Chapter 10 part 1: Ideal Gases

Read: BLB 10.1–5
HW: BLB 10.2, 19a,b, 23, 26, 30, 39, 41, 45, 49
Sup 10:1–6

Know:
What is pressure?

Gases
Pressure and Boyle’s Law
Temperature and Charles’ Law
Avogadro’s Law
Ideal gas equation of state \( PV = nRT \)
Density and Molecular Weight
\( d = \frac{PM}{RT} \)
\( M = \frac{dRT}{P} \)

Ideal Gas Law and Chemical Reactions
Stoichiometry
Partial Pressures
Dalton’s Law

Gases

Which elements exist as gases at ordinary temperature and pressure?

Some molecules also exist as gases at standard temperature and pressure (Table 10.1)

Gases:
• Have simple molecular formulas
• Consist of non-metallic elements
• Expand spontaneously to fill container

• Are very compressible
• Form homogenous mixtures
• Have KE >> IMF

NO SCORE FROM EXAM 2??
Not a problem - Go to 210 Whitmore and talk to Mike Joyce or email at mjj12@psu.edu
• PRESSURE

Pressure: force per area \[ \frac{F(\text{newtons})}{A(m^2)} \]

SI Units: 1N/ m² = 1Pa Pascal

Standard atmospheric pressure**:  
1 atm = 1.013x10⁵ Pa  
1 atm = 14.7 lb/in²  
1 atm = 760 torr (mm Hg)

*real atmospheric pressure varies with altitude and weather
What is Pressure?

Pressure is caused by Molecular Collisions!

- Function of density and temperature
- Earth’s gravity affects the density of gas at sea level

- Which has a higher pressure?
  A. 1 mol Ar gas on the moon (1L, 373 K)
  B. 1 mol Ar gas on Earth (1L, 373 K)
  C. Both are the same pressure.

How big is one atm?

If we had a box that measured 12 inches by 6 inches, the area of the top of the box would be:

So, 1 atm of force:
Pressure and altitude

• Pressure at any altitude depends on weight of gas above it.

• Pressure decreases exponentially with altitude.

<table>
<thead>
<tr>
<th>Altitude (km)</th>
<th>$P$ (atm)</th>
<th>collision frequency (sec$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
<td>$10^{10}$</td>
</tr>
<tr>
<td>50</td>
<td>$10^{-3}$</td>
<td>$10^{7}$</td>
</tr>
<tr>
<td>100</td>
<td>$10^{-6}$</td>
<td>$10^{3}$</td>
</tr>
<tr>
<td>200</td>
<td>$10^{-13}$</td>
<td>1</td>
</tr>
</tbody>
</table>

Measuring Pressure of the Atmosphere

Barometer is used to measure $P_{\text{atm}} = P_a$

In a closed tube, the forces balance each other:

\[ P_a = \frac{F_a}{A} = \frac{F_l}{A} = P_l \]

\[ P_l = \frac{F_l}{A} = g d_l h \]

Where:

$g =$ gravitational constant

$d_l =$ density of liquid

\[ P_{\text{atm}} = (g d_l) h \]

$P_{\text{atm}} \propto \text{height of column of liquid}$

measure $P$ in terms of height of Hg

1 atm $=$ 760 torr "$=$ 760 mmHg
**Mercury Manometer**

**Closed Ended:** \( P_g = h \) (in mm Hg)

**Open Ended:** Which P is greater?

IF \( P_{\text{gas}} > P_{\text{atm}} \)

\[
P_{\text{gas}} = P_{\text{atm}} + P_h
\]

IF \( P_{\text{gas}} < P_{\text{atm}} \)

**PVT relationships**

State of gas described by \((n,P,V,T)\)

- \( n \) – # moles
- \( P \) – pressure
- \( V \) – volume
- \( T \) – (absolute) temperature (K)

**Avogadro’s Law:** \( V \) of gas at constant \( T \) and \( P \) is proportional* to the number of moles of gas:

\[
V \propto n \quad \text{(P,T constant)}
\]

*constant of proportionality is the same for ALL gases.
**Boyles’ Law:** V of a fixed amount of gas at constant T is inversely proportional to P

\[ V \alpha \frac{1}{P} \quad (n,T \text{ fixed}) \]

<table>
<thead>
<tr>
<th>Pressure (atm)</th>
<th>Volume (V)</th>
<th>( V )</th>
<th>( \frac{1}{2}V )</th>
<th>( \frac{1}{4}V )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 atm</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 atm</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4 atm</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Charles’s Law:** V of fixed amount of gas at constant P is proportional to the absolute temperature

\[ V \propto T \quad (n,P \text{ fixed}) \]

\[ V \text{ vs } T \]

\[ 0 \text{ K} = -273.15^\circ C \]

