The Gaseous State of Matter

Preparation for College Chemistry
Columbia University
Department of Chemistry
Chapter Outline

KMT

Gas Laws

Ideal Gas Equation

Gas Stoichiometry

Air Pollution
Preliminary Observations

Molar mass of water: 18g /mole

$6.02 \times 10^{23}$ molecules weigh 18g

Density of water: 1g/cc

18 g liquid water occupies 18mL

18 g gaseous water occupies 22,400mL
Kinetic Molecular Theory of Gases

\[ KE = \frac{1}{2} m c^2 = \frac{p^2}{2m} \quad p = m c \]

\[ \frac{1}{2} mc^2 = \frac{3}{2} kT \]
Kinetic Molecular Theory of Gases
Distribution of Molecular Speeds
Maxwell-Boltzmann Distribution

O₂ at 25°C

O₂ at 1000°C

Molecular Speed (ms⁻¹)

# Molecules

0 200 600 1000 1400 1800
Graham’s Law of Effusion

At the same T and P, the rates of Effusion of two gases are inversely proportional to their densities or molar masses.

\[
\frac{\text{Rate}_{\text{gas}A}}{\text{Rate}_{\text{gas}B}} = \sqrt{\frac{d_B}{d_A}} = \sqrt{\frac{M_B}{M_A}}
\]
Naturally occurring Uranium: $U-235 / U238 = 1 / 140$

1st step: $U + 6 F \rightarrow \left\{ \begin{array}{c} 235 \text{UF}_6 \\ 238 \text{UF}_6 \end{array} \right\} (g)$

$$\frac{R_{235 \text{UF}_6}}{R_{238 \text{UF}_6}} = \sqrt{\frac{m_{238 \text{UF}_6}}{m_{235 \text{UF}_6}}} = \sqrt{\frac{352}{349}} = 1.0043$$

2nd step: Diffusion through thousands of membranes (cascades)

3rd step: $^{235}\text{UF}_6 \rightarrow ^{235}\text{U}$ Fully enriched weapons-grade Uranium
State Variables

\[ V = \text{volume (liters, cm}^3, m^3) \]

\[ T = \text{temperature (in K)} \]

\[ P = \text{pressure (atmospheres, mmHg, kPa)} \]
Torricelli’s barometer

At sea level

- 760 torr
- 760 mmHg
- 76 cmHg
- 101.325 mbar
- 29.9 in. Hg
- 14.7 lb/in² (PSI)
- 1 atm
Atmospheric Pressure

Hg height

150 km

air

Atmospheric Pressure
Boyle’s Law

At Constant $T$

For an Ideal Gas

$PV = C$

$P_1V_1 = P_2V_2$

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

$\Box_2 > \Box_1$
Boyle’s Law

At Constant T
For an Ideal Gas

\[ P = C \left( \frac{1}{V} \right) \]

\[ V_2 > V_1 \]
Boyle’s Law

At Constant $T$
For an Ideal Gas

$PV = \text{constant}$
Charles’ Law At Constant P for an Ideal Gas

\[ \frac{V_1}{V_2} = \frac{T_1}{T_2} \]

Absolute zero
-273°C
Gay-Lussac’s Law

At Constant V for an Ideal Gas

\[ \frac{P_1}{T_1} = \frac{P_2}{T_2} \]

\[ P = CT \]
Combined Gas Laws

Charles’

\[
\frac{V_1}{T_1} = \frac{V_2}{T_2}
\]

Boyle’s

\[
P_1 V_1 = P_2 V_2
\]

\[
\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}
\]

\[
V_2 = \frac{V_1 P_1 T_2}{P_2 T_1}
\]
STP Conditions

Reference Points for T and P for comparison

Standard Temperature: 273.15 K = 0°C

Standard Pressure: 1 atm
Dalton’s Law of Partial Pressures

\[ P_{\text{tot}} = P_1 + P_2 + P_3 + \ldots \]

where \( P_1 \) is the partial pressure of gas 1, etc...

\[ P_n = X_n P_{\text{total}} \]

\[ X_n = \frac{n_n}{n_1 + n_2 + n_3 + \ldots} \]

