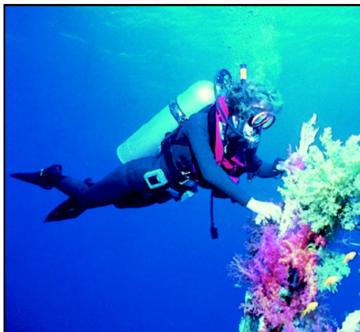

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Gases

Chapter 5

1

Elements that exist as gases at 25^{0}C and 1 atmosphere

1A	2A	3B	4B	5B	6B	7B	8B	8B	8B	1B	2B	3A	4A	5A	6A	7A	8A
H																	**He**
Li	Be											B	C	**N**	**O**	**F**	**Ne**
Na	Mg											Al	Si	P	S	**Cl**	**Ar**
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	**Kr**
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	**Xe**
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	**Rn**
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg							

2

TABLE 5.1 Some Substances Found as Gases at 1 atm and 25°C

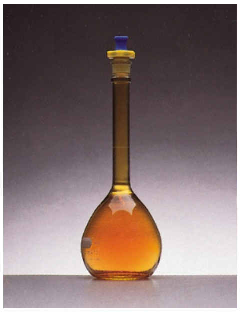
Elements	Compounds
H_2 (molecular hydrogen)	HF (hydrogen fluoride)
N_2 (molecular nitrogen)	HCl (hydrogen chloride)
O_2 (molecular oxygen)	HBr (hydrogen bromide)
O_3 (ozone)	HI (hydrogen iodide)
F_2 (molecular fluorine)	CO (carbon monoxide)
Cl_2 (molecular chlorine)	CO_2 (carbon dioxide)
He (helium)	NH_3 (ammonia)
Ne (neon)	NO (nitric oxide)
Ar (argon)	NO_2 (nitrogen dioxide)
Kr (krypton)	N_2O (nitrous oxide)
Xe (xenon)	SO_2 (sulfur dioxide)
Rn (radon)	H_2S (hydrogen sulfide)
	HCN (hydrogen cyanide)*

*The boiling point of HCN is 26°C, but it is close enough to qualify as a gas at ordinary atmospheric conditions.

3

Physical Characteristics of Gases

- Gases assume the volume and shape of their containers.
- Gases are the most compressible state of matter.
- Gases will mix evenly and completely when confined to the same container.
- Gases have much lower densities than liquids and solids.



NO_2 gas

4

Pressure = $\frac{\text{Force}}{\text{Area}}$

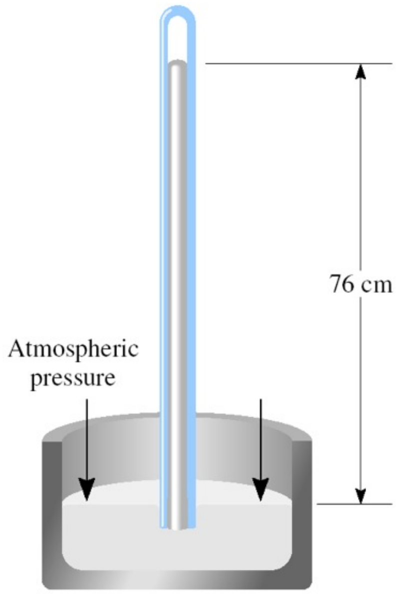
(force = mass x acceleration)

