Chapter 10: Gases

1. Gas Properties
2. Empirical Gas Laws
3. Ideal Gas Law
4. Gas Stoichiometry
5. Dalton’s Law of Partial Pressures
6. Kinetic Molecular Theory of Gases
7. Effusion & Diffusion
8. Real Gases

The Gaseous State

What are the Characteristics of the Gaseous State?

1. Fluid - Will Take the Shape of a Container
2. Compressible - Density Changes As the Volume Changes.
3. Forms Solutions (Homogeneous Mixtures)

How Can We Measure the Quantity of Molecules in the Gaseous State?

11.1 Pressure

Pressure is defined as the force per unit area.

\[ P = \frac{F}{A} \]

Units of Pressure:
- 1atm = 760 torr
- 1atm = 760mm Hg
- 1atm = 14.7lb/in²
- 1atm = 1.01x10⁵ Pa
- 1Pa = 1N/m²
  - = 1kg/(m·s²)

Pressure Measurement

The Barometer

Evangelista Torricelli (1608-1647)

Why Does the Weatherman Report the Barometric Pressure?

The Manometer

\[ P_g + P_c = P_{atm} \]

\[ P_g = P_{atm} + P_c \]

11.2 Empirical Gas Laws

Boyle’s Law, \( PV=k \)  @ const. \( n,T \)

Charle’s Law, \( V=bT \)  @ const. \( n,P \)

Avogadro’s Law, \( V=an \)  @ const. \( P,T \)
Boyle’s Law Data
From Boyle’s Law, PV=k, What Would You Graph?

\[ V = k \frac{1}{P} \quad \text{or} \quad P = k \frac{1}{V} \]

Knowing \( V \) at one \( P \), how do we determine it at another \( P \)?

This is a “Two State” Problem

\[ P_1 V_1 = k = P_2 V_2 \]

Class Problem, **If a sealed container at atmospheric pressure is doubled in size, what is the new pressure?**

\[ P_2 = P_1 \left( \frac{V_1}{V_2} \right) \]

Charles’s Law & Absolute Zero

What happens at pt. A?

Absolute Zero.

It has never been obtained. Negative Kelvin temperature implies negative volume

Avogadro’s Hypothesis

Equal Volumes of Gases at the Same Temperature and Pressure Have the Same Number of Molecules

Avogadro’s Law

- Effect of changing the number of gaseous molecules on the volume

\[ V = n \quad @ \quad \text{const.} \ P, T \]

What are the units of Avogadro’s Constant.

If 3 moles \( \text{H}_2(\text{g}) \) occupies 2L, what volume does 4 moles occupy?

This is a “Two State” Problem

\[ V_1 = n_1 \quad \text{and} \quad V_2 = n_2 \]

Dividing state one by the equality of state two cancels Avagardo’s constant:

\[
\frac{V_1}{V_2} = \frac{n_1}{n_2} \quad \implies \quad \frac{V_1}{V_2} = n_1 \quad \implies \quad V_1 = V_2 \left( \frac{n_1}{n_2} \right)
\]

Solve algebraically first, then assign state (State 1 is volume of 4 moles)
11.3 Ideal Gas Law: Eq of State

\[ PV = nRT \]

\[ R = 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \]

Note, from chapter 6, \((\Delta H = E + P \Delta V)\) and the ideal gas law relates the absolute temperature to the molar work of expansion. So \( R \) has units of energy/mol-K.

Summary of Gas Laws

<table>
<thead>
<tr>
<th>Equation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ideal Gas Law: ( PV = nRT )</td>
<td></td>
</tr>
<tr>
<td>Boyle’s Law: ( PV = k ), ( k = nRT )</td>
<td></td>
</tr>
<tr>
<td>Charles’s Law: ( V = bT ), ( b = nR/P )</td>
<td></td>
</tr>
<tr>
<td>Avogadro’s Law: ( V = an ), ( a = RT/P )</td>
<td></td>
</tr>
</tbody>
</table>

STP

Standard Temperature & Pressure
Properties of gases are often tabulated at STP:
- Standard Temperature = 0°C
- Standard Pressure = 1 Atm (actually 1 bar = .987 atm)

What is the Molar Volume of an Ideal Gas at STP?

Ideal Gas Molar Volume

\[ V = \frac{nRT}{P} \]

\[ V = \left(1 \text{ mol}\right)\left(0.0826 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right)\left(273K\right) \]

\[ V = 22.4 \text{ L at STP} \]

Interactive Quiz 12.4
Two State Eq. vs. Ideal Gas Laws

When would you want to use the Two State Equation instead of the Ideal Gas Law?

- Use Two State Eq. if given two sets of conditions for the same gas (say STP plus another)
- Use ideal gas law if given 3 of the 4 variables (P, V, n & T) or if n changes

Gas Density

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

Use units of g/L (not g/mL)

How can we determine the density of a gas?

The Problem is gasses are compressible and so the density is not a constant value like it is for solids and liquids.

