TMAS Academy

ACE AP Chemistry

2025

- 100+ Problems
- All Topics
- Detailed Solutions

Aditya Baisakh

Contents

§0.1 About TMAS Academy

TMAS Academy, previously known as Explore Math, was started by Ritvik Rustagi in 2020 to spread competition math. In full, it is **The Math and Science Academy**. Ritvik expanded the academy in October 2023 by releasing his AMC 10/12 prep book. After that, in March 2024, he released his free AP Physics 1, AP Calculus AB/BC, and AP Physics C: Mechanics books. Now, TMAS Academy has evolved into a large team of hard-working, passionate, and dedicated students who enjoy STEM and helping others. We believe that everyone should be able to achieve their full potential with learning, so we have channeled our efforts into making educational resources accessible to all.

You can learn more by visiting the website linked below.
Website: https://www.tmasacademy.com/

§0.2 Opportunities For You To Contribute To TMAS Academy

TMAS Academy is very inclusive and you can help support its cause in many ways.
You can **join the team** by filling out the form below:
https://forms.gle/VXGvj27UvcZPGhiJ8

Donations: If you want to assist us in our monthly payments to run TMAS Academy, which includes website, Overleaf (the platform used to write these books), and filming/editing costs, then please consider donating! For those willing to contribute, we have listed a few ways below. **Don't forget to write a message so we know who you are which will allow us to send you a thank you note!**

- You can donate through PayPal to the email: ritvikrustagi7@gmail.com
- If you want to donate and the above method doesn't work for you, then you can send an email directly to ritvikrustagi7@gmail.com

You can also contribute by **subscribing** to the YouTube channel:
https://www.youtube.com/@tmasacademy
Also, don't forget to join the Discord server to connect with other hardworking students preparing for AP exams and math competitions such as AMC 10/12 and AIME.
https://discord.gg/tmas-academy-1019082642794229870

There are occasional group study sessions and other review sessions led by Ritvik Rustagi and others from the server!

You can also follow all of our social media, such as the LinkedIn page and the Instagram account, both of which are run by the media team. Also, please join the mailing list to learn about all updates and our upcoming books and videos. All of that can be found at the bottom of the website: https://www.tmasacademy.com/

Finally, you can spread our efforts and initiative to anyone you know who may benefit from or support us, be it your classmates, teachers, or other nonprofit organizations focused on education.

§0.3 About the Author: Aditya Baisakh

My name is Aditya Baisakh and I am a student at Baton Rouge Magnet High School. In addition to being a STEM enthusiast, I enjoy playing chess, listening to music, practicing martial arts, programming, and sleeping.

I joined the TMAS Academy team in April 2024. I was impressed by the dedication Ritvik Rustagi has for spreading STEM education around the world without expecting anything in return. When I learned that he was actively recruiting new educators, I happily agreed to help out. My aptitude for science came from a strong math background, which allowed me to think more critically and made general subjects in school easier to grasp. However, my primary motivation for joining the team was my passion for simply helping others learn. Growing up in Baton Rouge, Louisiana, I realized just how difficult it was for many students to achieve their full academic potential. This is because many students in my school district are underprivileged. My love for learning, coupled with my desire to make education achievable for all, inspired me to join TMAS Academy and not only expand my own knowledge, but also demonstrate that anyone can learn anything, no matter their financial situation.

I dedicate this book to everyone who wants to excel in AP Chemistry. Due to the nature of this course, a solid grasp of concepts as well as a rich source of practice problems is necessary to perform well on this tough exam. Through my personal experience scoring a 5 on the exam, this is what my book aims to achieve. Many students these days struggle to prepare for AP exams due to the large amount of material. This book contains several well-written problems with detailed solutions that go along with the concepts, allowing even the most inexperienced students to have a productive time while studying theory and solving problems.

§0.4 Benefits of Taking and Preparing For AP Chemistry

Taking AP Chemistry is a great way to expand your science knowledge. As a college-level course, it goes a step further to deepen your knowledge of topics you have learned in middle school, and the potential to earn college credit if you do well. It is a great learning experience that can improve your problem solving skills that can serve as a life skill in many situations.

§0.5 What if there is an error in the book?

There are possibilities for errors such as typos or incorrect solutions to problems. If that is the case, please click on this link and fill out the form to report the error:
Error Form

§0.6 Any other questions or concerns?

If you have any other questions or concerns relevant to chemistry, feel free to reach out to **adityabaisakh123@gmail.com**
If you have any questions about TMAS Academy and its programs, feel free to email **ritvikrustagi7@gmail.com**

§0.7 Acknowledgements

- I want to thank **College Board, Khan Academy, The American Chemical Society (ACS), and Chemistry, Seventh Edition (Zumdahl)** for their resources that were used to help write this book.

- I would also like to thank the **Art of Problem Solving (AoPS)** for their supportive community of math and science enthusiasts. In addition, their LaTeX programming forums and tutorials were extremely helpful in writing this book.

- I would also like to thank **Evan Chen**, U.S. Math Olympiad Team coach, as well as a current Ph.D. student at MIT, for providing the template used in the book.

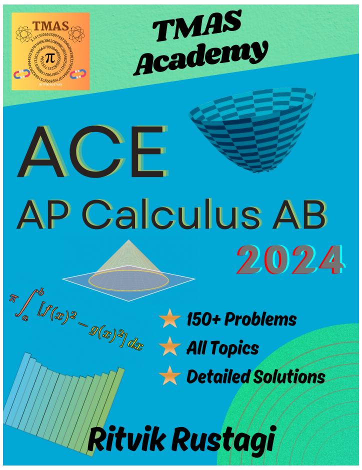
- I would also like to thank **Ritvik Rustagi**, founder and CEO of TMAS Academy, for honoring me with the opportunity to give back to the community through education. I especially appreciate his involvement with all on our team, ensuring that we were fully supported on this journey.

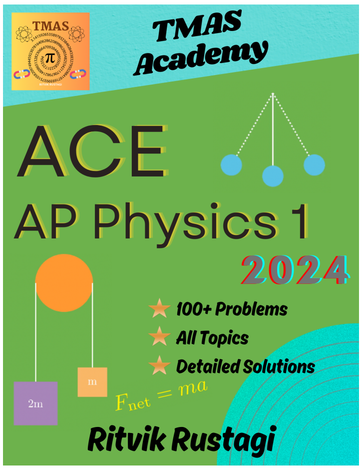
- I also thank my AP Chemistry teacher, Ms. Mathur, for encouraging me to enjoy chemistry and helping me earn a 5 on the exam.

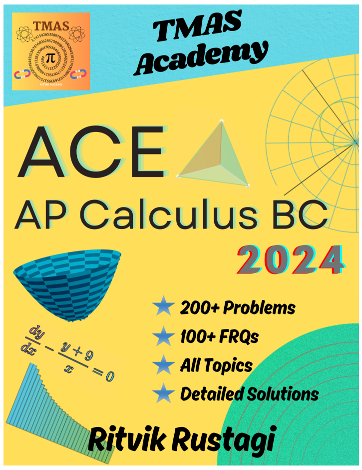
- I also would like to thank everyone who supports the work I have done and encourages me to continue.

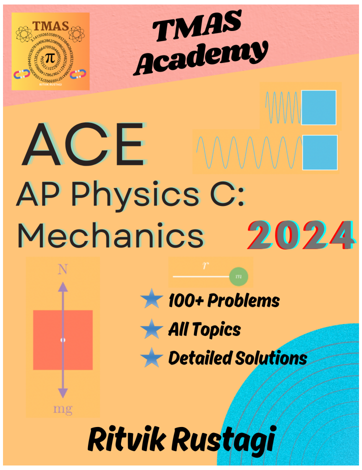
- Finally, I want to thank my parents for always motivating me to achieve my goals and for everything else they have done.

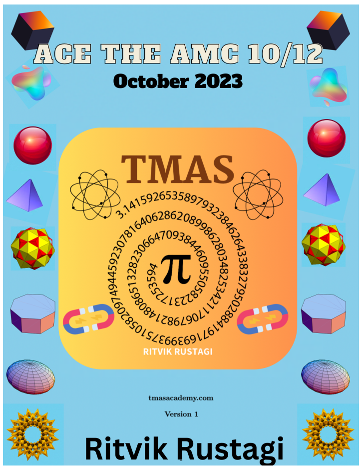
§0.8 Other Important Resources











These are some additional free books that everyone is encouraged to check out.

Make sure to check out the following playlists on the TMAS Academy YouTube channel! These are important to learn all the topics that appear on the following AP exams: AP Calculus AB/BC, AP Physics 1, and AP Physics C: Mechanics.

AP Calculus AB/BC Playlist

AP Physics 1 Playlist

AP Physics C: Mechanics Playlist

§0.9 Message From The Owner: Ritvik Rustagi

Throughout my life, I have tried to make education more accessible for students around the world. That inspired me to create the nonprofit organization TMAS Academy, for which I wrote 5 free books. These are my AP Calculus AB, AP Calculus BC, AP Physics 1, AP Physics C: Mechanics, and AMC 10/12 preparation books. However, to truly maximize growth in other students, I needed a team of students with similar goals.

I was extremely happy when Aditya showed passion and interest in helping students in both his area and around the world. His passion for STEM as well as helping others motivated him to pursue similar goals as me. I am extremely proud of his efforts to write this AP Chemistry book for the public. His book is very special for the TMAS Academy community and I, as it is the first to be authored by someone other than myself.

I really hope Aditya's efforts inspire others to take some time out of their daily lives to benefit others. People can receive a lot of satisfaction from helping others overcome various challenges to pursue a successful academic journey.

At TMAS Academy, we warmly welcome everyone with open arms. I am excited to meet all new writers and students! Please reach out to ritvikrustagi7@gmail.com if you are interested in being an author or if you have any questions! I respond to all emails.

1 Atomic Structure and Properties

This chapter begins our journey into AP Chemistry. Learn about the structure of atoms and how they make up matter. Pay close attention to these concepts: they will be critical for understanding the later units.

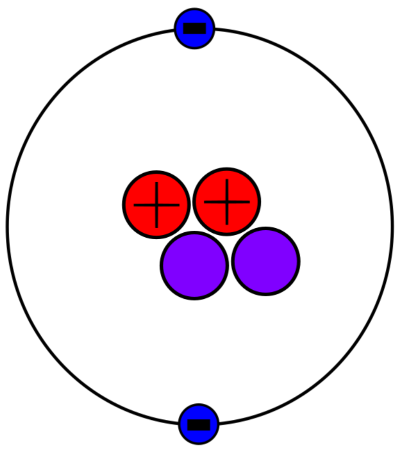
§1.1 Moles and Molar Mass

Definition 1.1.1

An **atom** is the smallest unit of matter that retains all the chemical properties of an element.

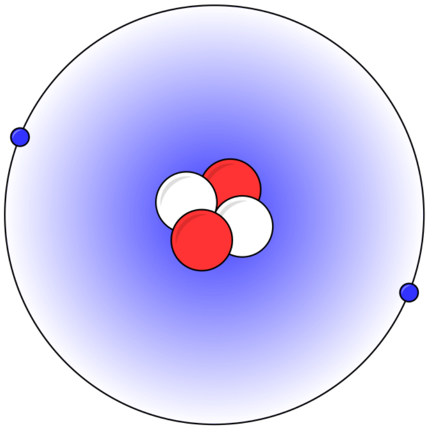
Atoms are also governed by three special **subatomic particles**:

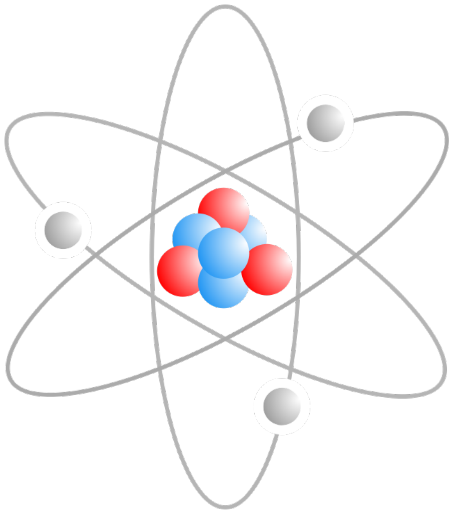
1. Protons: positively charged particles located at the center of an atom, also known as the nucleus.
2. Neutrons: neutral particles also located inside the nucleus of every atom (with the exception of hydrogen, which contains 1 proton).
3. Electrons: negatively charged particles located outside the nucleus. Unlike protons and neutrons, electrons have essentially no mass. Its charge is of equal magnitude as the proton, but with opposite sign.



For an atom of helium, the protons (shown with the + charge) and neutrons are situated at the nucleus, and the electrons (shown with the − charge) are located outside of the nucleus, as part of a region called the *electron cloud*.

While we will not explore atomic structure yet, know that atoms are *extremely small*; it is impossible to see them with the human eye, even with the most sophisticated microscopes.





Note 1.1.2

Now that we know how small atoms are, we propose:

One cannot directly count atoms or particles while performing laboratory work

Therefore, **a connection between masses of substances and the actual number of particles undergoing chemical changes** has been developed.

That standard which has been developed is known as the mole.

Definition 1.1.3

The **mole (mol)** is the amount of a substance that contains $6.022 \cdot 10^{23}$ formula units, e.g. 1 mole of H_2O molecules contains $6.022 \cdot 10^{23}$ molecules.

Formula units can represent anything, be it atoms, molecules, ions, photons, etc. For the purposes of this unit, our formula unit will be the *atom*.

Since 1 mole of anything represents $6.022 \cdot 10^{23}$ formula units of it, we can infer that it is much easier to measure substances by moles, rather than atoms in a laboratory setting.

Avogadro's Number

Definition 1.1.4

Avogadro's number, $N_A = 6.022 \cdot 10^{23}\,\text{mol}^{-1}$ provides the quantitative connection between the number of moles in a pure sample of a substance and the number of its constituent particles (or formula units).

Knowing this information, we can solve problems that ask for conversions involving the number of atoms, moles, formula units, grams, etc.

Problem 1.1.5 — Avogadro's Number I

Calculate the number of moles present in a sample of $1.31 \cdot 10^9$ helium atoms.

Solution: Since we are converting from atoms to moles, this problem definitely requires us to use Avogadro's number, which is $6.022 \cdot 10^{23}$ formula units mol^{-1}. For this problem, our formula unit is the helium atom. Therefore, we can rewrite the expression as

$$N_A = \frac{6.022 \cdot 10^{23} \text{ atoms}}{1 \text{ mol helium}}$$

Since the numerator and the denominator mean the same thing, we can use this fraction as a *conversion factor*. Its value is equal to 1 and it will be very useful for dimensional analysis.

Since we wish to convert from atoms to moles, the units of atoms should cancel. Therefore, our conversion factor for this problem should be written as

$$\frac{1 \text{ mol helium}}{6.022 \cdot 10^{23} \text{ atoms}}$$

We will use dimensional analysis to find our answer.

$$\frac{1.31 \cdot 10^9 \cancel{\text{atoms}}}{1} \cdot \frac{1 \text{ mol helium}}{6.022 \cdot 10^{23} \cancel{\text{atoms}}} = \boxed{2.18 \cdot 10^{-15} \text{ mol helium}}$$

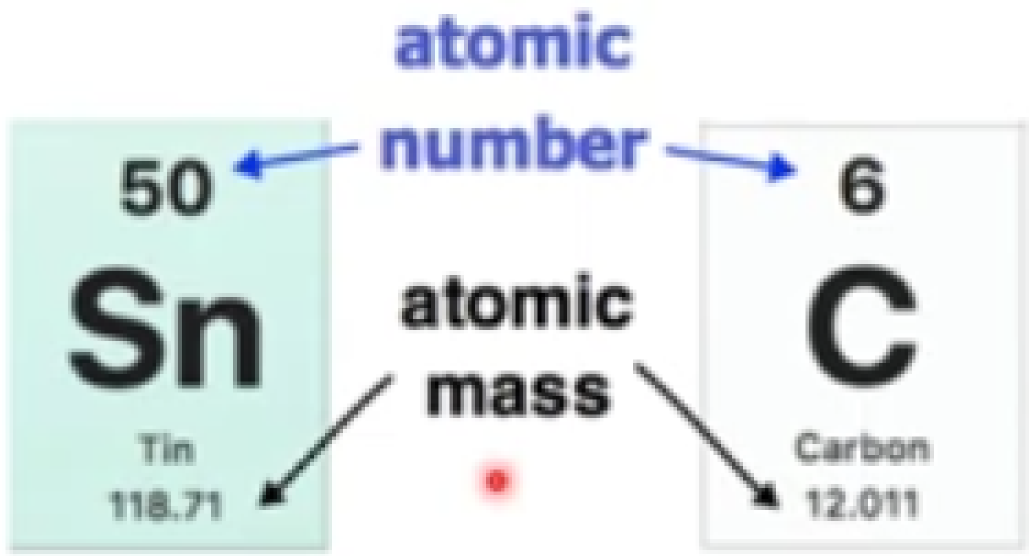
Atomic Mass and The Atomic Mass Unit

This section is all about the following idea:
Expressing the mass of an individual atom or molecule in terms of **atomic mass units (amu)** will be very useful since the average mass in amu of one formula unit or particle (atom or molecule) of a substance will always be numerically equal to the molar mass of that substance in grams. Thus, there is a quantitative connection between the mass of a substance and the number of particles contained in that substance.

$$\text{molar mass (g/mol)} = \frac{\text{mass (g)}}{\text{moles (mol)}}$$

Because measuring actual masses (in grams) of atoms and subatomic particles is absurd, units of **amu** are more convenient to use.

$$1 \text{ amu} = 1.6605 \cdot 10^{-24} \text{ g}$$



For example, we can compare the atomic mass unit and molar mass of hydrogen using the following:

- One atom of H has a mass of 1.008 amu: **atomic mass**
- One mole of H atoms has a mass of 1.008 g: **molar mass**

Additionally,

- Mass of a mole of particles = mass of 1 particle **x** $6.022 \cdot 10^{23}$
- Mass of 1 H atom $= 1.008\,\text{amu} \cdot 1.661 \cdot 10^{-24}\,\text{g/amu} = 1.674 \cdot 10^{-24}\,\text{g}$
- Mass of 1 mol H $= 1.674 \cdot 10^{-24}\,\text{g/H atoms} \cdot 6.022 \cdot 10^{23}\,\text{H atoms} = 1.008\,\text{g}$

Molar Mass of a Molecule

Molecules are groups of two or more atoms that form the smallest unit that retains all the properties of a pure substance.

Note 1.1.6
We will learn more about pure substances in sections 1.3 and 1.4.

We can calculate the molar mass of not only individual atoms, but also molecules.

Problem 1.1.7 — Molecular Mass

Find the molar mass of $CHCl_3$ in g/mol given that the atomic masses of C, H, and Cl are 12.01 amu, 1.008 amu, and 35.45 amu, respectively.

Solution: Since the mass in amu of an element is directly correlated to its molar mass, we know that the molar masses of C, H, and Cl are 12.01 g/mol, 1.008 g/mol and 35.45 g/mol, respectively. There is 1 atom of C, 1 atom of H, and 3 atoms of Cl in the molecule. Therefore, we can sum up these values and take into account their occurrences in the molecule. The total molar mass is $12.01\text{ g/mol} + 1.008\text{ g/mol} + 3 \cdot 35.45\text{ g/mol} = \boxed{119.37\text{ g/mol}}$.

Problem 1.1.8 — Avogadro's Number II

The molar mass of arsenic (As) is 74.92 g/mol. Calculate the mass in grams of a sample of As containing $1.35 \cdot 10^{25}$ atoms.

Solution: We can use Avogadro's number to convert from atoms of As to moles of As.

$$1.35 \cdot 10^{25}\,\cancel{\text{atoms As}} \cdot \frac{1\text{ mol As}}{6.022 \cdot 10^{23}\,\cancel{\text{atoms As}}} = 22.4\text{ mol As}$$

Now, we can multiply by the molar mass of As to determine the mass in grams of the sample.

$$22.4\,\cancel{\text{mol As}} \cdot \frac{74.92\text{ g As}}{1\,\cancel{\text{mol As}}} = \boxed{1.68 \cdot 10^{3}\text{ g As}}$$

Problem 1.1.9 — Using Molar Masses

Given that hydrogen, carbon, and oxygen have molar masses of 1.008 g/mol, 12.01 g/mol, and 16.00 g/mol, respectively, calculate the number of moles in a 4.06 kg sample of citric acid, $C_6H_8O_7$.

Solution: We can use the molar mass of a substance to convert number of grams to number of moles of that substance. That said, let us first calculate the molar mass of citric acid using the information in the problem.

$$6\,\cancel{\text{mol C}} \cdot \frac{12.01\text{ g C}}{1\,\cancel{\text{mol C}}} = 72.06\text{ g C}$$

$$8\,\cancel{\text{mol H}} \cdot \frac{1.008\text{ g H}}{1\,\cancel{\text{mol H}}} = 8.064\text{ g H}$$

$$7\,\cancel{\text{mol O}} \cdot \frac{16.00\text{ g O}}{1\,\cancel{\text{mol O}}} = 112.0\text{ g O}$$

Adding everything, we find that 1 mole of $C_6H_8O_7$ has a mass of 192.1 g.
Then, we use the molar mass of $C_6H_8O_7$ to to convert from grams of $C_6H_8O_7$ to moles of $C_6H_8O_7$. Since we were given the mass of $C_6H_8O_7$ in kilograms, we need to convert that into grams in the overall calculation.

$$4.06\,\cancel{\text{kg } C_6H_8O_7} \cdot \frac{1000\,\cancel{\text{g } C_6H_8O_7}}{1\,\cancel{\text{kg } C_6H_8O_7}} \cdot \frac{1\text{ mol } C_6H_8O_7}{192.1\,\cancel{\text{g } C_6H_8O_7}} = \boxed{21.1\text{ mol } C_6H_8O_7}$$

§1.2 Mass Spectrometry of Elements

If you look at the periodic table, you may wonder how scientists actually came up with all these numbers. As discussed previously, an atom is made up of protons, neutrons, and electrons. Understanding these three subatomic particles is significant because they relate to the very design of the periodic table.

Review: Periodic Table

In the periodic table, you can find the following information for each element.

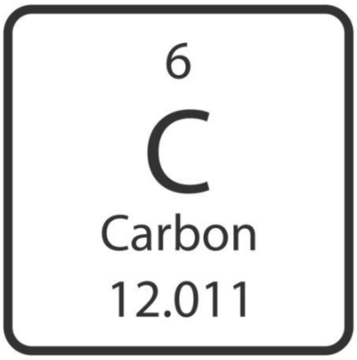
1. **Element symbol**: Each element is represented by a unique symbol, typically consisting of one or two letters.

2. **Atomic number**: The atomic number of each element, located above the elemental symbol, represents the number of protons in the nucleus of the atom of that element. It is also equal to the number of electrons in a neutral atom of that element, which we will discuss later on this unit.

3. **Atomic mass**: The atomic mass of an element is found below the element symbol and is typically expressed in units of atomic mass (amu). The atomic mass is a representation of the number of protons in an atom of that element + the number of neutrons in an atom of that element (**THIS WILL BE OUR KEY FOCUS IN THIS SECTION**).

Average Atomic Mass of an Element

Let's take a look at carbon on the Periodic Table, that will be given to you on the AP Exam:



We can make these three observations about carbon based on the periodic table.

1. Carbon is represented by the elemental symbol "C."

2. The atomic number of carbon is 6, which means that one atom of carbon has 6 protons in its nucleus and 6 electrons orbiting its nucleus.

3. Carbon's atomic mass looks to be 12.011, but how would this make sense? Since atomic mass = protons + neutrons, and we know we have 6 protons, that would give us 6.01 neutrons. As you may realize, this is impossible. Instead of a nice "12" or "13" under carbon, there is a really messy decimal value of 12.011. If you take a

look at other elements on the periodic table, you will notice a similar trend.

This is because the atomic masses that you are given on the periodic table are actually the *average* atomic masses. The **average atomic mass** of an element is the weighted average of the masses of the naturally occurring *isotopes* of that element, based on their relative abundances.

What are Isotopes?

Definition 1.2.1

Isotopes are variants of an element. They have the same number of protons and electrons, but a different number of neutrons. This means that isotopes have different atomic masses (total number of protons and neutrons).

Thus, the average atomic mass represents all isotopes of an atom and the frequency with which they occur naturally in the environment.

Worked Example: Determining Average Atomic Mass of Carbon

There are two naturally occurring carbon isotopes (in significant amounts): **carbon-12** and **carbon-13**.

- Carbon-12 is the most abundant isotope of carbon, making up about 98.9% of naturally occurring carbon. It has an atomic mass of 12 amu and is stable. Carbon-12 has 6 neutrons, which is calculated by taking the mass number of 12 and subtracting 6 protons.
- Carbon-13 is a less abundant isotope of carbon, making up about 1.1% of naturally occurring carbon. It has an atomic mass of 13 amu and is also stable. Carbon-13 has $13 - 6 = 7$ neutrons.

To calculate average atomic mass, we use the following formula:

$$\text{average} = \sum_{i=1}^{n} m_i \cdot p_i = m_1 \cdot p_1 + m_2 \cdot p_2 + \cdots + m_n \cdot p_n$$

for n isotopes in a sample of an element and where m_i and p_i are the masses and relative abundances, respectively, of the i-th isotope in the sample.

For carbon, to calculate its average atomic mass from the experimental data, we set up the following:

$$\text{average} = (0.989)(12) + (0.011)(13) = \boxed{12.01 \text{ amu}}$$

This is the same as the number on the periodic table!
Also, note that the abundance of isotopes has a significant effect on the average atomic mass of an element. If you are only given the mass numbers 12 and 13, as well as

the average atomic mass, you can easily tell which isotope is more abundant in nature. For example, 12.01 is much closer to 12 than 13, so clearly **carbon-12** is more abundant.

