

GENERAL CHEMISTRY SECTION III: PHYSICAL STATES

LECTURE 14: STATES OF MATTER AND AN INTRODUCTION TO THE IDEAL GAS LAW

Chapter Summary

Talk about a change of pace. After half a semester on the theoretical underpinnings for the chemical bond, we get decidedly practical and consider the simple idea that matter can be fairly simply categorized by whether it's a **gas, liquid, or solid**. The next several lectures will explore the theories that give rise to the empirical observations we can make about matter in its various states. The most interesting thing is that, when we explore condensed matter (liquids and solids), we will find that the concepts we developed in bonding can be applied to explain – and even predict – many of the properties that chemical compounds exhibit.

First, we'll consider gases. The simple models that explain most of gas behavior are actually founded on the idea that gas molecules are all the same, and, in fact, that everything we learned about the chemical bond is irrelevant to the study of gases. Yes, gases are both boring and easy.

This first lecture on gases is an elementary introduction, given in two parts:

Part 1 – **Nomenclature**. A brief bit of history on the scientists who investigated gases, and then we'll familiarize ourselves with some words used to discuss the nature of gases in a more sophisticated manner.

Part 2 – **Calculations**.

Type 1	Static system	$PV = nRT$
Type 2	Change of state	V_1T_1/V_2T_2

The second lecture develops somewhat more sophisticated ideas about gases.

Part 3 – **Theory**. We can use **Kinetic Molecular Theory (KMT)** to derive the **ideal gas law** ($PV = nRT$) and to calculate gas **velocity, diffusion, and effusion**.

Part 4 – **Ideal vs. non-ideal gases**. We'll see how $PV = nRT$ works for “ideal” gases but, since gases are not actually ideal, the truth is that $PV \neq nRT$ in reality. Gases' non-ideality is because of molecular attraction and size, both of which violate KMT.

Here's a helpful hint that will come in handy from here on out in the course: we often discuss **proportions/relationships between variables**, and to do that we use the symbol α , which signifies a **direct relationship** between variables (when one increases or decreases, the other does the same). Its reciprocal ($1/\alpha$ or α^{-1}) signifies an **inverse relationship** between variables (when one increases or decreases, the other does the opposite). For example, the more you watch or read the news, the more informed you are about the state of the world – directly proportional. But the more you watch or read the news, the less happy you are about the state of the world – inversely proportional. See? Easy.

USEFUL VARIABLES FOR GASES

In the lectures on thermodynamics we'll have in a few weeks, we'll learn a great deal about **chemical systems**: the **environment** in which our **chemical species are found**. They're characterized by **variables**, like pressure or volume. Those variables are called **state functions**: properties for which we care only about the values **before and after** a reaction. We will learn how to **quantify the relationship** between these state functions using the **ideal gas law**:

$$P_1, V_1, T_1, n_1$$

It'll often be the case that we will perturb our system with a reaction that changes the values of the state functions – giving us P_2, V_2, T_2, n_2 – and that the change in these state functions, represented as $\Delta P, \Delta V, \Delta T, \Delta n$, will be information that we want to know.

LET'S GET TO KNOW OUR STATE FUNCTIONS

n is the **moles** of a gas. The amount of gas is most easily defined by the mole and can be related through stoichiometry and other unit factors to other system parameters like:

$$n = g/MW$$

g = grams
MW = molecular weight

$$n = M \cdot V$$

M = molarity
V = volume

$$\rho = g/V$$

ρ = density
g = grams
V = volume

Note that the moles of gas are typically much smaller than other phases; gas density is much smaller than any of the others (about 1000 times less dense).

V is the **volume** of the gas and has units like mL, L, gallons, ounces, etc. It's defined by the **space** in which gases **travel**, which means it becomes very large in open environments.

P is **pressure**, in units like **atmospheres (atm)**. It tells the **number of times** gas molecules **hit the surface** of the container.

T is the **temperature** of the system, and has units like K, °C, °F. It's **directly proportional to energy** in the system.



Important note about units of T :

We most commonly use **K (degrees Kelvin)** and **°C** to measure T . You may not be familiar with K, and we'll learn more about it later, but for now, here's a conversion you should know:

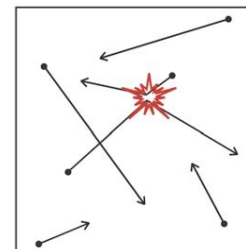
$$^{\circ}\text{C} + 273 = \text{K}$$

KINETIC MOLECULAR THEORY (KMT)

Scientists sat around, thinking really hard about a model for gases. They decide the following is a good way to think of them, given that they seem to be rather boring chemically and have very low densities*:

- Gas molecules are **hard spheres**.
- They are **infinitely small** in volume.
- They have **no attraction** for either each other or the surface of system; therefore, collisions are **elastic** (hitting another molecule or the container **does not cause any loss of energy**).
- The **energy** in a gas system is **constant** and is determined by **temperature**.
 - $T \propto E$ ← (temperature is directly proportional to energy; if one increases or decreases, the other does the same).
- The **velocity** of gas particles is determined by the equation:

$$E = \frac{1}{2} mv^2$$



*These are “ideal” notions and are used to derive the ideal gas law.

Note that gas particles are all the same according to KMT, regardless of type. For example, He is an infinitely small particle that undergoes elastic collisions, and the same goes for CO₂, N₂, NH₃, and H₂O.

FAMOUS EXPERIMENTS WITH GASES

As we go over the three gas laws, you'll see equations that include the constant "k". It must remain the same both before and after the reaction, and it is determined based on state functions in the ideal gas law.

Boyle's Law:

Boyle investigated the **pressure-volume** relationship and found they're **inversely** related: $P \uparrow, V \downarrow$ or $P \downarrow, V \uparrow$

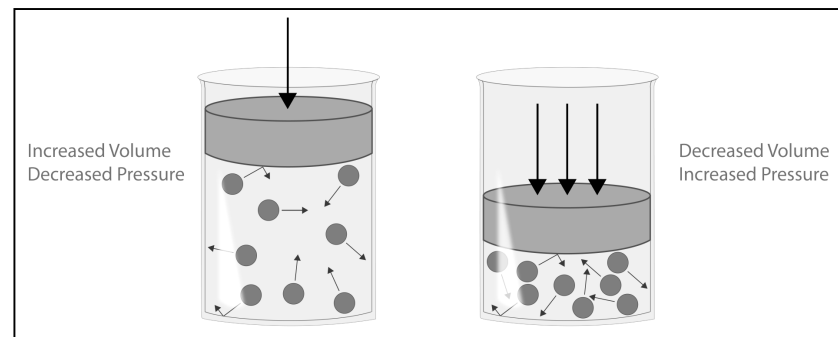
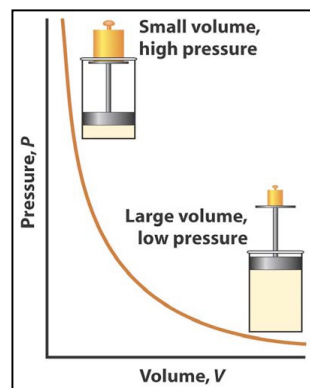
Mathematically, this relationship is expressed:

$$P \propto (1/V) \quad \text{or, equivalently,} \quad P \propto V^{-1}$$

And the equation in terms of k :

$$P = k (1/V)$$

So when you sit on a balloon, it's like repeating Boyle's experiments from centuries ago.



Charles' Law:

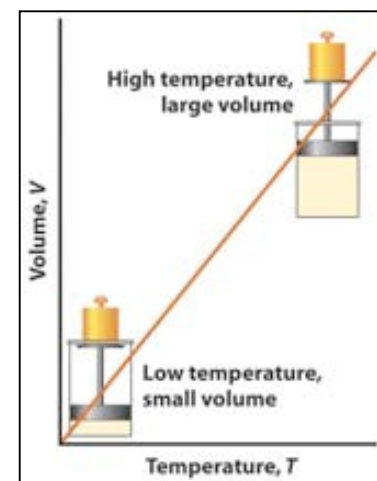
Charles investigated the **volume-temperature** relationship and that it's **direct**: $T \downarrow, V \downarrow$ or $T \uparrow, V \uparrow$

This relationship is:

$$V \propto T$$

And the equation is:

$$V = kT$$



Avogadro's Law:

Avogadro investigated the **mole-volume** relationship. He discovered the extraordinary idea that the **more moles** of gas you have, the **bigger** the balloon. In other words, n is **directly** proportional to V .