- Need an equation of state like the Ideal Gas Equation

Ideal Gas Density

\[ PV = nRT \]

\[ PV = \frac{mRT}{fw} \]

\[ d = \frac{m}{V} = \frac{P(fw)}{RT} \]

Note, \[ n \text{(moles)} = \frac{m(g)}{fw(g/mol)} \]

The mass of a gas can be determined from the # of moles (n) and molar mass (formula weight, fw) of the gas.

Molar Mass Problem

An unknown gas has a density of 4.08g/l at 88°C and 1.4 atm, what is its molar mass?

Density Problem

What is the density of sulfur dioxide gas at 88°C and 1.4 atm?
11.4 Gas Stoichiometry

Knowing the P,V & T, gives the moles of a gas, therefore we can use gas phase data in stoichiometric calculations.

Gas Stoichiometry

Consider the Decomposition of Potassium Chlorate

\[ 2\text{KClO}_3(\text{s}) \xrightleftharpoons{\text{MnO}_2, \Delta} 2\text{KCl}(\text{s}) + 3\text{O}_2(\text{g}) \]

How many grams KClO\textsubscript{3} would produce enough O\textsubscript{2}(\text{g}) to occupy 30mL at 1 atm and 68\degree F.

1. Gas Phase Step - Determine moles O\textsubscript{2} needed
2. Stoichiometric Step - Determine mass of KClO\textsubscript{3} required to produce the O\textsubscript{2}.

1. Gas Phase Calculations

\[ n = \frac{PV}{RT} \]

\[ T(K) = 273.15^\circ C + \frac{(68^\circ F + 40)}{1.8} - 40)^\circ C = 293.15 K \]

2. Stoichiometric Calculations

\[ 2\text{KClO}_3(\text{s}) \xrightarrow{\text{MnO}_2, \Delta} 2\text{KCl}(\text{s}) + 3\text{O}_2(\text{g}) \]

How Many Liters of Hydrogen Gas (at 35\degree C & 720 torr) Will Be Released

When 200.0 mL of 3.00 M HCl reacts with 10.0 g Mg?

1. This is a Single Replacement Reaction

\[ \text{Mg(s)} + 2 \text{HCl(aq)} \rightarrow \text{MgCl}_2(\text{aq}) + \text{H}_2(\text{g}) \]

-Note how this reaction equation involves species in all three phases

2. Determine Moles of Each Reactant

3. Determine Limiting Reagent
Calculate Volume of Hydrogen Gas

12.5 Dalton’s Law of Partial Pressure

For a mixture of gases, the total pressure is the sum of the pressures due to each type of gas.

Partial Pressure - is the pressure due to a specific type of gas.

\[
P_T = \sum_{i=1}^{\text{all gases}} P_i
\]

Consider a mixture of 3 gases, 1, 2 & 3

\[
P_T = P_1 + P_2 + P_3
\]

\[
P_T = n_1 \left( \frac{RT}{V} \right) + n_2 \left( \frac{RT}{V} \right) + n_3 \left( \frac{RT}{V} \right)
\]

\[
P_T = (n_1 + n_2 + n_3) \left( \frac{RT}{V} \right)
\]

\[
P_T = n_T \frac{RT}{V}
\]

Were \( n_T = n_1 + n_2 + n_3 \)

A Tank Contains 78.0 g of \( \text{N}_2 \) and 42 g of He at a total pressure of 3.75 atm and a temperature of 50.0°C.

Calculate

1. Moles \( \text{N}_2 \)
2. Moles He
3. Partial Pressure of \( \text{N}_2 \)
4. Partial Pressure of He

Mole Fraction

\( X_A \) is the mole fraction of species A, where

\[
X_A = \frac{n_A}{n_T}
\]

\[
\frac{P_A}{P_T} = \frac{n_A(\text{RT}/\text{V})}{n_T(\text{RT}/\text{V})} = \frac{n_A}{n_T} = X_A
\]

\[
P_A = X_A P_T
\]

Gasses Over Water

1. What Is the Partial Pressure of Oxygen If the Gas at 25°C Has a Pressure of 720 Torr?

\[
P_T = P_{\text{oxygen}} + P_{\text{water}}
\]

\[
P_{\text{oxygen}} = 720 - 23.756 = 696 \text{ Torr}
\]
### Gasses Over Water

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Pressure (torr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>9.209</td>
</tr>
<tr>
<td>20</td>
<td>17.535</td>
</tr>
<tr>
<td>25</td>
<td>23.756</td>
</tr>
<tr>
<td>30</td>
<td>31.824</td>
</tr>
<tr>
<td>40</td>
<td>55.324</td>
</tr>
<tr>
<td>60</td>
<td>149.4</td>
</tr>
<tr>
<td>70</td>
<td>233.7</td>
</tr>
<tr>
<td>90</td>
<td>525.8</td>
</tr>
<tr>
<td>100</td>
<td>760</td>
</tr>
</tbody>
</table>

2. If 0.50 L of Water Is Displaced, What Mass of Oxygen Was Produced?

\[
\text{O}_2(g) + \text{H}_2\text{O}(g) \rightarrow \text{H}_2\text{O}_2(g)
\]

### 12.6 Kinetic Molecular Theory of Gases (KMT)

1. The Volume of Gas Particles are Negligible Compared to the Total Gas Volume; Most of the Volume is Empty Space

2. Gas Particles are in Constant Motion, Pressure Results from Elastic Collisions with the Walls of the Container (the particles do not lose energy)

3. The Average Kinetic Energy of Gas Particles are Proportional to the Kelvin (Absolute) Temperature

4. There Are Negligible Intermolecular Forces

### KMT and Boyle’s Law (P,V)

\[ P = (K) \frac{1}{V} \quad K = nRT \]

As the volume gets smaller the mean free path decreases and the collision frequency goes up, therefore P increases as V decrease.

