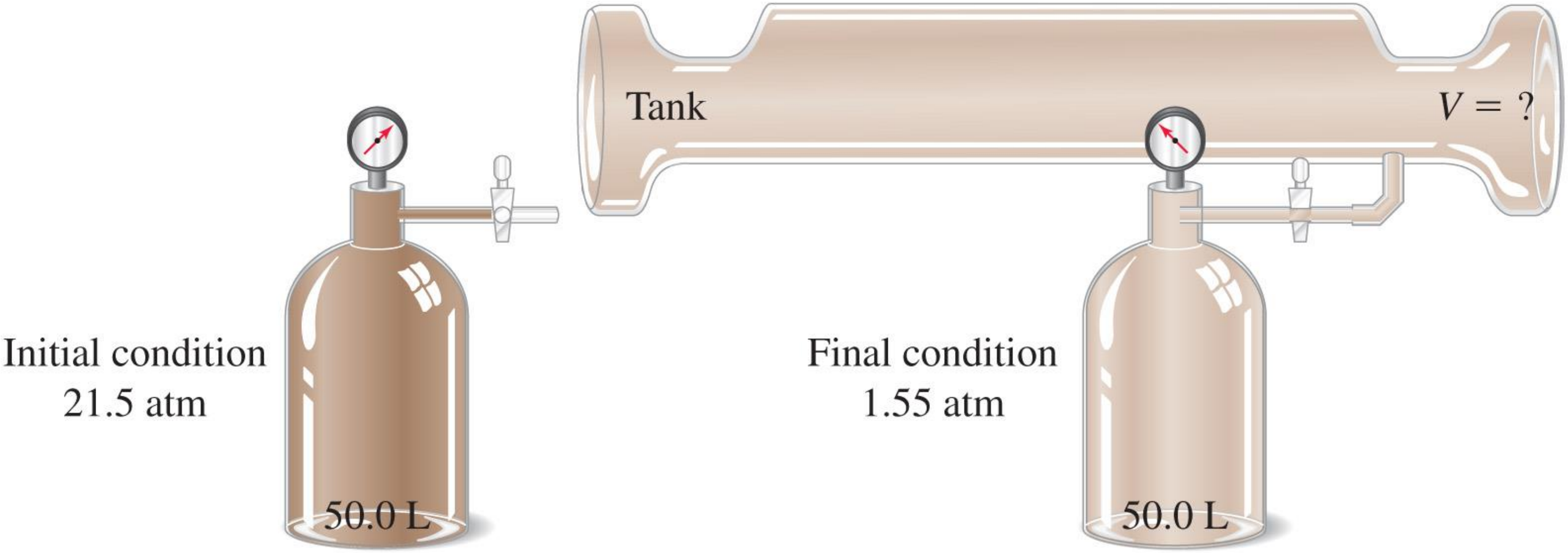


EXAMPLE

Relating Gas Volume and Pressure – Boyle's Law. The volume of a large irregularly shaped, closed tank can be determined. The tank is first evacuated and then connected to a 50.0 L cylinder of compressed nitrogen gas. The gas pressure in the cylinder, originally at 21.5 atm, falls to 1.55 atm after it is connected to the evacuated tank. What is the volume of the tank?



EXAMPLE



$$P_1V_1 = P_2V_2 \qquad V_2 = \frac{P_1V_1}{P_2} = 694\text{ L} \qquad V_{tank} = 644\text{ L}$$