Note 1.2.2

When finding average atomic mass, always convert the given % abundance to a decimal before proceeding with the formula.

Mass Spectrometry

Definition 1.2.3

Mass spectrometry is a technique used to measure the mass and relative abundance of isotopes in a sample. This technique produces a plot called the *mass spectrum*, which allows us to identify different isotopes of an element and the relative abundance of each isotope in nature.

Consider the mass spectrum for carbon below, we can identify the isotopes as carbon-12 and carbon-13.

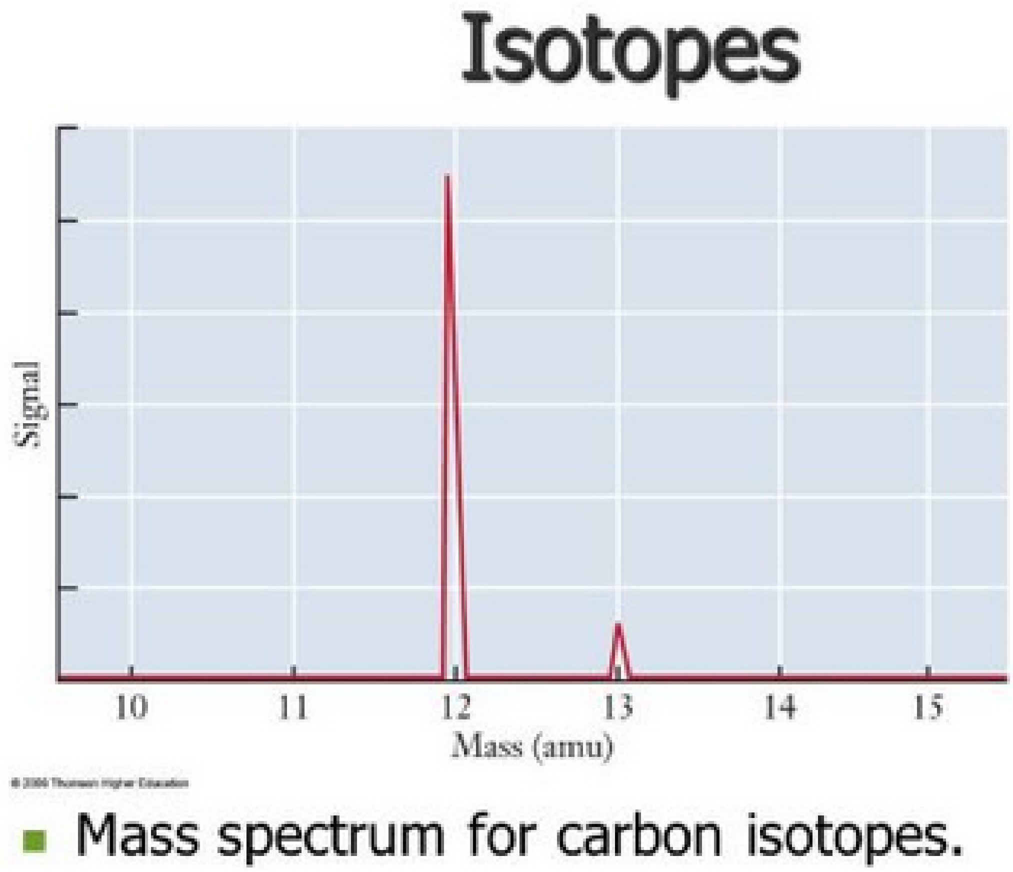


Image Courtesy of Professor Bensely

Also, the stronger signal of carbon-12 as opposed to carbon-13 indicates that the former is much more abundant than the latter.

Putting Everything Together

Our final challenge is to identify an unknown element given its mass spectrum.

Problem 1.2.4 — Identifying Unknown Element Given Mass Spectrum

The peaks below show a mass spectrum of element X. Based on this spectrum, what is the identity of element X?

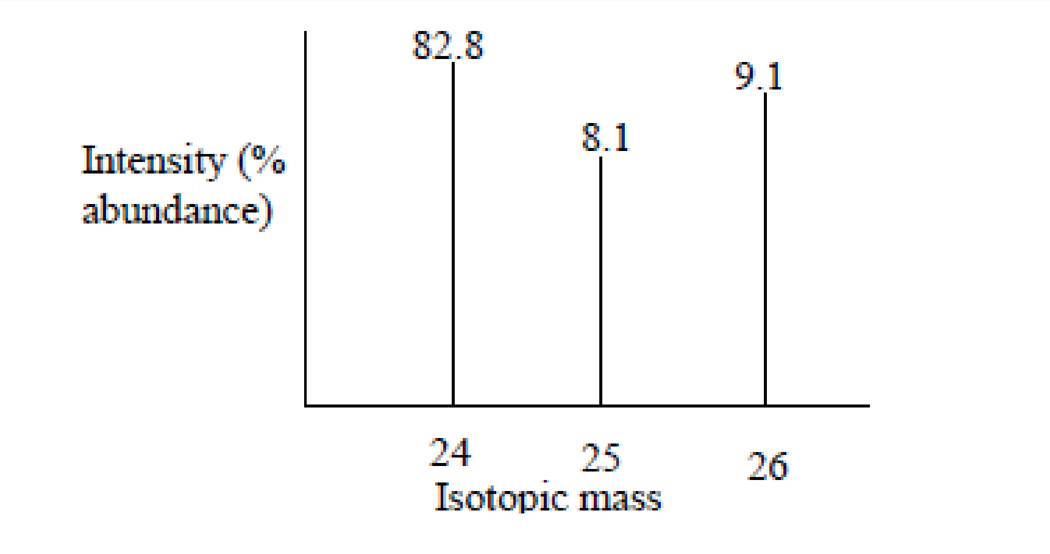


Image Courtesy of Kenyaplex

Solution: Without using a calculator, you can quickly infer that the average atomic mass should be somewhere between 24 and 25.

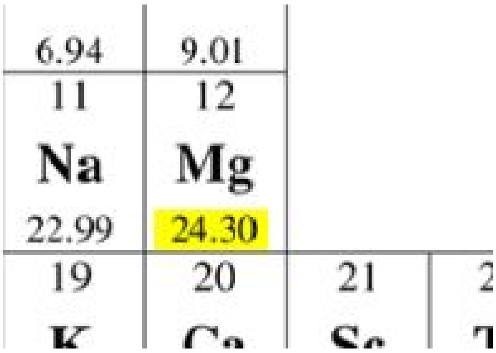
We set up the following

$$\text{average} = \sum_{i=1}^{n} m_i \cdot p_i$$

Plugging in our values, we have

$$\text{average} = (0.828)(24) + (0.081)(25) + (0.091)(26) = 24.263 \text{ amu}$$

This measurement is close to 24.3 amu. Looking at the periodic table, we can identify this element as $\boxed{\text{magnesium}}$, with an average atomic mass of 24.30 amu.



Recap of Section 1.2

- Mass spectrometry is a technique that allows you to determine the relative amounts of isotopes of an atom for a given sample of the element.
- This technique represents the laboratory aspect of AP Chemistry. You will likely conduct a related experiment in your classroom to enforce your understanding of the theory.

§1.3 Elemental Composition of Pure Substances

Definition 1.3.1

All **pure substances**, e.g. elements and compounds, consist of a fixed composition.

This means that the elements present and the ratio of their atoms is the same for every sample of the given compound. This is also known as the Law of Definite Proportions.

Example 1.3.2

Table salt, or sodium chloride, consists of a 1 : 1 ratio of sodium atoms to chlorine atoms. This is always true, regardless of the sample's size.

The fixed ratio of atoms of each element in a compound also means there is a fixed **mass ratio of elements** in every compound. For example, a sample of water will always be

11.11% hydrogen and 88.89% oxygen by mass.

Question: What is the Percent Composition of All Elements in Sucrose?

Answer: The chemical formula for sucrose is $C_{12}H_{22}O_{11}$.
First, we need to understand what the subscripts below carbon, hydrogen, and oxygen actually mean.

- C_{12} indicates that for one molecule of sucrose, there are 12 carbon atoms.
- H_{22} indicates that for one molecule of sucrose, there are 22 hydrogen atoms.
- O_{11} indicates that for one molecule of sucrose, there are 11 oxygen atoms.

We want to find the percent composition of each element in sucrose.

Step 1: Multiply the number of atoms for each element by atomic mass shown on the Periodic Table.

- C: $12 \cdot 12.01\,\text{amu} = 144.12\,\text{amu}$
- H: $22 \cdot 1.01\,\text{amu} = 22.22\,\text{amu}$
- O: $11 \cdot 16.00\,\text{amu} = 176.00\,\text{amu}$

Step 2: The sum of these results is referred to as the **formula mass** of sucrose.

$$144.12\,\text{amu} + 22.22\,\text{amu} + 176.00\,\text{amu} = 342.3\,\text{amu}$$

Step 3: Divide the mass of each element by the total formula mass and multiply by 100 to determine the percent composition per element.

$$\frac{144.12\,\text{amu C}}{342.3\,\text{amu}} \cdot 100\% = 42.10\%\,\text{C}$$
$$\frac{22.22\,\text{amu H}}{342.3\,\text{amu}} \cdot 100\% = 6.49\%\,\text{H}$$
$$\frac{176.00\,\text{amu O}}{342.3\,\text{amu}} \cdot 100\% = 51.40\%\,\text{O}$$

Note: Values may not exactly add up to 100 due to rounding.

Thus, we find that sucrose is $\boxed{42.10\%\,\text{C},\ 6.49\%\,\text{H, and}\,51.40\%\,\text{O}}$ by mass.

Understanding Percent Composition

Be sure to understand that it *is* possible for two different substances to have the same percent composition by mass.

Example 1.3.3

Consider two compounds: nitrogen dioxide and dinitrogen tetroxide. These compounds have chemical formulas NO_2 and N_2O_4, respectively.

- In both compounds, the ratio of nitrogen to oxygen atoms is $1 : 2$.
- Also, both compounds are 30.45% nitrogen and 69.55% oxygen by mass.

Question: Why is this the case?

Answer: Both compounds possess the same *empirical formula*, despite having different *molecular formulas*.

Definition 1.3.4

The smallest whole number ratio of atoms of each element in a compound is known as its **empirical formula**.

For example, dinitrogen tetroxide (N_2O_4) actually has an empirical formula of NO_2, similar to nitrogen dioxide (NO_2), which also happens to share the same formula mass.

Definition 1.3.5

The actual number of atoms of each element in a compound is known as its **molecular formula**.

Important! This means that for any compounds, regardless of their molecular formulas, if they share the same EMPIRICAL formulas, then their elemental composition by mass will be the same.

Example 1.3.6

Formaldehyde has molecular formula CH_2O and glucose has molecular formula $C_6H_{12}O_6$. Explain why formaldehyde and glucose share the same percent composition for all elements.

Answer: In both molecules, there is a $1 : 2 : 1$ ratio in carbon, hydrogen, and oxygen atoms as the $6 : 12 : 6$ ratio of atoms of all elements in glucose can be reduced to $1 : 2 : 1$. Thus, the empirical formula of both formaldehyde and glucose is CH_2O. Since the two compounds share the *same empirical formula*, they also share the same percent composition by mass for all elements.

Empirical Formula Determination

We know the definition of an empirical formula, but how can we actually determine one for a substance?
Answer: we need to use **mass data** from laboratory analysis.

In AP Chemistry, we can determine the empirical formula of a substance when a problem is framed in two possible ways:

- **Type I**: The masses of each element in the compound are stated.
- **Type II**: The percent composition of each element in the compound is provided.

For problems of **Type I**, the following steps are taken.

- Use molar masses to calculate the number of moles for each element present.
- Divide all calculated values by the smallest number of moles.
- Use the mole ratio to write the empirical formula.

Let's walk through the following problem.

Problem 1.3.7 — Empirical Formula I

Determine the empirical formula of the compound if a sample contains 5.28 g Sn and 3.37 g F.

Solution: First, let's convert the masses of each element to the number of moles using their respective molar masses.

$$5.28\,\cancel{\text{g Sn}} \cdot \frac{1 \text{ mol Sn}}{118.71\,\cancel{\text{g Sn}}} = 0.0445 \text{ mol Sn}$$
$$3.37\,\cancel{\text{g F}} \cdot \frac{1 \text{ mol F}}{19.00\,\cancel{\text{g F}}} = 0.177 \text{ mol F}$$

Next, divide all values by the smallest number of moles.

$$\frac{0.0445}{0.0445} \text{ mol Sn} = 1.00$$
$$\frac{0.177}{0.0445} \text{ mol F} = 3.98 \approx 4.00$$

Using the mole ratio, we determine the empirical formula of the compound to be $\boxed{SnF_4}$.

When empirical formula problems are of **Type II**, we use the following problem-solving strategy.

- Assume a 100 gram sample. Treat the percentages by mass as actual masses of the elements in the sample.
- Use molar masses to convert the masses to number of moles for each element.
- Same as Type I, divide by the smallest number of moles.
- If needed, multiply mole ratios by integers to get whole numbers.
- Finally, as with Type I, use the mole ratio to write the empirical formula.

Let's walk through the following problem.

Problem 1.3.8 — Empirical Formula II

A compound is determined to be 43.6% phosphorus and the remainder as oxygen. What is its empirical formula?

Solution: Since the compound is 43.6% phosphorus by mass, it is $100 - 43.6 = 56.4$ percent oxygen by mass.
If we assume that the sample of our compound is 100 grams, then the masses of phosphorus and oxygen are 43.6 and 56.4 grams, respectively. Let's convert these measurements to number of moles.

$$43.6\,\text{g}\,\cancel{\text{P}} \cdot \frac{1\text{ mol P}}{30.97\,\text{g}\,\cancel{\text{P}}} = 1.41\text{ mol P}$$
$$56.4\,\text{g}\,\cancel{\text{O}} \cdot \frac{1\text{ mol O}}{16.00\,\text{g}\,\cancel{\text{O}}} = 3.53\text{ mol O}$$

Next, we divide by the smallest number of moles.

$$\frac{1.41}{1.41}\text{ mol P} = 1.00$$
$$\frac{3.53}{1.41}\text{ mol O} = 2.50$$

Since we don't have whole numbers yet, we can multiply both these values by 2 to get whole number ratios.

$$1.00 \cdot 2 = 2.00\text{ mol P}$$
$$2.50 \cdot 2 = 5.00\text{ mol O}$$

These numbers become the subscripts in our empirical formula, which is $\boxed{P_2O_5}$.

Molecular Formula Determination

Sometimes, you will be asked to determine the molecular formula for a chemical compound. However, if you understood empirical formula determination well, this should be very easy for you, as there is only one extra step.

Recall that the molecular formula represents the **actual number of atoms** for each element in a compound, while the empirical formula only represents the *ratio of atoms* for each element. Simply put, the molecular formula of a compound is a **whole number multiple** of the empirical formula.

The relationship between a compound's empirical and molecular formula is

$$n = \frac{\text{molecular formula}}{\text{empirical formula}} = \frac{\text{molecular formula molar mass}}{\text{empirical formula molar mass}}$$

where n is any positive integer.

The most effective way to understand molecular and empirical formulas is by solving problems.

Problem 1.3.9 — Molecular Formula

In the previous problem, a compound containing phosphorus and oxygen was found to have empirical formula P_2O_5. Experimental data shows that the molar mass of the compound is 283.89 g/mol. What is the molecular formula of the compound?

Solution: We know that the empirical formula is P_2O_5 so we need to solve for the whole number multiple n, in order to determine the molecular formula.

We have the following.

$$n = \frac{\text{molecular formula molar mass}}{\text{empirical formula molar mass}}$$

We need to find the molar mass of our empirical formula, P_2O_5, which is equal to $2 \cdot 30.97\ \text{g/mol} + 5 \cdot 16.00\ \text{g/mol} = 141.94\ \text{g/mol}$.

Let's calculate the value of n.

$$n = \frac{283.89\ \text{g/mol}}{141.94\ \text{g/mol}} = 2.00$$

Now, we multiply the number of all atoms in the empirical formula by n.
Therefore, the molecular formula of the compound is

$$2 \cdot (\mathrm{P_2O_5}) = \boxed{\mathrm{P_4O_{10}}}$$

Combustion Analysis

In combustion analysis, an organic compound containing some combination of the elements carbon and hydrogen, also known as a *hydrocarbon*, is combusted in air, and the masses of the combustion products (carbon dioxide and water) are recorded. From this information, we can calculate the empirical formula of the original compound.

We will learn the strategy as we walk through this problem.

Problem 1.3.10 — Empirical Formula Given Combustion Data

A sample of a compound containing only carbon and hydrogen atoms is completely combusted, producing 5.65 g of CO_2 and 3.47 g of H_2O.

What is the empirical formula of the compound?

Solution: Since we do not know how carbon and hydrogen atoms are in the original compound, we can write the formula as C_xH_y. The equation that represents the combustion of our compound in air is

$$\mathrm{C}_x\mathrm{H}_y + \mathrm{O_2} \rightarrow \mathrm{CO_2} + \mathrm{H_2O}$$

Essentially, when a hydrocarbon combusts, we assume that all the carbon and hydrogen atoms are converted into CO_2 and H_2O, respectively.

A good first step is to have the atomic masses of carbon, hydrogen, and oxygen:

$$\text{H} : 1.008\,\text{g/mol}$$

$$\text{C} : 12.01\,\text{g/mol}$$

$$\text{O} : 16.00\,\text{g/mol}$$

Since all the carbon atoms in C_xH_y were transformed into CO_2, we can calculate the number of moles of carbon in the products by the following calculation:

$$\frac{5.65\,\cancel{\text{g CO}_2}}{1} \cdot \frac{1\,\cancel{\text{mol CO}_2}}{44.01\,\cancel{\text{g CO}_2}} \cdot \frac{1\,\text{mol C}}{1\,\cancel{\text{mol CO}_2}} = 0.128\,\text{mol C}$$

Similarly, we can calculate the number of moles of hydrogen in the products. However, you will need to be a little more careful. In one molecule of H_2O, there are 2 hydrogen atoms, so your mole ratio should be $2\,\text{mol H} : 1\,\text{mol H}_2\text{O}$, and not $1\,\text{mol H} : 1\,\text{mol H}_2\text{O}$.

$$\frac{3.47\,\cancel{\text{g H}_2\text{O}}}{1} \cdot \frac{1\,\cancel{\text{mol H}_2\text{O}}}{18.016\,\cancel{\text{g H}_2\text{O}}} \cdot \frac{2\,\text{mol H}}{1\,\cancel{\text{mol H}_2\text{O}}} = 0.385\,\text{mol H}$$

Now that we have the number of moles for both carbon and hydrogen in the original compound, we divide by the smallest value.

$$\frac{0.128}{0.128}\text{ mol C} = 1$$
$$\frac{0.385}{0.128}\text{ mol H} = 3.01 \approx 3$$

Since the ratio for carbon atoms to hydrogen atoms is 1 : 3, the empirical formula of the compound is $\boxed{CH_3}$.

§1.4 Composition of Mixtures

In the previous section, we studied the composition of various pure substances. In this section, it becomes a little more complicated. We will learn how to determine the composition of mixtures.

Definition 1.4.1

A **mixture** is a combination of two or more pure substances.

Mixture compositions depend on pure substances as well as the *relative* composition of those pure substances.
For example, solutions are a type of mixture (we will see this more in Unit 3).

Elemental analysis can be used to determine the amounts of substances in a mixture. On the AP Exam, this concept is tested very directly, so all you need to get the hang of it is practice.

Problem 1.4.2 — Calculating Mass of Substance in Mixture I

A 0.450 g potassium supplement contains 22.0% K by mass. The potassium is present in the supplement as KCl (molar mass 74.55 g/mol).

How many grams of KCl are in the potassium supplement?

Solution: Firstly, since we know what percent by mass in the supplement is potassium, we can find the exact mass of K.

$$\frac{0.450\,\cancel{\text{g sample}}}{1} \cdot \frac{22\text{ g K}}{100\,\cancel{\text{g sample}}} = 0.099\text{ g K}$$

Now that we know the mass of potassium in the supplement, we can use its molar mass to determine the number of moles.

$$0.099\,\cancel{\text{g K}} \cdot \frac{1\text{ mol}}{39.10\,\cancel{\text{g K}}} = 0.00253\text{ mol K}$$

Since there is 1 atom of K for every 1 molecule of KCl, we can convert from moles of K to moles of KCl using the following calculation:

$$0.00253\,\cancel{\text{mol K}} \cdot \frac{1\text{ mol KCl}}{1\,\cancel{\text{mol K}}} = 0.00253\text{ mol KCl}$$

Finally, we can use the molar mass of KCl (74.55 g/mol) to calculate the mass of KCl present in the supplement.

$$0.00253\,\cancel{\text{mol KCl}} \cdot \frac{74.55\text{ g KCl}}{1\,\cancel{\text{mol KCl}}} = \boxed{0.189\text{ g KCl}}$$

Problem 1.4.3 — Calculating Mass of Substance in Mixture II

A student determines that a 1.5 g mixture of $CaCO_3(s)$ and $NaHCO_3(s)$ contains 0.010 mol of $NaHCO_3(s)$.

Based on the student's measurement, what is the mass percent of Na in the mixture?

Solution: The mass percent of Na in the mixture can be determined by comparing the mass of Na to the total mass of the mixture.

We know that there are 0.010 mol $NaHCO_3(s)$ in the mixture. We can convert this to moles of Na using the fact that there is 1 atom of Na for every 1 molecule of $NaHCO_3(s)$. Finally, using the atomic mass of Na, we can convert to grams.

$$0.010\,\cancel{\text{mol NaHCO}_3} \cdot \frac{1\,\cancel{\text{mol Na}}}{1\,\cancel{\text{mol NaHCO}_3}} \cdot \frac{22.99\text{ g Na}}{1\,\cancel{\text{mol Na}}} = 0.23\text{ g Na}$$

Now, we can divide our calculated mass of Na by the total mass of the mixture to determine the mass percent of Na.

$$\text{mass percent of Na} = \frac{0.23\text{ g Na}}{1.5\text{ g mixture}} \cdot 100\% = \boxed{15\%}$$

Analyzing The Purity Of A Mixture

Elemental analysis can also be used to test the **purity** of a sample. For example, a pure sample of a generic compound AB should contain $x\%$ of A by mass. If the elemental analysis matches this value, then our sample is pure. Otherwise, it is contaminated.

Similarly to the masses of substances in mixtures, it is not very difficult to analyze whether a sample is pure. All it takes is practice.

Problem 1.4.4 — Multiple Choice Question

A student believes that a sample of solid KCl may be contaminated with NaCl(s). Knowing that pure KCl(s) contains 48% chlorine by mass, the student performs an experiment to determine the mass percent of chlorine in the sample of KCl(s).

Which of the following results for the mass percent would best support the student's claim that the sample of KCl(s) is contaminated with NaCl(s)?

(A) 37% chlorine by mass
(B) 41% chlorine by mass
(C) 48% chlorine by mass
(D) 55% chlorine by mass

Solution: Based on the relative molar masses of the two compounds, we know that NaCl contains more chlorine by mass than KCl. (You can verify this with the mass percent problem-solving strategy.) This means that if the student's sample of solid KCl was in fact contaminated, then the mass percent of chlorine in the sample would be *higher* than that in pure KCl(s), which is 48%. Among the answer choices, 55% chlorine by mass is greater than the 48% chlorine by mass for a pure sample. Thus, choice $\boxed{\textbf{(D)}}$ is correct.

§1.5 Atomic Structure and Electron Configuration

The very basics of atomic structure follow the same principle: *Protons and neutrons are positively and neutrally charged (respectively) subatomic particles that reside in the center or nucleus of an atom. Electrons are negatively charged and are localized outside the nucleus in a place called an electron cloud.*

Here is a list of reference properties for each of these subatomic particles:

- Protons are located within the atom's *nucleus*, with a mass of approximately 1 amu, a charge of +1, and is represented by the atomic number of an element and makes up part of the mass number.
- Neutrons are also located within the atom's nucleus, with a mass of approximately 1 amu, a charge of 0, and comprise the mass number of an element.

- Electrons are located within the **orbitals** (more on this later) of an atom, possess nearly zero mass, a charge of -1, and are represented by the atomic number of an element of zero charge.

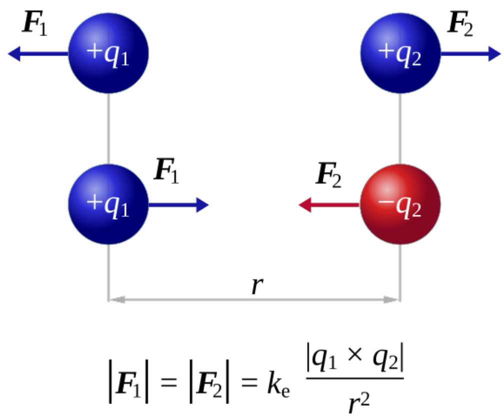
Representing the Atom: John Dalton And The Atomic Theory

Modern-day chemists use an important principle to understand the atom: **Dalton's Atomic Theory**. This theory is composed of four postulates:

1. Each element is made up of *indivisible* and *indestructible* atoms.
2. All atoms of a given element carry the *same* properties.
3. Atoms combine in whole-number ratios to form *compounds*.
4. A chemical reaction changes the way atoms are bound together. Alternatively, a chemical reaction is a simply a *rearrangement* of atoms.

Coulomb's Law

Now that we have learned the structure of an atom, we will need to quantitatively describe the *force*, or *interaction*, between two atoms. This can be determined by a relationship known as **Coulomb's Law**:



where F represents the calculated electric force, k_e is Coulomb's constant, q_1 and q_2 are the charges of the two particles, and r represents the separation distance between the nuclei of the two particles.