Units of Pressure

1 pascal (Pa) = 1 N/m^2

1 atm = 760 mmHg = 760 torr

1 atm = 101,325 Pa



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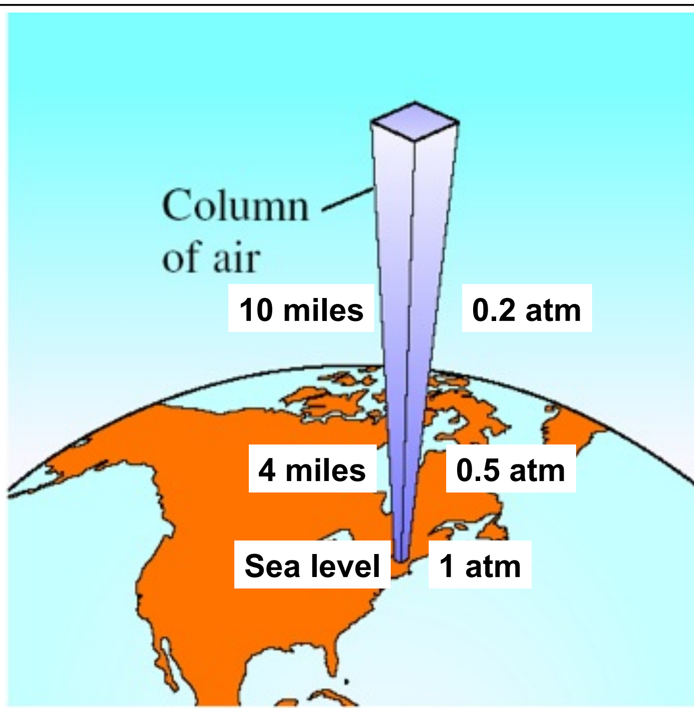

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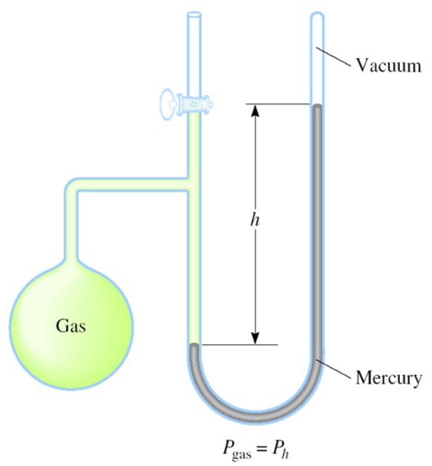
Manometers Used to Measure Gas Pressures

closed-tube

open-tube



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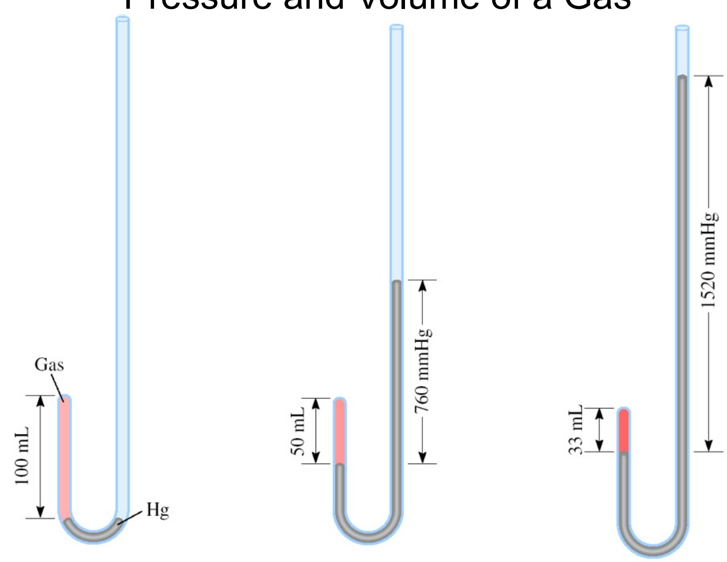
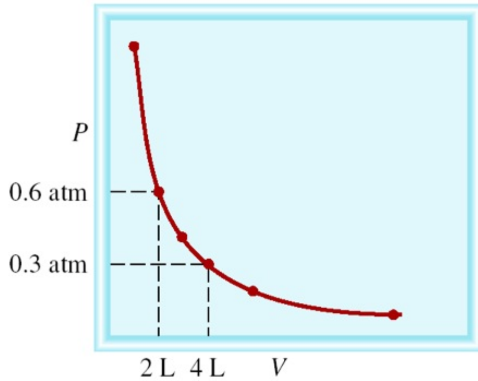
Apparatus for Studying the Relationship Between Pressure and Volume of a Gas