This relationship is:

$$n \propto V$$

And the equation is:

$$n = kV$$

COMBINING THREE LAWS GIVES US THE IDEAL GAS LAW

Using a little algebra to combine these three relationships, and after consolidating the three constants into one, we have the ideal gas equation:

$$PV = nRT$$

...where R is the ideal gas constant. Note the three experimental relationships are all present in this one equation. Also note this equation is true **only under ideal conditions (KMT conditions)**.

Let's talk some more about R . It quantifies the properties of an ideal gas, which is really just a gas under standard conditions. We consider standard conditions – or, STP (for standard temperature and pressure) – to be:

$$T = 273 \text{ K} = 0^\circ\text{C}$$

$$P = 1 \text{ atm} = 760 \text{ torr} = 101.3 \text{ kPa}$$

Like all constants, R can be expressed in different ways depending on its units. While we learn about gases, our units are typically: **atmospheres (atm)** for P ; **liters (L)** for V ; and **Kelvin (K)** for T . With these, the appropriate value for R is:

$$R = 0.082 \text{ L}\cdot\text{atm}/\text{mol}\cdot\text{K}$$

You should keep in mind, though, that R is also often used to relate energy (in Joules (J)) and T . In that case, it's $R = 8.314 \text{ J}/\text{mol}\cdot\text{K}$. But we'll focus on the former value for R during this unit on gases.

So let's see what kinds of problems can we work...

CALCULATIONS FOR A STATIC SYSTEM

For **static systems** (systems that are not perturbed), we can perform **simple calculations** with the ideal gas law equation ($P_1V_1=n_1RT_1$). These are classic plug-and-chug calculations in which we are given three values to hold constant while we solve for a fourth, unknown variable.

Example:

What is the volume of 1 mole of an ideal gas when it's held at 1 atm and 273 K?

Solution:

Let's first write down the variables we know (AKA "givens"):

$$P = 1 \text{ atm}$$

$$n = 1 \text{ mole}$$

$$T = 273 \text{ K}$$

$$R = 0.082 \text{ L}\cdot\text{atm}/\text{K}\cdot\text{mol}$$

Now we need to rearrange the ideal gas law before we plug-and-chug:

$$PV = nRT \rightarrow V = nRT/P \rightarrow [(1 \text{ mol}) \cdot (0.082 \text{ L}\cdot\text{atm}/\text{K}\cdot\text{mol}) \cdot (273 \text{ K})] / (1 \text{ atm}) = \mathbf{22.4 \text{ L}}$$

Look! All of the values we just used were those of the variables at STP! This means our answer tells us the neat fact that, at standard temperature and pressure, an ideal gas has a volume of 22.4 L.

Here are two good things to think about while doing problems that don't involve a change of state:

1. Remember how I said that there are many versions of R with different combinations of units? And that you should (for the most part) ignore those and just **plan to use $R = 0.082 \text{ L}\cdot\text{atm}/\text{K}\cdot\text{mol}$** while we work with gases? Good, because those things are still true.
2. The trick to doing these problems is that you'll often need to **convert the values given to you for P , V , T , and n , into values that are consistent with R** . That's really the only complication for these questions. And usually the biggest hassle comes from getting a value that you need to convert into a number of moles...

How about we address that last sentence? It was kind of daunting, and with good reason – you’ll need to have a value for n in these calculations, but there are three “disguises” in which it can present itself to you: molecular weight (MW), density (ρ), and molarity (M). If you’re given information about one of these, you need to recognize it as a stepping stone to find n , because that’s your real variable of interest. Each of them can be converted into a number of moles through an equation:

$$n = g/MW$$

$$n = M \cdot V$$

$$\rho = g/V$$

(Note: the “g” in these equations indicates a mass in units of grams.)

These hopefully look a little familiar to you, because we learned them a few pages ago...

CALCULATIONS FOR A SYSTEM WITH A CHANGE OF STATE

Anytime that a problem suggests that conditions in the system have been changed because of a perturbation, regardless of whether the change is happening to P , V , T , or n , you need to have an equation made from taking the ideal gas law, combining the two states you need, eliminating all other constants.

We’ll go over a derivation of one of these so you appreciate the idea behind them. Say we have a system in which only the volume and temperature change over the course of the reaction:

First off, since we know that only V and T changed, the other variables (n and P) must have stayed the same. So let’s rearrange the ideal gas law to have our changing-things on one side and our constant-things on the other: $V/T = nR/P$.

Now, using our rearranged gas law, we’ll write out the equation for state #1 of the system (before reaction): $V_1/T_1 = n_1R/P_1$, as well as the one for state #2 (after reaction): $V_2/T_2 = n_2R/P_2$.

In our new equations, the terms the right side (nR/P) contain all the states that didn’t change, meaning their before-reaction and after-reaction values are identical. This means that $n_1R/P_1 = n_2R/P_2$. And if that’s the case, then we our state #1 and state #2 equations can be set equal to each other: $V_1/T_1 = nR/P = V_2/T_2$.

Ta-da! You've now derived the equation needed to solve an ideal gas law question that involves a change of state. The equation we just derived was for a change in V and T (left equation), but others can be created for systems with changes in P and V (middle equation), and systems with changes in – brace yourself – P , V , and T (right equation).

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$P_1V_1 = P_2V_2$$

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

EXAMPLE CALCULATIONS: USING THE IDEAL GAS LAW

Example #1 – Simple ideal gas law:

What is the pressure when 2.5 moles of H_2 are placed in a 200 mL container at $50^\circ C$?

Solution:

First note that there is no change in state. We assume this is about ideal gases, so the equation is: $PV = nRT$.

Our givens:

$$n = 2.5 \text{ moles}$$

$$V = 200 \text{ mL} \rightarrow \text{Must convert this to L} \rightarrow V = 0.2 \text{ L}$$

$$T = 50^\circ C \rightarrow \text{Must convert this to K} \rightarrow T = 50^\circ C + 273 = 323 \text{ K}$$

$$R = 0.082 \text{ L}\cdot\text{atm}/\text{mol}\cdot\text{K}$$

Now we solve (while being aware that units are canceling):

$$P = [(2.5 \text{ mol}) \cdot (0.082 \text{ L}\cdot\text{atm}/\text{mol}\cdot\text{K}) \cdot (323 \text{ K})] / (0.2 \text{ L}) = \mathbf{331 \text{ atm}}$$

← That's some pressure!

Example #2 – Ideal gas law, solving for MW:

There are 0.87g of a gas put into a 5 L container at -50°C with a pressure of 76 torr. What is the MW of the gas?

Solution:

Derive an equation that includes our givens and MW:

$$PV = nRT \rightarrow PV = \frac{g}{MW} \cdot (RT) \rightarrow MW = \frac{g \cdot RT}{PV}$$

Givens:

$$g = 0.87\text{g}$$

$$V = 5\text{ L}$$

$$P = 76\text{ torr} \rightarrow \text{Must convert this to atm} \rightarrow P = (76\text{ torr}) / (760\text{ torr}) = 0.1\text{ atm}$$

$$T = -50^{\circ}\text{C} \rightarrow \text{Must convert this to K} \rightarrow T = (-50^{\circ}\text{C}) + 273 = 223\text{ K}$$

Plug and chug:

$$MW = [(0.87\text{g}) \cdot (0.082\text{ L}\cdot\text{atm}/\text{mol}\cdot\text{K}) \cdot (223\text{K})] / [(0.1\text{ atm}) \cdot (5\text{ L})] \approx \mathbf{32\text{ g/mol}}$$

Example #3 – Ideal gas law, solving for density:

What is the density of CH_4 while at a pressure of 0.1 atm and a temperature of 414 K?