Although you will not need to memorize or perform calculations with this formula, you should know that the strength of the forces depends on two factors:

1. **Charge magnitude** - the greater the charge, the stronger the attraction.
2. **Distance between particles' nuclei** - the closer the two particles, the stronger the attraction. The smaller the distance and the higher the charge, the stronger the attraction.

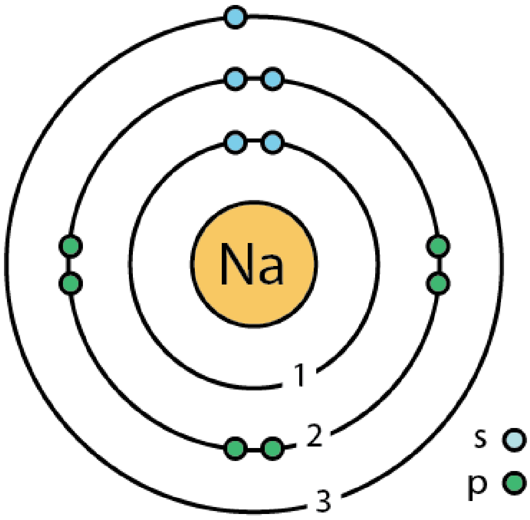
Don't worry about this too much. We will revisit Coulomb's law in much more detail in the next unit.

Bohr Model for Atoms

19th century Danish physicist Niels Bohr predicted that atoms orbit the nucleus in *circular paths*, similarly to how planets in our solar system orbit the Sun.

The main problem with this model was that unlike planets in our solar system, Bohr's orbits exist only at fixed distances from the nucleus. This causes the potential energy in each orbit to be quantized or stationary, occurring at discrete intervals.

To better illustrate this, let us look at the Bohr atomic model for sodium, which has 11 electrons.



According to the periodic table, the atomic number of sodium is 11, indicating that there are 11 protons and 11 electrons.

Bohr's main idea was that the electrons in an atom are arranged in a set of electron shells, or **energy levels**, around the nucleus. Each energy level corresponded to a specific potential energy state of the electron, which is fixed.

He also proposed that the distance from electrons to the nucleus was proportional to the potential energy stored in them. Therefore, **valence electrons**, or the outermost electrons, have the most energy. These electrons are found on the *valence shell* of an atom, or the outermost energy level, but we will get to these a little later.

Quantum Numbers

There are four special numbers that are used to describe the movement and path of electrons within an atom. These will help you understand the conventions associated with electron configurations as well as orbital diagrams.

These numbers are called **quantum numbers**, and they are:

- Principal quantum number, denoted by n.
- Angular momentum quantum number, denoted by l.
- Magnetic quantum number, denoted by m_l.
- Electron spin quantum number, denoted by m_s

The principal quantum number, n, designates the principal electron shell. The important generalization is that the larger n is, the farther an electron is from the nucleus, the larger the orbital's size, and finally the larger the atom. n can be any positive integer starting at 1, as $n = 1$ designates the innermost shell. This shell is also called the **ground state**, or lowest energy state. When an electron is **excited** state, it gains energy and can jump to the second principal shell, where $n = 2$. If you scroll up to the Bohr model for a sodium atom, the first circle represents $n = 1$, the second circle represents $n = 2$, and in general the kth circle represents $n = k$, pointing outward relative to the nucleus. This is called absorption because the electron is "absorbing" photons, or energy. Known as emission, electrons can also "emit" energy as they jump to lower principal shells, where n decreases by whole numbers.

The angular momentum (azimuthal) quantum number, l, determines the **shape** of an orbital. Each value of l represents a specific s, p, d, or f subshell (each distinctly shaped). The value of l depends on the principal quantum number. It can be at most one less than the principal quantum number:

$$l = 0, 1, 2, 3, 4 \ldots (n - 1)$$

The magnetic quantum number m_l determines the number of orbitals and their **orientation** within a subshell. Given a specific l, m_l can range from $-l$ to $+l$.

$$m_l = -l, (-l + 1) \cdots - 2, -1, 0, 1, 2 \ldots (l - 1), (l - 2), +l$$

Finally, the electron spin quantum number m_s is special because it does not depend on any of the other three quantum numbers. It designates the direction of the electron spin and may have a spin of $+\frac{1}{2}$, denoted by $\uparrow$, or $-\frac{1}{2}$, denoted by $\downarrow$. The main aspect of m_s is to determine the ability of an atom to generate a magnetic field.

The Electron Configuration of an Atom

First, we define what an electron configuration is.

Definition 1.5.1

Electron configuration refers to the arrangement of electrons in an atom or molecule. The idea behind electron configuration is a theoretical description of drawing the shells in the Bohr model, in that each shell has a specific capacity for electrons.

Not only are electrons in different energy levels or shells, they are also located in different **subshells**. There are four distinct subshells, namely, s, p, d, and f. The maximum number of electrons in each subshell, respectively, is 2, 6, 10, and 14.

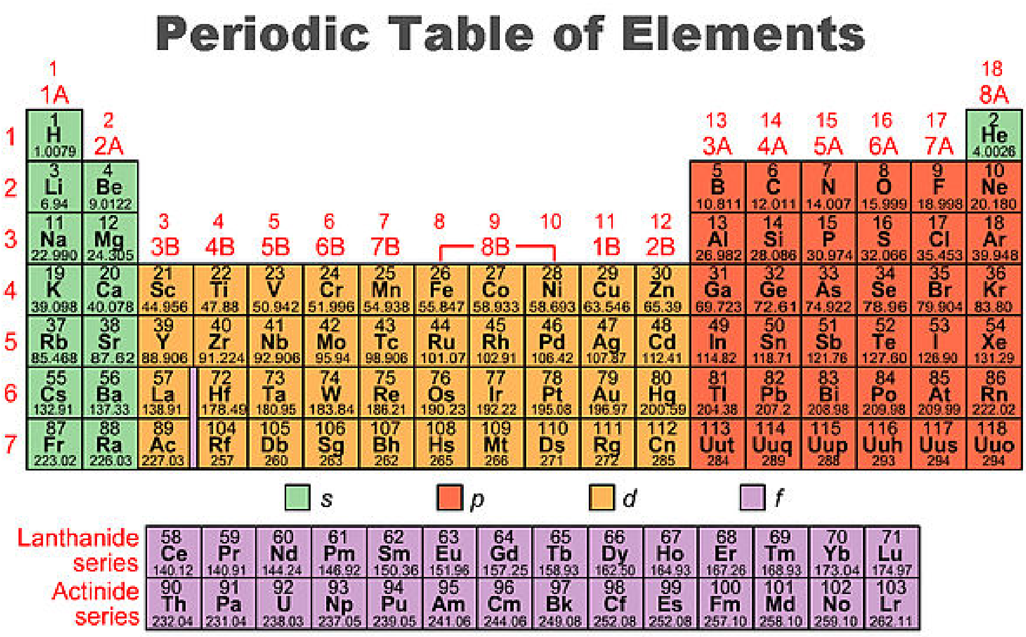
Core and Valence Electrons

The outermost electrons are called **valence electrons**, while the other (inner) electrons are called **core electrons**.

- Valence electrons occupy the outer s and p orbitals, farthest from the nucleus.
- Core electrons occupy the relatively closer d and f orbitals.

Electron Subshells on the Periodic Table

Here is a breakdown of the different subshells on the periodic table:



You should read this subshell version of the periodic table the same way you would read from a book: start at the upper-left corner of the "page," and work your way from there. The subshells in order of increasing energy are read as:

$$|1s|2s|2p|3s|3p|4s|3d|4p|5s|4d|5p|6s|4f|5d|6p|7s|$$

Alternatively, you could use the **diagonal rule** to read an electron configuration, represented below:

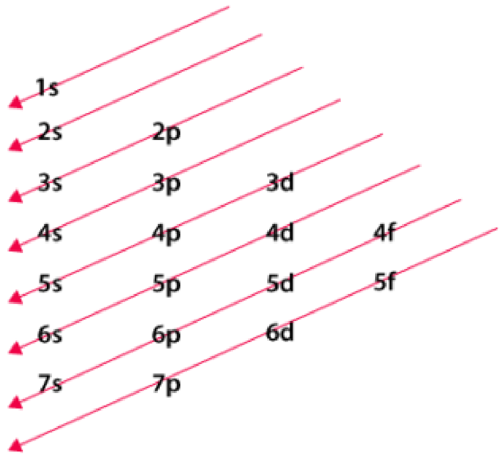


Image Courtesy of BYJU'S

For these, you read from right to left along the diagonal lines that travel downward.

Electron Configuration Rules

- The **Aufbau principle** states that electrons must be filled in order of increasing energy levels. Recall that Bohr discovered that the outermost electrons in the valence shell have the most energy, so the order of increasing energy is as follows: $1s \to 2s \to 2p \to 3s \to 3p \to$ etc.
- The **Pauli Exclusion Principle** states that no two electrons in the same orbital can have the same spin. One must spin clockwise, and the other must spin counterclockwise. We will see this in the **orbital diagrams** below.
- **Hund's Rule** states that unpaired electrons must fill an unoccupied orbital before pairing up with a single electron in previous orbitals. This rule is followed to minimize the sets of paired electrons, because this leads to significant repulsion. Think of Hund's rule as a corollary that follows from the Aufbau principle.

Note 1.5.2

Once you reach the elements of the d block, you might be confused as to why $3d$ is filled after $4s$, why $4d$ is filled after $5s$, etc. The reason for this is that while $4s$ and $5s$ are farther away from the nucleus than $3d$ and $4d$, respectively, the latter subshells experience more repulsions, which is responsible for the higher energy. Since subshells are filled in increasing order of energy, this scenario represents the Aufbau principle.

The best way to overcome this confusion is to practice dozens of electron configuration problems so that you will be able to internalize the order of increasing subshell energies. If you ever get stuck reading the periodic table to determine the electron configuration, knowing the Aufbau principle can help a lot.

Writing the Electron Configuration for an Atom

Let us use an easy example: boron (element 5)

Looking at boron's position on the periodic table above, you would realize that boron is in the $2p$ spot. It is highly recommended that you memorize the subshell-labeled periodic table so that you can write the electron configuration for atoms.

Step 1. Place your finger on the element you are trying to find.

Step 2. Start with hydrogen ($1s$) and then read the periodic table as if you were reading a book (left to right, then go down to the next "line," or this case, the next period).

Step 3. To keep track of the electron configuration, note all the subshells you have passed on your way down to boron, which in this case would be $1s$, $2s$, and $2p$.

Step 4. Count how many elements did you pass through in each block.

$$1s : \mathrm{H}, \mathrm{He} \to 2$$
$$2s : \mathrm{Li}, \mathrm{Be} \to 2$$
$$2p : \mathrm{B} \to 1$$

These numbers represent the electrons and are denoted by superscripts in the electron configuration. When we put everything together, boron's electron configuration is

$$1s^2 2s^2 2p^1$$

Conceptually, the superscripts represent the electron. The atomic number of the boron 5 indicates that it has 5 electrons, and thus all the superscripts should sum to 5. The electron configuration tells us that the 2 electrons occupy the $1s$ orbital, the 2 electrons occupy the $2s$ orbital and the 1 electron occupies the $2p$ orbital.

Noble Gas, or Short-Hand Configuration

The **noble gas shortcut** comes in handy when you are asked to find the electron configuration of an element that is really far into the periodic table, e.g. element 81. Let us use boron once again.

First, you would identify the noble gas prior to boron and then start reading the periodic table from there, rather than hydrogen. Since helium (He) is the first noble gas present before boron, the electron configuration would read as

$$[\mathrm{He}]2s^2 2p^1$$

You can use either method to write your configurations (make sure to do what the question asks!), but just remember to use the square brackets on the noble gas if you decide to use the shortcut.

Where do Electron Configuration Rules Apply?

Sometimes, you may see electron configurations represented visually, in orbital diagrams:

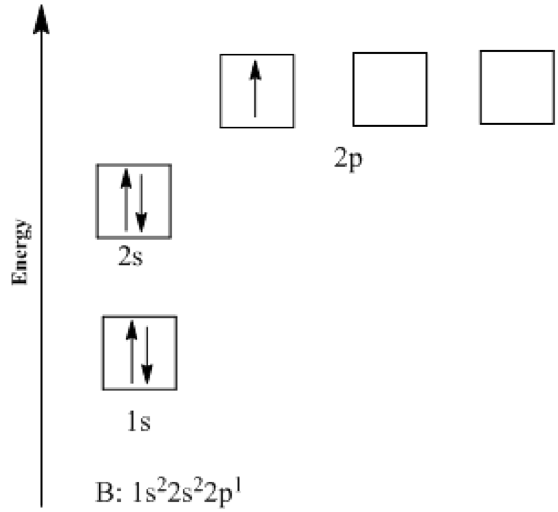


Image Courtesy of Chegg

Each arrow represents *one* electron. This image clearly demonstrates the Aufbau principle since the electrons are filling up orbitals in the order of increasing energy levels. ($1s \to 2s \to 2p$). Additionally, the arrows face opposite directions, indicating their spin. This is in accordance with Pauli's Exclusion Principle.

Meanwhile, Hund's rule is not actually represented because there is only 1 electron in the $2p$ orbital, but here is a generalized depiction of the proper filling of orbitals:

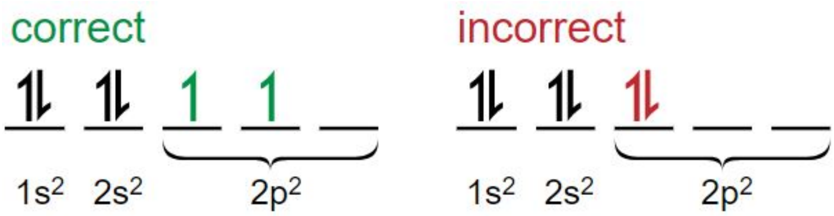


Image Courtesy of Chemistry 301

The left diagram is correct because electrons are filling unoccupied orbitals before pairing with one another. This phenomenon occurs because electrons fill the lowest energy first (Aufbau principle).

Let's try a sample problem where we write both the traditional and short-hand electron configuration of an element.

Problem 1.5.3 — Electron Configuration Practice

Construct the electron configuration for cobalt (Co), using both the traditional and shortcut methods.

Solution: Cobalt, Co, is element number 27. It has 27 electrons and is a *d*-block element, a transition metal. Using our increasing order of energy of subshells, we determine that the highest energy electrons of Co are located in the $3d$ subshell.

Reading the periodic table the same way we would read a book, we should get the electron configuration for Co as

$$\boxed{1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^7}$$

For the short-hand notation, we need to identify the last noble gas from cobalt on the periodic table. By inspection, we find that it is argon, Ar. From there, we have to count two electrons in the $4s$ subshell and seven electrons in the $3d$ subshell, in order to reach cobalt. Therefore, the short-hand electron configuration for Co is

$$\boxed{[\mathrm{Ar}]4s^2 3d^7}$$

Valence Electrons and Electron Configuration

Consider the electron configuration for arsenic, As:

$$[\mathrm{Ar}]4s^2 3d^{10} 4p^3$$

Remember that valence electrons are those furthest from the nucleus, so in our case, that is $n = 4$.

The *valence* electron configuration can be written as $ns^a np^b$, where a and b are the number of electrons in the s and p subshells of the atom.

Additionally, the total number of valence electrons is given by $a + b$.

For arsenic, we have $n = 4$, and there are 2 and 3 electrons in the $4s$ and $4p$ subshells, respectively. Therefore, the valence electron configuration reads

$$4s^2 4p^3$$

Finally, we find that there are $2 + 3 = \boxed{5}$ total valence electrons in arsenic.

§1.6 Photoelectron Spectroscopy

Definition 1.6.1

Photoelectron spectroscopy (PES) is an experimental procedure that measures the relative energies of electrons in atoms and/or molecules.

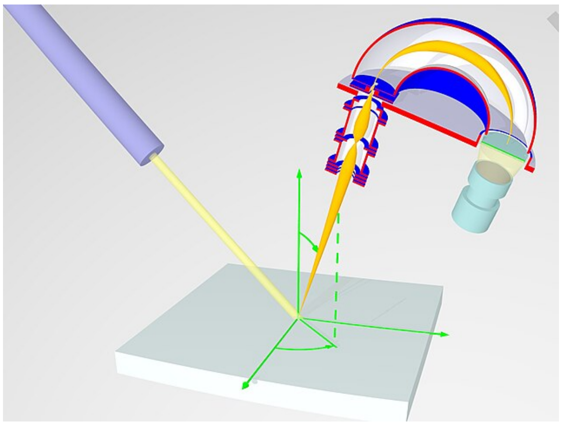
In this section, we will use PES to deepen our understanding of atomic structure. We will see how PES provides the foundation for the concepts of electron shells and subshells, electron configuration, etc.

Here's the theory behind it.

Introduction to Photoelectron Spectroscopy

In 1905, Albert Einstein characterized a phenomenon known as the *photoelectric effect* (more on this in Unit 3) and this is what he observed: when electrons in a metal surface were exposed to light with radiation energy at or above a certain threshold, the electrons are ejected, or "forced out", from the metal. If we know the kinetic energy KE of the ejected electrons (also called photoelectrons) and the energy of the incident radiation, we can calculate the energy of the electrons in the solid metal.

Photoelectric spectroscopy is essentially the same concept. The only difference is that it applies to atoms and/or molecules, instead of metal surfaces. In PES, a sample is subject to high-energy radiation which ejects the electrons from the sample. The released electrons travel to a device called an *energy analyzer*, which records the number of photoelectrons at different kinetic energies. See a simplified diagram below.



The image represents a light source of high-energy radiation striking a sample, thus causing electrons to eject and enter the energy analyzer.

The energy required to eject an electron from the sample is called the **binding energy**. We know the energy of radiation used to eject the electron. Therefore, by measuring the kinetic energy of the photoelectron ($\mathrm{KE}_{\mathrm{electron}}$), we can calculate the binding energy (BE) of the electron in the sample using the following equation:

$$\mathrm{BE} = \mathrm{E}_{\mathrm{radiation}} - \mathrm{KE}_{\mathrm{electron}}$$

This is better understood by

$$\text{Incoming Radiation Energy} = \text{Binding Energy} + \text{Kinetic Energy}$$

The binding energy of an electron depends on its location relative to the atom's nucleus. Electrons in the outermost shell are farther away from the nucleus, on average, so they have the *lowest* binding energies of all the electrons. In contrast, the inner-shell electrons are, on average, closer to the nucleus, so they have the *highest* binding energies. Soon, we will see how the location between an electron's binding energy and location is essential for interpreting PES data to atomic structure.

Analysis of PES Spectra

Data collected from PES experiments is usually plotted on a graph of **relative number of electrons** vs. *binding energy.* The units of binding energy are usually given in *electron volts* (eV) or *megajoules per mole* (MJ/mol). To make data analysis easier, PES data for elements is plotted such that binding energy *decreases* across the horizontal axis. You can think from the atom's perspective, with its nucleus at the origin.

Any given PES spectrum features peaks at different binding energies. Each of these peaks represent electrons in different subshells. A peak's binding energy indicates how much energy is required to remove an electron from the subshell, and the heights of the peaks indicate the relative number of electrons in each subshell.

For example, here is the PES spectra of lithium, Li. For reference, the ground-state electron configuration for Li is $1s^2 2s^1$.

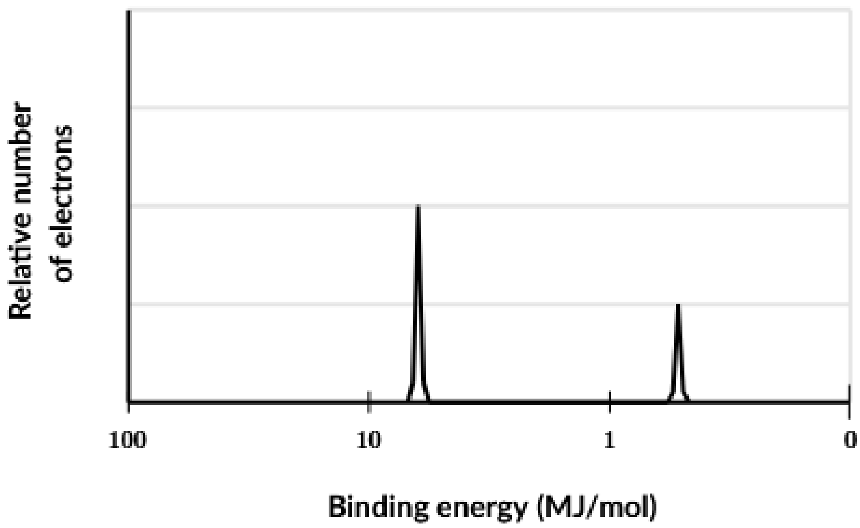


Image Courtesy of Khan Academy

The PES spectrum shows two peaks, representing the electrons in the 2 different subshells of a lithium atom, namely $1s$ and $2s$. Remember, the peak that is closer to the origin has a higher binding energy because its electrons are less shielded from the nucleus than those that are farther away. Therefore, it represents the $1s$ subshell. The farthest peak is the $2s$ subshell. As confirmed by the electron configuration for lithium, the $1s$ subshell contains 2 electrons, while the $2s$ subshell contains 1, for an overall configuration of $1s^2 2s^1$.

Note that the binding energy of Li's $2s$ peak is equal to the first ionization energy of lithium−the amount of energy required to remove the outermost electron from a neutral lithium atom. However, the binding energy of the $1s$ peak is NOT equal to the second ionization energy of lithium. In reality, once the first electron is removed from lithium, the $1s$ electrons would be held even more tightly by the nucleus, thus increasing their binding energy.

Note 1.6.2
The terms "first ionization energy" and "second ionization energy" will be studied in more detail throughout the next section.

Try this problem to test your understanding.

Problem 1.6.3 — Relative Number of Peaks on PES Spectrum

How many peaks would you expect in the PES spectrum of neutral magnesium?

Solution: First, let's write out the ground-state electron configuration for magnesium.

$$1s^2 2s^2 2p^6 3s^2$$

In the PES spectrum of any element, each peak corresponds to a different subshell of the element (or energy levels of its electrons). If we know how many subshells an element occupies, we can predict the number of peaks that will appear in its PES spectrum.

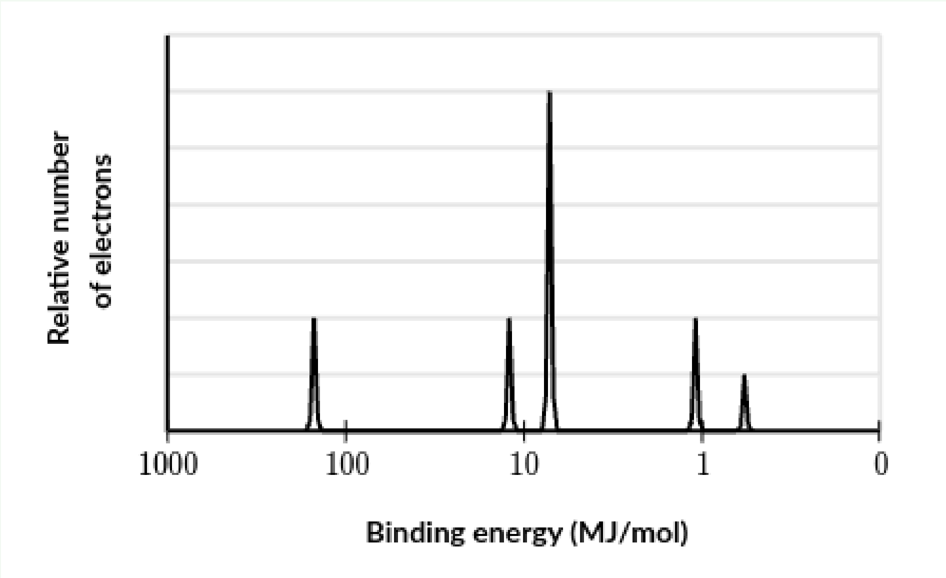
In the electron configuration for magnesium, we see that there are 4 different subshells (energy levels), namely $1s$, $2s$, $2p$, and $3s$ (in increasing energy). Thus, we would expect the corresponding PES spectrum to contain $\boxed{\text{four}}$ unique peaks.

Identifying an Element Based on PES Spectrum

In real-life situations, chemists may not always know what element they could be handling. Therefore, we must also be comfortable working backwards.

Problem 1.6.4 — Identifying Element Based on PES Spectrum

A pure sample of an unknown element was analyzed using a photoelectron spectrometer, producing the spectrum shown below. What is the identity of the element?



Example Courtesy of Khan Academy

Solution: The PES spectrum shows five peaks, indicating that the element's electrons are occupied in five different energy levels (subshells) with varying distances from the nucleus. We know from section 1.5 that the subshells in order of increasing distance are $1s$, $2s$, $2p$, $3s$, and $3p$. The peak with the highest binding energy (leftmost) must correspond to the $1s$ subshell, while the peak with the lowest binding energy (rightmost) must correspond to the $3p$ subshell. Notice that the $3p$ peak is half the height of the $1s$, $2s$, and $3s$ peaks, suggesting that there is only 1 electron in the $3p$ subshell of our mystery element.

Now we need to construct the electron configuration of our mystery element, determine the total number of electrons, and thus identify the (neutral) element. We ask ourselves, what element has only one electron in its $3p$ subshell? If we look at the periodic table, we can infer that the answer is aluminum, Al. However, we will just write the electron configuration to be sure.

$$1s^2 2s^2 2p^6 3s^2 3p^1$$

Finally, we can see that there are five regions/peaks in the spectrum, which makes sense considering that there are five occupied electron shells in Al. Overall, we can be confident that this element is indeed $\boxed{\text{aluminum}}$.