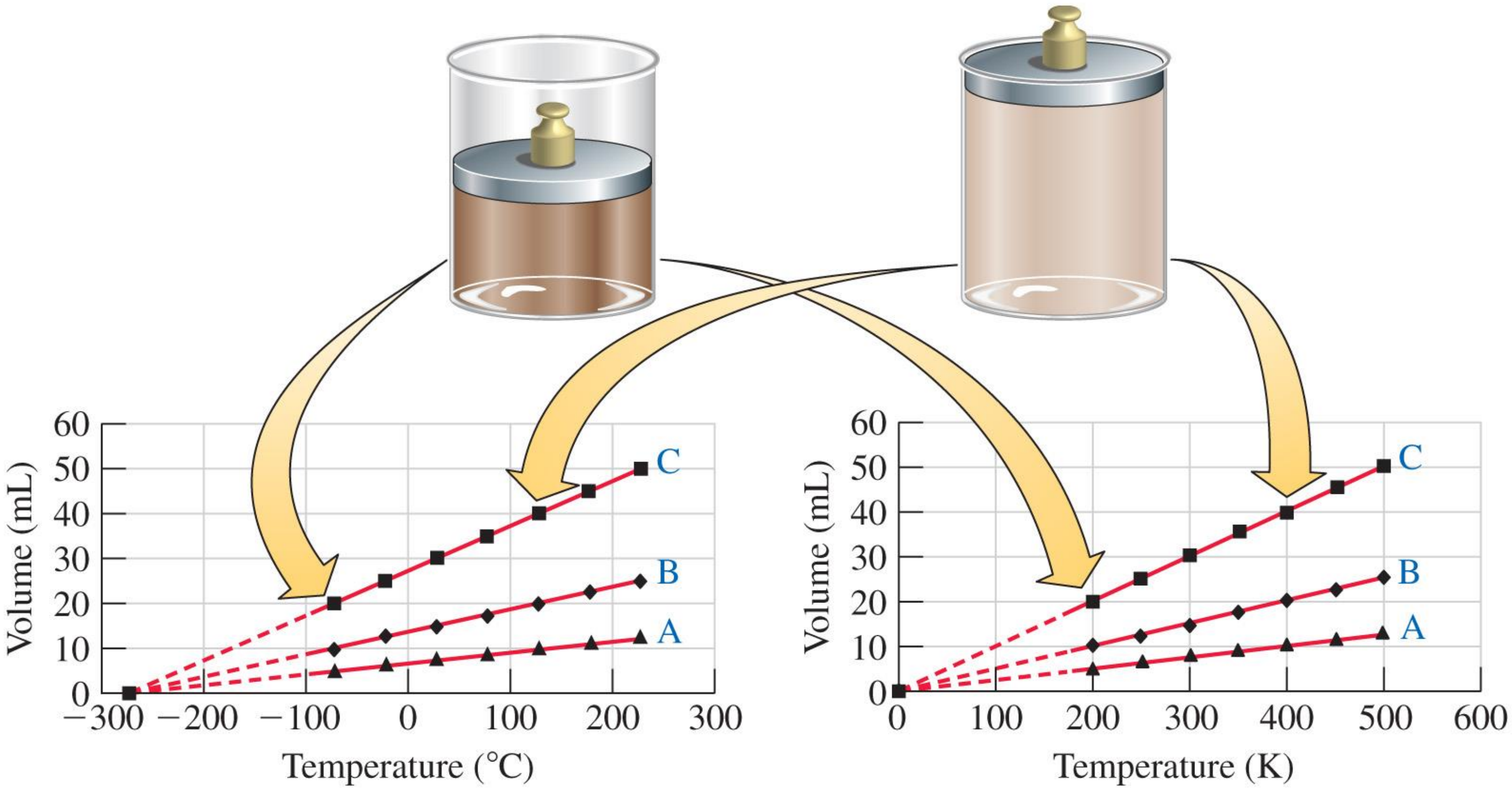
Charles's Law

Charles 1787

Gay-Lussac 1802

$V \propto T$

$V/T = \text{constant}$



Standard Temperature and Pressure

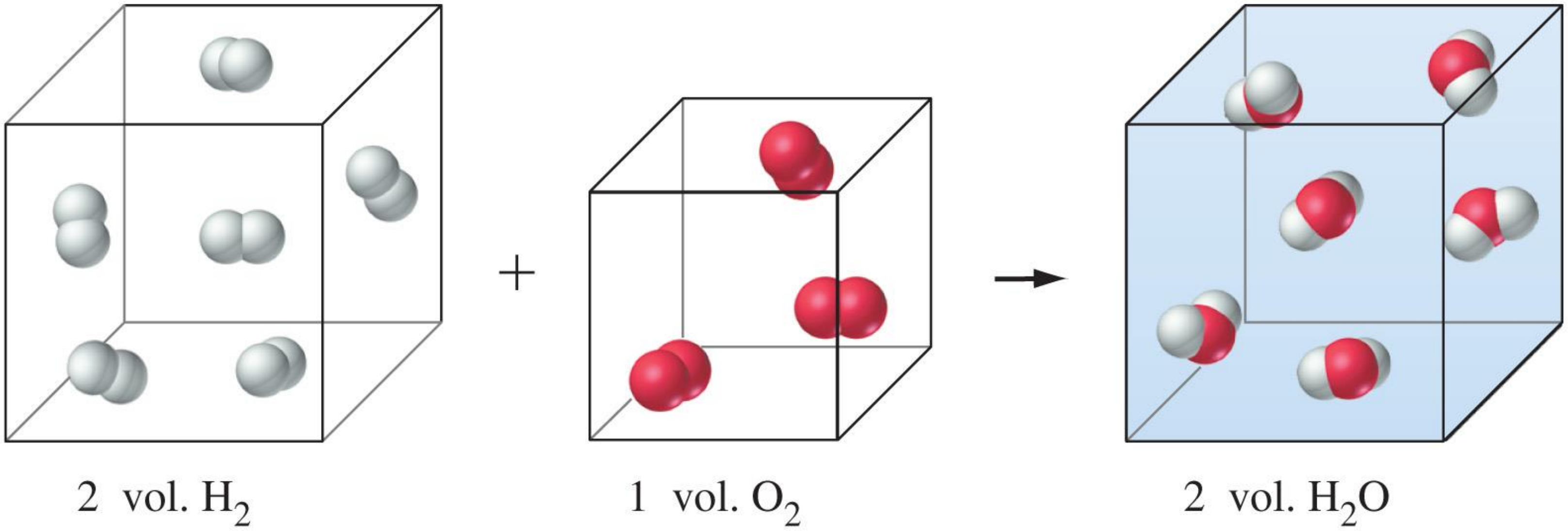
- Gas properties depend on conditions.
- Define standard conditions of temperature and pressure (STP).

P = 1 atm = 760 mm Hg

T = 0°C = 273.15 K

Gay-Lussac’s Law

- Gay-Lussac 1808
  - At a given pressure and temperature, the volumes of gases that react with one another are in the ratios of small whole numbers.



Avogadro’s Law

- Avogadro’s hypothesis
    - Equal volumes of gases have equal numbers of molecules *and*
    - Gas molecules may break up when they react.

- Avogadro’s Law
    - At an a fixed temperature and pressure:

$$V \propto n \qquad \text{or} \qquad V/n = \text{constant}$$

Molar volume is the volume of a 1 mol of a gas at STP and equals 22.41 L

10-4 The Ideal Gas Equation

- Boyle's law $V \propto 1/P$
- Charles's law $V \propto T$
- Avogadro's law $V \propto n$