Solution:

Derive an equation that includes our givens and density (ρ):

$$PV = nRT \rightarrow n = PV/RT \rightarrow P \cdot (g/\rho) / RT = (g/MW) \rightarrow \rho/MW = P/RT \rightarrow \rho = P \cdot (MW) / RT$$

Givens:

$$P = 0.1\text{ atm}$$

$$T = 414\text{ K}$$

$$MW \text{ of } \text{CH}_4 = 16\text{ g/mol} \leftarrow \text{Gotten from periodic table}$$

Plug and chug:

$$\rho = [(0.1\text{ atm}) \cdot (16\text{ g/mol})] / [(0.082\text{ L}\cdot\text{atm}/\text{mol}\cdot\text{K}) \cdot (414\text{ K})] = \mathbf{0.047\text{ g/L}} \quad \leftarrow \text{Not very dense.}$$

Example #4 – Ideal gas law, **using STP**:

What is the volume of C_3H_8 if 1 mole is kept at STP?

Solution:

We know that STP is $P = 1$ atm, and $T = 273$ K.

Plug and chug:

$$V = [(1 \text{ mol}) \cdot (0.082 \text{ L}\cdot\text{atm/mol}\cdot\text{K}) \cdot (273 \text{ K})] / 1 \text{ atm} = \mathbf{22.4 \text{ L}} \quad \leftarrow \text{A famous volume, true for all gases.}$$

Example #5 – Ideal gas law, **involving change of state in P and V** :

Dr. Laude fills a balloon to a pressure of 1 atm and volume of 500 mL at 273 K. He then sits on it, changing the pressure to 5 atm. What is the new volume?

Solution:

Identify which states are changing (P and V), and which are staying the same (n and T).

Use that information to decide the correct equation to use for a change-of-state-problem: $P_1V_1 = P_2V_2$

Plug and chug:

$$(1 \text{ atm})(500 \text{ mL}) = (5 \text{ atm})(X \text{ mL}) \rightarrow (500 / X) = 5 \rightarrow \mathbf{100 \text{ mL}} \quad \leftarrow \text{Or } \mathbf{0.1 \text{ L}}; \text{ you'd check the answer choices.}$$

Example #6 – Ideal gas law, **involving change of state in V and T** :

In a closed system at constant P and n , if the volume of the system is decreased by a factor of 10, the temperature:

- Goes up by a factor of 10.
- Goes down by a factor of 10.
- Remains constant.
- None of the above.

Solution:

The answer is **B**.

$V_1/T_1 = V_2/T_2 \rightarrow$ so if V goes from 10 L to 1L, then T must decrease 10-fold to keep the proportions equal.

LECTURE 15: MORE ADVANCED IDEAS INVOLVING GASES

HOW FAST ARE GAS MOLECULES?

From **kinetic molecular theory (KMT)** we know that:

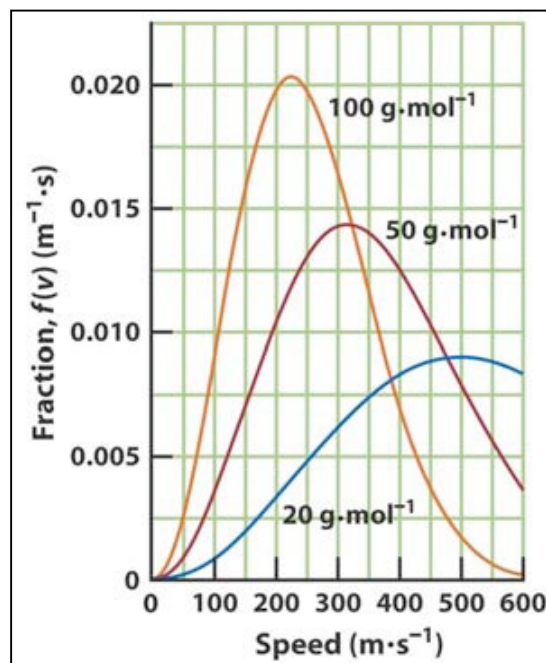
$$T \propto E = \frac{1}{2} kT = \frac{1}{2} mv^2$$

(Temperature term) (Velocity term)

Notice that the velocity can be easily determined from:

$$E = \frac{1}{2} mv^2$$

We can see from this that, the **higher the temperature**, the **higher the velocity (direct relationship between v and T)**. Depending on mass and T , gas molecules move at hundreds of miles per hour, just at room temperature!



Note that the equation tells indicates an **inverse square relationship** between molecular **speed and mass**.

Example:

At a certain temperature, H_2 is traveling 1000 mph. How quickly is O_2 moving at that temperature?

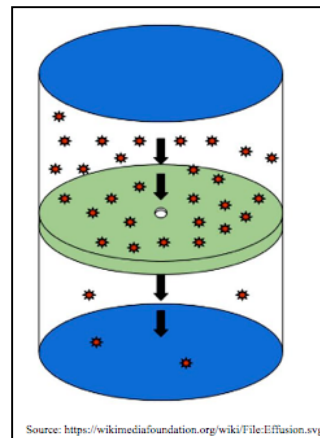
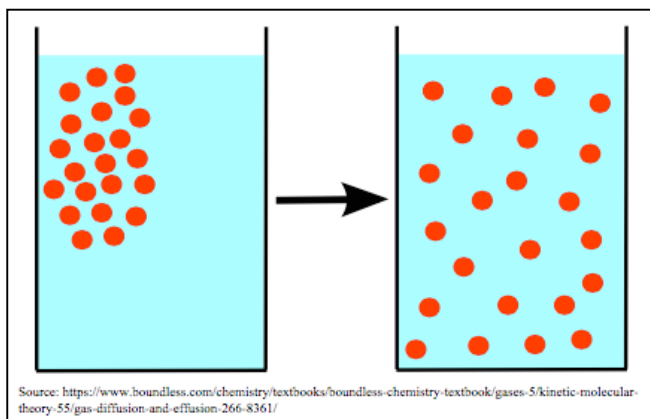
Solution:

The E of the gas is the same regardless of T , so:

$$\begin{aligned} \frac{1}{2} \cdot m_{\text{H}_2} \cdot v_{\text{H}_2}^2 &= \frac{1}{2} \cdot m_{\text{O}_2} \cdot v_{\text{O}_2}^2 \rightarrow 2 \cdot v_{\text{H}_2}^2 = 32 \cdot v_{\text{O}_2}^2 \rightarrow 32 / 2 = v_{\text{H}_2}^2 / v_{\text{O}_2}^2 \rightarrow \\ \rightarrow 16 &= (1000 / v_{\text{O}_2})^2 \rightarrow \sqrt{\text{everything}} \rightarrow 4 = (1000 / v_{\text{O}_2}) \rightarrow v_{\text{O}_2} = \mathbf{250 \text{ mph}}. \end{aligned}$$

GAS MOVEMENT: DIFFUSION AND EFFUSION

Despite that last answer, we know that gas molecules don't really get around the room going hundreds of miles per hour. If they did, smells would come (and go) much faster than they do. The reason for their **reduced speed** is that (at atmospheric pressure) **collisions constantly occur** between molecules, which decreases their speed by many orders of magnitude. So what do they call this **collisional velocity**? **Diffusion** (shown in the figure on the left). And a similar kind of velocity – called **effusion** (shown in the figure on the right) – has to do with the ability of gas molecules to get through a pin hole.



In both cases, the **rate of effusion and diffusion** is the **same inverse square relationship as speed**. So, if we know O_2 has a velocity that is 4-fold slower than that of H_2 , we also immediately know that its diffusion and effusion is also 4-fold slower.

NON-IDEALITY OF GASES

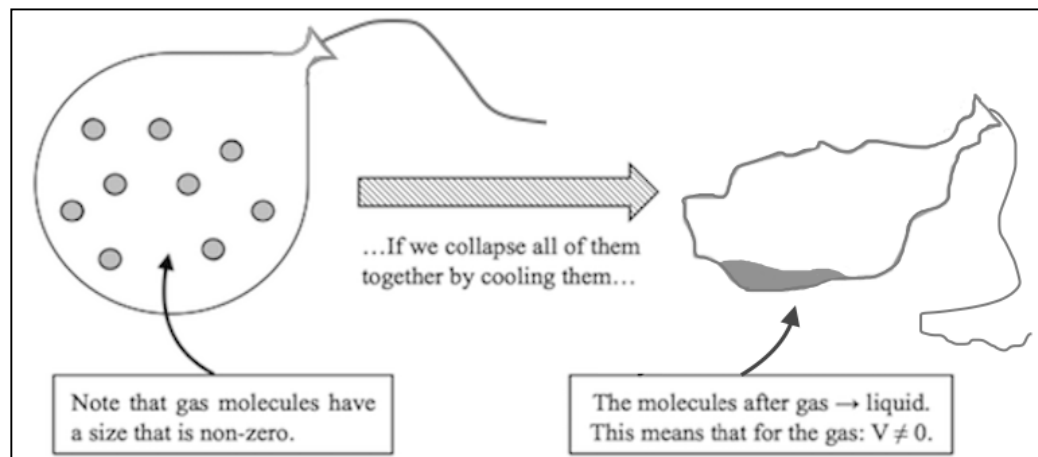
Is KMT flawed? Recall that when we were first introduced to gases, we learned that, according to KMT:

- Gas molecules have **no volume** (we called them infinitely small).
- Gas molecules are **not attracted** to each other, so all collisions are **elastic**.