**Ideal Gas Law**

\[ PV = nRT \]

Units of R are important

\[ R = 0.08206 \frac{\text{L atm}}{\text{mol K}} \quad R = 8.314 \frac{\text{J}}{\text{mol K}} \]
Example:

What is the volume (V) occupied by 1.00 mole of gas at exactly 0° C and 1 atm?

\[
V_{\text{STP}} = 22.4 \text{L/mol}
\]

Chapter 10 part 2: Partial Pressures, Kinetic Molecular Theory

Read: BLB 10.6-10.9
HW: BLB 10.5, 8, 59, 61, 71, 75, 77, 82, 83, 84
Supplemental 10.7-10.15

Know:
- kinetic-molecular theory
- partial pressures

When is Exam #3??

Locations will be posted on Chem 110 website

When is the Final Exam??

IGNORE THE ROOMS ON ELION: LOCATIONS WILL BE POSTED ON THE WEBSITE
Density and Molecular Weight of Gases

\[
density = \frac{\text{mass in g}}{\text{volume in L}} = \frac{m}{V}
\]

Molecular Weight \(= M = \frac{\text{mass in g}}{\# \text{ moles}} = \frac{m}{n}
\)

\[\Rightarrow m = n \cdot M\]

\[\Rightarrow d = \frac{m}{V} = \frac{n \cdot M}{V} = \frac{n}{V} \cdot M\]

Rearranged Ideal gas law

\[\frac{n}{V} = \frac{P}{RT}\]

What is the density of He gas in g/L at 21°C and 752 torr?

Under these conditions, the density of air is 1.188 g/L. The mass difference between 1 L of He and 1 L of air is

\[1.188 \text{ g/L} - 0.164 \text{ g/L} = 1.024 \text{ g/L}\]

This is the buoyant (lifting force) of He per L.
Which one of the following samples contains the largest number of molecules?

1. 1.0 L of H$_2$ (g) at STP
2. 1.0 L of N$_2$ (g) at 0°C and 800 mm Hg
3. 1.0 L of CO$_2$ (g) at 0°C and 600 mm Hg

Which one of the following gas samples has the highest density?

1. 1 mole of He (g) in a 10 L flask at STP
2. 1 mole of N$_2$ (g) in a 10 L flask at STP
3. 1 mole of CO$_2$ (g) in a 10 L flask at STP

Mixtures of gases

<table>
<thead>
<tr>
<th>Mix</th>
<th>Volume (L)</th>
<th>Mole Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. 5 moles of CO$_2$</td>
<td>40 L</td>
<td></td>
</tr>
<tr>
<td>2. 2 moles of N$_2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3. 1 mole of Cl$_2$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

What is P ?

$$P_{\text{TOT}} = n_{\text{TOT}} \frac{RT}{V}$$

$$P_{\text{TOT}} = (n_{CO_2} + n_{N_2} + n_{Cl_2}) \frac{RT}{V}$$

$$= \frac{(5 + 2 + 1) \text{ moles}(0.0821 \frac{L - \text{atm}}{K - \text{mole}})(273 \text{K})}{40 L}$$

$$= 4.5 \text{ atm}$$

Can also Rearrange:

$$P_{\text{TOT}} = n_{CO_2} \frac{RT}{V} + n_{N_2} \frac{RT}{V} + n_{Cl_2} \frac{RT}{V}$$

$$P_{\text{TOT}} = P_{CO_2} + P_{N_2} + P_{Cl_2}$$

$$P_{\text{TOT}} = 2.8 \text{ atm} + 1.1 \text{ atm} + 0.56 \text{ atm}$$

$$= 4.5 \text{ atm}$$
Dalton’s Law of Partial Pressures

Total pressure is equal to the sum of partial pressures:

\[
\text{Total pressure} = \sum \text{partial pressures}
\]

Example: 3.0L of He at 5.0 atm and 25°C is combined with 4.5 L of Ne at 2.0 atm and 25°C at constant T into a 10 L vessel. What is the partial pressure of the He in the 10 L vessel?

What is the total pressure in the 10 L vessel?

Mole Fraction and Partial Pressure
The fraction of the total pressure contributed by each gas is equal to its mole fraction: \( X_i \)

\[
X_i = \frac{P_i}{P_{tot}} = \frac{n_i}{n_{tot}}
\]

Example From Previous Page:

\[
X_{CO_2} = \frac{P_{CO_2}}{P_{tot}} = \frac{2.8 \text{ atm}}{4.5 \text{ atm}} = 0.622
\]

Example 2: What is the partial pressure of O₂ in the vessel below?