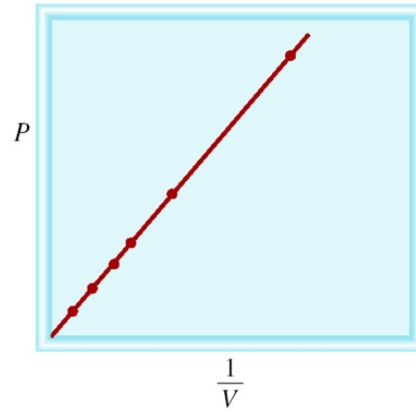


As P (h) increases V decreases

8

Boyle's Law





$P \propto 1/V$

$P \times V = \text{constant}$

$P_1 \times V_1 = P_2 \times V_2$

Constant temperature
Constant amount of gas

9

A sample of chlorine gas occupies a volume of 946 mL at a pressure of 726 mmHg. What is the pressure of the gas (in mmHg) if the volume is reduced at constant temperature to 154 mL?

$$P \times V = constant$$

$$P_1 \times V_1 = P_2 \times V_2$$

$P_1 = 726$ mmHg $\quad P_2 = ?$

$V_1 = 946$ mL $\quad V_2 = 154$ mL

$$P_2 = \frac{P_1 \times V_1}{V_2} = \frac{726 \text{ mmHg} \times 946 \cancel{\text{mL}}}{154 \cancel{\text{mL}}} = 4460 \text{ mmHg}$$

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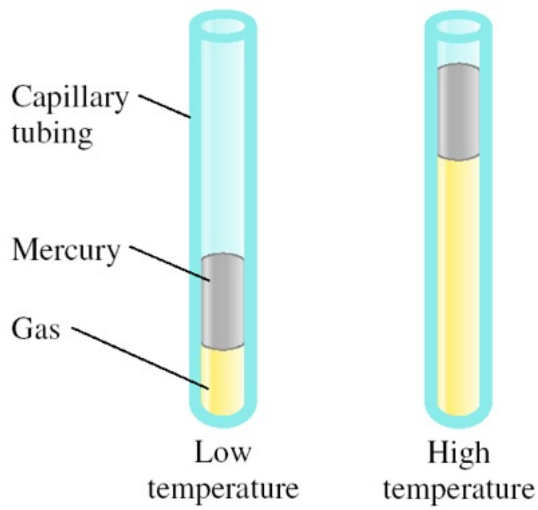
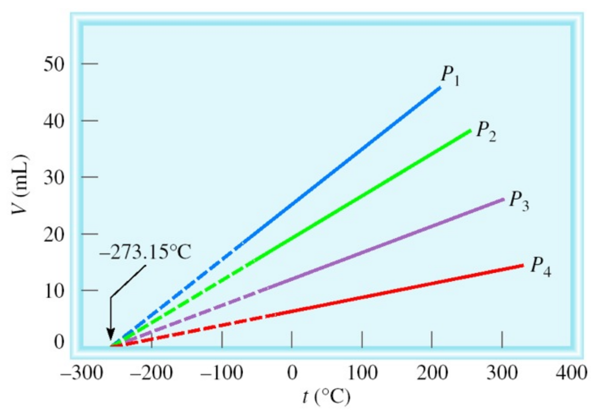
Variation in Gas Volume with Temperature at Constant Pressure



As T increases V increases

11

Variation of Gas Volume with Temperature at Constant Pressure



Charles' & Gay-Lussac's Law

$V \propto T$

V = constant x T

$V_1/T_1 = V_2/T_2$

Temperature **must** be in Kelvin

T (K) = t (˚C) + 273.15

12

A sample of carbon monoxide gas occupies 3.20 L at 125 ˚C. At what temperature will the gas occupy a volume of 1.54 L if the pressure remains constant?

$$V_1/T_1 = V_2/T_2$$

V_1 = 3.20 L $\qquad$ V_2 = 1.54 L

T_1 = 398.15 K $\qquad$ T_2 = ?

T_1 = 125 (˚C) + 273.15 (K) = 398.15 K

$$T_2 = \frac{V_2 \times T_1}{V_1} = \frac{1.54\ \cancel{\text{L}} \times 398.15\ \text{K}}{3.20\ \cancel{\text{L}}} = 192\ \text{K}$$

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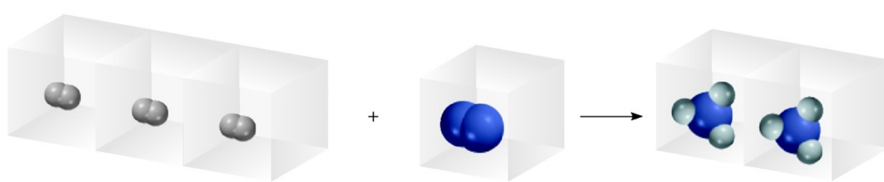
Avogadro's Law