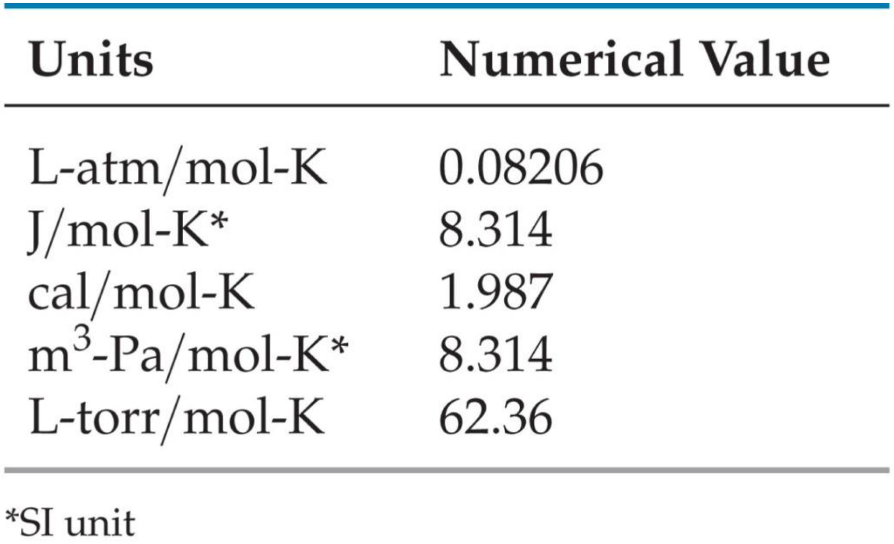
$$V \propto \frac{nT}{P}$$

$$PV = nRT$$

The Gas Constant

$$PV = nRT$$

$$R = \frac{PV}{nT}$$

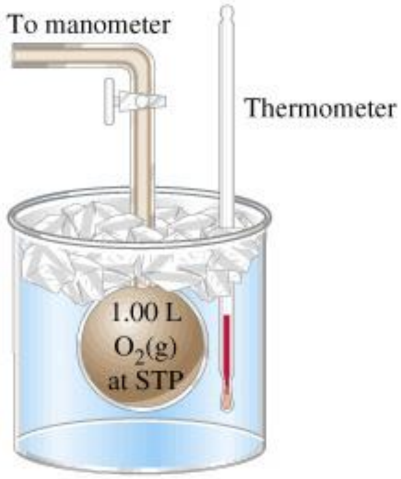


Units	Numerical Value
L-atm/mol-K	0.08206
J/mol-K*	8.314
cal/mol-K	1.987
m^3-Pa/mol-K*	8.314
L-torr/mol-K	62.36

*SI unit

The General Gas Equation

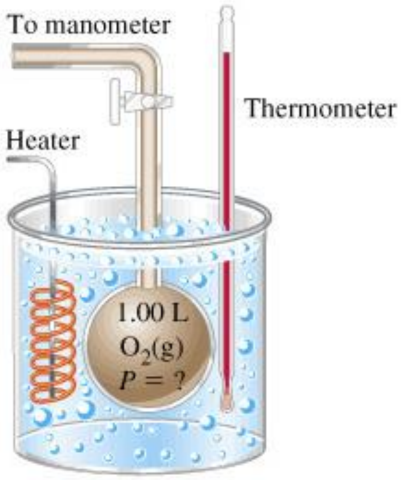
$$R = \frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2}$$



(a) Ice bath

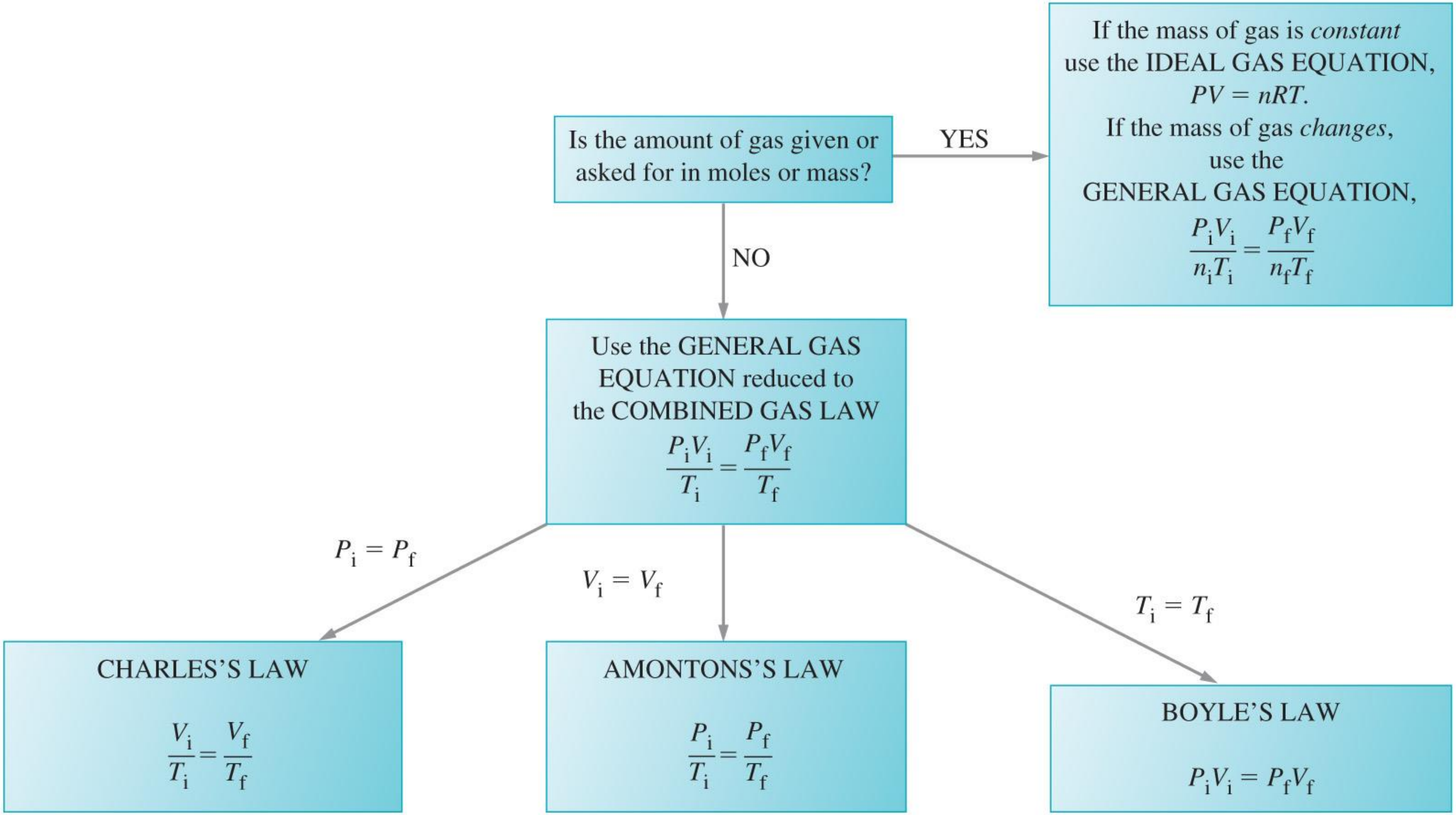
If we hold the amount and volume constant:

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$



(b) Boiling water

Using the Gas Laws



Is the amount of gas given or asked for in moles or mass?