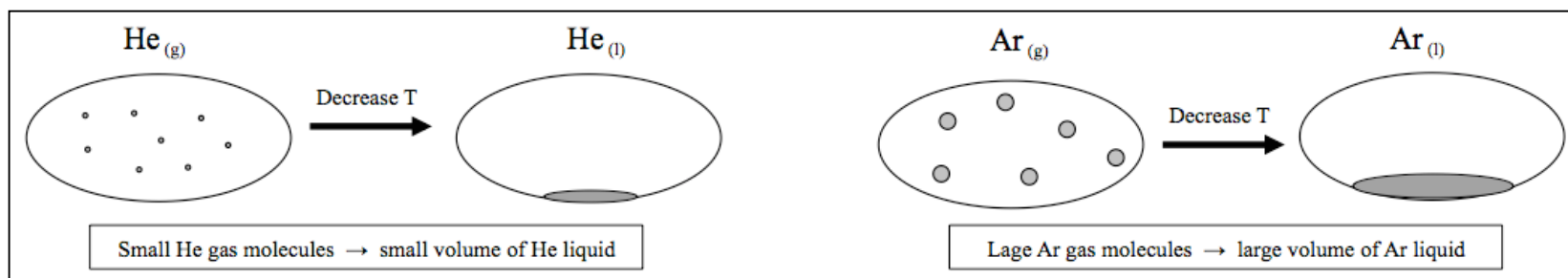
But in reality, neither of those statements is completely true...

GAS MOLECULES' VOLUME IS NOT ZERO

Consider whether a **gas atom or molecule takes up physical space**. Of course it does! In fact, here's something neat: have you ever seen liquid air? (Just normal air, like what you're surrounded by right now.) To see that gas atoms and molecules have a volume, we can pour liquid N_2 over a balloon (filled with said normal air) and watch the air liquefy:



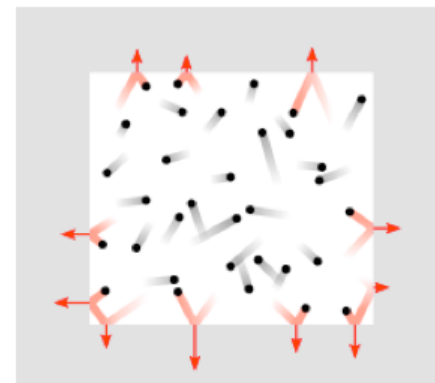
You should also note that (as is obvious) **bigger molecules** have **larger volumes**. This means they have **less ideality**, or, equivalently, **more non-ideality** – the ideal **gas law applies to them less** than it does gases that better meet its criteria.



ATTRACTION BETWEEN GASES

Gases bump into each other and will momentarily “stick” together. So their **collisions** are actually somewhat **inelastic** – not by much (or they wouldn’t be gases), but still by an amount worth mentioning. And the **bigger** the molecule, the more polar – and “sticky” – it is.

Why does this matter? – Because if at any given time some particles are stuck together, the number of particles hitting the sides of the container decreases, which means that $P \downarrow$.



Source: https://commons.wikimedia.org/wiki/File:Pressure_exerted_by_collisions.svg

CORRECTING FOR NON-IDEALITY

How do we **correct** for gases that are **not ideal**? – By using **fudge factors** that are **specific to each gas** and **account for its non-ideality**; so if $PV \neq nRT$, then we use:

$$(P + \text{“fudge factor”}) \cdot (V + \text{“fudge factor”}) = nRT$$

...Where P 's fudge factor accounts for the attractive forces the gas law ignores, and V 's accounts for molecules' volume. **Non-ideal gas laws** incorporate these **fudge factors**; one such law is the **van der Waals equation**:

$$(P + n^2a / v^2)(v - nb) = nRT$$

Here, **a** and **b** are **fudge factors** that are **specific to the kind of gas**. The **bigger** any gas' **a** and **b**, the **more non-ideal** it is – so there's a **direct relationship** between the **magnitude** of the fudge factors, and the **non-ideality** of the gas.

For example, consider the following:

$$\text{Helium} \rightarrow a = .0034 \text{ and } b = 0.237$$

$$\text{NH}_3 \rightarrow a = 4.17 \text{ and } b = 3.71$$

This means helium is small and not attracted (or attractive) to NH_3 , while NH_3 is bigger and very attracted to most gases.

WHEN IS A GAS MORE IDEAL?

Gases behave more ideally when **fewer collisions** are taking place between molecules, which happens at **high temperature and low pressure**. Specifically regarding small, non-polar gases: since both their volume and attractive forces are small, they behave more ideally than larger and/or polar gases.

SUMMARIZING TRENDS BASED ON SIZE

As mentioned in the last sentence: for **small gases**, like He and H₂, $PV = nRT$ is a good equation to use, because of their **high ideality**.

For **large gases**, like CO₂ or H₂O, we must use $(P + n^2a / v^2) \cdot (v - nb) = nRT$ as our equation. This is necessary because they have strong attractive forces and take up more volume, meaning they're **less ideal**.

For the other properties we've discussed, here are the trends based on molecules' size:

Size of Molecules	Small	Large
Velocity	Fast	Slow
Rate of Diffusion	Fast	Slow
Rate of Effusion	Fast	Slow

Example:

Rank ideality, speed, diffusion, and effusion for the following gases, in increasing order: He, CO₂, N₂, and O₂.

Solution:

All of the trends (ideality, speed, diffusion, effusion) are directly related, and we know that smaller gases more ideal. So:
He > N₂ > O₂ > CO₂.

Example:

At a certain temperature, helium travels with a velocity of 300 mph. What is the MW of a gas that, at the same temperature, has a velocity of 150 mph?

Solution:

First off, we know that, at the same temperature, the E of the system is constant, so we don't have to worry about T .

We also know that the equation relating V and E for all gases is: $E_{\text{sys}} = \frac{1}{2}mv^2$. So for our two gases:

$$E_{\text{He}} = \frac{1}{2}m_1v_1^2 \quad \text{and,} \quad E_{\text{other gas}} = \frac{1}{2}m_2v_2^2$$

Now let's rearrange them to put our variable of interest (m_2) on one side of the equation:

$$m_2 = m_1v_1^2/v_2^2$$

Plug and chug:

$$m_2 = (4 \text{ g/mol})(300 \text{ mph} / 150 \text{ mph})^2 = 16 \text{ g/mol}$$

Example – Ranking ideality (which also means velocity):

Rank the following gases in terms of increasing non-ideality: He, O₂, N₂, and CH₄.

- He < N₂ < O₂ < CH₄.
- He < CH₄ < N₂ < O₂.
- O₂ < N₂ < CH₄ < He.
- CH₄ < O₂ < N₂ < He.

Solution:

The answer is **B**.

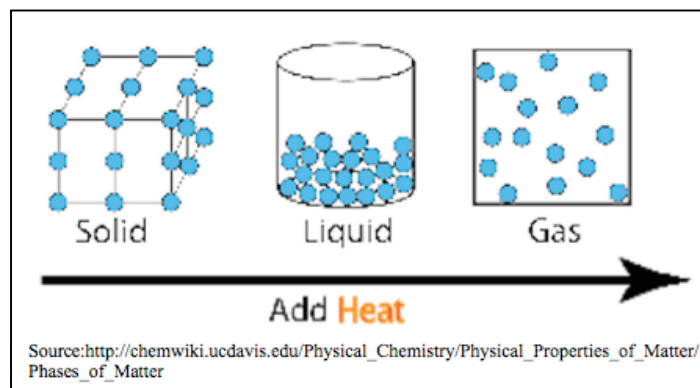
In general, the **bigger and slower** the gas molecule, the **less ideal**. Among these gases, O₂ is biggest and He smallest; therefore He is *most* ideal, and O₂ *least* ideal. In class we'll assume that **size is proportional to molecular weight**.