$V \propto$ number of moles (n)

V = constant x n

Constant temperature
Constant pressure

$$V_1 / n_1 = V_2 / n_2$$



$3H_2(g)$	+	$N_2(g)$	⟶	$2NH_3(g)$
3 molecules	+	1 molecule	⟶	2 molecules
3 moles	+	1 mole	⟶	2 moles
3 volumes	+	1 volume	⟶	2 volumes

14

Ammonia burns in oxygen to form nitric oxide (NO) and water vapor. How many volumes of NO are obtained from one volume of ammonia at the same temperature and pressure?

$$4NH_3 + 5O_2 \longrightarrow 4NO + 6H_2O$$

$$1 \text{ mole } NH_3 \longrightarrow 1 \text{ mole NO}$$

At constant T and P

$$1 \text{ volume } NH_3 \longrightarrow 1 \text{ volume NO}$$

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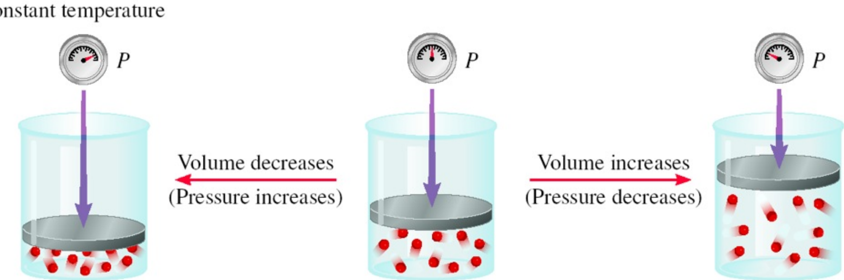
Summary of Gas Laws

Boyle's Law

Increasing or decreasing the volume of a gas at a constant temperature



Boyle's Law

$P = (nRT)\frac{1}{V}$ $\quad nRT$ is constant

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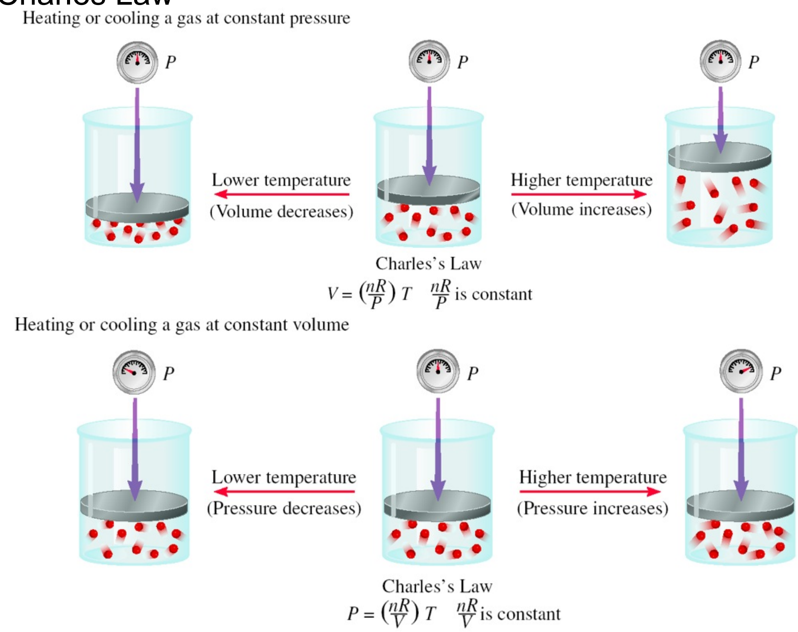
Charles Law



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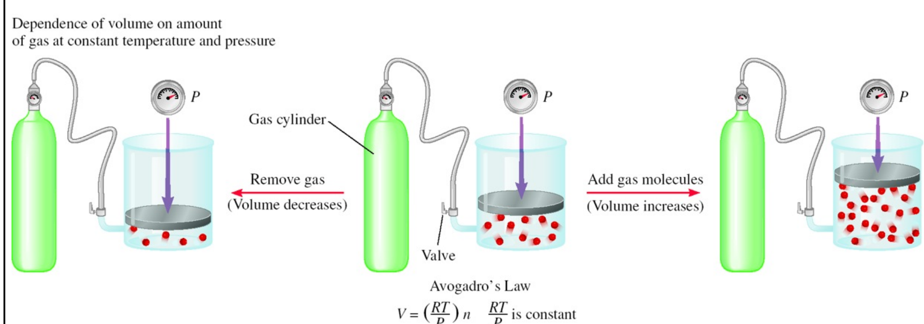
Avogadro's Law