YES

If the mass of gas is *constant* use the IDEAL GAS EQUATION, $PV = nRT$.

If the mass of gas *changes*, use the GENERAL GAS EQUATION,

$$\frac{P_iV_i}{n_iT_i} = \frac{P_fV_f}{n_fT_f}$$

NO

Use the GENERAL GAS EQUATION reduced to the COMBINED GAS LAW

$$\frac{P_iV_i}{T_i} = \frac{P_fV_f}{T_f}$$

$P_i = P_f$

$V_i = V_f$

$T_i = T_f$

CHARLES'S LAW

$$\frac{V_i}{T_i} = \frac{V_f}{T_f}$$

AMONTONS'S LAW

$$\frac{P_i}{T_i} = \frac{P_f}{T_f}$$

BOYLE'S LAW

$$P_iV_i = P_fV_f$$

10-5 Further Applications of the Ideal Gas Equation

Molar Mass Determination

$$PV = nRT \qquad \text{and} \qquad n = \frac{m}{M}$$

$$PV = \frac{m}{M} RT$$

$$M = \frac{m\,RT}{PV}$$

EXAMPLE 6-10

Determining a Molar Mass with the Ideal Gas Equation. Polypropylene is an important commercial chemical. It is used in the synthesis of other organic chemicals and in plastics production. A glass vessel weighs 40.1305 g when clean, dry and evacuated; it weighs 138.2410 when filled with water at 25°C ($\delta_{water} = 0.9970\ \text{g cm}^{-3}$) and 40.2959 g when filled with propylene gas at 740.3 mm Hg and 24.0°C. What is the molar mass of polypropylene?

Strategy:

Determine V_{flask}. Determine m_{gas}. Use the Gas Equation.

EXAMPLE 6-10

Determine V_{flask}:

$$V_{\text{flask}} = m_{H_2O} \div d_{H_2O} = (138.2410\ \text{g} - 40.1305\ \text{g}) \div (0.9970\ \text{g cm}^{-3})$$

$$= 98.41\ \text{cm}^3 = 0.09841\ \text{L}$$

Determine m_{gas}:

$$m_{\text{gas}} = m_{\text{filled}} - m_{\text{empty}} = (40.2959\ \text{g} - 40.1305\ \text{g})$$

$$= 0.1654\ \text{g}$$

EXAMPLE 5-6

Use the Gas Equation:

$$PV = nRT \qquad PV = \frac{m}{M} RT \qquad M = \frac{m\,RT}{PV}$$

$$M = \frac{(0.6145\ \boxed{\text{g}})(0.08206\ \cancel{\text{L}}\ \cancel{\text{atm}}\ \boxed{\text{mol}^{-1}}\ \cancel{\text{K}}^{-1})(297.2\ \cancel{\text{K}})}{(0.9741\ \cancel{\text{atm}})(0.09841\ \cancel{\text{L}})}$$

$$M = 42.08\ \text{g/mol}$$

Gas Densities

$$PV = nRT \quad \text{and} \quad d = \frac{m}{V}, \quad n = \frac{m}{M}$$

$$PV = \frac{m}{M} RT$$

$$\frac{m}{V} = d = \frac{MP}{RT}$$

Gases in Chemical Reactions

- Stoichiometric factors relate gas quantities to quantities of other reactants or products.
- Ideal gas equation relates the amount of a gas to volume, temperature and pressure.
- *Law of combining volumes* can be developed using the gas law.

EXAMPLE 6-12

Using the Ideal gas Equation in Reaction Stoichiometry Calculations. The decomposition of sodium azide, NaN_3, at high temperatures produces $N_2(g)$. Together with the necessary devices to initiate the reaction and trap the sodium metal formed, this reaction is used in air-bag safety systems. What volume of $N_2(g)$, measured at 735 mm Hg and 26°C, is produced when 70.0 g NaN_3 is decomposed?

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

EXAMPLE 6-12

Determine moles of N_2:

$$n_{N_2} = 70\ \cancel{\text{g NaN}_3} \times \frac{1\ \cancel{\text{mol NaN}_3}}{65.01\ \cancel{\text{g NaN}_3}} \times \frac{\boxed{3\text{ mol N}_2}}{2\ \cancel{\text{mol NaN}_3}} = 1.62\text{ mol N}_2$$

Determine volume of N_2:

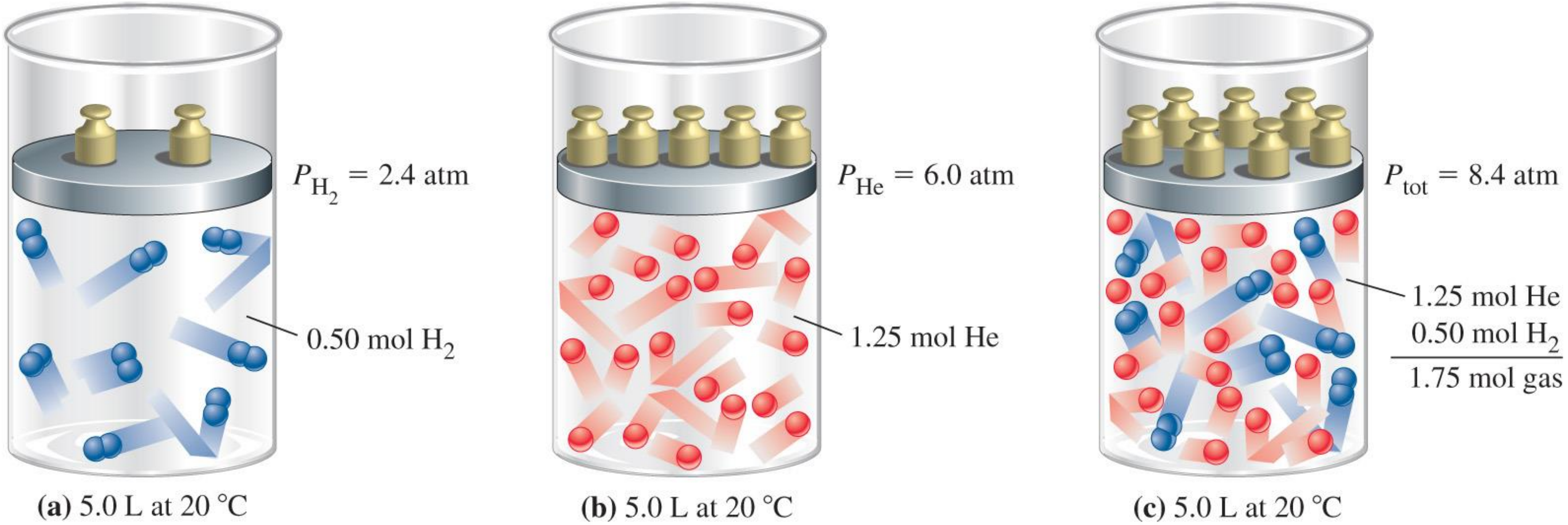
$$V = \frac{nRT}{P} = \frac{(1.62\ \cancel{\text{mol}})(0.08206\ \boxed{\text{L}}\ \cancel{\text{atm}}\ \cancel{\text{mol}^{-1}}\ \cancel{\text{K}^{-1}})(299\ \cancel{\text{K}})}{\left\{(735\ \cancel{\text{mm Hg}}) \times \dfrac{1.00\ \cancel{\text{atm}}}{760\ \cancel{\text{mm Hg}}}\right\}} = 41.1\text{ L}$$

10-6 Gas Mixtures and Partial Pressures

- Gas laws apply to *mixtures* of gases.
- Simplest approach is to use n_{total}, but....

- Partial pressure
  - Each component of a gas mixture exerts a pressure that it would exert if it were in the container alone.

Dalton’s Law of Partial Pressure



The total pressure of a mixture of gases is the sum of the partial pressures of the components of the mixture.

Partial Pressure

$P_{tot} = P_a + P_b + \ldots$

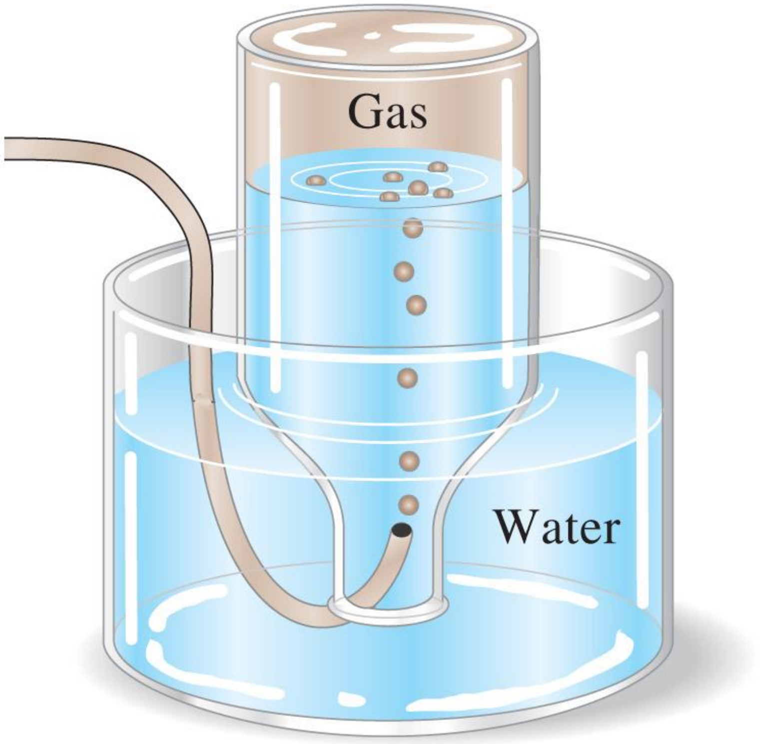
$V_a = n_aRT/P_{tot}$ and $V_{tot} = V_a + V_b + \ldots$

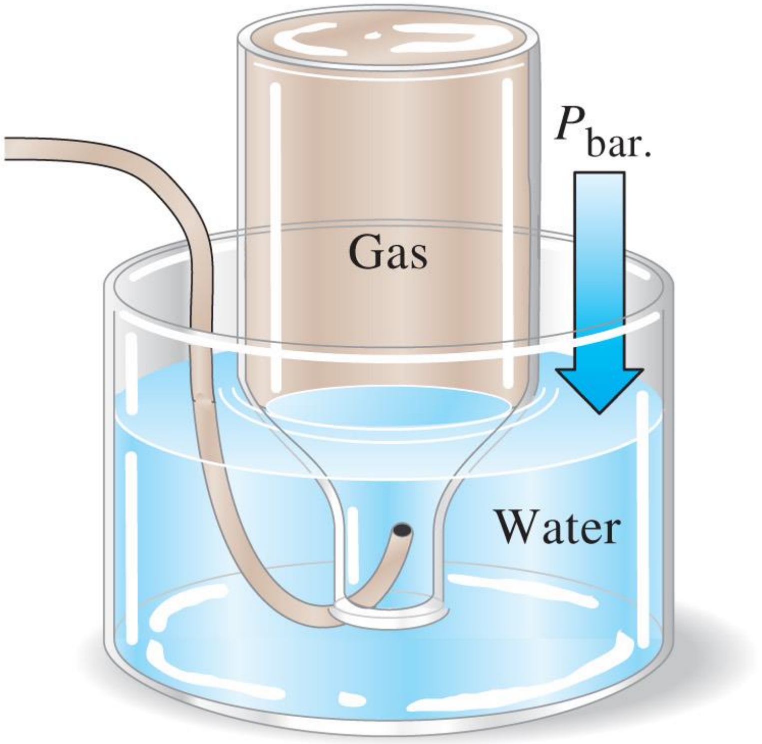
$$\frac{V_a}{V_{tot}} = \frac{n_aRT/P_{tot}}{n_{tot}RT/P_{tot}} = \frac{n_a}{n_{tot}}$$