§1.7 Periodic Trends

In a laboratory, chemists often work with multiple elements at once. Therefore, it is very useful to immediately determine elemental properties. Periodic trends are special patterns that exist within the periodic table that represent many aspects of the elements, e.g.

atomic radii, ionization energies, electronegativity, electron affinity, melting point, and metallic character. For the purposes of the AP exam, knowledge of the first three trends is significant. The existence of these trends occurs because elements sharing a row (period) or column (group) in the periodic table share similar atomic structures.

Definition 1.7.1

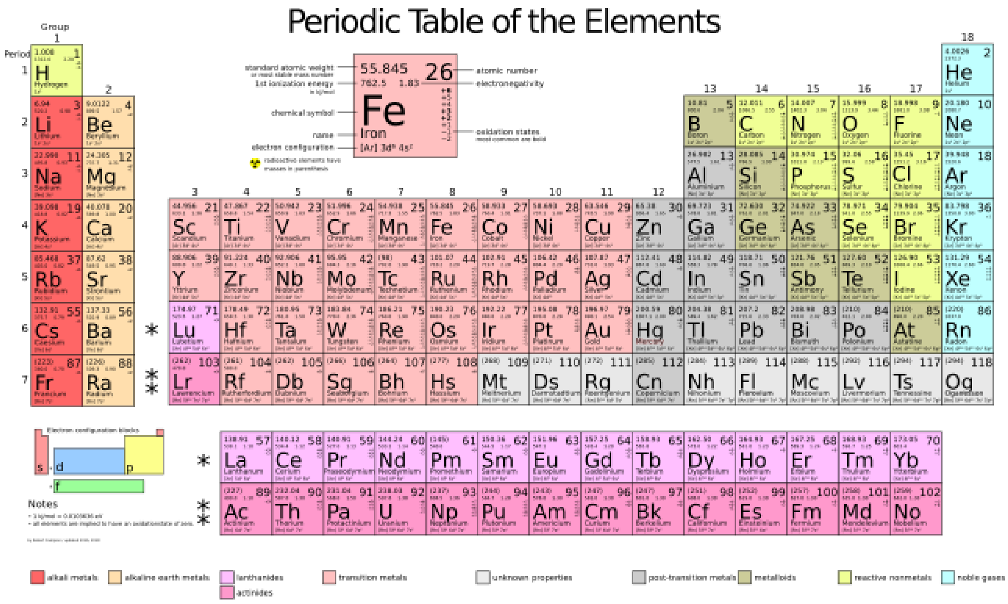
The manner in which scientists can quickly make predictions on certain elements without *any* experimental data is known as **periodicity**, or repeating patterns.

Before we can fully understand the trends of atomic radii, ionization energy, and electronegativity, there are three terms that we must be familiar with: **effective nuclear charge**, **shielding**, and **electron-electron repulsions**.

1. Effective nuclear charge,z_{eff} is the net *positive* charge from the nucleus that electrons can "feel" its attractions.

2. Shielding occurs when the core (inner-shell, nonvalence) electrons prevent valence electrons (farthest from the nucleus) from being fully attracted by the nucleus.

3. Electron-electron repulsions are caused by like negative charges on electron pairs orienting them as far away possible from each other. When this occurs, the electron cloud expands, which explains atomic radii across periods (horizontal rows).



Atomic Radii Trend

Definition 1.7.2

Atomic radius is the distance from the nucleus (or geometric center) to the outer edge of the electron cloud.

More generally, we can imagine two circular-shaped atoms of the same element "stuck" together. For contest math enthusiasts, we call such an arrangement *mutually externally* *tangent*, with two circles in a plane touching at exactly one point. We can determine the center-to-center distance from both atoms' nuclei, and then divide by 2.

If you prefer a visual explanation, the diagram below represents the same idea.

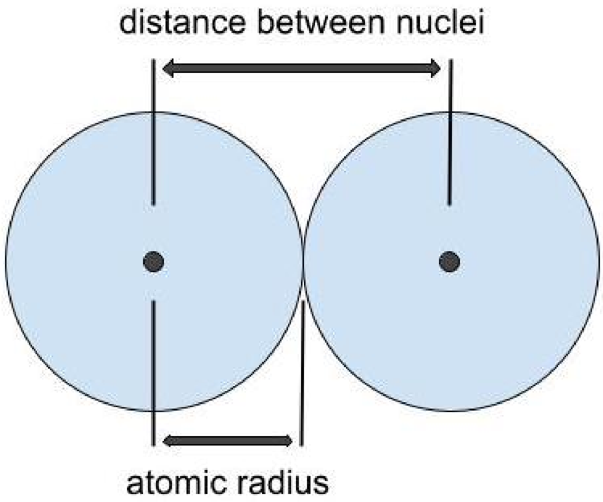


Image Courtesy of ChemTalk

For the purposes of the periodic table, atomic radius generally **decreases across a period and increases down a group**.

Let's consider period 3. Mg has a larger radii than Na, Al has a larger radii than Mg, and so on. This is because the number of protons in each element is increasing, and so is their effective nuclear charge. However, electron shielding remains the same because each of Na, Mg, Al, Si, etc. have the same number of core electrons. A higher effective nuclear charge results in greater attractions to the electrons, pulling the electron cloud closer to the nucleus. As we can imagine, if the electron cloud moves closer to the nucleus, the atomic radius *decreases.*

Now consider group 1, the alkali metals: Li, Na, K, Rb, etc. As we travel down the group, the principal quantum number n increases as there are more energy levels. Therefore, there is a greater distance between the atom's nucleus and the outermost orbital of electrons. This causes the atomic radius to *increase.*

Ionic Radii Trend

The **ionic radius** is the distance between the nucleus of an ion and the valence electrons of that said ion.

When dealing with the same element, there are two comparisons that will significantly help us retain the information regarding ionic size.

- **+ Ions (Cations) < Atoms for the Same Element**:
  - When metals ionize, they lose an electron and become cations, with a *positive* charge. Losing an electron causes the atom to *decrease* in size. Additionally,

there is less shielding and electron-electron repulsion present, so the remaining valence electrons are thus closer to the nucleus.

- **- Ions (Anions) > Atoms for the Same Element**:
  - When nonmetals ionize, they gain an electron and thus become anions, with a *negative* charge. Gaining an electron causes the atom to *increase* in size. There is more electron-electron repulsion present as a result, due to the increased number of negatively charged particles.

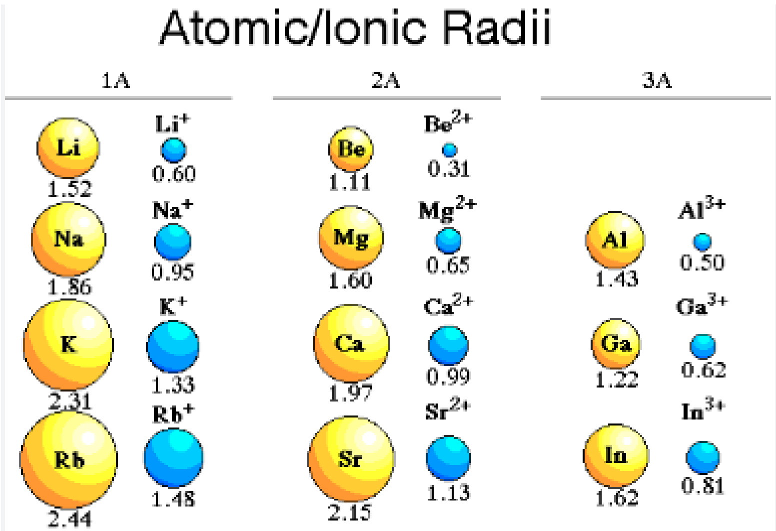


Image Courtesy of Quora

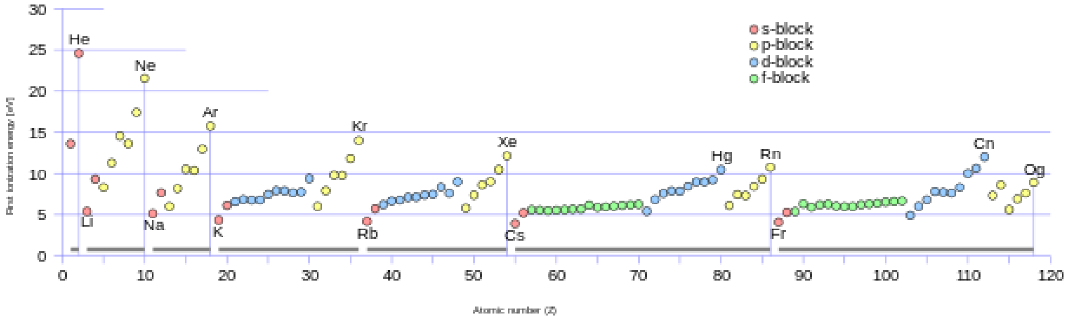
Isoelectronic Species

At this point, we also need to define **isoelectronic species**. These are groups of atoms/ions that have the same electrons. College Board sometimes likes to confuse students by asking them to compare sizes of species that have the same number of electrons. Fortunately, we can clear that up in a jiffy!

One example of an isoelectronic series are N^{3-}, O^{2-}, F^-, Ne, Na^+, Mg^{2+}, and Al^{3+}. For these species, the number of protons (and thus the effective nuclear charge) determines the relative sizes. The greater the nuclear charge, the smaller the radius in such a series. Therefore, the order of increasing radii for this series is:

$$\boxed{Al^{3+} < Mg^{2+} < Na^+ < Ne < F^- < O^{2-} < N^{3-}}$$

Ionization Energy Trend



For the above graph, the horizontal axis indicates the atomic number (increasing number of protons) and the vertical axis indicates the first ionization energy, in kJ/mol. We will explore what ionization energy is and its relevance to the data shown above.

Definition 1.7.3

Ionization energy (IE) is the energy required to remove the *highest-energy* electron from a neutral atom.

To successfully understand the relative IE values for different elements, we will first unpack Coulomb's law.

Definition 1.7.4

Coulomb's law is a formula used to calculate the electrostatic force of interaction between two charged particles.

$$F = k\frac{q_1 q_2}{r^2}$$

where k is a proportionality constant, q_1 and q_2 represent electrical charges in the particles 1 and 2, respectively, and r is the center-to-center distance between them.

We can use Coulomb's law to predict the amount of energy required to remove an electron from an atom.

For the purposes of the AP exam, you will never have to quantitatively determine the force of interaction between two charged particles.
You only need to know this key fact for qualitative comparisons: *the magnitude of the electrostatic force of attraction or repulsion is directly proportional to the product of the magnitudes of point charges and inversely proportional to the square of the distance between them.*

The general trend for ionization energy is that it **increases across a period and decreases traveling down a group**. Notice that this is the opposite of the atomic radii trend!

Go back to period 3. We know that as we move across the period, the effective nuclear charge on the electrons increases. College Board tends to say that there are *stronger Coulombic attractions* between the electrons and the nucleus. Since the attractive force increases, *more* energy is required to remove the highest-energy electron from a neutral atom. Therefore, the ionization energy *increases* going across a period.

Let's now consider group 2, the alkaline earth metals: Be, Mg, Ca, Sr, etc. As you travel down the group, the highest-energy electrons are moving farther away from the nucleus. If we think about Coulomb's law, as r grows larger, then the force of attraction decreases exponentially. Since the valence electrons feel less attraction to the atom's nucleus, *less* energy is required to remove them from a neutral atom. Therefore, the ionization energy *decreases* going down a group.

Successive Ionization Energies

If atoms possess more than one electron, then they can have more than one ionization energy. This introduces the concept of *successive ionization energies*.

Note: The amount of energy required to remove successive electrons increases steadily. We can define a *first ionization energy* I_1, a *second ionization energy* I_2, and in general the nth ionization energy I_n.

Example 1.7.5

For silicon (Si), the 5 successive ionization energies are determined by experiment as:

- $I_1 = 780\,\text{kJ/mol}$
- $I_2 = 1575\,\text{kJ/mol}$
- $I_3 = 3220\,\text{kJ/mol}$
- $I_4 = 4350\,\text{kJ/mol}$
- $I_5 = 16100\,\text{kJ/mol}$

First, we need to establish an answer to the following question: **Why do successive ionization energy values of an atom always increase?**

Answer: A neutral atom of each element feels the same nuclear charge (attraction from the nucleus). However, each time it is ionized (an electron is removed), there are fewer electrons remaining, and thus more energy is required to remove successive electrons.

Additionally, the energy jumps associated with successive ionization energy values can help you determine the number of valence electrons in an element. As shown above, the values of I_1, I_2, I_3, and I_4 for silicon are all comparable. However, there is a huge jump from the fourth and fifth ionization energies. This occurs because of the distinction between **valence** and **core** electrons. The former are furthest from the nucleus so they experience the least shielding from core electrons and require less energy to remove. Meanwhile, the latter are closer and shielded significantly from the nucleus, so the amount of energy required to remove them is much larger.

More generally, if an element undergoes a large, non-comparable change in ionization energy from the nth electron to the $(n + 1)$th electron, then we can say it has n

valence electrons. In the case of silicon, there was a huge jump from the fourth and fifth ionization energy values, meaning that silicon has $\boxed{\text{four}}$ valence electrons.

Electronegativity Trend

Definition 1.7.6

Electronegativity is the ability of an atom in a molecule to attract shared pairs of electrons to itself.

Suppose we have a molecule XZ, represented by

X**:**Z

where the **:** represents a pair of electrons.

To better understand this concept in action, if element X is more electronegative than element Z, then it will have a tendency to attract the pair of electrons to itself, and the molecular structure will look more like this (in space):

X**:** Z

As we can see, the electron pair is oriented more towards element X than element Z.

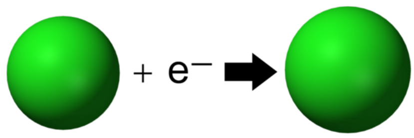
The periodicity for electronegativity is that it **increases across a period and decreases going down a group**. Note that this is the **same** pattern as ionization energy. Why is this?

Explanation: For larger atomic radii, there is a greater distance between the nucleus of an atom and the valence electrons of the other atom, so the Coulombic attractions are much smaller, resulting in a smaller electronegativity. Meanwhile, for smaller atomic radii, the nucleus of one atom is closer to the valence electrons of the other, so the Coulombic attractions are larger, resulting in a greater electronegativity.

Important! It is important to understand that the relative atomic radii predict the relative electronegativity values, not the other way around. For example, consider our molecule XZ again. We know that element X is smaller than element Z. We also know that the pair of electrons is closer to atom X as it is more electronegative. However, it is *incorrect* to state, "Atom X has a small radius because it is more electronegative." Atomic radius is only affected by effective nuclear charge and distance between the nucleus and valence electrons. The *correct* statement is, "Atom X has a high electronegativity due to a small atomic radius." The small atomic radius indicates a greater force of attraction between the nucleus of one atom and the valence electrons of the other. This results in the increased electronegativity.

Electron Affinity Trend

For this trend, we only need minimal knowledge, as opposed to the previous three.



Definition 1.7.7

Electron affinity is the *energy change* when an atom gains an electron to form a negatively charged ion, or anion.

This process can be endothermic (gains energy) or exothermic (loses energy), from the atom's perspective.

Electron affinity works in different ways for different elements, depending on their metallic character.

Metals:

- It is easier to lose electrons because the valence electrons are only held loosely by the nucleus.
- Adding an electron to a metal atom is either endothermic or slightly exothermic, so the electron affinity is either positive or slightly negative.

Nonmetals:

- It is easier to gain electrons because the valence electrons are held very tightly by the nucleus.
- For nonmetals, the addition of an electron is always exothermic, so the electron affinity is negative.

Note 1.7.8

For the purposes of the AP Exam, you will not need any quantitative applications of electron affinity. The most important aspect is the periodic trend, which follows here.

The general trend for electron affinity is that it **increases traveling across a period and decreases traveling down a group**.

Before we move on to the last section of this unit, we will walk through some short problems to solidify your understanding of periodic trends.

Problem 1.7.9 — Relative Atomic Radii I

Which element has the smallest atomic radius: carbon, nitrogen, or chlorine?

Solution: First off, eliminate chlorine. Its highest-energy electrons are in the third subshell, while those of carbon and nitrogen are in the second subshell. Therefore, chlorine has the largest radius. Between carbon and nitrogen, the latter has more protons, and therefore a higher effective nuclear charge. Its outermost electrons will feel a greater attraction to the nucleus than those of the former. Thus, $\boxed{\text{nitrogen}}$ has the smallest atomic radius.

Problem 1.7.10 — Relative Ionization Energy I

Which element has the larger first ionization energy: calcium or scandium?

Solution: Look at your Periodic Table. Both Ca and Sc are in the second period. Therefore, we must compare the effective nuclear charge on atoms of both elements. Scandium has more protons than calcium, so it has a greater z_{eff}. More energy is required to pull its outermost electrons to the nucleus compared to for calcium. Therefore, $\boxed{\text{scandium}}$ has the larger first ionization energy.

Here are some questions that require more critical thinking. Try these on your own before looking at the solution!

Problem 1.7.11 — Relative Atomic Radii II

In terms of atomic structure, explain why the atomic radius of arsenic is smaller than that of chromium.

Solution: As we can see in the periodic table, both arsenic (As) and chromium (Cr) are located in the fourth period (energy level), so the difference in atomic radii must be attributed to a difference in effective nuclear charge, not distance from the nucleus. We observe that arsenic is further across the period than chromium, so it has more protons (greater atomic number). More protons indicates a greater effective nuclear charge, so electrons are more attracted to the nucleus, resulting in a smaller radius.

Problem 1.7.12 — Relative Ionization Energy II

One student claims that the first ionization energy for F is greater than that of I. Is this a true statement? Explain why or why not in terms of atomic structure and Coulomb's law.

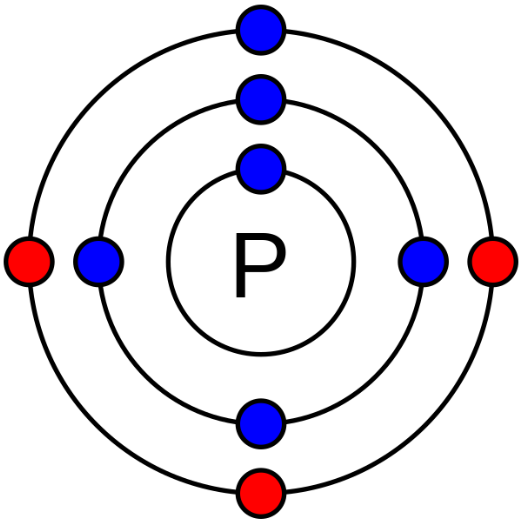
Solution: Fluorine (F) and iodine (I) are halogens located in Group 7A of the periodic table. Therefore, we can account for differences in ionization energy using differences in distances from the nuclei. Fluorine is three periods above iodine on the periodic table, so its electrons are at a lower energy state and much closer to the nucleus. This results in a reduced shielding effect on the electrons in fluorine compared to iodine, and more energy is required to remove electrons from the nucleus of fluorine than for iodine. The statement is true.

§1.8 Valence Electrons and Ionic Compounds

The periodic table shows patterns in electronic structure and trends in atomic properties, as we saw in the previous section. In this section, we will take a step further, exploring the relationship between trends in the reactivity of elements and periodicity.

Definition 1.8.1

Valence electrons are electrons located in the outermost shell of an atom, and are able to interact with other atoms to facilitate chemical bonding.



The above picture shows the atomic structure of phosphorus (P). The ground-state electron configuration of P is $1s^2 2s^2 2p^6 3s^2 3p^3$. The outermost electrons are in the $3s$ and $3p$ subshells, in the third energy level, or $n = 3$. Since the valence electron configuration is $3s^2 3p^3$, there are $2 + 3 = 5$ total valence electrons in phosphorus.

Essential Knowledge

In this chapter, we apply the following information.

- **Concept 1:** The likelihood that two elements will form a chemical bond is determined by the interactions between their valence electrons and nuclei.
- **Concept 2:** Elements in the same group tend to form *analogous compounds*. This means, elements in the same group tend to share similar chemical properties. When a molecule has one element replaced with another from the same column, the two compounds are said to be analogous.

- **Concept 3:** Typical charges of elements in ionic compounds are governed by their location on the periodic table and the relative number of valence electrons.

- Group 1A: H, Li, Na, K, etc.: **one** valence electron.
- Group 2A: Be, Mg, Ca, etc.: **two** valence electrons.
- Group 3A: B, Al, Ga, etc.: **three** valence electrons.
- Group 4A: C, Si, Ge, etc.: **four** valence electrons.
- Group 5A: N, P, As, etc.: **five** valence electrons.
- Group 6A: O, S, Se, etc.: **six** valence electrons.
- Group 7A: F, Cl, Br, etc.: **seven** valence electrons.
- Group 8A: He, Ne, Ar, Kr, etc.: **eight** valence electrons.

Recall from previous sections that a group is a vertical column, and the periodic table contains 18 of them. For quick counting of valence electrons, the contents of 8 groups are classified as "Group A" elements.

This series continues until we reach the Group 8A elements: the **noble (inert) gases**. These elements always exist in nature as gases, and because their atoms do not react with atoms of other elements, they are referred to as *inert*. The reason is that they have little tendency to gain or lose electrons. Their electron configurations are the most stable; these elements contain a *full octet* of 8 valence electrons with the exception of helium (containing 2).

Two General Cases of Noble Gases

- The electron configuration of helium is $1s^2$. The $1s$ subshell is the outermost relative to the nucleus. Therefore, helium is stable with only 2 valence electrons.
- As per the other noble gases, their valence electron configuration is ns^2np^6, where n is in the set of integers from 2 to 7, inclusive. Therefore, they have a total of $2 + 6 = 8$ valence electrons, a full octet.

You may have noticed that we skipped over the *transition metals*, or d-block elements, because they are much less predictable in terms of properties. The AP Chemistry exam is going to primarily focus on the main elements, but it is good to be familiar with several transition metals, such as Co, Cu, and Zn.

By merely observing the periodic table, you can infer that oxygen has 6 valence electrons and carbon has 4 valence electrons. The number of valence electrons in an atom affects the process by which it bonds with others. Therefore, elements in the same group tend to bond with similar elements and form similar compounds. For example:

- Elements in Group 1A can all bond with chlorine; LiCl, NaCl, KCl, RbCl.

- Elements in Group 2A can all bond with oxygen; MgO, CaO, SrO, BaO.

Charges of Ions

Before studying chemical bonds (more detailed in Unit 2), it is beneficial to memorize the charges of most elements on the periodic table when they bond with another element. This will make more sense once we look at what actually happens to each element in a pair that forms a bond.

Ions are charged atoms or molecules that have gained or lost electrons and as a result, possess a positive or negative charge. Atoms may *ionize* in order to achieve a more stable **electron configuration**.

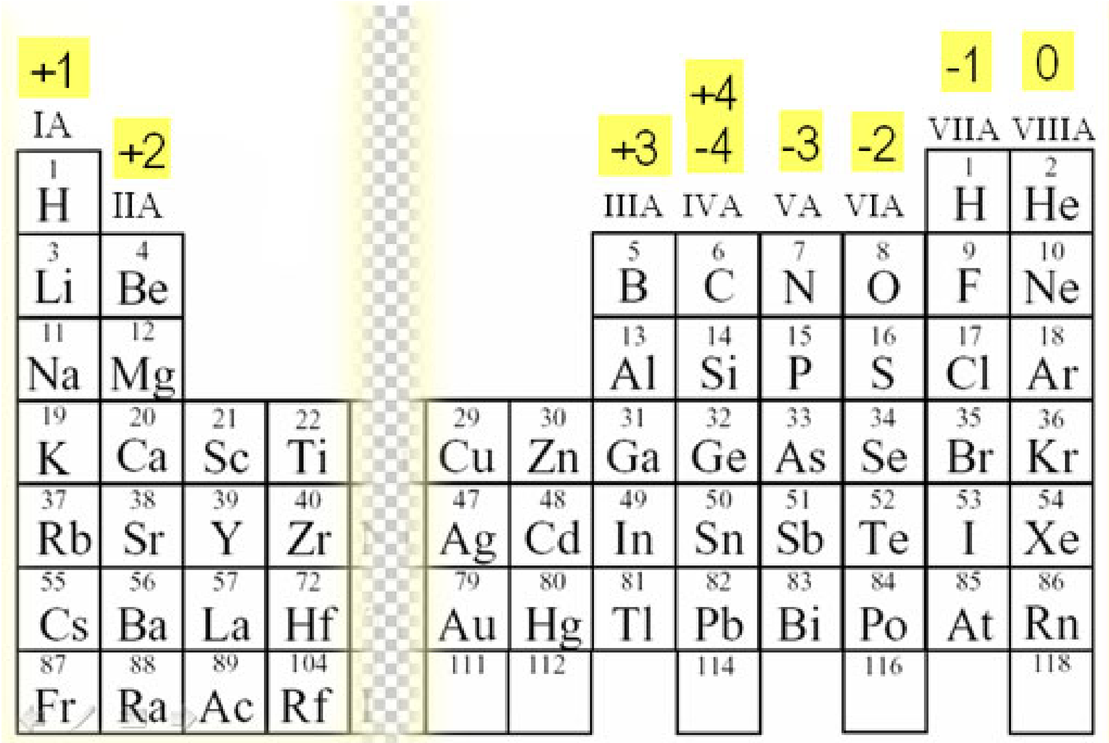


Image Courtesy of Chemistry Land

Again, the transition metals are not included here because they have multiple charges and vary in chemical properties. Don't worry about this, at most, you will only need to write out their electron configurations.

Types of Elements

There are three different types of elements with distinct properties: metals, nonmetals, and metalloids.

- **Metals** are good conductors of heat and electricity, shiny, malleable (can bend), and ductile (can be formed into a wire).