A word of caution about ranking problems: Make sure you pay attention to the rank you're asked for, and that you're actually ordering it correctly; that might sound stupidly obvious, but backwards-ranking is a common mistake. In the last example, we were asked for "increasing non-ideality"; you obviously know what this means, but make sure you think about it – the *least non-ideal* (or, equivalently, the *most ideal*) should be listed first, and the *most non-ideal* (or, equivalently, the *least ideal*) should be last. Be careful that you don't think of it backwards, because that will always be an answer choice.

LECTURE 16: INTRODUCTION TO INTERMOLECULAR FORCES (IMF's)

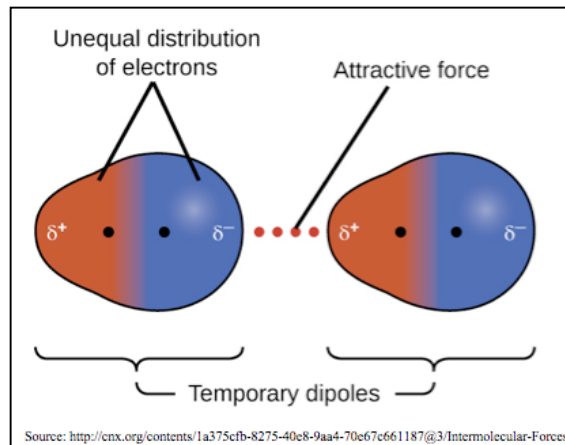
As we ended the lectures on gases, we were introduced to an idea that serves as foundation for the material in this lecture: kinetic molecular theory says that colliding gas molecules exhibit that no attractive forces to each other – but that's not actually the case. We learned that non-ideality arises because of the **attractive forces between colliding molecules**, and that consequently, $PV \neq nRT$.

So can we explain the source of this non-ideality? It is important because this **non-ideality from attractive collisions** explains how **liquids and solids form**.

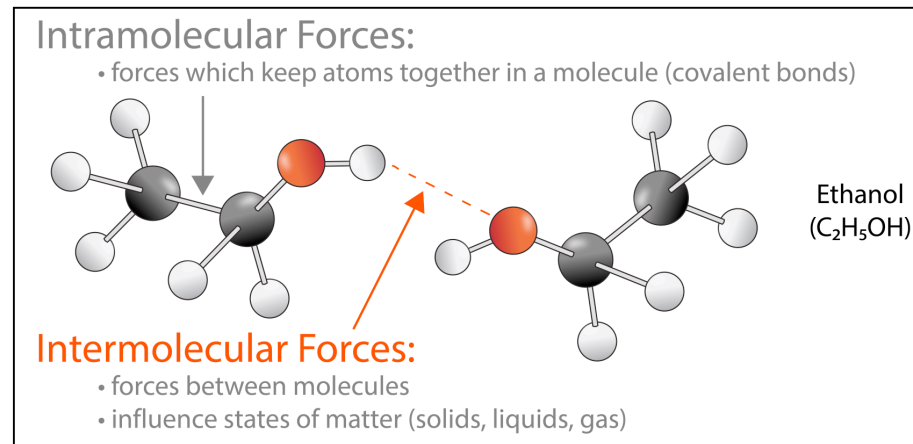


...And we see that as **T increases, P decreases** – they are **inversely proportional**.

So the lectures on liquids and solids must begin with a better understanding of intermolecular attraction. Let's get started by looking at attractive forces more generally:



Two examples of Coulombic attraction can be distinguished in matter:



Intramolecular forces are bonds **inside** molecules (holding them together); these are either ionic or covalent.

Intermolecular forces (IMF's) are attractions **between** molecules; they exist outside the molecules.

INTERMOLECULAR BOND STRENGTHS

So now let's get quantitative with bonding.

Notice that **intramolecular bonds are 1 to 2 orders of magnitude stronger than intermolecular forces**. (Even still, it is the weak intermolecular forces that allow liquids and solids to form.) Here are some facts about IMF's:

- They are responsible for solution properties like boiling point and viscosity.
- Their relative magnitude is determined from the existence of dipoles in molecules (which comes from ΔEN).
- You can rank solution properties based on ΔEN calculations.

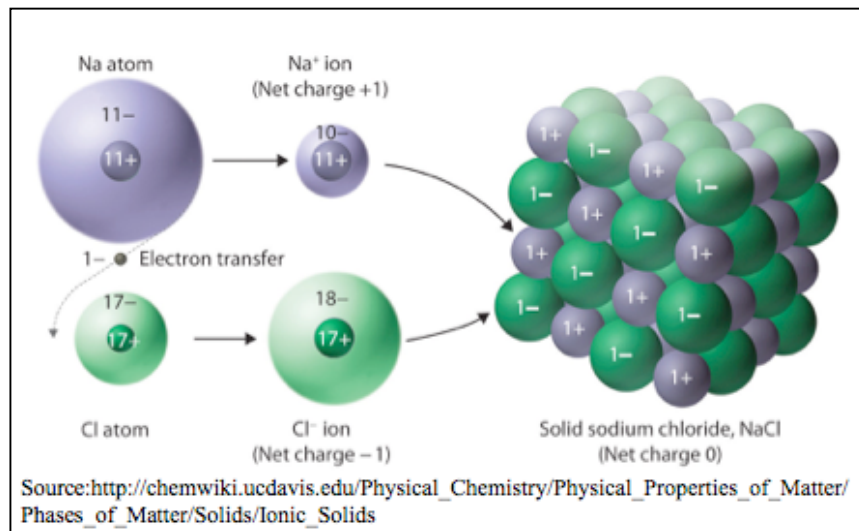
TABLE 5.1 Interionic and Intermolecular Interactions*

Type of interaction	Typical energy (kJ·mol ⁻¹)	Interacting species
ion-ion	250	ions only
ion-dipole	15	ions and polar molecules
dipole-dipole	2	stationary polar molecules
	0.3	rotating polar molecules
dipole-induced dipole	2	at least one molecule must be polar
London (dispersion) [†]	2	all types of molecules
hydrogen bonding	20	molecules containing N, O, F; the link is a shared H atom

*The total interaction experienced by a species is the sum of all the interactions in which it can participate.

[†]Also known as the induced-dipole-induced-dipole interaction.

An interesting side note about **ionic bonds**: they are *both* inter- and intramolecular. Why?



The bonds in a crystal are not as distinct as they are in a molecule. Hence the ambiguity in inter- and intramolecular bonds.

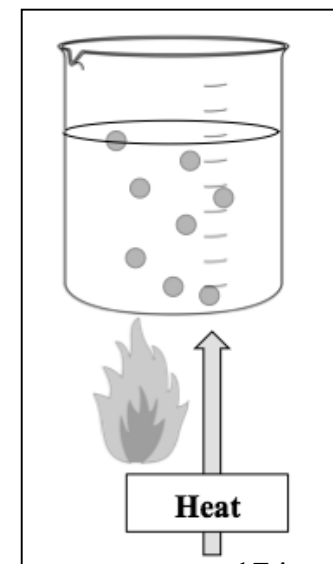
Look at the salt crystal on the left. Notice that there is no single Na—Cl unit anywhere. Instead, each Na⁺ has ionic bonds to all 6 of the Cl⁻ molecules around it (or <6 if the Na⁺ is on the side of the crystal); the same goes for each Cl⁻.

Now on to the rest of the lecture. What are the solution properties we're interested in? (You need only to know their definitions and a brief theoretical explanation about their relationship to intermolecular forces.)

BOILING POINT

This is a process that happens when an **increase in temperature** causes a system's **energy to increase**, thus **breaking IMF's** and resulting in a **vaporized (gas) molecule**. However, for a molecule to **escape liquid**, enough gas molecules need to be made in order to **raise the vapor pressure above atmospheric pressure**. This is the definition of **boiling**. The **boiling point** reflects the **energy needed** to induce boiling.