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Ideal Gas Equation

Boyle's law: $P \propto \frac{1}{V}$ (at constant n and T)

Charles' law: $V \propto T$ (at constant n and P)

Avogadro's law: $V \propto n$ (at constant P and T)

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

$$V = \text{constant} \times \frac{nT}{P} = R\frac{nT}{P}$$

R is the **gas constant**

$$\boxed{PV = nRT}$$

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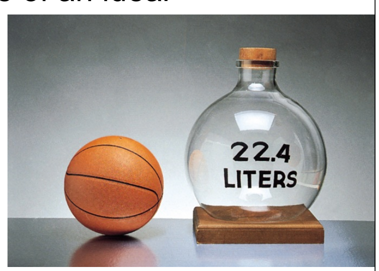
The conditions 0 °C and 1 atm are called **standard temperature and pressure (STP).**

Experiments show that at STP, 1 mole of an ideal gas occupies 22.414 L.



$$PV = nRT$$

$$R = \frac{PV}{nT} = \frac{(1\ \text{atm})(22.414\text{L})}{(1\ \text{mol})(273.15\ \text{K})}$$

$$R = 0.082057\ \text{L} \bullet \text{atm} / (\text{mol} \bullet \text{K})$$

20

What is the volume (in liters) occupied by 49.8 g of HCl at STP?

$T = 0\ ^\circ\mathrm{C} = 273.15\ \mathrm{K}$

$P = 1\ atm$

$PV = nRT$

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

$n = 49.8\ \mathrm{g} \times \frac{1\ \mathrm{mol\ HCl}}{36.45\ \mathrm{g\ HCl}} = 1.37\ \mathrm{mol}$

$$V = \frac{1.37\ \cancel{\mathrm{mol}} \times 0.0821\ \frac{\mathrm{L}\bullet\cancel{\mathrm{atm}}}{\cancel{\mathrm{mol}\bullet\mathrm{K}}} \times 273.15\ \cancel{\mathrm{K}}}{1\ \cancel{\mathrm{atm}}}$$

$V = 30.7\ \mathrm{L}$

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Density (d) Calculations

$$d = \frac{m}{V} = \frac{P\mathcal{M}}{RT}$$

m is the mass of the gas in g

$\mathcal{M}$ is the molar mass of the gas

Molar Mass ($\mathcal{M}$) of a Gaseous Substance

$$\mathcal{M} = \frac{dRT}{P}$$

d is the density of the gas in g/L

22

A 2.10-L vessel contains 4.65 g of a gas at 1.00 atm and 27.0 ˚C. What is the molar mass of the gas?

$$\mathcal{M} = \frac{dRT}{P} \qquad d = \frac{m}{V} = \frac{4.65\ \text{g}}{2.10\ \text{L}} = 2.21\,\frac{\text{g}}{\text{L}}$$

$$\mathcal{M} = \frac{2.21\,\frac{\text{g}}{\cancel{\text{L}}} \times 0.0821\,\frac{\cancel{\text{L•atm}}}{\text{mol•}\cancel{\text{K}}} \times 300.15\ \cancel{\text{K}}}{1\ \cancel{\text{atm}}}$$

$$\mathcal{M} = 54.5\ \text{g/mol}$$

Gas Stoichiometry

Amount of reactant (grams or volume) → Moles of reactant → Moles of product → Amount of product (grams or volume)