- **Nonmetals** are polar opposites: poor conductors of heat and electricity and brittle (easily broken and/or deformed).
- **Metalloids** share properties of both metals and nonmetals. Their existence occurs with very low frequency, with only 7 of them.

Revisiting Electronegativity

Recall that **electronegativity** refers to how strongly a nucleus of one atom attracts electrons of an atom. This comes into play when two atoms are sharing valence electrons because the relative pull on each other's electrons depends on the relative electronegativity values for each element!

Note 1.8.2

Electronegativity is one of the five essential periodic trends for AP Chemistry. Remember that fluorine is the most electronegative element, with a value of 4.0. From here, you can use the periodic trend to compare the electronegativity values for other elements, using the fluorine atom as a reference.

Do you want a quick refresher on periodic trends and electronegativity? If so, feel free to skim over the last section (1.7)!

Ionic Bonds and Compounds

The reason why elements bond is to achieve the lowest possible energy state, and therefore, the highest stability. There are two different types of bonds that you should know: **ionic bonds** and **covalent bonds**. In this section, we will focus on the former; Unit 2 will explore covalent bonds in more detail.

Definition 1.8.3

Ionic bonds result from the *transfer* of electrons from one atom to another, usually from a metal to a nonmetal.

The atom that loses the electron gains a positive charge and is called a **cation** (usually a metal). Meanwhile, the atom that gains the electron will gain a negative charge and is called an **anion** (usually a nonmetal).

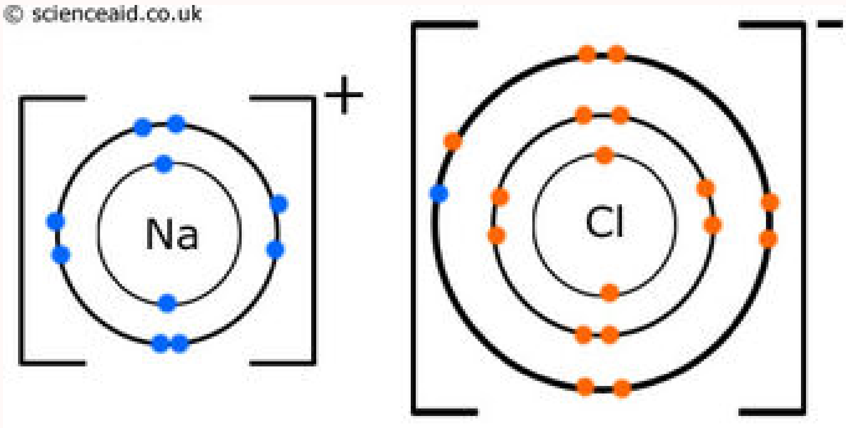
Many of the properties of ionic compounds include:

- **Very strong bonds**.
- **High solubility in water**.
- **Ability to strongly conduct heat and electricity in certain phases of matter**.

Example 1.8.4

In the ionic compound NaCl, sodium (Na) loses one electron and obtains a positive charge, becoming Na^+ while chlorine (Cl) gains one electron and therefore obtains a negative charge, becoming Cl^-.

Visually, we can represent it as



The one valence electron in Na was transferred to the chlorine atom in order for both ions to achieve a stable, full octet. The **octet rule** is a standard based on the idea that atoms are most stable when they contain eight valence electrons in their outermost shell.

Note 1.8.5

The octet rule will be more relevant and better defined in Unit 2. Don't panic if you don't fully understand it right away.

Generally, Group 1A and 7A elements bond so well this way because they achieve stability very easily. They both achieve the proper number of valence electrons that enable them to both reach a full octet. In fact, when alkali metals form ionic compounds with halogens, they lose an entire electron shell.

Specifically, when Na and Cl ionize as Na^+ and Cl^-, their electron configurations are modified to those of the adjacent noble gases on the periodic table.

$$\text{Na:}\quad 1s^2 2s^2 2p^6 3s^1 \qquad\qquad \text{Na}^+/\text{Ne:}\quad 1s^2 2s^2 2p^6$$
$$\text{Cl:}\quad 1s^2 2s^2 2p^6 3s^2 3p^5 \qquad\qquad \text{Cl}^-/\text{Ar:}\quad 1s^2 2s^2 2p^6 3s^2 3p^6$$

§1.9 Practice Problems

Problem 1.9.1 — Free-Response Question

Answer the following questions related to the analysis of $CaBr_2$.

(a) A student has a 10.0 g sample of $CaBr_2$. Show the setup of the calculation to determine the number of moles of $CaBr_2$ in the sample. Include units in your setup.
(b) What number, in addition to the answer in part (a), is needed to determine the number of atoms of Ca in the sample?
(c) A different student is given a 10.0 g sample labeled $CaBr_2$ that may contain an inert (nonreacting) impurity. Identify a quantity from the results of laboratory analysis that the student could use to determine whether the sample was pure.
(d) Explain why $CaCl_2$ is likely to have properties similar to those of $CaBr_2$.

Solution to part a: We know that we can use the molar mass to quantitatively describe the mass, in grams, of a substance that are present in ONE MOLE of that substance. The molar mass of a compound is equal to the sum of the masses of each elements' atoms in that compound.

$$\text{molar mass of } \mathrm{CaBr_2} = \text{molar mass of Ca} + 2 \cdot \text{molar mass of Br}$$

$$40.08\,\mathrm{g/mol} + 2 \cdot 79.90\,\mathrm{g/mol} = 199.88\,\mathrm{g/mol}$$

Now, we will use dimensional analysis to convert our units. Since we are starting with grams but want to end in moles, our conversion factor will take the form

$$\frac{1 \text{ mol } \mathrm{CaBr_2}}{199.88 \text{ g } \mathrm{CaBr_2}} = 1$$

and to find our answer, we multiply our initial value with this conversion factor:

$$10.0\,\cancel{\mathrm{g\ CaBr_2}} \cdot \frac{1 \text{ mol } \mathrm{CaBr_2}}{199.88\,\cancel{\mathrm{g\ CaBr_2}}} = \boxed{0.0500\,\mathrm{mol\ CaBr_2}}$$

Solution to part b: There is an important constant in chemistry that relates the number of moles of a substance to formula units. Here, our formula unit is atoms of Ca. The constant is called Avogadro's number, with a value of $N_A = 6.022 \cdot 10^{23}\,\mathrm{mol^{-1}}$. Since we wish to convert from moles to atoms, we can use the following conversion factor:

$$\frac{6.022 \cdot 10^{23} \text{ atoms}}{1 \text{ mol}}$$

We will proceed with dimensional analysis.

$$0.0500\,\cancel{\mathrm{mol\ CaBr_2}} \cdot \frac{1\,\cancel{\mathrm{mol\ Ca}}}{1\,\cancel{\mathrm{mol\ CaBr_2}}} \cdot \frac{6.022 \cdot 10^{23} \text{ atoms Ca}}{1\,\cancel{\mathrm{mol\ Ca}}} = \boxed{3.01 \cdot 10^{22} \text{ atoms Ca}}$$

Solution to part c: For the compound $CaBr_2$, we should expect the following percent composition for each element: 20.04% Ca and 79.96% Br, by mass. If these percentages do not match the values just established, then there must be an impurity in the mixture. Intuitively, the presence of any element other than Ca or Br would cause the mass percent of Ca and Br to decrease relative to the total mass of the mixture. Any relevant response will earn college credit, as long as you can quantitatively explain how and why the mass percents of Ca and Br will change.

Solution to part d: The easiest way to answer such questions is to observe the atoms that make up these compounds. Specifically, both $CaCl_2$ and $CaBr_2$ are both composed of calcium, Ca. Additionally, both Cl and Br are halogens, located in Group 7A of the periodic table. This indicates that they both have the same number (seven) of valence electrons, which means that both $CaCl_2$ and $CaBr_2$ will display similar chemical properties, especially in bonding, which we will explore in the next unit.

Problem 1.9.2 — Free-Response Question

Using your knowledge of atomic structure and periodicity, explain the following scenarios.

(a) Experimental data shows the radius of a Ca atom is 0.197 nm and that of the Ca^{2+} ion is 0.099 nm. Account for this difference.
(b) Explain the difference in first ionization energies for Ca and K.
(c) Explain the difference in second ionization energies for Ca and K.

Solution to part a: The problem statement tells us that a neutral Ca atom is larger than the Ca^{2+} cation. Using our knowledge of periodic trends, we know that cations are generally smaller than their parent (corresponding, neutral) atoms because they contain less protons. As the number of protons increases from Ca^{2+} to Ca, the effective nuclear charge increases, so the nucleus can attract valence electrons towards itself more tightly.

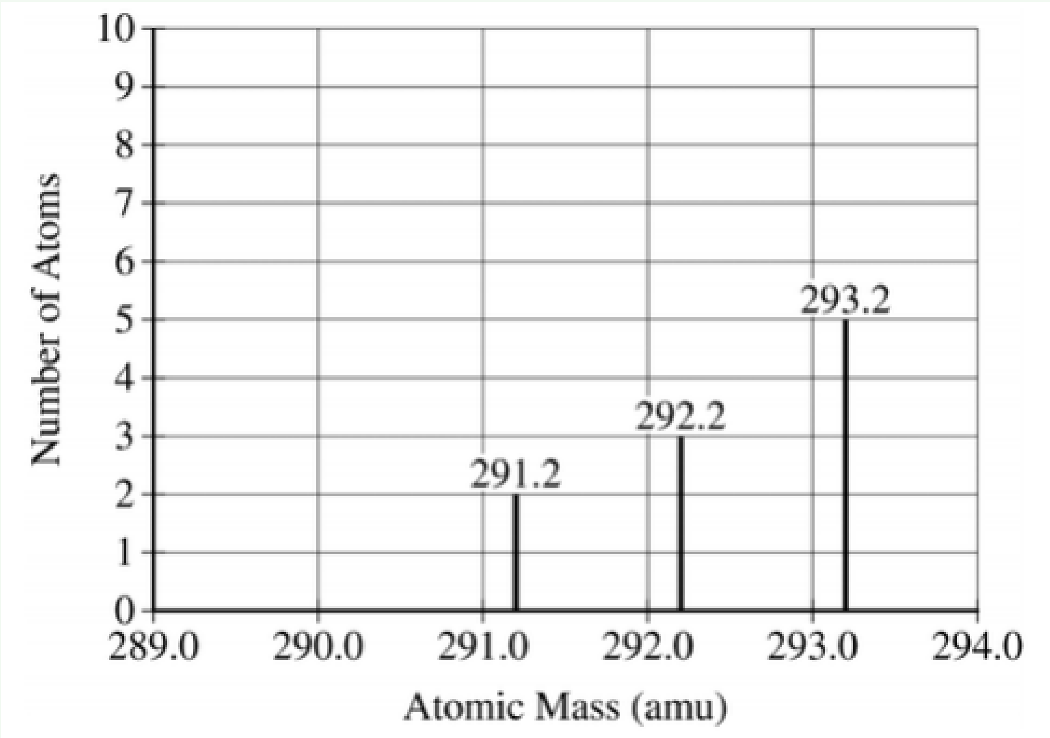
Solution to part b: Ca and K are in the same period (row on the periodic table), so difference in ionization energies must be attributed to their effective nuclear charge. These elements have the same number of occupied electron shells, but Ca has one more proton than K, so there is more attraction between the nucleus and its electron, so more energy is required to remove it. Therefore, Ca has a $\boxed{\text{greater}}$ first ionization energy than K.

Solution to part c: When dealing with successive ionization energies, we must consider the number of valence electrons of each element. Specifically, potassium has one valence electron ($4s^1$ configuration) and calcium has two ($4s^2$ configuration). When one electron is removed from potassium, its highest energy electron configuration is a stable $3s^2 3p^6$. However, if another electron is removed, the ionization energy would experience a large jump because core electrons are closer to the nucleus and are held much more tightly. This is different with calcium, where if two electrons are removed, the highest energy electron configuration is still a stable $3s^2 3p^6$. Therefore, the second ionization energy for K is much $\boxed{\text{greater}}$ than that of Ca.

Problem 1.9.3 — Free-Response Question

A new element with atomic number 116 was discovered in 2000. In 2012 it was named livermorium, Lv. Although Lv is radioactive and short-lived, its chemical properties and reactivity should follow periodic trends.

(a) Write the electron configuration for the outermost shell electrons of Lv in the ground state.
(b) According to periodic properties, what would be the most likely formula for the product obtained when Lv reacts with $H_2(g)$?
(c) The first ionization energy of polonium, Po, is 812 kJ/mol. Is the first ionization energy of Lv expected to be greater than, less than, or equal to that of Po? Justify your answer in terms of Coulomb's law.
(d) Shown below is a hypothetical mass spectrum for a sample of Lv containing 10 atoms.



Using the information in the graph, determine the average atomic mass of Lv in the sample to four significant figures.

Solution to part a: For this problem, use the diagonal short-cut that you were introduced to in section 1.5. Since Lv has atomic number 116, we should be looking somewhere around the $6p$-$7s$-$7p$ subshell series. Using this, it becomes easy to read the periodic table. Since valence electrons are represented by the ns and np configurations, we need to count the number of electrons in the $7s$ and $7p$ subshells. Additionally, $7s$ has less energy than $7p$, so it must be filled first according to the Aufbau principle. Finally, Lv is two electrons away from achieving a stable octet of $7s^2 7p^6$, so we can be sure that the outermost shell electrons have a configuration of $\boxed{7s^2 7p^4}$.

Solution to part b: For this, it becomes useful to consider valence electrons. Lv is one of the Group 6A elements, and it contains $2 + 4 = 6$ (derived from its outermost electron configuration of $7s^2 7p^4$) valence electrons. Another element containing 6 valence electrons hat comes into mind is oxygen, O. We know that oxygen has outermost electron configuration $2s^2 2p^4$, so it is 2 valence electrons away from reaching a fully stable octet. Now, consider hydrogen. An atom of H contains 1 valence electron, so H_2(g) would contain $1 \cdot 2 = 2$ valence electrons in total. This means H_2(g) can share 2 electrons with Lv, and because of that, the product would be $\boxed{H_2Lv}$.

Solution to part c: Let's look at the locations of both Po and Lv. Both elements are positioned in Group 6A, with Lv being in the row directly below Po. Let's review basic implications of periodicity: as you travel down a group on the periodic table, atomic size increases because the number of occupied electron shells increases and the valence electrons grow further apart from the nucleus. Recall that Coulomb's law states $F \propto \frac{1}{r^2}$, so as electrons move further away from the nucleus, the nucleus has a weaker attraction for them, and less energy is required to remove an electron from the atom. Therefore, we should expect the first ionization energy of Lv to be $\boxed{\text{less than}}$ that of Po.

Solution to part d: To find the average atomic mass of a sample of one atom containing several isotopes, we apply the formula

$$\text{average} = \sum_{i=1}^{n} m_i \cdot p_i$$

for n isotopes in the sample - where m_i and p_i are the masses and percent abundances (values from 0 to 1), respectively for each of the i-th isotopes.

While we aren't directly given the abundance of each isotope, we DO know the number of atoms of each isotope present. The overall sample contains 10 atoms, so we can determine the percent abundance for each isotope.

- Isotope 1: atomic mass of 291.2 amu, 2 atoms in the whole sample, so $\frac{2}{10} = 20\%$ abundance.
- Isotope 2: atomic mass of 292.2 amu, 3 atoms in the whole sample, so $\frac{3}{10} = 30\%$ abundance.
- Isotope 3: atomic mass of 293.2 amu, 5 atoms in the whole sample, so $\frac{5}{10} = 50\%$ abundance.

Therefore, we can now use the formula:

$$\text{average} = \sum_{i=1}^{n} m_i \cdot p_i$$

and accounting for the decimal to percentage conversion:

$$\text{average} = \frac{(291.2)(20) + (292.2)(30) + (293.2)(50)}{100} = \boxed{292.5 \text{ amu}}$$

2 Molecular and Ionic Compound Structure and Properties

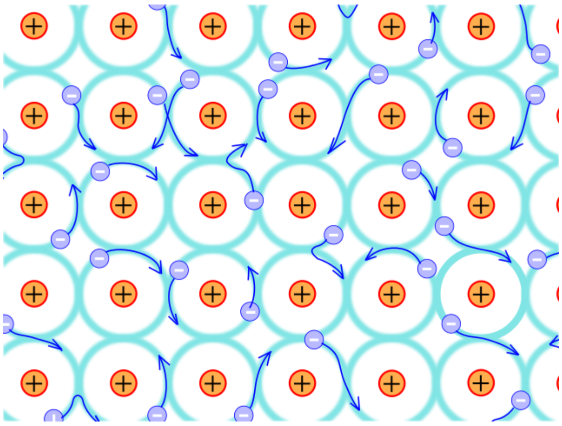
This unit examines how atomic structure relates to the macroscopic properties (those that we can physically see) of substances. We will learn all about chemical bonding, Lewis diagrams, resonance, VSEPR theory, predicting shapes of molecules, and more.

§2.1 Types of Chemical Bonds

Definition 2.1.1

Chemical bonds are forces that hold atoms together to make compounds or molecules.

In this unit, we will focus on three main types of chemical bonding: **ionic, covalent, and metallic bonding**.



The image above demonstrates metallic bonding.

Electronegativity and Bonding

Recall from Unit 1 that electronegativity is the tendency of an element to attract shared pairs of electrons (or electron density) to itself.

Electronegativity values increase across a period and decrease across a group. **One very important fact you must remember is that fluorine is the MOST electronegative element**. It is a Group 7A element, and this group of species is extremely unstable. They are short of 1 electron to complete their outermost subshell. Therefore, these elements have a great tendency to attract electrons to themselves, which explains their high electronegativity values.

Meanwhile, on the very left of the periodic table are the Group 1A elements: the alkali metals. These elements have very low electronegativity values because they do not attract electrons strongly in chemical bonds. They contain 1 valence electron in the s subshell, and are very eager to shed this and reach a full stable octet of 8 valence electrons.

Ionic Bonding

Definition 2.1.2

Ionic compounds are compounds made up of ions that form charged particles when an atom gains or loses electrons.

Definition 2.1.3

An **ionic bond** is formed by the electrostatic interaction between oppositely charged ions in a chemical compound.

A classic example of an ionic compound is NaCl.

$$\mathrm{Na(s)} + \frac{1}{2}\mathrm{Cl_2(g)} \rightarrow \mathrm{NaCl(s)}$$

NaCl, a brittle salt with a high melting point, was formed in the above chemical reaction. Ionic bonds are held together by strong electromagnetic forces that keep oppositely charged ions together. The forces are so strong, requiring considerable energy to break apart, hence the high melting point.

Using concepts we learned previously, when sodium and chlorine react to form an ionic bond, sodium gives off a valence electron to chlorine. This gain and loss of an electron creates sodium and chloride ions, arranged in a crystal lattice of NaCl. Sodium loses the valence electron, becoming sodium ion, a **cation** having positive charge. Meanwhile, chlorine gains the valence electron, becoming chloride ion, an **anion** with negative charge.

Coulomb's Law, Again

Coulomb's law, given by

$$F \propto \frac{q_1 q_2}{r^2}$$

states that greater charges q and smaller separation distances r lead to the strongest interactions between ionic species.

For example, you may be asked to compare the boiling or melting points of two or more ionic substances. In such scenarios, always look for any differences in size (periodic trends will help you here) as well as charges on the constituent ions (this is why valence electrons are so important for this course). The higher the charge of the ions, the stronger the electrostatic attraction between the ions and the greater amount of energy required to break the bond.

PRO TIP: Many students get confused by the formula and wonder whether charge or size has a greater or lesser effect on electrostatic attractions. Therefore, for simplicity, we will establish the following:
For all problems given by the College Board, look for differences in charge before distance; the former has a greater impact on melting/boiling points than the latter.

This concept is difficult to retain without practice, so let's solve some problems!

Problem 2.1.4 — Ionic Bond Strength I

Which ionic compound, NaF or SrF_2, should you expect to have the higher melting point? Justify your answer.

Solution: According to Coulomb's Law, stronger attractions (and higher melting points) are associated with higher charges and smaller distances between the ions. First, we look at the charges of the ions. We notice that Sr has a +2 charge, while Na only has a +1 charge. Without even considering the ions' sizes, this must mean that stronger attractions are associated with $\boxed{SrF_2}$, and therefore it has the higher melting point.

Problem 2.1.5 — Ionic Bond Strength II

Which ionic compound has a higher boiling point: LiF or NaF? Justify your answer?

Solution: Using the same logic in the previous problem, we need to look for differences in ionic charge as well as size. Since both sets of ionic charges are $\{1, -1\}$, the difference in boiling points must be attributed to the size of the ions.

Since both ionic compounds consist of F^-, we need to consider the relative sizes of Li^+ and Na^+ ions. Using periodic trends, we know that Li^+ has a smaller radius than Na^+, because the former's valence electrons are closer to the nucleus and Li occupies fewer electron shells than Na (visually, it is one period above Na^+ on the periodic table). Coulomb's Law indicates the shorter separation distances between ions indicates stronger electrostatic forces, so we should expect $\boxed{\text{LiF}}$ to have the higher boiling point.

Covalent Bonding

The other important type of chemical bonding for this course is covalent bonding. This involves the *sharing* of electrons between two or more atoms. Because metals and nonmetals are prone to ionize when they interact, covalent bonding usually involves two nonmetals.

Covalent bonding in a molecule can be divided into two categories:

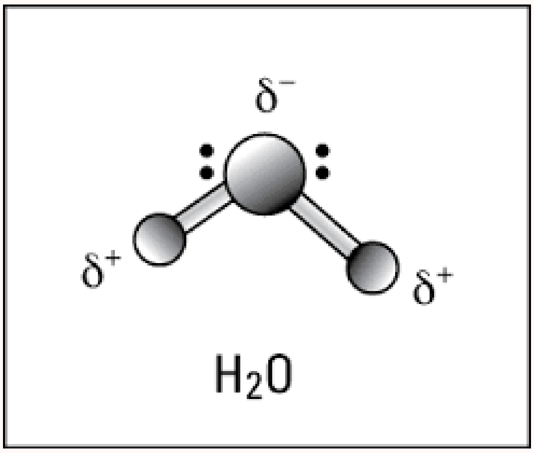
1. **Polar covalent bonds** arise when there is an unequal distribution of charge.
2. **Nonpolar covalent bonds** arise when there is an equal distribution of charge.

We'll go more in detail into polarity for sections 2.5 and 2.7: Lewis Diagrams and VSEPR and Bond Hybridization, respectively. For now, just remember the difference between nonpolar vs. polar covalent bonds. There will also be some examples that follow!

Example 2.1.6

Polar Covalent Bonding - H_2O

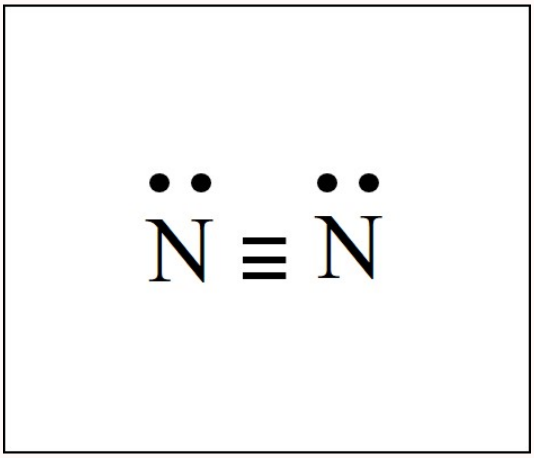
Water, as we know, is essential for all life on Earth. It is formed by hydrogen and oxygen atoms, which are held together by very strong attractions. More specifically, a water molecule contains two polar covalent $O-H$ bonds, and the charge distribution is uneven (electrons are shared unequally), concentrating on the oxygen atom.



Example 2.1.7

Nonpolar Covalent Bonding - H_2

Diatomic nitrogen, N_2, is the gas present in greatest amounts in Earth's atmosphere (it constitutes nearly 80% of the total content!). It contains one nonpolar covalent bond between two nitrogen atoms ($N-N$). The atoms share the electrons equally, so the charge is distributed evenly.



Electronegativity to Distinguish Nonpolar and Polar Covalent Bonds

To analyze the difference between polar covalent and nonpolar covalent bonds, compare the electronegativity values for each element's atoms in the covalent bond. Specifically, valence electrons that are shared between atoms with similar electronegativity result in a nonpolar covalent bond, and if shared unequally, it is a polar covalent bond.

We saw in Example 2.1.6 that water is formed by hydrogen and oxygen atoms in a polar covalent bond. Hydrogen has an electronegativity value of 2.2 while oxygen has an electronegativity of 3.44. Therefore, electron has a greater tendency to attract electron density to itself. This unequal charge distribution is seen by oxygen developing a partial negative charge, denoted by the lowercase Greek letter delta, δ^-, and the significant difference in electronegativity forms what are called **bond dipoles**, which will be more important in Unit 3.

The basic idea of bond dipoles for this unit is that they become more prominent as the electronegativity values for constituent elements increase.

Predicting Chemical Bonds

You can use the electronegativity difference between elements to predict the type of chemical bonding that they will engage in:

- Ionic: Two elements whose electronegativity values differ by more than 1.70.
- Covalent: Usually formed between two metals.
  - Polar Covalent Bonds: Form between two elements that have an electronegativity difference of $0.45 - 1.70$ (somewhat arbitrary).
  - Nonpolar Covalent Bonds: Form between two elements that have an electronegativity difference of $0.0 - 0.45$ (again, somewhat arbitrary).

Overlap Between Ionic and Covalent Bonds

We will emphasize solids more in later sections, but we should generally know these two principles:

- If a solid has a high melting point and conducts electricity well when *dissolved* in water, it is almost always an **ionic** compound. This is because ions (charged particles) flow very freely through liquids.
- On the other hand, a solid that melts at a low temperature and is a poor conductor of electricity in all states of matter, it is most likely a **molecular** compound, composed of covalent bonds.