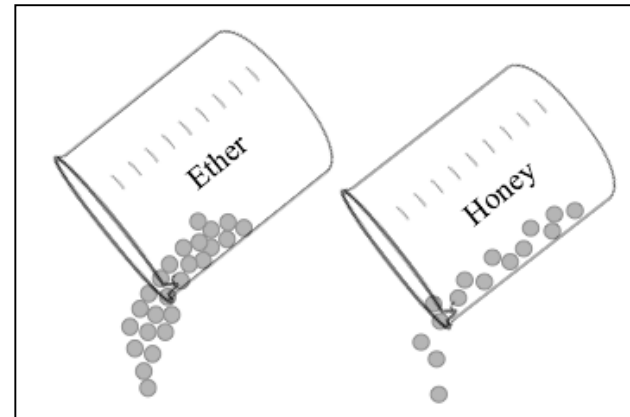
Relationship to IMF's – **directly proportional**.



VISCOSITY

This is the “**stickiness**” liquids exhibit when **being poured**, and it’s caused by the attractions of IMF’s. It is a surface phenomenon that makes it appear that the liquid has a “**resistance to flow.**” The figure below shows the viscosities of honey and ether.

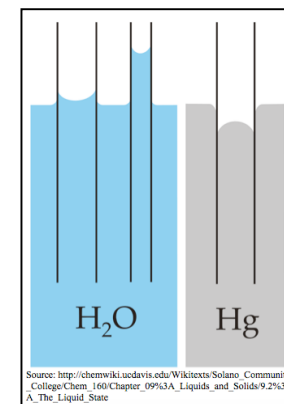
Relationship to IMF’s – **directly proportional.**



CAPILLARY ACTION

This is the tendency to **climb the walls of a capillary** (a tube with a thin diameter). It’s what creates the **meniscus** you see in burettes and straws filled with water. This property is why water seems to almost crawl up capillary walls.

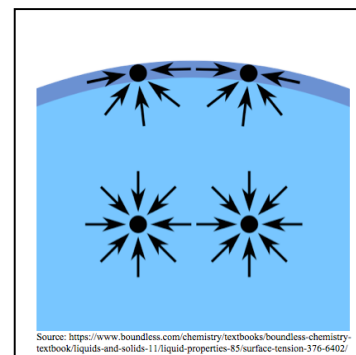
Relationship to IMF’s – **directly proportional.**



SURFACE TENSION

The phenomenon that maintains the **surface interface between liquid and gas**. It allows you to place needles and insects on surfaces despite being denser, like the water strider in the left image. The figure on the right shows molecules’ interactions while in the solution vs. on the surface.

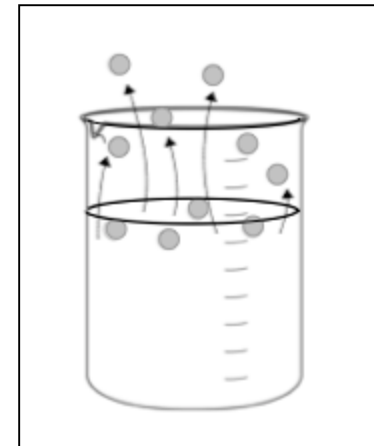
Relationship to IMF’s – **directly proportional.**



EVAPORATION

This is a surface phenomenon that explains why **solution molecules enter gas phase**. This is **different from boiling** in that it occurs at surface, but it is also temperature dependent.

Relationship to IMF's – **inversely proportional** (in reference to the evaporation rate).



$$\Delta H_{\text{VAP}}$$

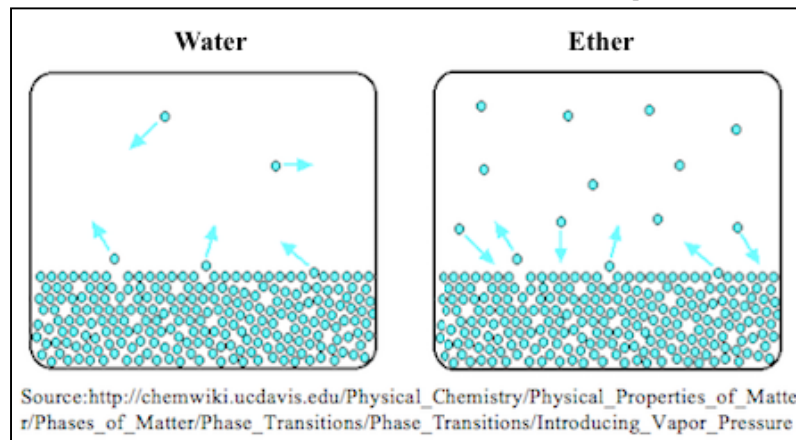
Technically called the “enthalpy of vaporization,” this is a thermodynamic term that tells you the amount of **energy required for a liquid to become a gas**. It is found in boiling and evaporation equations.

Relationship to IMF's – **directly proportional**.

VAPOR PRESSURE

This is the flip side of evaporation – it is the **pressure pushing down on liquid by its already-evaporated molecules**. Obviously, if ΔH_{vap} is small, vapor pressure is large – there is an inverse relationship between ΔH_{vap} and vapor pressure.

Relationship to IMF's – **inversely proportional**.



RANKING SOLUTION PROPERTIES: OUR PREDICTIONS

Now that we have seen the various **solution properties** and how they **relate to IMF's**, let's see whether we can **predict the ranking** of various molecules for a solution property.

Can I rank the solution properties of compounds? Yes, and it's easy. For example, I can rank H₂O, CH₃Cl, and N₂ in order of increasing ΔH_{vap} in less than ten seconds. The answer is: N₂ < CH₃Cl < H₂O. ...How'd I do that?

ELECTRONEGATIVITY: AN OLD FRIEND

In a nutshell, you can relate the three kinds of intermolecular forces directly to the magnitude of solutions' properties:

Type of IMF	<u>Instantaneous Dipole</u>	<u>Dipole-Dipole</u>	<u>H-bond</u>
Energy (kJ/mol)	< 1	5	10-20
Specifications for molecules	Symmetrical, nonpolar molecules	Asymmetrical, polar molecules	Polar molecules with an H atom bonded to a highly-EN atom , like N or O
Examples	N ₂ , CH ₄ , BF ₃	CH ₃ Cl, H ₂ O, NH ₃	NH ₃ , H ₂ O

Summary of relationships to IMF's:

IMF's are *directly proportional* to: **boiling point, viscosity, capillary action, surface tension, and ΔH_{vap}** .
As IMF magnitude increases, so do the magnitudes of the above properties.

IMF's are *inversely proportional* to: **evaporation and vapor pressure**.
As IMF magnitudes increase, the magnitudes of the above properties decrease.

To figure out the magnitude of IMF's, you need to be able to create 3D Lewis structures for molecules, assign atoms' EN's, identify all dipoles, cancel them out if possible), and determine whether a net dipole exists. (You did all of this in unit #2, when we learned how to draw the 3D structures of molecules.)

Example, part #1:

Predict the ranking of solution properties for N_2 , CH_3Cl , and H_2O .

Solution:

The steps to take:

1. Create the 3D Lewis structures.
2. Assign EN to each atom.
3. Identify all dipoles.
4. Determine whether a net dipole is present ($\Sigma \Delta\text{EN} \neq 0$).

When you do these, you find:

$\text{N}_2 \rightarrow$ no net dipole \rightarrow nonpolar.
 $\text{CH}_3\text{Cl} \rightarrow$ has a net dipole \rightarrow polar.
 $\text{H}_2\text{O} \rightarrow$ has a net dipole \rightarrow polar.

Example, part #2:

What does the above information tell us about the solution properties of these molecules?

Solution:

$\text{N}_2 \rightarrow$ Since it's nonpolar \rightarrow it only forms *instantaneous dipoles*.
 $\text{CH}_3\text{Cl} \rightarrow$ Since it has a net dipole \rightarrow *strongest* IMF is *dipole-dipole*; instantaneous dipoles are also present.
 $\text{H}_2\text{O} \rightarrow$ Since it has a net dipole \rightarrow forms dipole-dipole; BUT it has an H bonded to an EN atom \rightarrow also *H-bonding*, which is its *strongest* IMF. (Also has instantaneous dipoles.)

So in terms of solutions properties, we can say generally that:

For properties directly proportional to IMF strength $\rightarrow \text{N}_2 < \text{CH}_3\text{Cl} < \text{H}_2\text{O}$.
 For properties inversely proportional to IMF strength $\rightarrow \text{H}_2\text{O} < \text{CH}_3 < \text{N}_2$.