Recall $\frac{n_a}{n_{tot}} = \chi_a$

$$\frac{P_a}{P_{tot}} = \frac{n_aRT/V_{tot}}{n_{tot}RT/V_{tot}} = \frac{n_a}{n_{tot}}$$

Pneumatic Trough



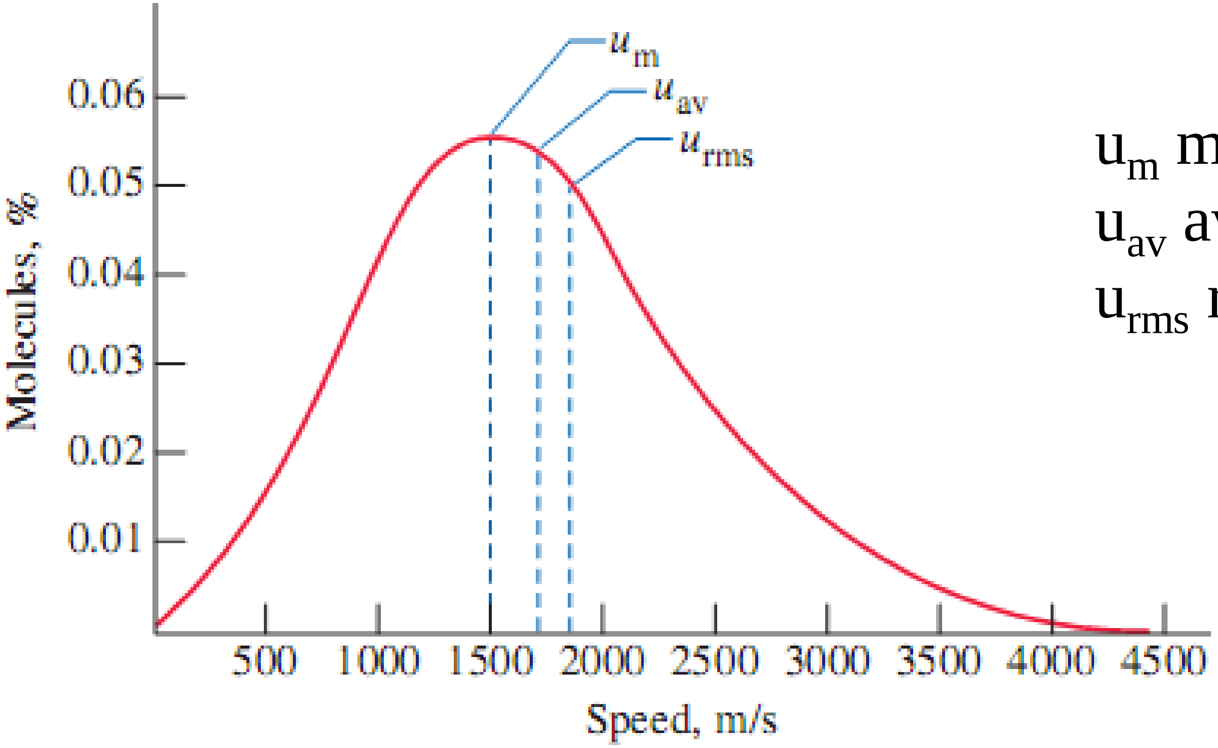


$$P_{tot} = P_{bar} = P_{gas} + P_{H_2O}$$

10-7 Kinetic-Molecular Theory of Gases

- Random motion:
- Negligible molecular volume
- Negligible attractive and repulsive forces
- Constant average kinetic energy
- Average kinetic energy proportional to temperature

Distributions of Molecular Speed



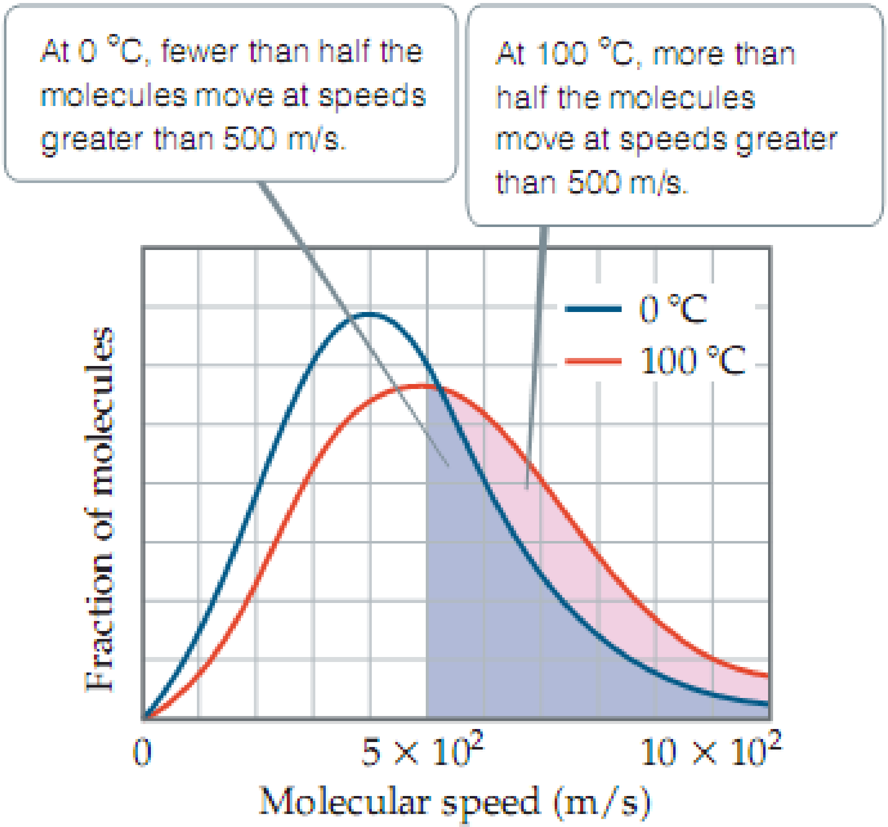
u_m most probable speed,
u_{av} average speed
u_{rms} root mean square speed

$$F(u) = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} u^2 e^{-(Mu^2/2RT)}$$

F: fraction of molecules having speed between u and (u + 1) m/s
M: molar mass,
T: absolute temperature

Effects of temperature on molecular speed.

