Chapter 8 Part 1 - Gases

8.1 States of Matter and Their Changes

Matter can exist in 3 primary states or phases: _____________________________.

Review the overall Kinetic Molecular Theory of Matter.

- **Solid** particles are in fixed positions relative to each other: they have only vibrational movements. They have ________________.
- **Liquid** particles are still touching, but they have the freedom to slide past each other. They have ________________.
- **Gas** particles are far apart and are in constant motion. They have _______.

The state of matter depends on the strength of the attractive forces between the particles.

- Solids have the ___________ attractive forces.
- Gases have the ___________ attractive forces.

**Changes of State**

Transformation from one phase to another is called a **change of state**.

Changes of state take place at a given temperature.

- __________________________ – the *temperature* at which solid ↔ liquid.
  The two phases can exist in equilibrium at this temperature.
- __________________________ – the *temperature* at which liquid ↔ gas.
  The two phases can exist in equilibrium at this temperature.
- It is possible for a solid to change directly to a gas in a process called _______________.

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**Gibbs Free Energy**

Since different phases are associated with different energy levels, we can calculate the change in energy using the Gibbs Free Energy equation we learned in the last chapter.

\[ \Delta G = \Delta H - T\Delta S \]

- $\Delta H$ is a measure of the heat absorbed or released.
- $\Delta S$ is a measure of the change in molecular disorder.

The energy changes associated with phase changes can be summarized as:

Every phase change is __________ by one factor (Enthalpy or Entropy) and ________________ by the other!
**Problem:** The change of state from liquid H$_2$O to gaseous H$_2$O has $\Delta H = +9.74$ kcal/mol and $\Delta S = +26.1$ cal/(mol·K).

a) Is the change from liquid to gaseous H$_2$O favored or disfavored by $\Delta H$?
   by $\Delta S$?

- Spontineity depends on the temperature!

**Problem:** What do we call the temperature at which the change of state from a liquid to a gas goes from nonspontaneous to spontaneous?

Example: above 100°C the water boils spontaneously.
   below 100°C the boiling of water is nonspontaneous.

**Problem:** What do we call the temperature at which the change of state from a solid to a liquid goes from nonspontaneous to spontaneous?

**Problem:** Let’s calculate for ourselves what the boiling point of water would be based on the values of $\Delta H$ & $\Delta S$.

We need the same energy units of entropy and enthalpy (kcal vs cal).

When it is not spontaneous in the forward direction (vaporizing) nor spontaneous in the reverse direction (condensing), the two phases are in equilibrium with each other and:
8.2 Intermolecular Forces

Intermolecular forces - attractive forces between molecules that hold them together.

1. Overall referred to as **Van der Waals forces**.
2. Big for ______, moderate for ________, negligible for ________.
3. ______________ in nature (+ attracted to -).
   a. The bigger the charges the ______________ the force
   b. The larger the particles (and farther apart the charges are) the ______________ the attractive force.

The greater the forces of attraction,

the ____________________________________________________________________________

(It takes more energy to break the forces of attraction.)

Types of Intermolecular Forces

**Note: Ion-ion and ion-dipole forces not covered in CHEM305**

1. **Dipole-Dipole Forces**

In ______________ there is a dipole: a positive and a negative end of the molecule.

The ________ end of one is attracted to the ________ end of another.

![Butane (C₂H₆O) and Acetone (C₂H₄O)]

This accounts for why non-polar butane (mw= 58) has a low bp (-0.5 °C) and polar acetone (mw=58) has a higher bp (56 °C)

On the order of 1 kcal/mol.

**Weak** compared to ion – ion attractions.
2. London Dispersion Forces (LDF)

- _______ molecules experience these forces.
  - only important in nonpolar
- LDF are _____________. On the order of 0.5-2.5 kcal/mol.
  The weakest of the IMFs.
- Aka instantaneous dipole forces.
  - At any given *instant* there may be
    - more electrons at one end of a molecule than at the other,
    - giving a short-lived polarity

![Diagram of molecular structures showing London Dispersion Forces](image)

- The _________ the molecular weight & the __________ the surface area,
  - the _____________ the temporary polarization of a molecule.
  - The _____________ the LDF.
- MW comparison: Cl₂ is a gas, Br₂ is a liquid, I₂ is a solid at room temp.