Molar fraction of gas \( n \)

\[ P_{\text{gas}} = P_{\text{total}} - P_{H_2O} \text{ (table 11.3 p. 387)} \]

where \( P_{H_2O} \) is the vapor pressure of water at the specified temperature. Most often used in collection of insoluble gases over water. In open systems, \( P_{\text{total}} = P_{\text{atm}} \)
Gay-Lussac’s Law of combining volumes

“When measured at the same $T$ and $P$, the ratios of the $V$ of reacting gases are small whole numbers”

Avogadro’s Law

“Equal volumes of different gases at the same $T$ and $P$ contain the same number of molecules”
Consequences of Avogadro’s Law


3. Firm foundation of KMT: gases consists of microscopic particles
**Density of Gases**

\[ d = \frac{m}{V} \]

But \( V = f(P, T) \)  \( \rightarrow d_{gas}^{T,P} \)

<table>
<thead>
<tr>
<th>Gas</th>
<th>( M \text{(g/mol)} )</th>
<th>STP ( d \text{(g/L)} )</th>
<th>Gas</th>
<th>( M \text{(g/mol)} )</th>
<th>STP ( d \text{(g/L)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( H_2 )</td>
<td>2.016</td>
<td>0.900</td>
<td>( H_2S )</td>
<td>34.09</td>
<td>1.52</td>
</tr>
<tr>
<td>( CH_4 )</td>
<td>16.04</td>
<td>0.716</td>
<td>( HCl )</td>
<td>36.46</td>
<td>1.63</td>
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<tr>
<td>( NH_3 )</td>
<td>17.03</td>
<td>0.760</td>
<td>( F_2 )</td>
<td>38.00</td>
<td>1.70</td>
</tr>
<tr>
<td>( C_2H_2 )</td>
<td>26.04</td>
<td>1.16</td>
<td>( CO_2 )</td>
<td>44.01</td>
<td>1.96</td>
</tr>
<tr>
<td>( HCN )</td>
<td>27.03</td>
<td>1.21</td>
<td>( C_3H_8 )</td>
<td>44.09</td>
<td>1.97</td>
</tr>
<tr>
<td>( CO )</td>
<td>28.01</td>
<td>1.25</td>
<td>( O_3 )</td>
<td>48.00</td>
<td>2.14</td>
</tr>
<tr>
<td>( N_2 )</td>
<td>28.02</td>
<td>1.25</td>
<td>( SO_2 )</td>
<td>64.07</td>
<td>2.86</td>
</tr>
<tr>
<td>air</td>
<td>28.9</td>
<td>1.29</td>
<td>( Cl_2 )</td>
<td>70.90</td>
<td>3.17</td>
</tr>
<tr>
<td>( O_2 )</td>
<td>32.00</td>
<td>1.43</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
**Ideal Gas Equation**  

\[
V = \frac{1}{P} \quad V = R \frac{nT}{P} \quad PV = nRT
\]

\[
\begin{align*}
V & = \frac{n}{P} \\
V & = \frac{T}{P}
\end{align*}
\]

\[
PV = \frac{mRT}{M} \quad M = \frac{mRT}{PV} \quad d = \frac{PM}{RT}
\]

**For one mole of a gas at STP, R constant:**

\[
R = \frac{(1 \text{ atm})(22.4L)}{273K} = 0.082 \ \frac{L\text{-atm}}{mol\text{-K}}
\]
Ideal Gas Equation

The ideal gas constant has energy/mol degrees dimensions

\[ R = \frac{[\text{pressure}][\text{Volume}]}{[\text{temperature}][\text{mol}]} = \frac{[\text{force}][\text{volume}]}{[\text{area}][\text{temperature}][\text{mol}]} \]

\[ R = \frac{[\text{force}][\text{length}]}{[\text{temperature}][\text{mol}]} = \frac{[\text{energy}]}{[\text{temperature}][\text{mol}]} \]

\[ R = 8.134 \text{ J mol}^{-1} \text{ K}^{-1} \sim 2 \text{ Cal mol}^{-1} \text{ K}^{-1} \]
**Gas Stoichiometry**