Notice that the ranking is the same for properties that are directly vs. inversely proportional, except that their orders are reversed.

Get really good at creating 3D structures and assigning polarity – it is the essential step in explaining IMF's in solutions.

LECTURE 17: THEORY BEHIND INTERMOLECULAR FORCES

Intermolecular forces (IMF's) are forces of attraction *between* individual molecules.

As we have just seen, there exists a **direct correlation** between the **strength of IMF's in a solution** and the **magnitude of its properties** (e.g., viscosity, boiling point, ΔH_{vap} , evaporation).

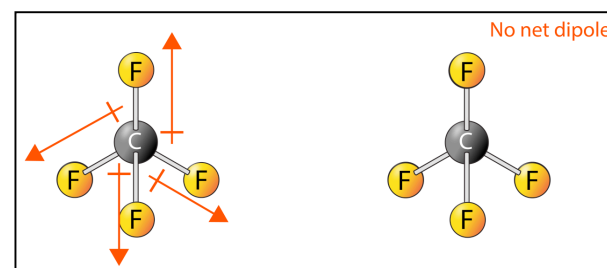
Type of IMF	Strength (kJ/mol)
Instantaneous Dipole	<1
Permanent Dipole	1-5
Hydrogen Bonding	10-20

Let's look more deeply at reasons for the magnitude of each of these kinds of intermolecular forces.

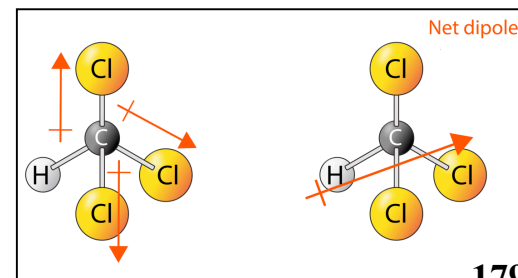
PERMANENT DIPOLES

Permanent dipoles occur in molecules that are **not completely symmetrical**, which, as we learned in previous lectures, are also molecules with a **total electronegativity that does not equal zero** ($\sum \Delta \text{EN} \neq 0$). (Recall: "total/overall electronegativity" is the electronegativity values of all the species are added together.)

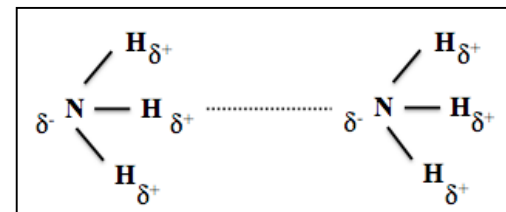
CF_4 does *not* have a permanent dipole \rightarrow it is **symmetrical** (and $\sum \Delta \text{EN} = 0$).



CCl_3H does have a permanent dipole \rightarrow it is **not symmetrical** (and $\sum \Delta \text{EN} \neq 0$).



Permanent dipoles are one type of IMF's. **Each molecule possesses an area of δ^- with a relatively high electron density** ("partial positive charge"), as well as an **area of δ^+ with a relatively low electron density** ("partial negative charge"). As dipoles of nearby molecules align, attractions are created (figure below); to the left is a figure of NH_3 's dipoles.

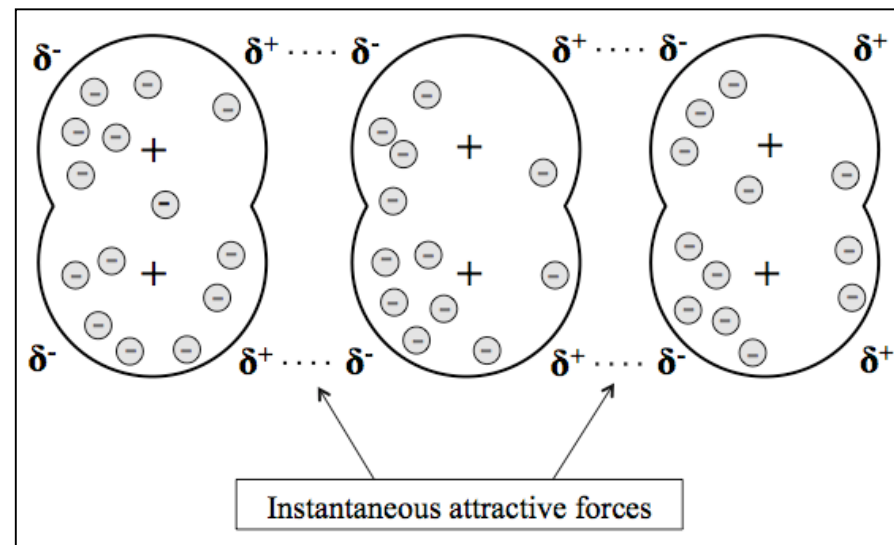


$(\delta^+) \dots (\delta^-) \dots (\delta^+) \dots (\delta^-) \dots (\delta^+) \dots (\delta^-)$

INSTANTANEOUS DIPOLES

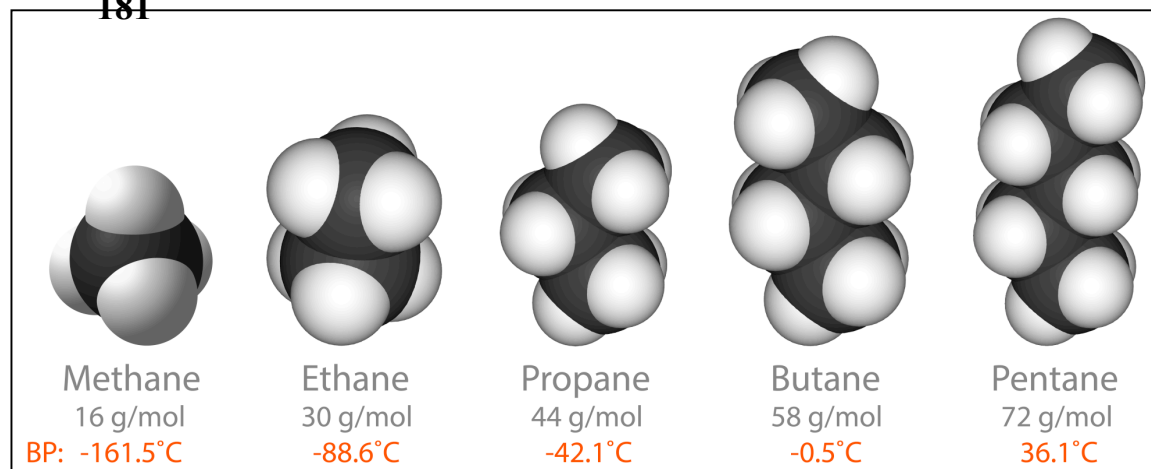
Unlike asymmetrical molecules, **symmetrical molecules have weak IMF's!** This is why N_2 or He can be liquid at room temperature. But why do symmetrical molecules – with $\sum \Delta \text{EN} = 0$ and no permanent partial charges – have any attraction at all? Because of **instantaneous dipoles**.

So what are these instantaneous dipoles? Well, although it's true that **symmetrical** molecules have $\sum \Delta \text{EN} = 0$ over time, they will actually have moments where – for an *instant* – a **dipole will exist** in the molecules, and a **weak attraction** forms. These occur because electrons are constantly whizzing around, so even though a molecule might not have any atoms that are more electronegative than others, the **electrons may just happen to be briefly near each other**; for that tiny instant, the e^- -density is, in fact, higher on one side of the molecule, and it therefore has a partial charge. If this happens to adjacent molecules, their **momentary partial charges can experience a short-lived attraction**.



Important facts about instantaneous dipoles:

- 1) They are also known as **London forces**, **dispersion forces**, or **Van der Waals forces**.
- 2) They are the reason that noble gases can form liquids and solids.
- 3) Alone, they are mostly insignificant; but as molecules increase in magnitude, dispersive forces can integrate and add up to be something quite substantial, kind of like Velcro.