- The larger the surface contact, the greater the close interaction between the molecules.

![Molecular structures of 2,2-Dimethylpropane and Pentane](image)
3. Hydrogen Bonding

Hydrogen bonding is just an especially strong kind of dipole-dipole interaction.

Poor name because these are not bonds (which are within a molecule) but are IMFs (which are between molecules).

These are an attractive interaction between:

- between a hydrogen atom
- bonded to an electronegative O, N, or F atom

and

- and an unshared electron pair on a nearby
- electronegative O; N; or (F bonded to H) atom.

H-bonds are on the order of 2-10 kcal/mol.

In water, each oxygen atom has two lone pairs and two hydrogen atoms, allowing the formation of ________ hydrogen bonds.

This accounts for the unusually high boiling point of water.

Water forms a vast array of hydrogen bonds because each water has two δ+ hydrogens and two δ- oxygens.

Hydrogen bonding increases the boiling points of NH₃, H₂O, and HF beyond what would otherwise be predicted.
**Problem:** Would you expect the boiling points to increase or decrease in each of the following series?

a) Kr, Ar, Ne

Decision Tree for possible molecular IMFs:

1. **Polar Molecule?**
   - **NO**
     - LDF only
   - **YES**
     - O, N, F Present?
       - H-bond: NO LDF & dipole-dipole
       - H-bond: YES LDF & dipole-dipole & H-bonding

*The boiling points generally increase with increasing molecular mass down a group of the periodic table, but the hydrides of nitrogen (NH₃), oxygen (H₂O), and fluorine (HF) have abnormally high boiling points because these molecules have hydrogen bonds.*
**Problem:** Describe the intermolecular forces at play in pure samples of

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Bonding Forces</th>
</tr>
</thead>
<tbody>
<tr>
<td>a) CH₃CH₃</td>
<td></td>
</tr>
<tr>
<td>b) CH₃CH₂OH</td>
<td></td>
</tr>
<tr>
<td>c) CH₃CH₂Cl</td>
<td></td>
</tr>
<tr>
<td>d) CH₃CCH₃</td>
<td></td>
</tr>
</tbody>
</table>

**Ranking of IMFs (Strongest to weakest)**

1. ___________________ (full charge to full charge)
2. ___________________ (full charge to partial charge)
3. ___________________ (strong partial to strong partial charge)
4. ___________________ (partial charge to partial charge)
5. ___________________ (temp partial charge to temp partial charge)
8.3 Gases and the Kinetic Molecular Theory of Matter

The KMT of matter can be further refined for gases.

**The 5 assumptions of Kinetic Molecular Theory:**

**Real vs Ideal Gases**

<table>
<thead>
<tr>
<th>True for all gases</th>
<th>Ideal Gas Assumptions</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) The molecules of a gas are in continual, random, rapid straight-line motion.</td>
<td></td>
</tr>
<tr>
<td>2) Gases consist of small particles. The volume of the particles is very small compared to the total volume.</td>
<td></td>
</tr>
<tr>
<td>3) The average Kinetic Energy (KE) of the gas is directly proportional to the temp. of the gas in Kelvin.</td>
<td></td>
</tr>
<tr>
<td>4) Collisions with the wall lead to the pressure that is observed.</td>
<td></td>
</tr>
<tr>
<td>5) Particles are so far apart that they exert very little forces on each other.</td>
<td></td>
</tr>
</tbody>
</table>

An ________________ is one that obeys all of the assumptions of the kinetic molecular theory of gasses.
8.4 Pressure
Pressure is a measure of the force of the particles hitting the walls of the container.

**Definition of Pressure**
Pressure is the *force* exerted over a given *area* $= \text{force} / \text{area}$.

**How do we measure pressure?**

— Atmospheric pressure is measured with a ____________________.

— The pressure is proportional to the ____________ of the column of Hg.

— The *greater* the atmospheric pressure, the greater the height of mercury that will be supported.

— Therefore, pressure can be expressed in units of ______________________

— $1 \text{ mm Hg} = ___$

(named for Evangelista Torricelli born: 15 Oct. 1608 who conceptually invented the barometer.)

— $1 \text{ atmosphere (atm)} =

\begin{align*}
&= 101325 \text{ Pa (Pascals, the SI unit for pressure)} \\
&= 14.7 \text{ lb/ in}^2 \text{ (psi)}
\end{align*}$

A **barometer** measures ____________ pressure while

A **manometer** measures ____________ pressure.