What is the volume of CO_2 produced at 37 ^{0}C and 1.00 atm when 5.60 g of glucose are used up in the reaction:

$$C_6H_{12}O_6(s) + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(l)$$

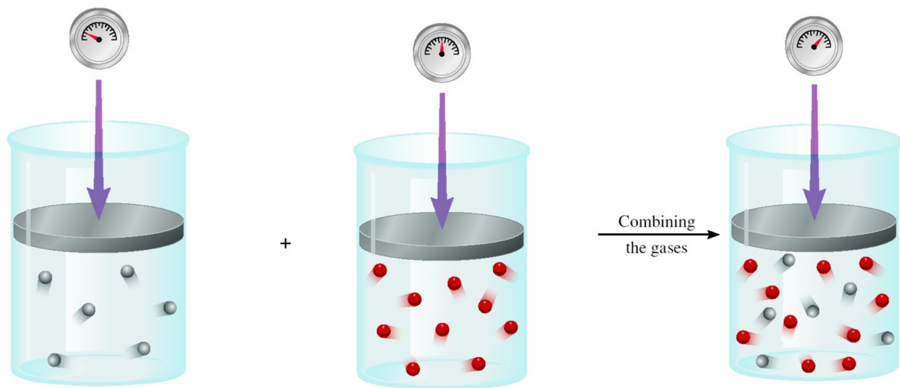
$$\text{g } C_6H_{12}O_6 \longrightarrow \text{mol } C_6H_{12}O_6 \longrightarrow \text{mol } CO_2 \longrightarrow V\ CO_2$$

$$5.60\ \cancel{\text{g } C_6H_{12}O_6} \times \frac{1\ \cancel{\text{mol } C_6H_{12}O_6}}{180\ \cancel{\text{g } C_6H_{12}O_6}} \times \frac{6\ \text{mol } CO_2}{1\ \cancel{\text{mol } C_6H_{12}O_6}} = 0.187\ \text{mol } CO_2$$

$$V = \frac{nRT}{P} = \frac{0.187\ \cancel{\text{mol}} \times 0.0821\,\frac{\cancel{\text{L•atm}}}{\cancel{\text{mol•K}}} \times 310.15\ \cancel{\text{K}}}{1.00\ \cancel{\text{atm}}} = 4.76\ \text{L}$$

Dalton's Law of Partial Pressures

V and *T* are **constant**



P_1 P_2 $P_{total} = P_1 + P_2$

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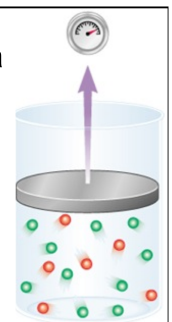
Consider a case in which two gases, A and B, are in a container of volume V.



$$P_A = \frac{n_A RT}{V}$$ n_A is the number of moles of A

$$P_B = \frac{n_B RT}{V}$$ n_B is the number of moles of B

$$P_T = P_A + P_B \qquad X_A = \frac{n_A}{n_A + n_B} \qquad X_B = \frac{n_B}{n_A + n_B}$$

$$P_A = X_A P_T \qquad P_B = X_B P_T$$

$$\boxed{P_i = X_i P_T}$$

mole fraction (X_i) = $\frac{n_i}{n_T}$

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A sample of natural gas contains 8.24 moles of CH_4, 0.421 moles of C_2H_6, and 0.116 moles of C_3H_8. If the total pressure of the gases is 1.37 atm, what is the partial pressure of propane (C_3H_8)?

$P_i = X_i P_T \qquad P_T = 1.37 \text{ atm}$

$$X_{propane} = \frac{0.116}{8.24 + 0.421 + 0.116} = 0.0132$$

$P_{propane} = 0.0132 \times 1.37 \text{ atm} = 0.0181 \text{ atm}$

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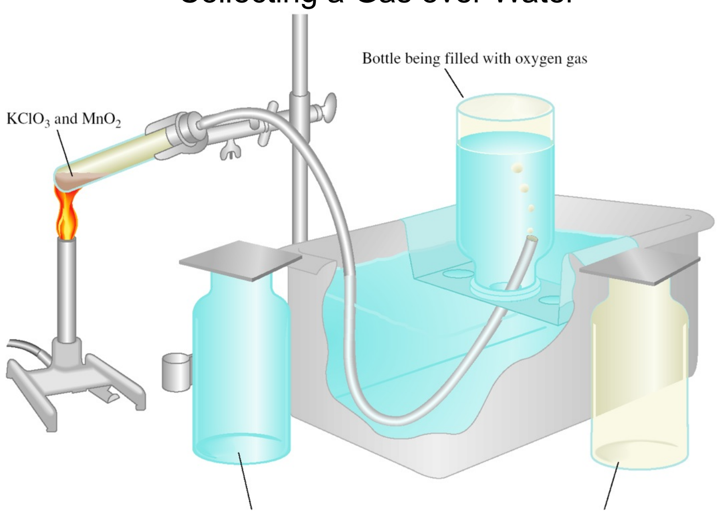
Collecting a Gas over Water