<table>
<thead>
<tr>
<th>P_{TOT} = 756 TORR</th>
<th>GAS</th>
<th>MOLE FRACTION</th>
</tr>
</thead>
<tbody>
<tr>
<td>T = 300.0°C</td>
<td>Ar</td>
<td>0.320</td>
</tr>
<tr>
<td>V_{TOT} = 5.00 L</td>
<td>N₂</td>
<td>0.270</td>
</tr>
<tr>
<td></td>
<td>CO₂</td>
<td>0.150</td>
</tr>
<tr>
<td></td>
<td>Ne</td>
<td>0.160</td>
</tr>
<tr>
<td></td>
<td>O₂</td>
<td>?</td>
</tr>
</tbody>
</table>

1.756 torr
2.378 torr
3.680 torr
4.756 torr
5. There is not enough data to determine this.
If you know the barometric pressure, you can determine the partial pressure.

**Collecting a gas over water; use the vapor pressure of H₂O**

During a reaction, N₂ is collected over H₂O. Using the following data, find out how much N₂ was collected. Note: \( P_{\text{TOT}} = P_{N_2} + P_{H_2O} \)

\[
\begin{align*}
P_{H_2O} &= 21 \text{ torr (Appendix B, } P_{\text{vap}} \text{ of } H_2O) \\
P_{\text{bar}} &= 742 \text{ torr (} = P_{\text{TOT}}) \\
V &= 55.7 \text{ ml} \\
T &= 23°C
\end{align*}
\]

**Review Ideal Gas Law Relationships**

If P and T are constant:
Avagadro’s Law

If n and T are constant:
Boyle’s Law

If n and P are constant:
Charles’ Law

Combined, we get the Ideal Gas Law:

At STP (What T and P? ___________):
\[
V_{\text{STP}} = \frac{nRT}{P_{\text{bar}}}
\]
Regions of the Atmosphere are defined by Temperature:

1. **Troposphere**: $T \downarrow$ as altitude $\uparrow$
   - Where we live!
   - Weather
   - Airplanes
2. **Stratosphere**: $T \uparrow$
   - Warming caused by ozone cycle
   - Ultraviolet light absorbed
3. **Mesosphere**: $T \downarrow$
   - Density of gases is small.
4. **Thermosphere**: $T \uparrow$
   - High energy radiation is absorbed
   - Ions formed.

**So - What is temperature?**

KINETIC MOLECULAR THEORY

1. Molecules move in straight lines; their direction is random.
2. Molecules are small. (The volume they occupy is small compared to the total V.)
3. Molecules do not attract or repel each other (no intermolecular forces).
4. Elastic collisions
5. **Mean kinetic energy** $\epsilon \propto T(K)$.

**Ideal Gas Law**

$$PV = nRT$$
**Effect of Temperature on Molecular Speeds**

![Graph showing effect of temperature on molecular speeds]

- **Blue line** is $N_2$ at 0°C
- **Red line** is $N_2$ at 100°C

Increasing $T$ increases both the most probable speed (peak of curve) and the rms speed $u$ ($\propto$ average speed)

---

**Chapter 10 part 3: Kinetic Molecular Theory, Real Gases**

- **Read:** BLB 10.6-10.9
- **HW:** BLB 10.5, 8, 59, 61, 71, 75, 77, 82, 83, 84  
  Supplemental 10.7-10.15

- **Know:**
  - kinetic-molecular theory
  - effusion & diffusion
  - real gases (van der Waals)

---

**When is Exam #3??**

Locations will be posted on Chem 110 website

---

**When is the Final Exam??**

*IGNORE THE ROOMS ON ELION: LOCATIONS WILL BE POSTED ON THE WEBSITE*
**Distribution of Molecular Speeds**

\[ T(K) \propto \varepsilon = \frac{1}{2}mu^2 \]

\[ \varepsilon = \text{average kinetic energy of molecule} \]
\[ u = \text{(root mean square) speed of molecule} \]
\[ m = \text{mass of molecule (in kg)} \]

Where is the root mean square speed \((u)\) on this graph?

![Graph showing distribution of molecular speeds.](image)

**When T increases:**

- less molecules move _________
- more molecules move _________

What happens to average speed??

---

**Kinetic Molecular Theory:**

explanations for why gases behave as they do.