However, there is some overlap between the two types of bonding. For example, a solid that is a poor conductor of electricity in any state but also has a high melting point is classified as a **covalent network solid**, composed of very strong covalent bonds. (We will emphasize all the types of solids you need to know later in this course.)

§2.2 Intramolecular Force and Potential Energy

This section discusses chemical bonds and the *potential* energy that is stored within them. The prefix "**intra**" means "*within*", so intramolecular forces are the forces within a molecule formed by its chemical bonds, which are classified as either ionic or covalent.

Defining Bond Energy

- This is the energy that is stored in a chemical bond.
- Its magnitude gives us information about the relative strength of the atoms' bonding interaction.

Potential Energy and Chemical Bonding

In chemistry and in general science, we are always trying to do things the most efficient way. In chemical bonding, this means striving to reach the highest stability. Therefore, it follows that in this course, whenever we see potential energy involved, we should always be looking to minimize it to achieve maximum stability.

Anyways, all physical and chemical processes can be represented through energy diagrams. For the purposes of this unit, energy diagrams will consist of a graph of potential energy versus internuclear distance between two atoms to simulate chemical bonding. There are several aspects of this graph that College Board requires us to understand:

1. The "**equilibrium bond length**" is defined by the distance between the two atoms where the potential energy of the system is minimized. To simplify it further, it is the internuclear at which the atoms are most stable.
2. The **bond energy**, as we defined earlier, is the energy supplied to separate two atoms in a chemical bond. Conceptually, this is the difference between the potential energy of atoms at their maximum distance and the potential energy of atoms at their equilibrium bond length.
3. The **bond strength** can be inferred from the bond energy. Higher bond energies correspond to stronger and more stable bonds, and vice versa.
4. The **bond length** of the bond, when the atoms are at any given internuclear distance.

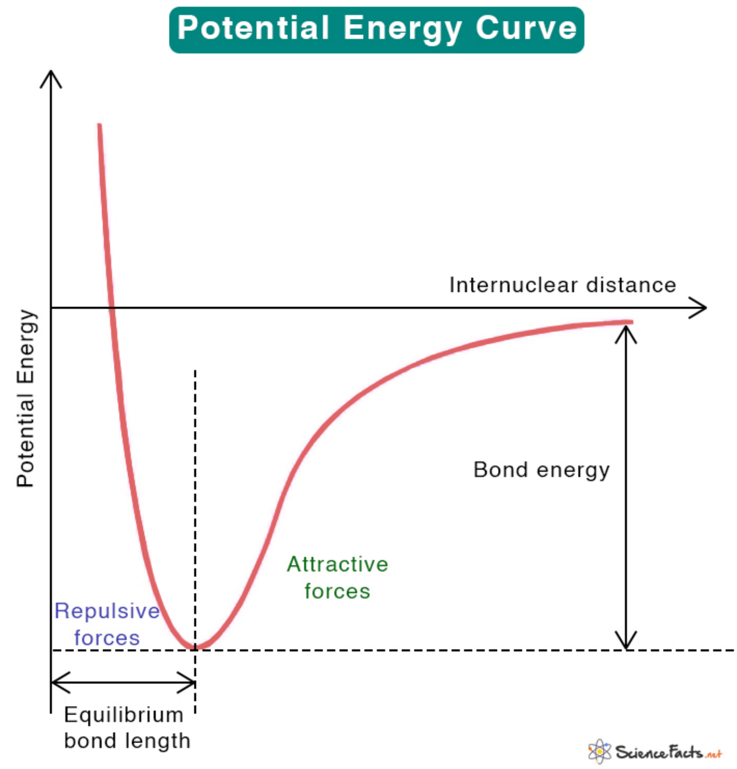


Image Courtesy of Science Facts

A More Detailed Discussion of Covalent Bonds and Potential Energy

Theoretically, we can represent the bond length of a covalent bond using both the size of atoms and the bond order.

Definition 2.2.1

Bond order is the number of chemical bonds between a pair of atoms. It describes the stability of a bond.

In this way, bonds can be classified as single, double, or triple, depending on their order.

Bond Order	Electrons	Bond Length	Bond Energy
Single Bond ($-$)	2	Longest	Largest
Double Bond ($=$)	4	Medium	Medium
Triple Bond ($\equiv$)	6	Shortest	Smallest

An easy way to determine the number of electrons associated with a bond (and therefore the order) is to keep in mind that each dash on a Lewis diagram represents a shared pair of electrons.

For example,

- H_2; $H - H$, single bond, bond order of 1,
- CO; $C = O$, double bond, bond order of 2, and

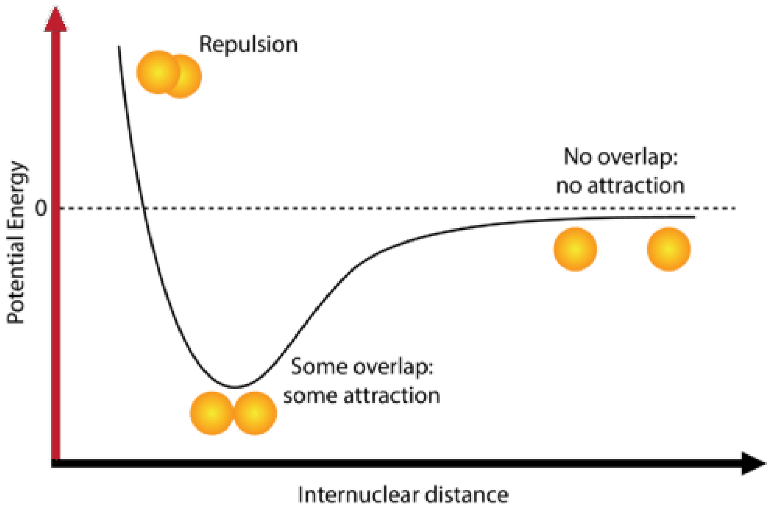
- N_2; $N \equiv N$, triple bond, bond order of 3.

Note 2.2.2

If you didn't understand anything regarding Lewis diagrams in the earlier discussion, don't worry. This concept is actually covered in section 2.5.

Since higher bond energies correspond to greater bond strength and stability, we should expect triple bonds to be the most stable, and vice versa. However, stability also depends on the size and charge of atoms involved in a bond. Let's see how we can put this information together in a potential energy diagram.

For covalent bonds, the bond length is influenced by the bond order as well as the mixture of forces of interaction (attractive and repulsive). The bond energy in this graph displays maximum potential energy as repulsion between two atoms.



We need to analyze three regions, namely:

1. **Repulsion**: when atoms are in very close proximity, the internuclear distance is minimized. Therefore, the atoms are experiencing significant repulsion between their electrons, causing the potential energy to be greater than 0 and the bond to be very unstable.

2. Some overlap/**attraction**: This is the most stable state, and the internuclear distance is at the "equilibrium bond length," which we had defined earlier. A balance between the attractive and repulsive forces occurs, forming a stable bond. At this point, we should infer that the potential energy is lowest because it is equal to the bond energy.

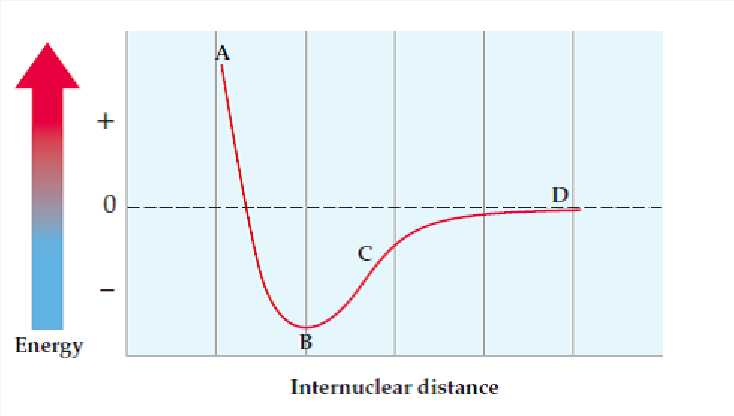
3. No overlap/attraction: When atoms are so far apart, their internuclear distance is largely unbounded, making all potential interactions between the atoms virtually impossible. As a result, no bond is formed and the potential energy is about 0.

Sometimes, you might be given the potential energy vs. internuclear distance diagram for one element and your task is to draw the curve for another element on the same graph.

Important Note: The following images associated with this problem and its solution are both courtesy of Chegg.

Problem 2.2.3 — Two Elements on a Potential Energy vs. Internuclear Distance Curve

Suppose the following image is a diagram of chlorine atoms bonded together ($Cl-Cl$). Where would $Br-Br$ fall in comparison to this curve?



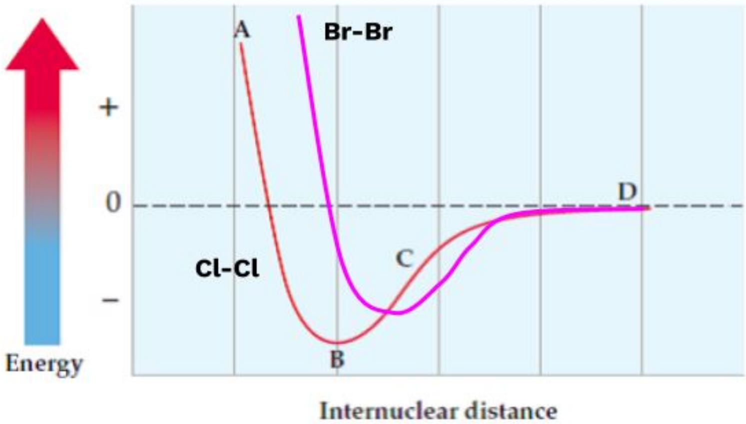
Solution: We need to use our knowledge of periodic trends as well as split this problem into two cases.

In the first case, we will consider the relative positions of the x-axis, and in the second case, we will consider the y-axis.

- Internuclear distance: We need to compare the values for $Cl-Cl$ and $Br-Br$. How can we do so? Well, the element with the larger atomic radius will have the larger internuclear distance. Since bromine is below chlorine on the periodic table, the $Br-Br$ bond is longer than the $Cl-Cl$ bond. This means that the $Br-Br$ curve should be to the right of $Cl-Cl$.

- Potential energy: We need to ask ourselves which bond is easier to break, $Cl-Cl$ or $Br-Br$? The answer lies in remembering the ionization energy trend. Specifically, a lower ionization energy means it is easier to break the bond. Br and Cl are both halogens, and as you move down a group, ionization energy decreases because more electron shells are occupied and the nucleus' attraction to valence electrons becomes weaker. Therefore, bromine has a lower ionization energy than chlorine, and the $Br-Br$ bond is easier to break. This means that the curve's vertical component should be graphed above the curve for chlorine.

Combining both cases, our final answer should look like this:



§2.3 Structure of Ionic Solids

Definition 2.3.1

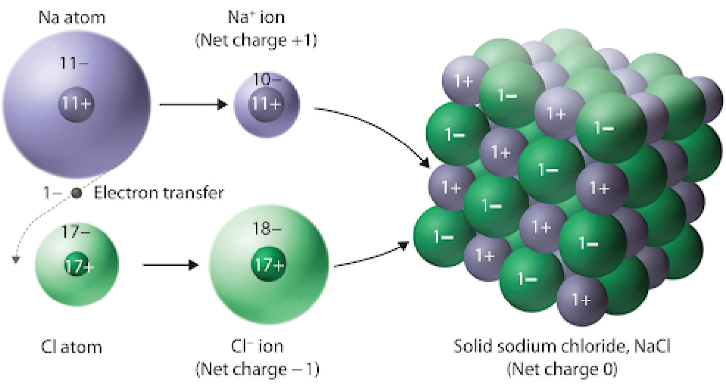
An **ionic solid** is a solid representation of an ionic compound that is composed up of a *positively-charged* cation and a *negatively-charged* anion.

Ionic bonding typically occurs between a metal and a nonmetal, i.e. a metal transfers a number of its valence electrons to a nonmetal. Since the metal loses a valence electron, it becomes a cation and the nonmetal gains a valence electron, becoming an anion.

The cation and anion interact because they are attracted to each other's opposite charges. The extent to their interaction is governed by Coulomb's Law.

Structure of Ionic Solids

We discussed earlier that ionic bonding can produce brittle, hard solids with very high melting points. This is due to the structural properties of an ionic solid, which is arranged in a 3D array known as a **crystal lattice**.



Because ions are attracted to their opposite charges, the anions surround the cations and vice versa. You can consider this as an arrangement to maximize the attractive forces between ions and minimize the repulsive forces.

But why do the sizes fit so well? The reason is that when metals ionize, they lose valence electrons, thus decreasing in size. However, when nonmetals ionize, they gain valence electrons, thus increasing in size. This doesn't happen for *all* ionic solids, but it is significant as it impacts the forces that hold the ions together in the lattice.

Representing Ionic Solids

You must know that *particle diagrams* for ionic substances look much different compared to molecular substances (composed of covalent bonds). These substances are usually presented as an array of molecules oriented such that more covalent bonds can form, while ionic substances are represented by a network of cations and anions.

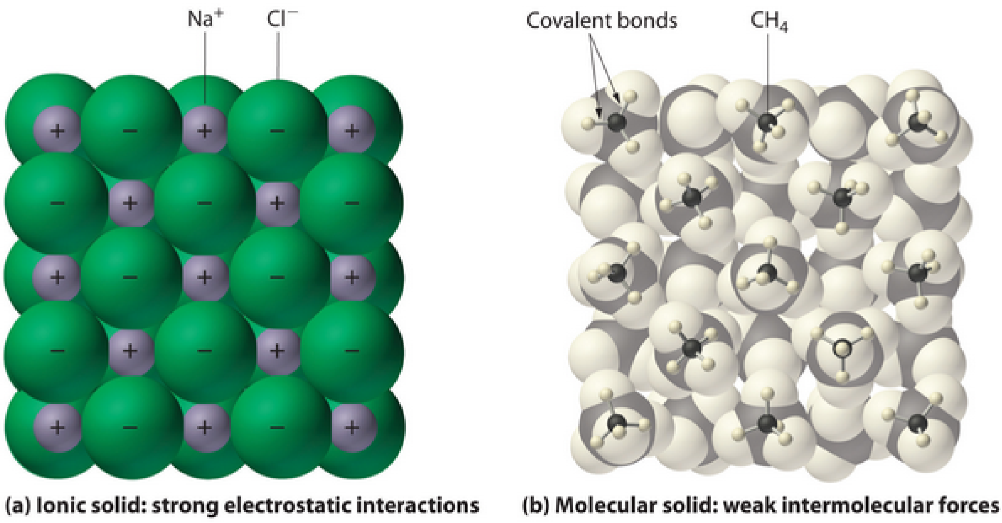


Image Courtesy of Principles of General Chemistry

Why Does The Lattice Structure Exist?

The lattice structure of ionic solids is caused by the strong *electrostatic forces* between the cations and anions with opposing charges. **Coulomb's law** states that the electrostatic force between a cation and an anion is directly proportional to their charges and inversely proportional to their center-to-center distance.

$$F = k\frac{q_1 q_2}{r^2}$$

We saw this formula in Unit 1! Coulomb's law is referenced A LOT in this course.

Note: Unless you are also enrolled in AP Physics C: Electricity and Magnetism, you do not need to memorize this formula.

Rather, you should know that the relative electrostatic force strength depends on these two factors:

1. **Charge magnitude** - The greater the magnitude of charge on the ions, the stronger the interaction between them.

2. **Distance between the ions' nuclei** - The closer the cation and anion are located, the stronger the attractive force between the two. This is where our knowledge of periodic trends from Unit 1 becomes useful!

Properties of Ionic Substances

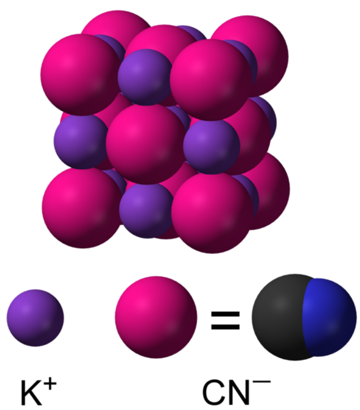
At room temperature, ionic solids are typically in the solid state of matter. They are also known for their very high melting and boiling points. Here are some of the general properties that apply to virtually all ionic substances:

- The strong electrostatic forces that comprise an ionic solid require significant energy to overcome. As a result, these substances have very high melting and boiling points.
- In a lattice structure, the electrons are "stuck" in place. College Board deems them as **localized**. Since no electrons are moving around, no current is flowing, so ionic solids are generally poor conductors of heat and electricity.
- When ionic solids melt, their ions can move freely. In other words, electrons are **delocalized**. Therefore, ionic substances are excellent conductors of heat and electricity in the aqueous and liquid phases.
- Ionic solids are hard and brittle because the electrostatic forces make them very difficult to deform.

The Concept of Lattice Energy

When ions engage in ionic bonding, they do so with the purpose of reducing their potential energy, thus reaching a more stable state.

Therefore, when ions bond to form an ionic solid, this process releases an amount of energy, known as **lattice energy**. Coulomb's law goes hand in hand with it.



Lattice energy involves the same two concepts that we used in the previous example: charge and distance. Coulomb's law correlates with lattice energy and melting point so make sure to remember this: *The smaller the distance between ions and the higher their charges, the greater the lattice energy.* Therefore, the higher the melting point of an ionic solid, the higher the lattice energy.

Let's try out one final example for the concepts to sink in.

Problem 2.3.2 — Relative Lattice Energies

For each of the following pairs of ionic compounds, predict the one with the higher lattice energy and explain why.

(a) MgO and NaF
(b) NaF and KCl
(c) $MgCl_2$ and $MgBr_2$

Solution to part a: Mg^{2+} and O^{2-} ions have charges of +2 and −2 respectively, while Na^+ and F^- only have charges of +1 and −1 respectively. Without checking the relative ion sizes, $\boxed{\text{MgO}}$ must have a higher lattice energy.

Solution to part b: These ions are located in the same groups, so they have the same charges. To compare the sizes of NaF and KCl, we must use periodic trends. We find that K^+ and Cl^- are larger than Na^+ and F^-. With a smaller size, $\boxed{\text{NaF}}$ has the higher lattice energy.

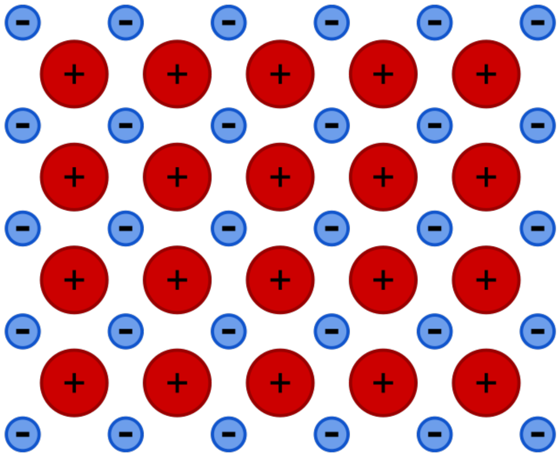
Solution to part c: Both ionic solids consist of Mg^{2+} ions, so we need to compare the sizes of Cl^- and Br^-. Because Cl^- contains one less $3d$ electron shell, it is smaller. Thus, $\boxed{MgCl_2}$ has the higher lattice energy.

§2.4 Structure of Metals and Alloys

The objective of this topic is to effectively represent a metallic solid and/or alloy using a model to display significant characteristics of the solid's structure as well as the interactions occurring within.

Review of Metallic Bonding

Recall that metallic bonding is represented as an array of positive metal ions surrounded by delocalized valence electrons (i.e. a "sea of electrons").



Alloys: An Overview

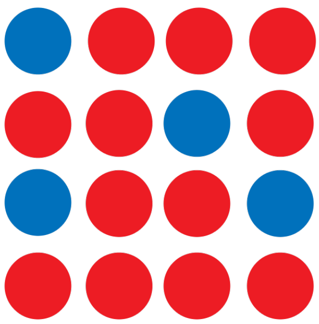
- Alloys are mixtures of metals or a mixture of a metal and another element.
- Their properties are *usually* (not always) different from those of its component elements. For example, rust is much weaker than iron metal, even though it is a corroded form of iron.
- Examples of alloys include brass, bronze, steel, etc.

Alloys: Types

Alloys can be classified into three types: **pure metals, substitutional alloys**, and **interstitial alloys**.

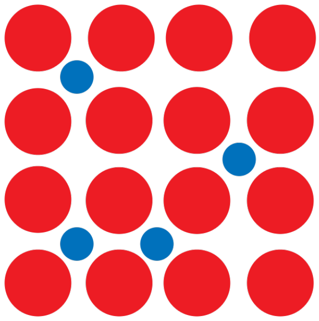
Definition 2.4.1

Substitutional alloys are formed between atoms of similar radii, when one atom substitutes for another in the structure. For example, zinc can substitute for copper in certain brass alloys.



Definition 2.4.2

Interstitial alloys are formed between atoms of much different radii, where the smaller atoms fill the *interstitial spaces* between the larger atoms (for example, carbon occasionally occupies the interstices in iron in steel alloys).



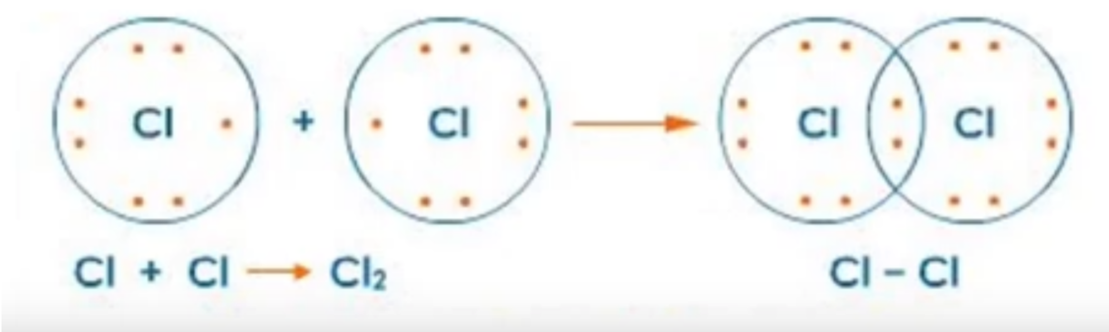
This concludes our discussion of alloys. "Wow, that was fast!" you might think. You are correct! Metal alloys are one of the shortest and simplest topics in the AP Chemistry syllabus.

§2.5 Lewis Diagrams

In this section, we will learn about visual representations of molecules called Lewis diagrams. We will learn the process of drawing them and understand their importance later in the course.

What is the Octet Rule?

Atoms of various elements tend to gain, lose, or share valence electrons during the formation of molecules such that there are eight electrons, or a complete octet, in their valence shells.



We will analyze the above image.
Chlorine has seven valence electrons. A lone Cl atom is very unstable, since it is eager to gain one more valence electron and completely fill its outermost shell. Therefore, it can combine with another Cl atom and form diatomic chlorine, Cl_2. Now, both chlorine atoms have a pair of electrons that are equally shared. Since the Cl_2 atom consists of Cl atoms with a full octet in their valence shells, the overall system becomes more stable.

What are Lewis Diagrams?

Lewis diagrams, or Lewis dot structures, are a way of drawing molecular structures and representing the valence electrons and bonds that are formed between atoms. The ability to understand and draw Lewis structures opens up many more possibilities in this course.

Lewis structures are also used to predict the shapes of molecules as well as the type of reactions they can undergo. This theory is based on the octet rule, which we talked about earlier.

These diagrams are best summarized as a type of **localized electron model**, which means that the electrons are "stuck" within the structure. The valence electrons in a Lewis structure are of two types:

1. **Lone pairs -** pairs of electrons that are localized around a single atom and are not shared with any other atoms (represented as two dots).
2. **Bonding pairs -** pairs of electrons found in the shared space between atoms (represented by a dash).

Drawing a Lewis Diagram

Generally, we do not draw the Lewis diagrams for ionic substances since valence electrons are being transferred. In this section, we are more concerned with covalent bonds, so we will focus on molecular substances where valence electrons are shared.

We will follow these steps for drawing the Lewis diagrams for molecular substances:

- Count the total number of valence electrons in the molecule by observing the chemical formula.
- Draw the **central atom**. Here are some simple ways to determine which atom is to be placed in the center: carbon is always placed in the center, the least electronegative element is placed in the center, the element that contains the least number of atoms is placed in the center, and carbon is always placed in the center. Also note that hydrogen *cannot* be placed in the center because it can only hold 2 valence electrons.
- The outside atoms are drawn and single bonds (one dashed line) are placed to connect them.
- Draw electron pairs (2 dots per pair) on each outside atom, ensuring that they have full octets. Most elements are stable with 8 electrons.
- At this point, count the valence electrons that are present so far. If there are *too many*, remove lone pairs from the central atom and instead form double/triple bonds. If there are *too few*, add some to the central atom, with exceptions (we will see them soon). Note that fluorine is the most electronegative element and therefore cannot form a bond with an order greater than 1.

Exceptions to the Octet Rule

When drawing Lewis structures, it's important to recognize certain exceptions to the octet rule. This is where many students doubt themselves and tend to mess up on otherwise straightforward problems.

- Some atoms have fewer valence electrons than a full octet of 8. For example, hydrogen has 2, beryllium can have at most 4, and boron can have at most 6.
- If there are too few valence electrons in your structure, you can break the octet rule on the central atom **if and only if** the element has an atomic number of at least 14. In this way, you can add extra electrons to the central atom to meet the required total.
- Some atoms have an odd number of valence electrons. You just can't always pair an octet completely.
- Some compounds contain multiple bonds (double and/or triple) between the atoms if there are not enough electrons. For example, CS_2 is represented as a carbon joined to two sulfur atoms by **double bonds**.