### KMT and Charle’s Law (V,T)

\[ V = (b)T \quad b = nR \frac{1}{P} \]

As the temperature increases the pressure tends to increase but since this is at constant pressure, the volume increases to compensate.
KMT and Avogadro’s Law (V,n)

\[ V = (a)T \quad a = \frac{RT}{P} \]

As the number of molecules increases, the collision frequency increases causing the volume to increase at constant pressure.

KMT and Daltons’s Law of Partial Pressures

Since there are no intermolecular interactions, the total pressure is proportional to the total number of molecules regardless of their identity.

Kinetic Energy

\[ E_K = \text{The Energy of Motion} \]

For a Particle (molecule)

\[ E_K = \frac{1}{2} (\text{mass})(\text{speed})^2 = \frac{1}{2}mv^2 \]

What Variables Effect the Kinetic Energy?

The Absolute Temperature (K)

Not Molecular Size!

Larger Molecules Have a Lower Average Velocity

Note, a small gas particle like H\(_2\) has the same average kinetic energy as a large particle like Cl\(_2\), (H\(_2\) having the smaller mass, has the greater average velocity).

KMT & Temperature

Kinetic Energy = \(1/2mv^2\)

How will increasing the temperature effect the distribution of molecular speeds?

Does the area under the curve change as the temperature changes?

KMT & Temperature

How does the molecular size influence the velocity distribution at constant temperature?

Heaviest Molecules
Middle Weight Molecules
Lighter Molecules
Root Mean Square Velocity
Note velocity is a vector and in 3D space the average velocity of random motion is zero as the components in opposite directions cancel.

\[ \mu^2 = \mu_x^2 + \mu_y^2 + \mu_z^2 \]

\[ \mu_{rms} = \sqrt{\mu_x^2 + \mu_y^2 + \mu_z^2} \]

For an ensemble of molecules

\[ \overline{KE} = \text{Ave Kinetic Energy} \]

\[ \overline{KE} = \frac{1}{2} \mu^2 \]

\[ \mu = \text{root mean square velocity} \]

\[ E_{k,ave} = N_A \left( \frac{1}{2} m \mu^2 \right) = \frac{1}{2} RT \]

\[ \mu = \sqrt{\frac{mE}{nRT}} \]

Graham’s Law:
Diffusion: Process where gas mix through random motion

Effusion: Process of collision less movement of gasses into a vacuum

Graham’s Law: Rate of Effusion is Inversely Proportional to Molar Mass

\[ E_k = \frac{1}{2} RT = N_A \frac{1}{2} m \mu^2 \]

At Constant Temperature both gases have same kinetic energy

\[ \left( \frac{1}{2} m_1 \mu_1^2 \right)_{gas1} = \left( \frac{1}{2} m_2 \mu_2^2 \right)_{gas2} \]

\[ m_1 \mu_1^2 = m_2 \mu_2^2 \]

\[ \frac{m_1}{m_2} = \left( \frac{\mu_1}{\mu_2} \right)^2 \quad \text{and} \quad \frac{\mu_1}{\mu_2} = \sqrt{\frac{m_2}{m_1}} = \sqrt{\frac{m_1}{m_2}} \]

Real Gasses:
When Do Real Gasses Deviate From Ideal?
-When the Postulates of the Kinetic Molecular Theory Break Down

-High Pressure: Gas Molecules Take up Substantial Space of Container and Being Closer Together, Have Greater Intermolecular Interactions

-Low Temperature: The Average Kinetic Energy Is Decreased Causing a Greater Influence of Intermolecular Forces on the Gas Species Trajectory

Non Ideal Gases
Van Der Waals Equation

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

Correction Term for Intermolecular Forces
Correction Term for Molecular Volume
Van Der Waals Equation

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

<table>
<thead>
<tr>
<th>Gas</th>
<th>a (atm-L^2) mol^2</th>
<th>b (L) mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>0.0341</td>
<td>0.0237</td>
</tr>
<tr>
<td>Xe</td>
<td>4.19</td>
<td>0.0511</td>
</tr>
<tr>
<td>CH₄</td>
<td>2.25</td>
<td>0.0428</td>
</tr>
<tr>
<td>NH₃</td>
<td>4.17</td>
<td>0.0371</td>
</tr>
<tr>
<td>H₂O</td>
<td>5.46</td>
<td>0.0305</td>
</tr>
</tbody>
</table>