**Experimentally Observed \(P\) vs. \(T\) Behavior**

\[ P \propto T \quad (n,V \text{ fixed}) \]

- Increase \(T\) \((n,V \text{ constant})\); \(P\) increases. WHY?
Relate KMT to Observed Behavior

Experimentally Observed P vs. V Behavior

\[ V \propto \frac{1}{P} \quad (n,T \text{ constant}) \]

- Increase \( V \) (\( n,T \) constant); \( P \) decreases

WHY?

Using KMT to describe Speed of Gases

\[ \varepsilon = \frac{1}{2} m u^2 \]

\[ \varepsilon \propto \frac{1}{2} M u^2 \]

- different gases (at the same \( T \)) have different average speeds (but same \( \varepsilon \))

\[ u = \sqrt{\frac{3RT}{M}} \]

- On average: lighter gases move faster
  heavier gases move slower

\[ \frac{\text{Fraction of molecules within } 10 \text{ m/s of indicated speed}}{\text{Molecular speed (m/s)}} \]

Dr. Lori Van Der Sluys Page 29 Chapter 10

Dr. Lori Van Der Sluys Page 30 Chapter 10
Example:

- Speed of N\textsubscript{2} at 20°C?  \[M = 0.028 \text{kg/mol}\]
  \[u = 511 \text{m/sec (≈ 1100 mph)}\]

- Speed of He at 20°C?  \[M = 0.004 \text{ kg/mol}\]
  \[u = 1360 \text{m/sec}\]

Note: use \(R = 8.31 \text{J/mol•K}\) and \(M\) in kg/mol

Other Properties of Gases:

**Effusion:** leakage of gas through a small opening

**Diffusion:** spread of gas through space.

\[
\text{Rate of effusion (or diffusion)} \propto \sqrt{\frac{1}{M}}
\]

Usually we compare the diffusion rate of two gases.

\[
\text{Graham’s Law} \quad \frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}
\]

⇒ Heavy molecules effuse (or diffuse) more slowly than lighter molecules.

An unknown gas effuses at a rate 1.49 times as fast as Cl\textsubscript{2}. What is the molecular weight of the gas?
Collisions and Diffusion

Rate of diffusion follows Graham's Law:
- Depends on $\sqrt{\frac{T}{M}}$ and molecular speed
- Depends on molecular size ($\mathcal{M}$)
- What happens to the diffusion rate as size increases?

At STP molecules collide $\sim 10^{10}$ times per second.

$N_2$ speed = 511 m/s @ 20°C

but...

in 1 s it collides $10^{10}$ times

Measuring the Result of Collisions on Diffusion

The MEAN FREE PATH (MFP) is the distance between collisions. For air molecules, this is $\sim 60$ nm ($6 \times 10^{-8}$ m) at 1 atm. What happens to the MFP as density and pressure decrease?
**Real gases deviate from ideal behavior**

For an ideal gas:

\[ PV = nRT \]

\[ \frac{PV}{nRT} = 1 \]

For a non-ideal gas (real gas) this is not true for two types of conditions:

- high P
- low T

**2 Reasons:**

1. Molecules have finite size.

\[ \frac{PV}{nRT} > 1 \quad \text{(high P)} \]

2. Molecules exert attractive forces.

\[ \frac{PV}{nRT} \neq 1 \quad \text{(high P, low T)} \]

**In general**

- As P increases, non-ideality increases.
- As T decreases, non-ideality increases.

**At high P, Postulate 2 in KMT is not true.**

![Graph showing deviation from ideal gas behavior](image)

As P increases PV/RT increases  (Ex: H₂)

If the V of the container is not that much smaller than V of the gas, use of the ideal gas law leads to an appearance of larger n.

- At low pressures, deviation from ideal is small and the ideal-gas equation doesn't generate serious error.
At low $T$, postulate 3 in KMT is not true. 

As $P$ increases $PV/RT$ decreases (Ex: 1 mol N$_2$)

At low $T$ or high $P$, attractive forces lead to the appearance of a smaller $n$ (molecules stick together)

. Different gases deviate from the ideal gas law by different amounts

WHY?

Compare CO$_2$ to CH$_4$; which deviates more from ideality at low pressures?

How do intermolecular forces affect the expected pressure on the wall?
Correcting the ideal gas law: the van der Waals Equation

- At intermediate pressures, the ideal gas law calculates a $P$ that is too small. Deviation is related to:
  - size of attractive interactions ($a$)
  - frequency of collisions $\left(\frac{n}{V}\right)^2$

- At high pressure, the ideal gas law calculates a $V$ that is too large.
  - actual $V = V_{\text{cont}} - V_{\text{excluded}}$
    - $V = V - nb$
    - $b \Rightarrow$ volume per mole of molecules

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

Table 10.3 lists van der Waals constants ($a$, $b$) for various gas molecules.