$2KClO_3\ (s) \longrightarrow 2KCl\ (s) + 3O_2\ (g)$

$P_T = P_{O_2} + P_{H_2O}$

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Table 5.2

Pressure of Water Vapor at Various Temperatures

Temperature (°C)	Water Vapor Pressure (mmHg)
0	4.58
5	6.54
10	9.21
15	12.79
20	17.54
25	23.76
30	31.82
35	42.18
40	55.32
45	71.88
50	92.51
55	118.04
60	149.38
65	187.54
70	233.7
75	289.1
80	355.1
85	433.6
90	525.76
95	633.90
100	760.00

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Kinetic Molecular Theory of Gases

1. A gas is composed of molecules that are separated from each other by distances far greater than their own dimensions. The molecules can be considered to be *points*; that is, they possess mass but have negligible volume.
2. Gas molecules are in constant motion in random directions, and they frequently collide with one another. Collisions among molecules are perfectly elastic.
3. Gas molecules exert neither attractive nor repulsive forces on one another.
4. The average kinetic energy of the molecules is proportional to the temperature of the gas in kelvins. Any two gases at the same temperature will have the same average kinetic energy

$$\overline{KE} = \frac{1}{2} m\overline{u^2}$$

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Kinetic theory of gases and …

- Compressibility of Gases
- Boyle's Law

  $P \propto$ collision rate with wall

  Collision rate $\propto$ number density

  Number density $\propto 1/V$

  $P \propto 1/V$
- Charles' Law

  $P \propto$ collision rate with wall

  Collision rate $\propto$ average kinetic energy of gas molecules

  Average kinetic energy $\propto T$

  $P \propto T$

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Kinetic theory of gases and …

- Avogadro's Law

  $P \propto$ collision rate with wall

  Collision rate $\propto$ number density

  Number density $\propto n$

  $P \propto n$
- Dalton's Law of Partial Pressures

  Molecules do not attract or repel one another

  P exerted by one type of molecule is unaffected by the presence of another gas

  $P_{total} = \Sigma P_i$

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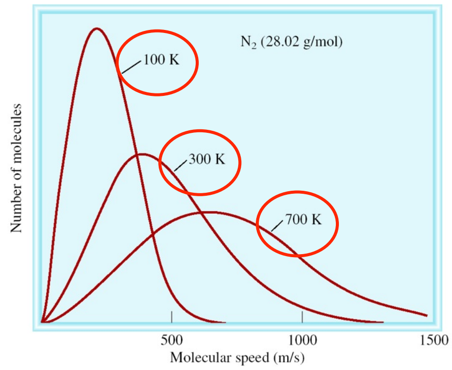
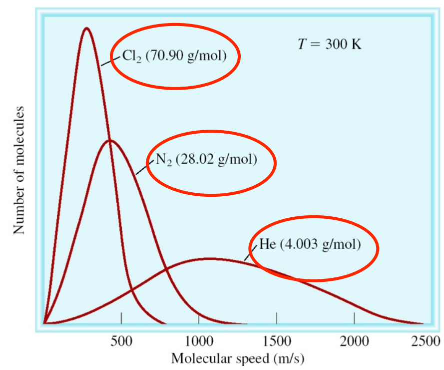


The distribution of speeds for nitrogen gas molecules at three different temperatures

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

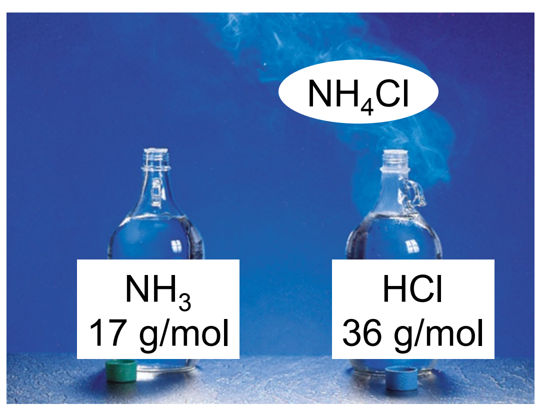
The distribution of speeds of three different gases at the same temperature