Let's try some practice problems.

Problem 2.5.1 — Lewis Diagrams that Obey the Octet Rule

Give the Lewis structures for the following:
(a) N_2, diatomic nitrogen
(b) CH_4, methane gas

Solution to part a: Our first step is to count the total number of valence electrons. Nitrogen has 5 valence electrons, so a neutral N_2 molecule should have $5 \cdot 2 = 10$ valence electrons in total.

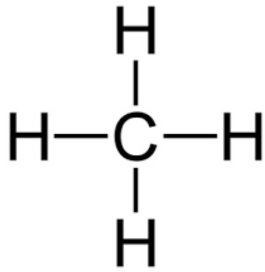
Also, we don't necessarily have a central atom, so we will just start with this structure: $N - N$. Remember that the dash represents one pair of (two) electrons, meaning that we have $10 - 2 = 8$ available valence electrons left to complete the Lewis diagram. Now, we must fill up the octets on each N atom. As a result, we have the bonded pair of electrons as well as 3 pairs of electrons, represented by dots, on each N, for a total of $1 \cdot 2 + 3 \cdot 2 = 3 \cdot 2 = 14$ valence electrons.

However, this is not allowed. We know that the N_2 molecule contains only $2 \cdot 5 = 10$ valence electrons, so we have an excess of 4 electrons. Fortunately, we can use double and/or triple bonds to ensure that each atom is as stable as possible, without going above our limit on the number of valence electrons.

Using some trial and error, we determine that the Lewis diagram for N_2 will involve a triple bond ($2 \cdot 3 = 6$ electrons are **shared** between the two atoms), and a lone pair of electrons on both ($2 \cdot 2 = 4$), for a total of $6 + 4 = 10$ valence electrons.

Solution to part b: Carbon has 4 valence electrons, and hydrogen has 1, so methane (CH_4) should contain $1 \cdot 4 + 4 \cdot 1 = 8$ valence electrons in total.

Now we need to follow the steps to draw the Lewis diagram. First, we know that carbon must be placed in the center because it can form four bonds with hydrogen. More specifically, carbon has 4 valence electrons and needs 8 for a stable octet. Each of the four hydrogen atoms has 1 valence electron, so all H can share $4 \cdot 1 = 4$ valence electrons with carbon, giving a total of $4 + 4 = 8$ electrons: a stable octet. Hydrogen is a special case; it only requires 2 valence electrons for a stable octet. Therefore, we should expect a symmetric structure of covalent $C - H$ bonds that would look like this:



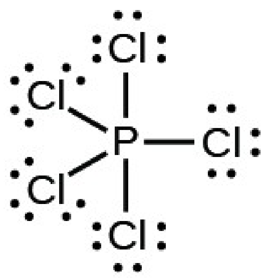
Problem 2.5.2 — Lewis Diagrams that Violate the Octet Rule

Give the Lewis structures for the following:
(a) PCl_5, phosphorus pentachloride
(b) XeO_3, xenon trioxide

Solution to part a: Phosphorus contains 5 valence electrons, while chlorine is a halogen that contains 7. Therefore, PCl_5 has a total of $5 + 5 \cdot 7 = 40$ valence electrons. Placing phosphorus at the center, we will perform the following:

1. We can draw 5 dashes from the P atom to the five Cl atoms.
2. P has an atomic number of 15, which is greater than 14, so its octet can be stable even with more than 8 electrons.
3. Using this fact, we can assign 10 electrons to P, represented by the five dashes as polar covalent $P - Cl$ bonds.
4. Then we add the remaining three lone pairs of electrons on each Cl atom (so that they can also have a full octet), for a total of $3 \cdot 2 \cdot 5 = 30$ electrons.

Since we have kept track of the number of valence electrons used in developing our diagram, it is easier for us to determine if we need to add more lone pairs of electrons (too few) or replace single bonds with double/triple bonds (too many). Since 10 valence electrons were shared between all 5 $P-Cl$ bonds and 30 valence electrons as lone pairs were added to all Cl atoms, we used a total of $10+30=40$ in total, which is actually the number of valence electrons in a molecule of PCl_5, so we distributed just the right amount of valence electrons. Therefore, we should expect a symmetric structure of covalent $P-Cl$ bonds that would look like this:

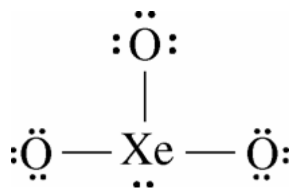


Solution to part b: Xenon is a noble gas, so it contains 8 valence electrons, a stable octet for its atoms. Meanwhile, oxygen has 6 valence electrons. Therefore, the total number of valence electrons in XeO_3 is $8+3\cdot 6=26$.

Note 2.5.3

Generally, we established that noble gases do not react with other elements, but in certain situations we can force them to react with atoms of other elements, as we see in this problem. Keep this fact in the back of your head; you do not need to know the mechanism behind forcing Xe to react with 3 atoms of O.

We use the same logic involved in part (a) of this problem. We will start by drawing three $Xe-O$ bonds and leaving them all as single bonds for the time being. Each $Xe-O$ bond represents a shared pair of electrons, for a total of $3\cdot 2=6$ electrons. Next, we complete the octets on the surrounding atoms (in this case, the oxygen atoms). For each of three O atoms, we will have to add three lone electron pairs, which requires $3\cdot 2\cdot 3=18$ electrons. At this point, we have used 24 of the available valence electrons in XeO_3. Since we have extras, we add a lone pair on the central atom, Xe (effectively giving it a full octet). The Lewis diagram for XeO_3 is therefore



Remark. In other places, you may see that the Lewis diagram for XeO_3 actually contains 3 double bonds for $Xe-O$ ($Xe=O$) and one less lone pair of electrons on each O atom. This is done to minimize the *formal charge* on the molecule, which is the topic of the next section, so keep reading!

§2.6 Resonance and Formal Charge

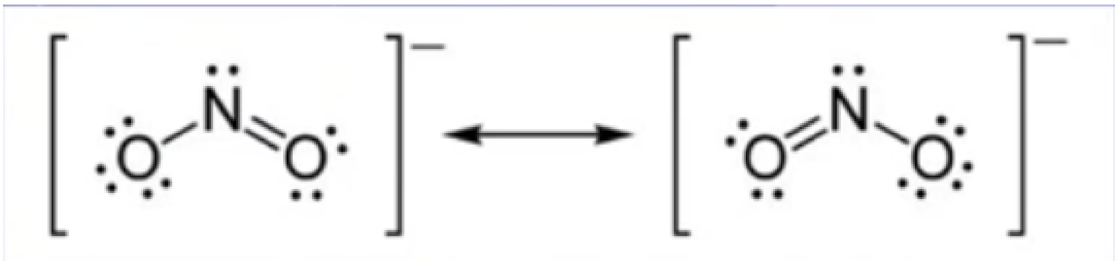
Definition 2.6.1

Resonance describes the scenario in which more than one valid Lewis structure can be written for a particular molecule.

On the AP Chemistry exam, resonance is denoted by the double arrow, or $\leftrightarrow$.

Example 2.6.2

The Lewis structure for the nitrite ion, NO_2^-, consists of one double bond and one single bond. NO_2^- displays resonance because you can interchange the double and single bonds.



These are resonance structures of NO_2^-. The actual structure is the *average* of the resonance structures. This is due to the delocalization of electrons. They can move to help stabilize the molecule. Recall that resonance structures always have the same number of electrons and the same net charge. However, individual charges on the atoms could be different (We will talk about this a little later!).

Resonance and Bond Order

When you actually draw multiple resonance structures for a molecule, they constitute the entire molecule. The actual structure in space is the average of all resonance structures, which can lead to bond orders that are fractions (interesting, isn't it?).

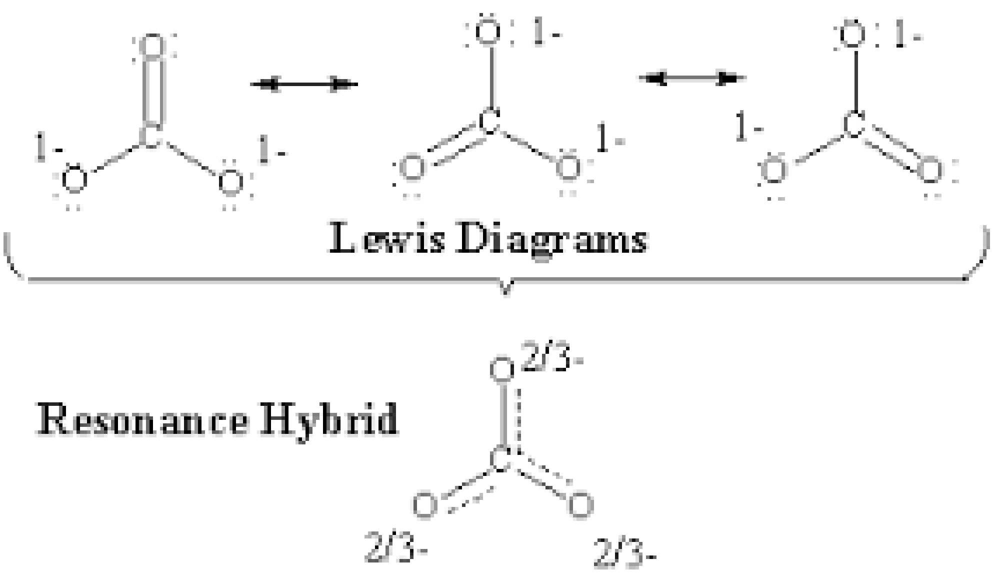


Image Courtesy of University of Calgary

Many students have the misconception that resonance structures can actually exist with different bond connections. However, resonance is mainly done to represent a molecule in slightly different ways to emphasize that the molecule is just the average of those representations in space. This will make more sense in the example that follows on the next page.

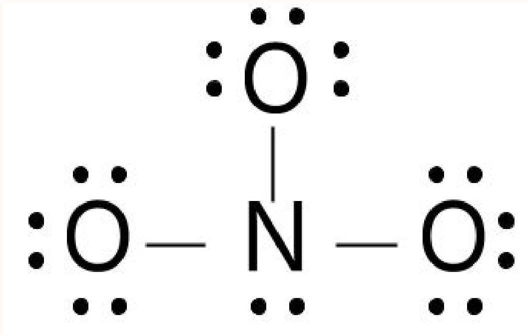
Example 2.6.3

Let's try drawing the Lewis structure of nitrate ion, NO_3^-.

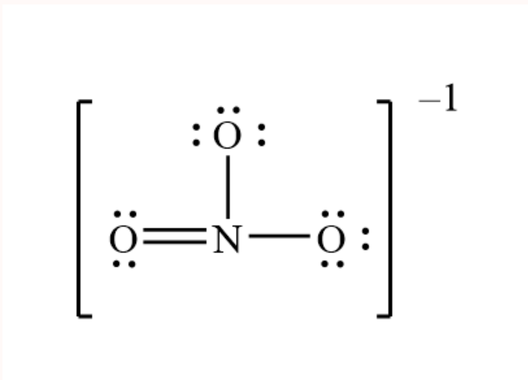
1. Count the total number of valence electrons. Nitrogen has 5 and oxygen has 6 so we will account for all three oxygen atoms in the calculation as $5 + 3 \cdot 6 = 23$. However, NO_3^- has a -1 charge, indicating that we need to add 1 more electron, so there must be a total of 24 valence electrons in NO_3^-.

2. Draw the central atom, which in this case is nitrogen since there is only one N atom.

3. Draw the 3 surrounding O atoms and 3 single bonds connecting them to N. Then complete the octets on the oxygen atoms.



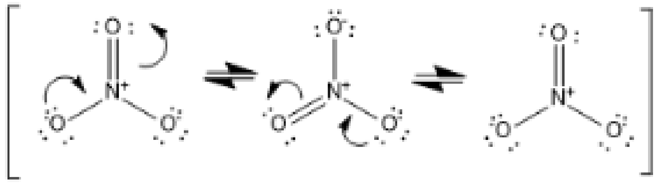
4. At this point, the current number of valence electrons is 26. Since NO_3^- has 24, we have 2 extra on our Lewis structure. We can eliminate them by replacing a single bond and a lone pair with a double bond.



Make sure you include the brackets and charge for polyatomic ion structures.

Now we count the number of valence electrons. Due to the double bond, we get 24! Note that this is *one* way to draw the Lewis diagram for NO_3^-. How do we know which $N-O$ bond to assign a double bond?

Well, the simple answer is any one of them. This is because each of the three possibilities simultaneously exist in space. Specifically, there are three ways to draw this structure using resonance.



nitrate

Note that for practical purposes, NO_3^- does not actually have 2 single bonds and 1 double bond. In fact, it has a 4/3 **bond order**, and we only use resonance because there is no way to actually represent a fractional bond order in three-dimensional space.

Bond Order

You must be wondering as to how did I know the bond order was 4/3? There is actually a quick way to determine this in a Lewis structure:

$$\text{bond order} = \frac{\text{number of bonds}}{\text{number of bonding regions}}$$

For NO_3^-, there is one double bond and two single bonds, for a total of 4 bonds. There are 3 regions for these bonds to form, so the bond order is simply $\boxed{4/3}$. This bond is intermediate between a single bond and a double bond, which means it is stronger than the former but weaker than the latter.

As mentioned before, make sure to draw all resonance structures side-by-side using the double arrow notation. You may also write the word "resonance" if you need to clarify your knowledge and answer the question for yourself.

Formal Charge

Definition 2.6.4

Formal charge is the charge assigned to an atom in a molecule, assuming electrons in all chemical bonds are shared equally between atoms.

The implication of this statement is that it reflects the electron count associated with the atom **as part of the molecule** compared to the atom **as neutral and isolated**. It is used to predict the correct placement of electrons as well as the bond order for certain bonds in Lewis diagrams.

Calculating Formal Charge

The easiest way to calculate formal charge is to use the following equation:

$$\# \text{ of valence electrons} - \# \text{ of dots} - \# \text{ of dashes}$$

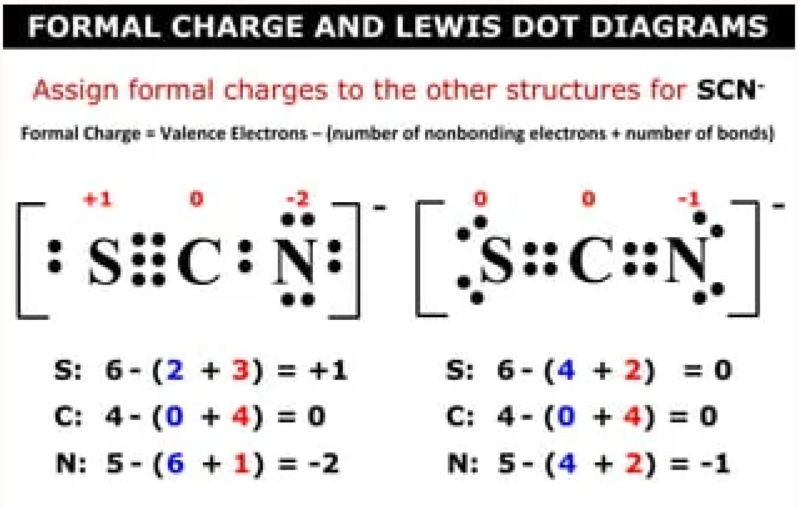
The technical definition is

$$\# \text{ of valence electrons in free atom} - (\# \text{ of lone electrons} + \# \text{ of bonds})$$

but students generally grasp the concept better using the first definition!

Example 2.6.5

Consider the thiocyanate ion, SCN^-, with Lewis structures shown below.



For this example, we will focus on the structure on the left.

For the sulfur atom, we begin with the number of its valence electrons assuming a free atom. This implies sulfur has 6 valence electrons. Then, we subtract by the number of lone electrons (2) and single bonds with carbon (3, but it is actually a triple bond!). This tells us that sulfur has a formal charge of $6 - (2 + 3) = +1$ when drawn as SCN^- with this representation.

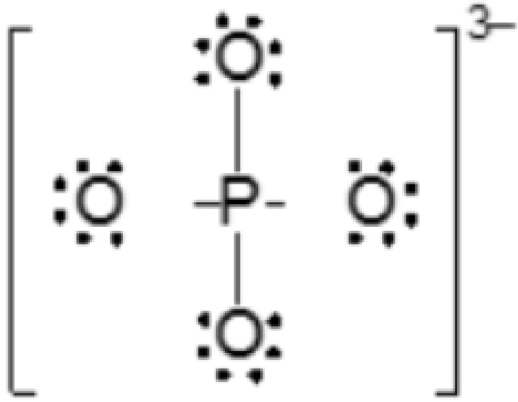
Important. It is always a good idea to double-check your formal charge to minimize careless mistakes. Actually, you only have to check whether or not an element past atomic number of 14 is involved, because only then we are allowed to break the octet rule!

Problem 2.6.6 — Formal Charge for Phosphate Ion

Draw the structure of phosphate ion. Be sure to consider the formal charge on atoms of each element in PO_4^{3-}.

Solution: Let's draw the Lewis diagram of PO_4^{3-}.

1. There should be $5 + 4 \cdot 6 + 3$ valence electrons, for a total of 32.
2. Place phosphorus in the center and four oxygen atoms surrounding it with single bonds and full octets.



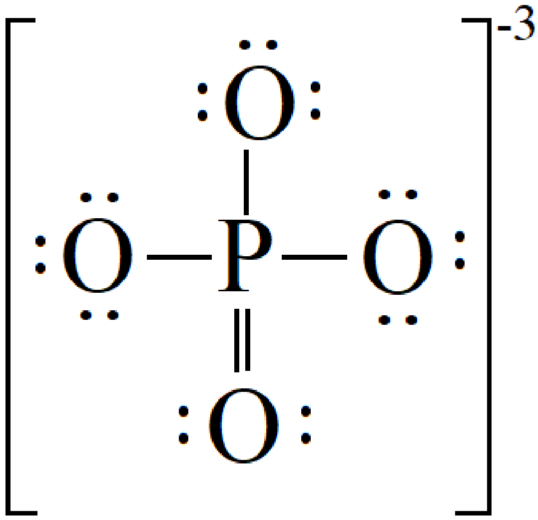
At this point, we count the total valence electrons. There are 32, so we think it's perfect. However, the central atom (phosphorus) represents element 15 (> 14), so we should be checking formal charge to ensure the proper placement of electrons.

Applying the dots and dashes trick, we have

$$\text{P} : 5 - (0 + 4) = +1 \qquad \text{O} : 6 - (6 + 1) = -1$$

Generally, there are two criteria for formal charges: we want the central atom to have zero formal charge and the most electronegative atom to have a negative formal charge. This is because a formal charge of 0 means that the electrons are **localized** (not moving), which is the most stable representation of a molecule.

We can reduce the formal charge on phosphorus from $+1$ to 0 by replacing one of the single bonds with a double bond.



Check:

- formal charge (P) $= 5 - (0 + 5) = 0$,
- formal charge (O, double-bonded) $= 6 - (4 + 2) = 0$, and
- formal charge (O, single-bonded) $= 6 - (6 + 1) = -1$ ✓

The electrons are placed correctly, and therefore we have a stable bond! You can also recognize that the PO_4^{3-} molecule displays resonance, so make sure to draw it all four ways and know that the bonds are of 5/4 order.

Note 2.6.7
A quick way to check that you calculated formal charge correctly is if the sum of formal charges is equal to the overall charge of the molecule/ion.

Because we had three oxygen atoms with a formal charge of -1, the total is $-1 \cdot 3 = -3$, which is equal to the net charge of the PO_4^{3-} ion.

§2.7 VSEPR and Bond Hybridization

In this section, we will use the relationship between Lewis diagrams, bond orders, and bond polarities to explain both structural and electronic properties of molecules.

VSEPR Theory

Definition 2.7.1
The **valence shell electron pair repulsion (VSEPR) theory** presents a method to predict the shape of molecules consisting of covalently-bonded atoms.

The following statements are referred to as the *postulates* of VSEPR Theory:

- The geometry of a molecule depends upon the number of electron pairs (both bonded and non-bonded, demonstrated by the Lewis diagram) in the valence shell of the *central atom only*.
- Electron pairs tend to occupy such positions in space so that the distance between them is *maximized*, thus *minimizing* the repulsion between them.
- The repulsion of electron pairs can be ranked by the following interactions:

  $$\mathrm{lp} - \mathrm{lp} > \mathrm{lp} - \mathrm{bp} > \mathrm{bp} - \mathrm{bp}$$

  where lp and bp represent lone (non-bonded) and shared (bonded) pairs of electrons, respectively.

Note 2.7.2
The electron cloud spreads apart and occupies more space with the presence of a lone pair of electrons. This causes differences in the expected shapes and bond angles.

Steps to Predict Molecular Geometry

To determine the shape or geometry of a molecule, follow these steps:

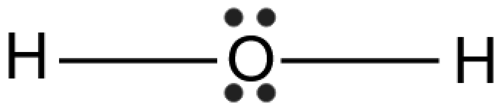
1. Draw the Lewis diagram for the molecule.
2. Count the number of electron pairs on the central atom, and classify them as bonding pairs or lone pairs.
3. Count the number of bonding and lone pairs.
4. Looking at the positions of other atoms around the central atom, name the molecular geometry.

Problem 2.7.3 — Predicting Molecular Shape

Using the above steps, predict the geometry of a water molecule, H_2O.

Solution: First, let's draw the Lewis diagram for H_2O. Since O has the lowest subscript in the molecular formula for H_2O, it can form the most bonds and its atom will be in the center.

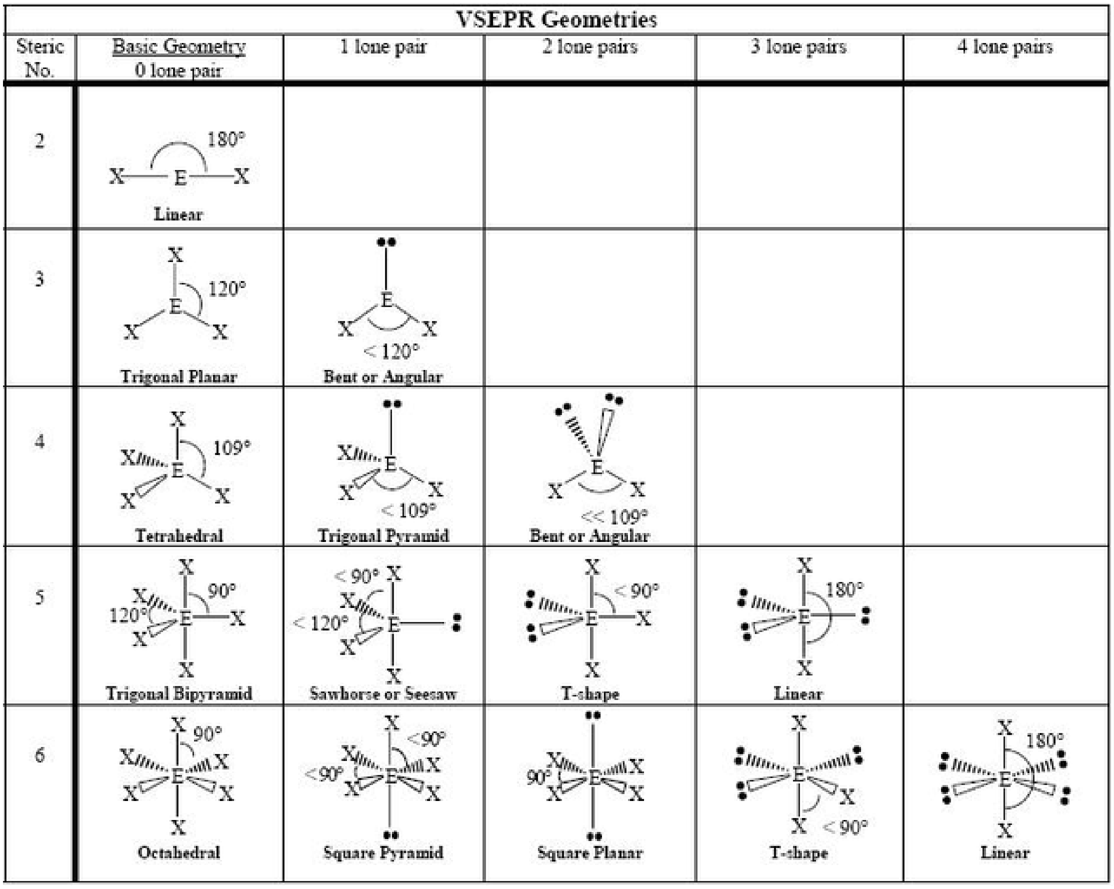
The Lewis diagram for H_2O is:



Let's classify the electron pairs surrounding our central atom, O. There are two bonded pairs, shared between the hydrogen and oxygen atoms, and two lone pairs, located on the oxygen atom. Since lone electron pairs require more space than bonded pairs, the shape of H_2O won't be a straight line; its structure will be $\boxed{\text{bent}}$.

Okay, now that was a bit unfair. You all must be thinking, "How am I supposed to know the geometry just by counting the number of lone and bonded pairs of electrons on the central atom?"

Below is a chart that summarizes the molecular geometry of covalent compounds with a given number of bonded and non-bonded pairs of electrons on the central atom.



Unfortunately, you will not be provided with this resource on the AP Exam - you must memorize this. However, don't panic. The more you practice with these, retaining them will get much easier.

Definition 2.7.4

A **bond angle** is the geometric angle formed by two adjacent bonds originating from the same atom in a covalent compound.

Note 2.7.5

A useful approximation for the bond angle without rote memorization is:
"For every lone pair, the bond angle will decrease by two degrees, compared to as if all electron pairs were bonded."