The relative area under the curve for a range of speeds gives the relative fraction of molecules that have those speeds



- The average kinetic energy of the molecules is proportional to the absolute temperature
- Energy can be transferred between molecules during collisions, but the average kinetic energy of the molecules does not change with time, as long as the temperature of the gas remains constant.

Distribution of molecular speeds for nitrogen gas

Application of Kinetic-Molecular Theory to the Gas Laws

An increase in volume at constant temperature causes pressure to decrease

A temperature increase at constant volume causes pressure to increase

$P \propto$ impulse imparted per collision * collision rate

Pressure – Assessing Collision Forces

- Translational kinetic energy, $e_k = \frac{1}{2} mu^2$
- Frequency of collisions, $v = u \frac{N}{V}$
- Impulse or momentum transfer, $I = mu$
- Pressure proportional to impulse times frequency $P \propto \frac{N}{V} mu^2$

P ∝ impulse imparted per collision * collision rate

Pressure

Assume one mole:
$$\mathrm{PV} = \frac{1}{3} N_{\mathrm{A}} \mathrm{m}\, \overline{\mathrm{u}}^2$$

PV=RT so:
$$3\mathrm{RT} = N_{\mathrm{A}} \mathrm{m}\, \overline{\mathrm{u}}^2$$

N_Am = M:
$$3\mathrm{RT} = \mathrm{M}\, \overline{\mathrm{u}}^2$$

Rearrange:
$$\mathrm{u}_{\mathrm{rms}} = \sqrt{\frac{3\mathrm{RT}}{\mathrm{M}}}$$

Temperature

Modify:

$$PV = \frac{1}{3} N_A m \bar{u}^2 = \frac{2}{3} N_A (\frac{1}{2} m \bar{u}^2)$$

PV=RT so:

$$RT = \frac{2}{3} N_A \bar{e}_k$$

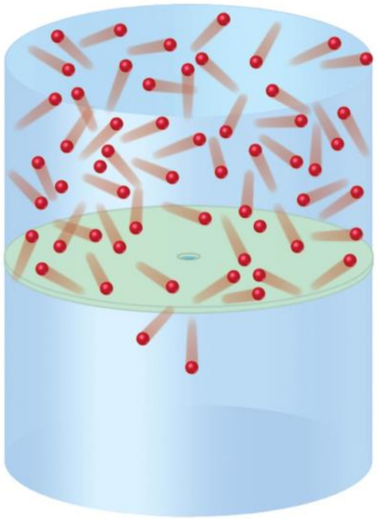
Solve for $\bar{e}_k$:

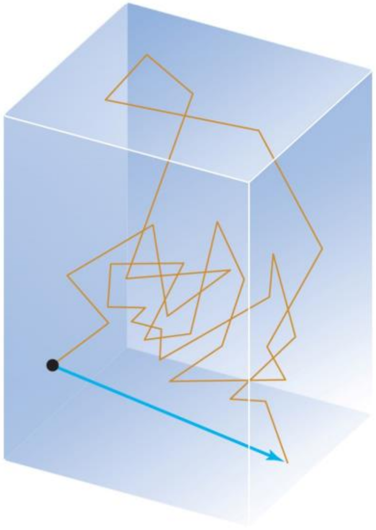
$$\bar{e}_k = \frac{3}{2} \frac{R}{N_A} (T)$$

Average kinetic energy is directly proportional to temperature!

10-8 Molecular Effusion and Diffusion

- Effusion is the escape of gas molecules through a tiny hole into an evacuated space.
- Diffusion is the spreading of one substance throughout a space or throughout a second substance.





Graham’s Law

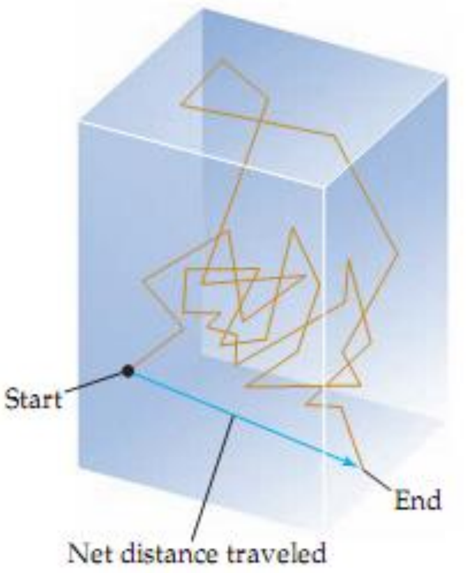
$$\frac{\textit{rateof effusionof A}}{\textit{rateof effusionof B}} = \frac{(u_{\mathrm{rms}})_A}{(u_{\mathrm{rms}})_B} = \sqrt{\frac{3RT/M_A}{3RT/MB}} = \sqrt{\frac{M_B}{M_A}}$$

- Only for gases at low pressure (natural escape, not a jet).
- Tiny orifice (no collisions)
- Does not apply to diffusion.