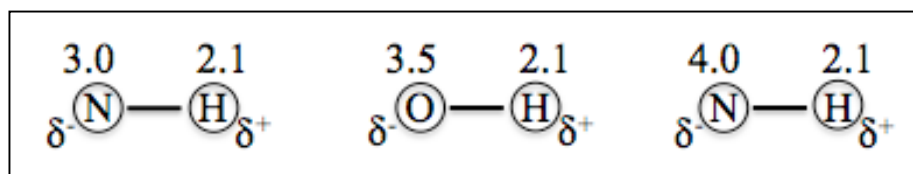


Instantaneous dipoles are the reason some **hydrocarbons** (molecules consisting only of H and C) are **liquids** at **room temperature** – the more C's and H's in the hydrocarbon, the more opportunities for instantaneous dipoles; more instantaneous dipoles makes a compound harder to change from solid → liquid → gas. Hence, **longer hydrocarbons** have **higher boiling points**.

HYDROGEN BONDS: A PERMANENT DIPOLE SPECIAL CASE

Hydrogen bonds (H-bonds) are the **strongest IMF's**, and they're the rationale behind the phenomenon of H₂O – a molecule with a molecular weight of 18 g/mol that doesn't boil until 100°C.

The permanent dipoles we just learned about are indeed found in water, but they're exceptional in its case – the bond contains an extremely electropositive hydrogen:

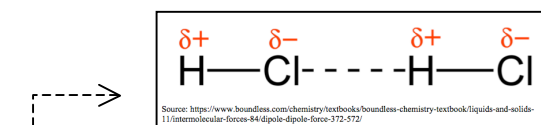


The atom bonded to hydrogen pulls the electron density away from it, which results in a small, densely, positively-charged region on the molecule. This is a prime δ^+ for other molecules to be attracted to (via their δ^- regions).

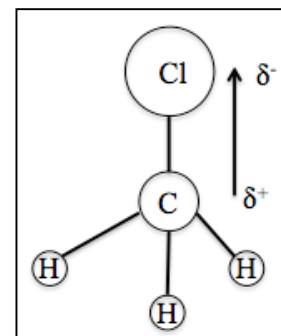
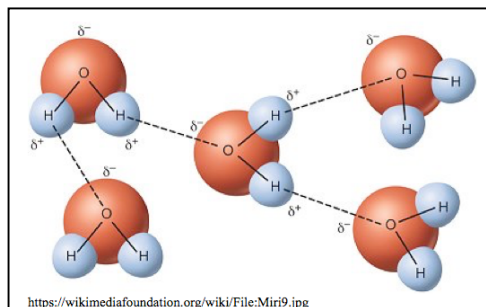
H-bonding is especially strong in atoms of the **second row** because of the **high electronegativity** values of nitrogen, oxygen, and fluorine. Those elements with high EN have a strong pull on their bonded electrons, which results in regions of δ^+ and δ^- on the molecule. With these things in mind, our definition for a **hydrogen bond** should make sense:

- A **hydrogen must be one of the atoms** of the bond.
- The hydrogen must be attached to an **highly EN atom**, such as **N, O, F, or Cl**.

This means that H_2O , HF , HCl , and NH_3 all exhibit H-bonding. On the other hand, CH_3Cl *does not* because **chlorine is not the atom bonded to the hydrogen** in the molecule:

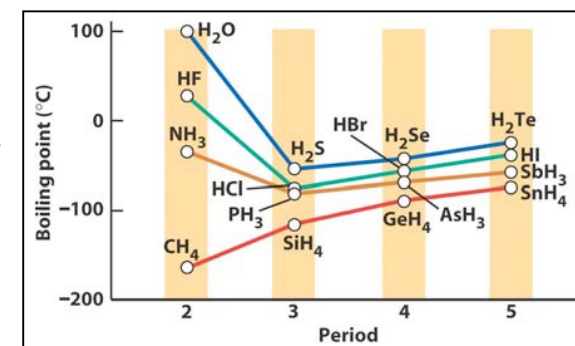


Hydrogen bonding is possible.



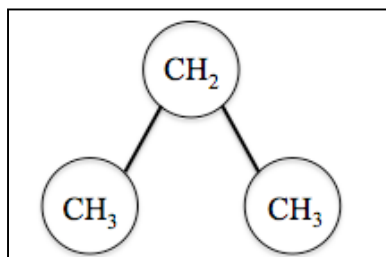
Hydrogen bonding is not possible.

A more general definition is that H-bonding occurs for any hydrogen bonded to another atom. Thus, H_2S , H_2Te , and PH_3 all have hydrogen bonding, though it is very weak:



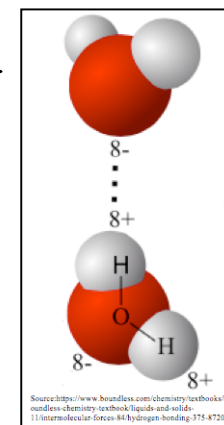
A final example – let's compare IMF's and solution properties in propane (C_3H_8) vs. water:

Solution	Propane	Water
Polarity	Nonpolar	Polar
Strongest IMF	Instantaneous dipoles	Hydrogen bonding
Boiling point	-42°C	100°C
Vapor pressure	4500 torr	18 torr
$\Delta H_{\text{vaporization}}$	16 kJ/mol	41 kJ/mol



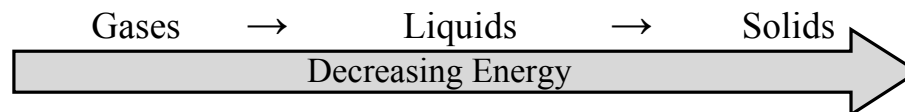
Since H_2O has H-bonding, its:

1. Boiling point is larger.
2. Vapor pressure is lower.
3. ΔH_{vap} is higher.



LECTURE 18: SOLIDS

As you **remove energy** from a system, **IMF attractions increase**. Once enough energy is lost, gases turn into liquids, and liquids turn into solids.



Not all solids are ordered (e.g., plastic), but under certain circumstances, crystalline solids can form with specific geometrics.

There are **seven types** of primitive geometric cells (three-dimensional), called **unit cells**: one is cubic, comprised entirely of right angles and sides of equal length; the other six are slightly less simple, as they vary in angle measure and side lengths.

These **unit cells** can be merged by **overlapping** them to form more complex structures – **crystals**.

BONDING IN SOLIDS

There are **four types of bonds in solids**, and molecules' position in periodic table determine their bond as solids:

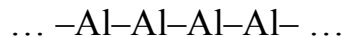
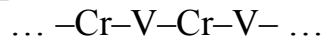
	1A	2A											3A	4A	5A	6A	7A	8A
1	H																	He
2	Li	Be											B	C	N	O	F	Ne
3	Na	Mg	3B	4B	5B	6B	7B	8B	1B	2B	Al	Si	P	S	Cl	Ar		
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6	Cs	Ba		Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
7	Fr	Ra		Unq	Unp	Unh	Uns	Uno	Uue									
			6	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
			7	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

 dual properties
 Metals
 Nonmetals and Noble gases

As you can see from the periodic table on the previous page, the **majority** of elements form **metallic bonds** when in solid form. However, the **nonmetals and noble gases** on the right form the **other three types** of bonds:

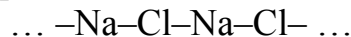
1) **Metallic bond**: a **metal** bonding with another **metal**; these are very strong bonds.

Examples:



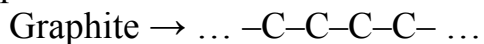
2) **Ionic bond**: a **metal** bonding with a **nonmetal**; these have ~ 200 kJ/mol.

Example:



3) **Covalent bond**: a **nonmetal** bonding with another **nonmetal**; these have ~ 400 kJ/mol.

Examples:



4) **IMF's between molecules**: solids can also be formed from H-bonds, dipoles, and/or dispersion; these are the weakest solids at ~ 1 -20 kJ/mol.

Example:



TABLE 5.4 Typical Characteristics of Solids

Class	Examples	Characteristics
metallic	<i>s</i> - and <i>d</i> -block elements	malleable, ductile, lustrous, electrically and thermally conducting
ionic	NaCl, KNO ₃ , CuSO ₄ ·5H ₂ O	hard, rigid, brittle; high melting and boiling points; those soluble in water give conducting solutions
network	B, C, black P, BN, SiO ₂	hard, rigid, brittle; very high melting points; insoluble in water
molecular	BeCl ₂ , S ₈ , P ₄ , I ₂ , ice, glucose, naphthalene	relatively low melting and boiling points; brittle if pure