On the left, the pressure of the gas is ____________ than atmospheric

On the right, the pressure of the gas is ____________ than atmospheric
Differential pressure is measured often as psig (pounds per square inch on the gauge.) Only showing amount above atmospheric pressure.

**Problem:** The atmospheric pressure outside is 745 mmHg.

a) Is the pressure inside the flask greater or less than atmospheric pressure?

b) by how much?

c) What is the pressure in the flask?

d) What is the pressure in atmospheres?

**P, V, n & T Relationships for Gases**

An ideal gas can be described using 4 variables:

____ (pressure); ____ (volume); ____ (number of moles) & ____ (temp in K)

We will try to explain the relationships between these variables using the Kinetic Molecular Theory of Gases.
8.5 Boyles Law: The Relationship Between Volume (V) and Pressure (P) (when n & T are constant)

The volume of a confined gas is *inversely proportional* to its pressure. (at const n & T)

**KMT explanation:** *Smaller volume means that there are more frequent collisions with the walls of the container, leading to increased pressure.* (Think of squeezing a balloon to make it smaller.)

**Problem:** A sample of HCl(g) at P = 67.5 mm Hg with a volume of 256 mL is transferred to a new flask; new P = 23.6 mm Hg. What is the volume of the new flask?

**Problem:** A sample of propane is in a 3.50 L container at 25 °C. Its pressure is 735 mm Hg. If the gas is transferred to a 15.0 L container, also at 25 °C, what is the pressure in the larger container?
Breathing and Gas Pressure

Blood Pressure

- A normal adult male has a reading near 120/80 mmHg, and a normal adult female has a reading near 110/70 mmHg. Abnormally high values signal an increased risk of heart attack and stroke.

- __________ pressure is the maximum pressure developed in the artery just after contraction, as the heart forces the maximum amount of blood into the artery.

- __________ pressure is the minimum pressure that occurs at the end of the heart cycle.

- Blood pressure is often measured by a sphygmomanometer or sphygmometer, a device consisting of a squeeze bulb, a flexible cuff, and a mercury manometer.

- The cuff is placed around the upper arm over the brachial artery and inflated by the squeeze bulb to about 200 mmHg pressure, an amount great enough to squeeze the artery shut and prevent blood flow. Air is then slowly released from the cuff, and pressure drops. As cuff pressure reaches the systolic pressure, blood spurts through the artery, creating a turbulent tapping sound that can be heard through a stethoscope. The pressure registered at the moment the first sounds are heard is the systolic blood pressure.
When the pressure in the cuff becomes low, blood flow becomes smooth, and a diastolic blood pressure reading is recorded on the manometer.
8.6 Charles’s Law: The Relationship Between Temperature (T) and Volume (V) (when n & P are constant)

The **volume** of a fixed amount of gas is *directly proportional* to the **absolute temperature**. (constant n & P)

**KMT explanation:** Higher temp means higher KE particles that move faster hitting the walls more frequently.

If we lower the temperature, then the particles do not move as fast or push as hard on the walls of the container so the volume will reduce if it can.

**Demo:**
Crush soda can containing steaming water by inversion in cold water.

**Problem:** A 25.0 mL sample of a gas is enclosed in a gas tight syringe at 22 °C. If the syringe is immersed in an ice bath at 0 °C, what is the new gas volume, assuming that the pressure is constant?
8.7 Gay-Lussac’s Law: The Relationship Between Pressure (P) and Temperature (T) (n & V are constant)

The pressure of a fixed amount of gas is directly proportional to the absolute temperature. (constant n & P)

**KMT explanation:** Higher temp means higher KE; particles that move faster hit the walls harder and more frequently, increasing the pressure.

**Problem:** Driving on a hot day causes tire temperature to rise. What is the pressure inside an automobile tire at 45°C if the tire has a pressure of 30 psi at 15°C?

8.9 Avogadro’s Law: The Relationship Between Volume (V) and Molar Amount (n) (P & T are constant)

The volume of a confined gas is directly proportional to the number of moles (n). (const. P & T.)

**KMT explanation:** When you put more particles into an expandable container, if the pressure (# of collisions) is to stay constant, the volume must increase. (Think of blowing up a balloon.)