Concentrated nitric acid acts on copper and produces nitrogen dioxide and dissolved copper. 6.80 g Cu is consumed and NO₂ is collected at a pressure of .970 atm and a temperature of 45°C (318 K). Calculate the volume of NO₂ produced.

\[
\text{Cu(s) + 4H}^+ + 2\text{NO}_3^- (\text{aq}) \rightarrow \text{Cu}^{+2} (\text{aq}) + 2\text{NO}_2 (\text{aq}) + 2\text{H}_2\text{O}
\]

\[
6.80 \text{ g Cu} \times \frac{1 \text{ mol Cu}}{63.55 \text{ g Cu}} \times \frac{2 \text{ mol NO}_2}{1 \text{ mol Cu}} = 0.214 \text{ mol NO}_2
\]

\[
V = \frac{nRT}{P} = 5.76 \text{ L NO}_2
\]
Real Gases

Follow the ideal gas law at sufficiently low densities

- Gas molecules attract one another
- Gas molecules occupy a finite volume

Both factors increase in importance when the molecules are close together (high P. low T).

Deviations from ideality are quantified by the Compressibility factor $z$

$$z = \frac{P V}{n R T}$$
Real Gases

Intermolecular Forces

Compressibility factor

Ideal Gas

$N_2$

$H_2$

$CH_4$

$P$ (atm)
Nitrogen at several $T$

Compressibility factor vs. $P$ (atm) at different temperatures:
- 25 °C
- 600 °C
- -100 °C

The graph compares nitrogen data to the ideal gas behavior.
Van der Waals Equation (1873)

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

- \( b \) = constant representing volume excluded per mole of molecules
- \( a \) = depends on the strength of attractive forces

\( \frac{n^2}{V^2} \) Proportional to reduction of wall collisions due to cluster formation.
Air Pollution

Upper and Lower Atmosphere Ozone

Sulfur Dioxide

Nitrogen Oxides

Green House Effect
Upper atmosphere Ozone

\[ \text{O}_2 \xrightarrow{\text{h illuminated}} 2\text{O} \]

\[ \text{O}_2 + \text{O} \rightarrow \text{O}_3 \quad \text{Allotropic Transformation} \]

\[ \text{O}_3 \xrightarrow{\text{h illuminated}} \text{O}_2 + \text{O} + \text{heat} \quad \text{Ozone shield} \]

\[ \text{CCl}_3\text{F} \xrightarrow{\text{h illuminated}} \text{CCl}_2\text{F} \cdot + \text{Cl} \cdot \quad \text{Ozone Layer Destruction} \]

\[ \text{Cl} \cdot + \text{O}_3 \rightarrow \text{ClO} \cdot + \text{O}_2 \quad \text{Chain propagation} \]

\[ \text{ClO} \cdot + \text{O} \rightarrow \text{O}_2 + \text{Cl} \cdot \]
**Tropospheric Chemistry**

\[ \text{NO}_2 \xrightarrow{h\nu} \text{NO} + \text{O} \]  
*Photochemical Smog*

\[ \text{O}_2 + \text{O} + \text{M} \rightarrow \text{O}_3 \]  
*< 3 ppm Ozone alert, M= N\textsubscript{2} or O\textsubscript{2}*

\[ \text{SO}_2 + \text{OH} \rightarrow \text{SO}_2\text{OH} \]  
*Radical Oxidation*

\[ \text{SO}_2\text{OH} + \text{O}_2 \rightarrow \text{SO}_3 + \text{OOH} \]  
*Acid Rain Precursor*

\[ \text{OOH} \rightarrow \text{O} + \text{OH} \]
The Greenhouse Effect

Some of the infrared radiation passes through the atmosphere, and some is absorbed and re-emitted in all directions by greenhouse gas molecules. The effect of this is to warm the earth's surface and the lower atmosphere.

Solar radiation passes through the clear atmosphere

Some solar radiation is reflected by the earth and the atmosphere

Most radiation is absorbed by the earth's surface and warms it

Infrared radiation is emitted from the earth's surface
Emissions increasing
Carbon (billion tonnes)