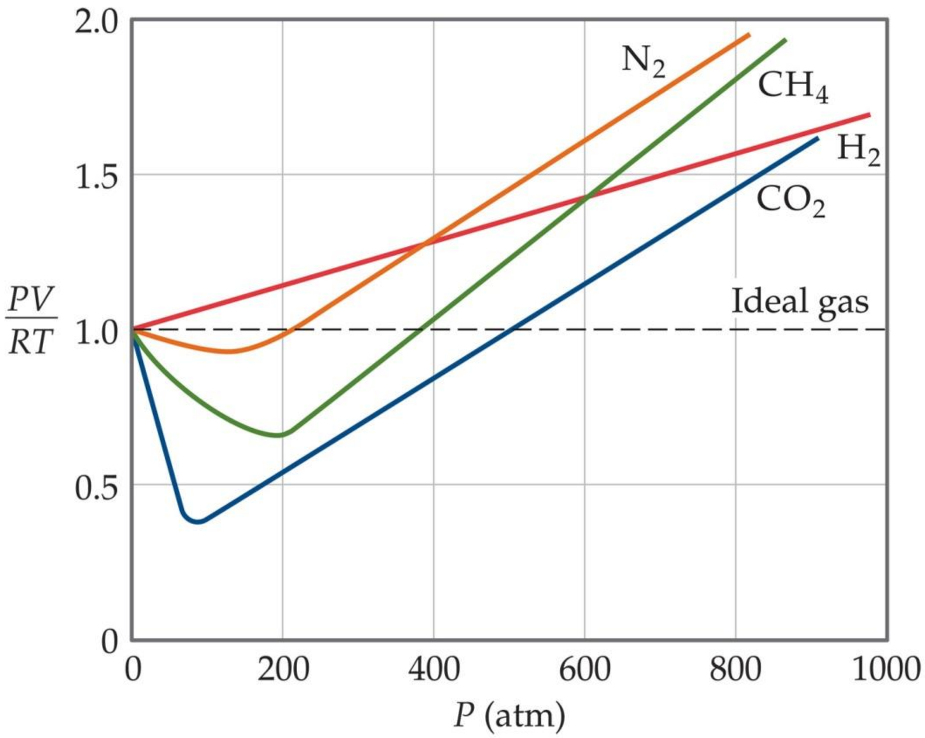
- Ratio used can be:
  - Rate of effusion (as above)
  - Molecular speeds
  - Effusion times
  - Distances traveled by molecules
  - Amounts of gas effused.

Diffusion and Mean Free Path

- The diffusion of a molecule from one point to another consists of many short, straight-line segments as collisions buffet it around in random directions
- The average distance traveled by a molecule between collisions, called the molecule's **mean free path**

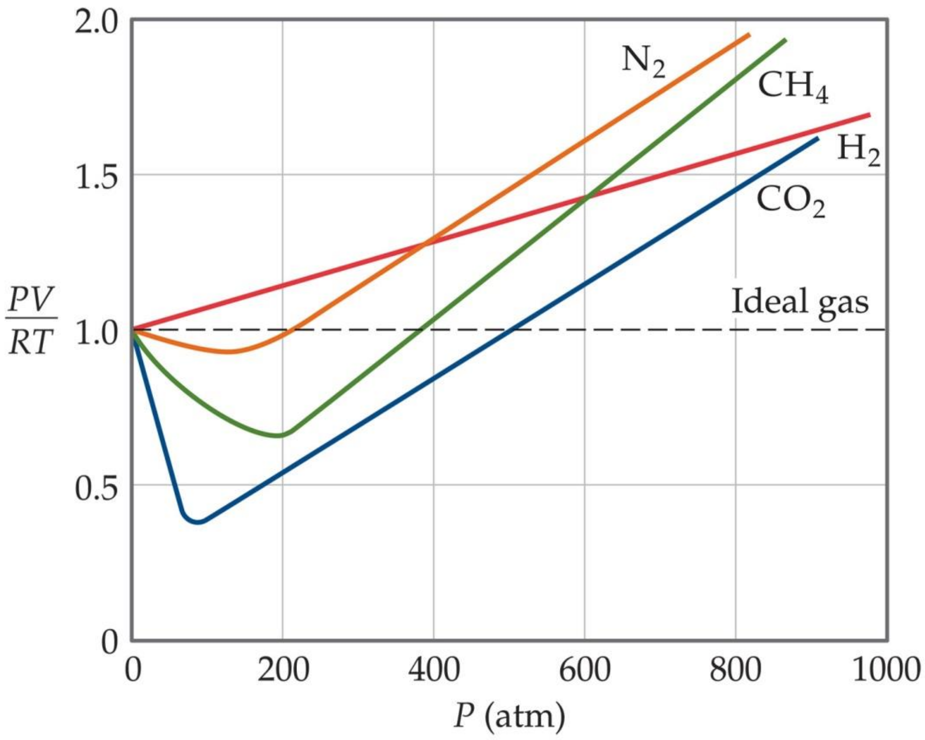


10-9 Real Gases: Deviations from Ideal Behavior



In the real world, the behavior of gases only conforms to the ideal-gas equation at relatively high temperature and low pressure.

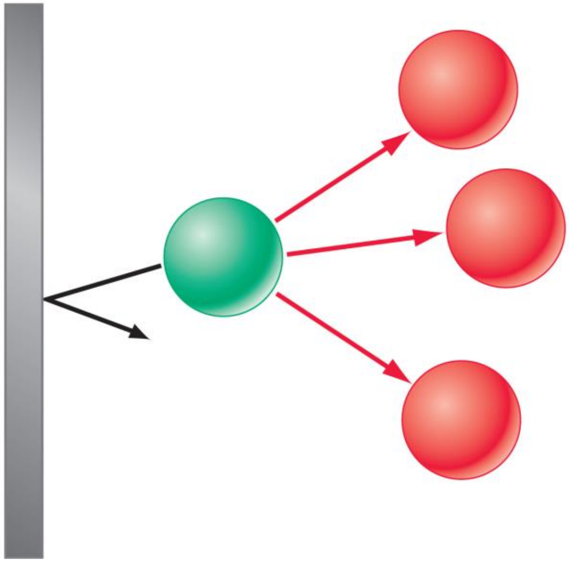
10-9 Real Gases: Deviations from Ideal Behavior



In the real world, the behavior of gases only conforms to the ideal-gas equation at relatively high temperature and low pressure.

10-9 Real Gases: Deviations from Ideal Behavior

- Compressibility factor PV/nRT = 1
- Deviations occur for real gases.
  - PV/nRT > 1 - molecular volume is significant.
  - PV/nRT < 1 – intermolecular forces of attraction.



van der Waals Equation

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

a: a measure of how strongly the gas molecules attract one another,

b: a measure of the finite volume occupied by the molecules

Homeworks

Chemistry
The Central Science
Fourteenth Edition in SI Units

All "Practice Exercise 1" of Chapter 10