Gas diffusion is the gradual mixing of molecules of one gas with molecules of another by virtue of their kinetic properties.

molecular path

$$\frac{r_1}{r_2} = \sqrt{\frac{\mathcal{M}_2}{\mathcal{M}_1}}$$



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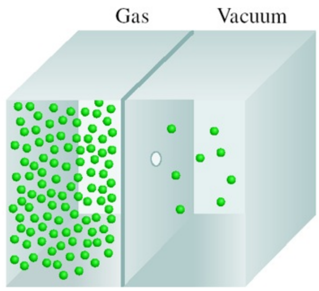
Gas effusion is the is the process by which gas under pressure escapes from one compartment of a container to another by passing through a small opening.



$$\frac{r_1}{r_2} = \frac{t_2}{t_1} = \sqrt{\frac{\mathcal{M}_2}{\mathcal{M}_1}}$$

Nickel forms a gaseous compound of the formula $Ni(CO)_x$ What is the value of x given that under the same conditions methane (CH_4) effuses 3.3 times faster than the compound?

$r_1 = 3.3 \times r_2$ $\qquad \mathcal{M}_2 = \left(\frac{r_1}{r_2}\right)^2 \times \mathcal{M}_1 = (3.3)^2 \times 16 = 174.2$

$\mathcal{M}_1 = 16$ g/mol $\qquad 58.7 + x \cdot 28 = 174.2 \qquad x = 4.1 \sim 4$

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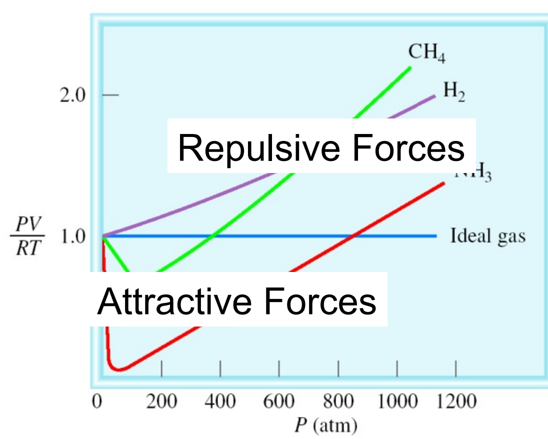
Deviations from Ideal Behavior

<u>1 mole of ideal gas</u>

$$PV = nRT$$

$$n = \frac{PV}{RT} = 1.0$$



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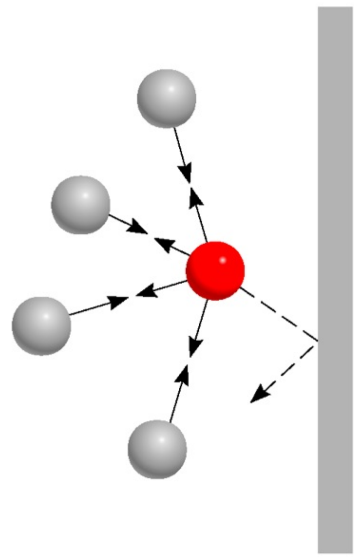
Effect of intermolecular forces on the pressure exerted by a gas.



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Van der Waals equation

nonideal gas

$$\underbrace{\left(P + \frac{an^2}{V^2}\right)}_{\text{corrected pressure}}\underbrace{(V - nb)}_{\text{corrected volume}} = nRT$$

Table 5.3

van der Waals Constants of Some Common Gases

Gas	a $\left(\frac{atm \cdot L^2}{mol^2}\right)$	b $\left(\frac{L}{mol}\right)$
He	0.034	0.0237
Ne	0.211	0.0171
Ar	1.34	0.0322
Kr	2.32	0.0398
Xe	4.19	0.0266
H_2	0.244	0.0266
N_2	1.39	0.0391
O_2	1.36	0.0318
Cl_2	6.49	0.0562
CO_2	3.59	0.0427
CH_4	2.25	0.0428
CCl_4	20.4	0.138
NH_3	4.17	0.0371
H_2O	5.46	0.0305

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