Let's go back to our H_2O molecule. In total, there are 4 electron pairs. Thus, the electron geometry is tetrahedral, with an expected bond angle of 109.5°. However, 2 of these electron pairs are non-bonding. The bond angle generally decreases by 2° for every lone pair, so the overall bond angle of a water molecule is expected to be approximately 104.5°, with a **bent or angular** structure, according to VSEPR theory.

Alright, you're probably asking this: "What exactly is electron geometry and how is it different from molecular geometry?"

Answer: *Electron geometry* is determined by the **overall** number of electron pairs surrounding the central atom, while *molecular geometry* is affected by the number of bonded and non-bonded electron pairs.

Regardless of the number of bonded vs. lone electron pairs, the following electron-domain geometry holds:

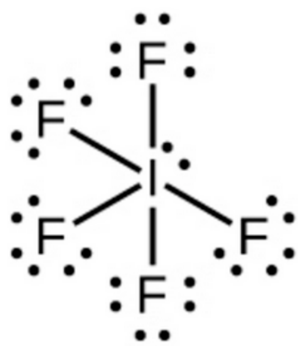
- For two electron pairs, the electron geometry is **linear**.
- For three electron pairs, the electron geometry is **trigonal planar**.
- For four electron pairs, the electron geometry is **tetrahedral**.
- For five electron pairs, the electron geometry is **trigonal bipyramidal**.
- Finally, for six electron pairs, the electron geometry is **octahedral**.

Let's work through these problems.

Problem 2.7.6 — VSEPR Theory I

Determine the electron geometry of iodine pentafluorine, IF_5.

Solution: First, draw the Lewis diagram for IF_5:

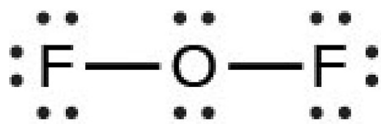


Since we are asked to find the electron geometry, we only need to find the number of electron pairs surrounding iodine, located in the center. We count 5 bonded pairs and 1 lone pair, for a total of 6 electron pairs. The electron geometry of IF_5 is $\boxed{\text{octahedral}}$.

Problem 2.7.7 — VSEPR Theory II

Determine the molecular geometry of oxygen difluoride, OF_2.

Solution: Once again, we start by drawing the Lewis diagram.

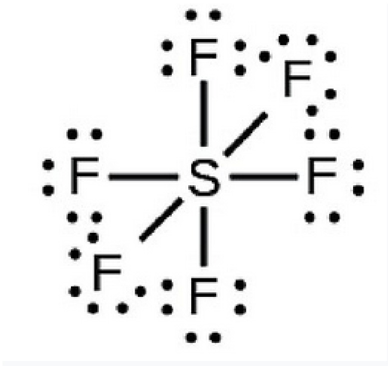


On the central atom O, there are four electron pairs surrounding it. Therefore, the electron geometry is tetrahedral. Now, we need to check for any lone electron pairs. We find that two of the electron pairs are shared between the oxygen and fluorine atoms, so there are 2 bonded pairs. Thus, the molecular geometry of OF_2 is $\boxed{\text{bent}}$.

Problem 2.7.8 — VSEPR Theory III

Determine the bond angle of sulfur hexafluoride, SF_6.

Solution: The Lewis diagram for SF_6 is



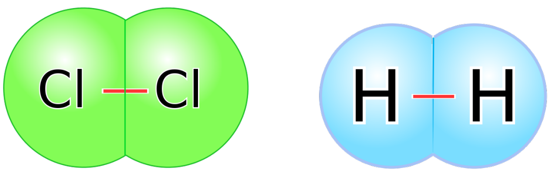
First, let's determine the electron geometry of SF_6. There are six total electron pairs surrounding sulfur, the central atom, so the electron geometry is octahedral. Now, we need to count for non-bonding electron pairs. Since we see no lone pairs, the molecular geometry of SF_6 is octahedral, and its bond angle is thus $\boxed{90^\circ}$.

Bond Polarity

Previously, we distinguished between ionic and covalent bonding. However, in the case of covalent bonds, some ionic character *does* exist. For example, recall that there are two classes of covalent bonds: **non-polar covalent** and **polar covalent** bonds.

Definition 2.7.9

In a nonpolar covalent bond, electrons are shared equally between two atoms. There is no charge situated on either atom.



A great example of nonpolar covalent bonding is described in diatomic hydrogen gas, or H_2. The actual bonding can be represented by $H-H$, a bond between two unstable hydrogen atoms. The reason why one H atom pairs with another is to achieve an overall decrease in potential energy, i.e. for the two atoms, to collectively become more stable.

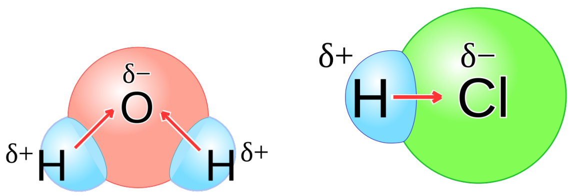
In fact, all of the diatomic elements display nonpolar covalent bonding. Here are the seven diatomic elements you should know.

- Gases at room temperature are
  - Hydrogen (H_2), nitrogen (N_2), oxygen (O_2), fluorine (F_2), and chlorine (Cl_2).
- When the temperature is slightly raised, these molecules are liquid:
  - Bromine (Br_2) and iodine (I_2).

A cool way to remember the seven diatomic elements is to use the mnemonic device: **H**ave **N**o **F**ear **O**f **I**ce **C**old **B**eer.
(Technically, you should fear it, as you are not yet of legal age. Jokes apart, this device works extremely well for many students!)

Definition 2.7.10

In a polar covalent bond, electrons are shared unequally between two atoms. There are partial charges present on each atom.



Polar covalent bonding arises when a more electronegative element tends to attract electron density to itself, causing an uneven distribution. When this occurs, the atoms are assigned partial charges.

Consider the molecule hydrochloric acid, HCl, composed of a hydrogen atom and a chlorine atom. From periodic trends, we know that chlorine is far more electronegative than hydrogen. Therefore, we can see (in the images above) that chlorine holds a higher density of electrons.

When assigning partial charges on each atom, we follow this convention: *the less electronegative element is assigned a partial positive charge and the more electronegative element is assigned a partial negative charge*. Thus, we assign to hydrogen the partial positive charge δ^+ and to chlorine the partial negative charge δ^-.

Earlier, I introduced the concept of **ionic character** in covalent bonding. But what exactly does that mean?

Definition 2.7.11

Ionic character is a measure of the difference in electronegativity between atoms in a covalent bond.

Therefore, the *greater* the difference in electronegativities, the *higher* the percentage of ionic character in the bond.

Let's try a practice problem.

Problem 2.7.12 — Comparison of Ionic Character

Which acid molecule has more ionic character, HCl or HF? Justify your answer.

Solution: The ionic character of a molecule is correlated with the electronegativity difference between its atoms. Since both HCl and HF contain hydrogen, we only need to compare the electronegativity values of fluorine and chlorine. Using periodic trends, fluorine is more electronegative than chlorine (remember that it's also the most electronegative element on the periodic table). Therefore, the electronegativity difference between hydrogen and fluorine is greater than that of hydrogen and chlorine, which means that $\boxed{\text{HF}}$ has more ionic character.

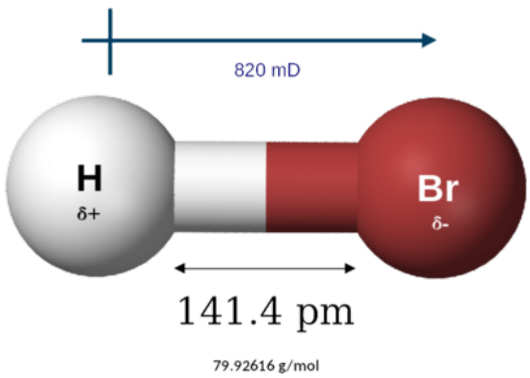
Dipole Moment

Definition 2.7.13

The **dipole moment** results from the unequal distribution of electrons in a bond or a molecule. In polar covalent compounds, electrons move towards more electronegative atoms, leading to an uneven charge distribution.

Fun Fact: The units for dipole moment are given in Debye (D).

The dipole moment is a **vector quantity**, so it has a magnitude as well as a direction.
Its direction is represented by a small arrow with its *tail* on the positive end and its *head* on the negative end.



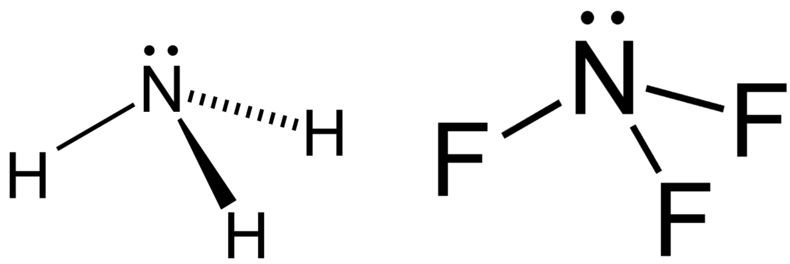
Above shows the dipole moment in the polar covalent bond of HBr. The arrow starts at the partial positive end (tail), represented by hydrogen, the less electronegative element. It continues toward the partial negative end (head), represented by bromine, which has greater electronegativity.

Dipole Moment as it Relates to Molecular Structure

In a molecule, the *net* dipole moment depends on the dipole moments of all the bonds. It is the sum of these individual dipole moments.

For example, CO_2 and H_2O are both triatomic (contain three atoms), but the former has zero net dipole moment and the latter has a net dipole moment of 1.85 D, because of its two lone pairs. They affect the overall geometry of the molecule, which is related to the net dipole moment.

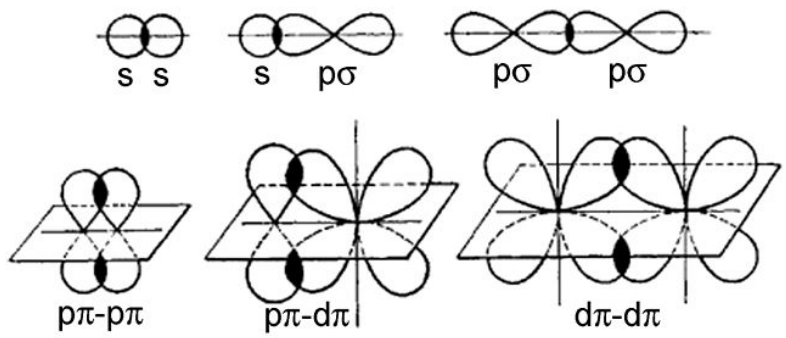
When molecules have the same number of lone pairs, it can get tricky comparing their dipole moments. For example, NH_3 and NF_3 are both trigonal pyramidal according to VSEPR Theory. However, it is found that the dipole moment of NF_3 (1.47 D) is higher than that of NH_3 (0.23 D). In each molecule, the central atom (N) has one lone pair. However, fluorine is much more electronegative than hydrogen, so the $\mathrm{N-F}$ bond is more polar than the $\mathrm{N-H}$ bond, causing the higher dipole moment in NF_3. Also, you could say that the NF_3 molecule is *more polar* than the NH_3 molecule.



Bonding: Sigma and Pi Bonds

Sigma and pi bonds are important aspects of valence bond theory and molecular orbital theory that explains the existence of double and triple bonds in certain molecules' Lewis diagrams.

- **Sigma** (σ) **bonds** form as a result of "head-to-head" overlapping of atomic orbitals.
- **Pi** (π) **bonds** form as a result of *lateral*, or "side-by-side" overlapping of atomic orbitals.



You don't really have to memorize those definitions, but you MUST be aware of the following:

1. A single bond is made up of 1 σ bond.

2. A double bond is made up of 1 σ and 1 π bond.

3. A triple bond is made up of 1 σ and 2 π bonds.

Therefore, the more pi bonds in a molecule, the greater the **bond energy** (and higher order) and the shorter the **bond length**.

Let's try this example.

Example 2.7.14

Count the number of σ and π bonds in acetylene (HCCH) and benzene (C_6H_6), shown below.

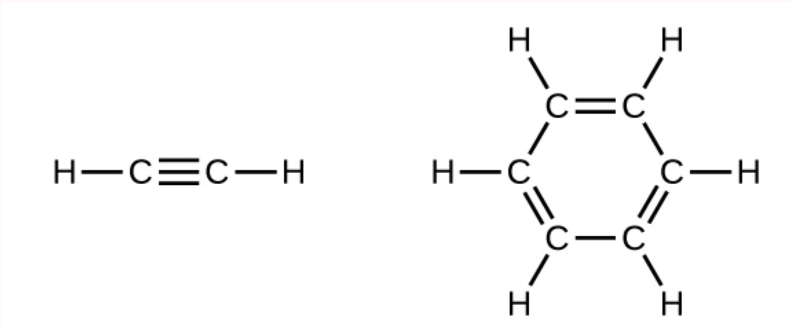


Image Courtesy of BC Open Textbooks

Solution: Let's just focus on each molecule at a time. On the left, we have HCCH (acetylene). There is 1 triple bond and 2 single bonds. The triple bond contains 1 σ and 2 π bonds, while the single bond contains only 1 σ bond. Therefore, in total, acetylene contains $\boxed{3\,\sigma \text{ and } 2\,\pi \text{ bonds}}$.
For C_6H_6 (benzene), we count 3 double bonds and 9 single bonds. Doing the math, we find that this molecule contains $\boxed{12\,\sigma \text{ and } 3\,\pi \text{ bonds}}$.

Hybridization

Ever heard of the term "hybrid" before? Essentially, it's a *blend* of two different things to create something new.

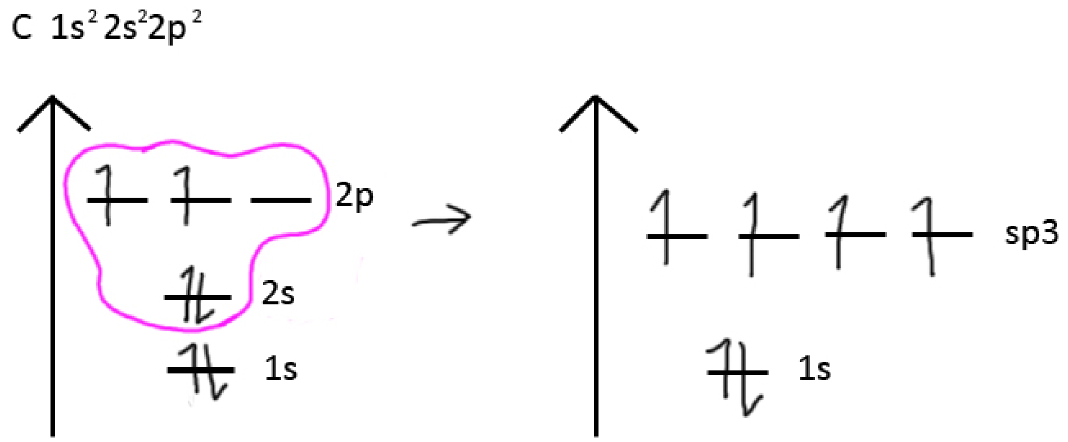
Definition 2.7.15

Hybridization is the mixing of atomic orbitals to form special orbitals for covalent bonding in molecules. Atoms respond as needed to provide the *minimum threshold energy* of the moleclue.

The reason the atoms are so responsive to achieve the process of hybridization lies in the *weakness of their orbitals.*

Example 2.7.16

In methane, CH_4, the molecular shape is tetrahedral. Carbon contains two valence orbitals in the *s* orbital and 2 in the *p* orbital. However, the two valence electrons in carbon's *p* orbital are *unpaired*. Only the 2*s* electrons are paired with each other. This would indicate that carbon can only form two bonds, but in reality we know that it forms **four**. For this reason, electron orbitals *fuse* together to fill subshells and reach a *more stable* (lower energy) state. Thus, we can count 4 sigma bonds in a CH_4 molecule.



In the above example, carbon's 2*p* and 2*s* orbitals fuse into 4 half-filled sp^3 orbitals which make 4 sp^3-orbital sigma bonds. The same principle applies to other hybridizations.

Bond Hybridization from Electron-Domain Geometry

Hybridization is based on the electron geometry of a molecule. This is where VSEPR theory becomes very useful, as we can easily determine the hybridization of the central atom in a proper Lewis diagram.

Here are the common hybridization states (the ones you will need to recognize for the AP exam):

- sp - one s and one p orbital combine to form two sp hybrid orbitals.
- sp^2 - one s and two p orbitals combine to form three sp^2 orbitals.
- sp^3 - one s and three p orbitals combine to form four sp^3 hybrid orbitals.
- dsp^3 - one s, three p, and one d orbital combine to form five dsp^3 hybrid orbitals.
- d^2sp^3 - one s, three p, and two d orbitals combine to form six d^2sp^3 orbitals.

Question: "How are sp^3 orbitals formed?"
Answer: One s and three p orbitals combine to give four sp^3 orbitals:

$$s + p_x + p_y + p_z = sp^3 + sp^3 + sp^3 + sp^3$$

You generate four sp^3 orbitals because you put in 4 orbitals to make them, i.e. you input 4 orbitals so you output 4 orbitals.

Similarly, you make three sp^2 orbitals because you put in 3 orbitals to make them:

$$s + p_x + p_y = sp^2 + sp^2 + sp^2$$

Here is a chart of electron domain geometry as it corresponds to hybridization for the *central* atom. This is precisely what College Board loves to test students on!

Electron Geometry	**Hybridization**
linear	sp
trigonal planar	sp^2
tetrahedral	sp^3
trigonal bipyramidal	dsp^3
octahedral	d^2sp^3

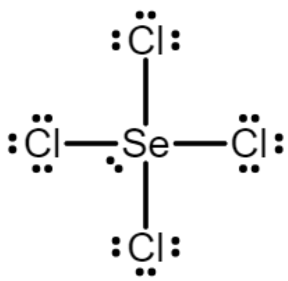
Note that electron geometry is about the overall number of electron domains surrounding the central atom, not considering the number of bonding vs. non-bonding pairs. For example, H_2O and NH_3 have different molecular geometry (bent and trigonal pyramidal, respectively), but the overall number of electron domains in both is 4, so their electron geometry is tetrahedral, and the hybridization of their central atoms is sp^3.

Let's try some problems to wrap up this section.

Problem 2.7.17 — Central Atom Hybridization I

For $SeCl_4$, find the number of electron groups and predict the hybridization of the central atom.

Solution: Here is the Lewis diagram for $SeCl_4$:

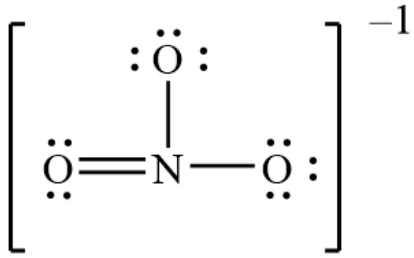


The central atom is Se, so we'll count the number of electron groups that surround it. There are four regions of bonding pairs between Se and each Cl atom, along with one lone pair on the former. This is a total of $4 + 1 = 5$ domains, so the electron geometry of $SeCl_4$ is trigonal bipyramidal and the hybridization around Se is $\boxed{dsp^3}$.

Problem 2.7.18 — Central Atom Hybridization II

For NO_3^-, find the number of electron groups and predict the hybridization of the central atom.

Solution: The central atom is N, and the Lewis diagram for NO_3^- will display resonance:



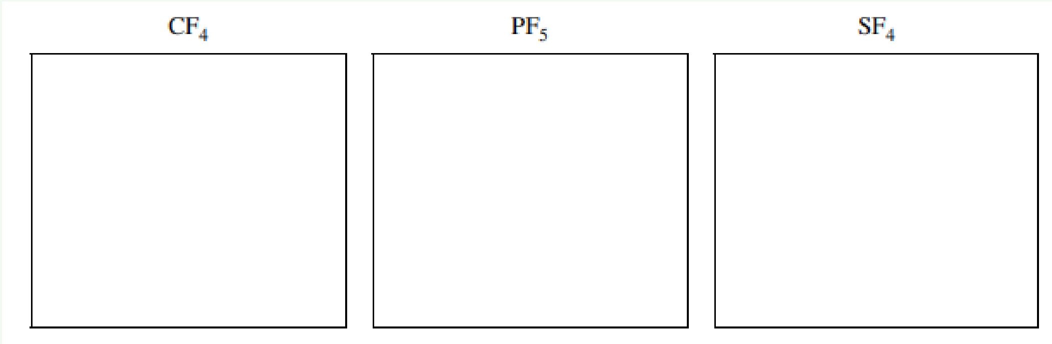
The important thing to notice here is that a double bond does **not** mean two electron groups! Regardless of the bond order, one bond always represents one electron domain. Therefore, NO_3^- has three electron domains, and the hybridization around N is $\boxed{sp^2}$.

§2.8 Practice Problems

Problem 2.8.1 — 2005 AP Chemistry FRQ

Answer the following questions that relate to chemical bonding.

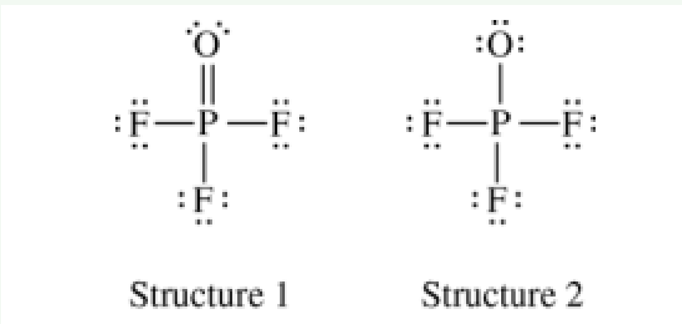
(a) In the boxes below, draw the complete Lewis structure (electron-dot diagram) for each of the three molecules represented below.



(b) On the basis of the Lewis structures drawn above, answer the following questions about the particular molecule indicated.

(i) What is the $F-C-F$ bond angle in CF_4?
(ii) What is the hybridization of the valence orbitals of P in PF_5?
(iii) What is the geometric shape formed by the atoms in SF_4?

(c) Two Lewis structures can be drawn for the OPF_3 molecule, as shown below.

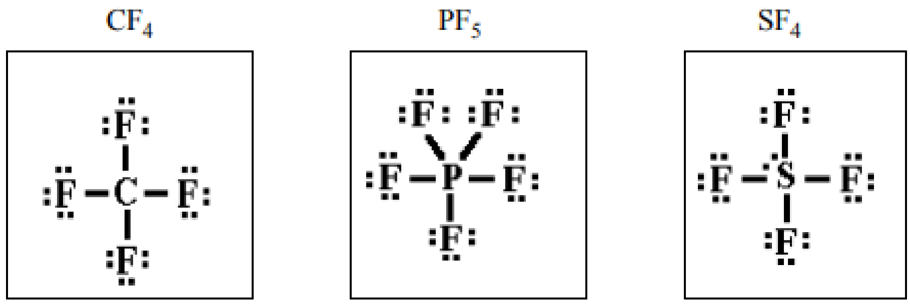


(i) How many sigma bonds and how many pi bonds are in structure 1?
(ii) Which one of the two structures best represents a molecule of OPF_3? Justify your answer in terms of formal charge.

Solution to part a: CF_4 contains $4 \cdot 1 + 4 \cdot 7 = 32$ valence electrons in total. Placing carbon in the center and recognizing that fluorine cannot form double or triple bonds, we should end up with a tetrahedral structure, where the $C-F$ bond dipoles cancel out, leaving us with a nonpolar molecule.
For PF_5, we have a total of $5 + 7 \cdot 5 = 40$ valence electrons. Placing phosphorus in the center, and drawing 5 single bonds, because P has atomic number past 14 so its octet can contain more than 8 electrons. After filling up the octets on each F atom, we should end up with a symmetrical structure, where the individual $P-F$ bonds are evenly distributed

and cancel out. PF_5 is also a nonpolar molecule.
Finally, SF_4 contains $6 + 4 \cdot 7 = 34$ valence electrons in total. At this point, you should be comfortable drawing Lewis dot diagrams, so I will skip one step here. We have 2 extra valence electrons, after placing sulfur in the center, drawing four single S-F bonds, and filling the octets for all F atoms. Therefore, we will need to attach it to sulfur, which will cause it to have a nonzero net dipole, making SF_4 a polar molecule.

Putting everything together, our boxes should resemble the following:



Solution to part b(i): Since CF_4 consists of four C − F bonds and a tetrahedral molecular geometry, VSEPR theory guarantees the bond angle between adjacent atoms (F − C − F) to be $\boxed{109.5°}$. According to the 2005 AP Chemistry Scoring Guidelines, College Board would have accepted any answer within the range of 109° to 110°.

Solution to part b(ii): This question requires us to use our knowledge of electron geometry. Since we are looking for the hybridization of the valence electrons of P in PF_5, we should count the number of electron pairs that surround this atom. We see that there are 5 electron domains, all of them are shared pairs with the F atoms. Therefore, the hybridization of the central P atom should be $\boxed{dsp^3}$.

Solution to part b(iii): This question involves molecular geometry. In SF_4, we have 5 electron domains in total, but 4 of them are bonded pairs and 1 of them is a lone pair. According to VSEPR theory, this arrangement of electrons around the central atom is called a $\boxed{\text{seesaw}}$ structure.

Solution to part c(i): In structure 1, we count three single bonds (P − F) and one double bond (P = O). We know that all sigma bonds represent one single bond, and for higher order (two and three) bonds, the first bond is sigma and the remaining are pi. Therefore, for the three single bonds, we have three sigma bonds and for the double bond, we have one sigma and one pi bond. This leads us to a total of $\boxed{4\ \sigma \text{ bonds and } 1\ \pi \text{ bond}}$.

Solution to part c(ii): Since we are asked to pick the best representation of a molecule, we should choose the structure that minimizes formal charge, i.e. zero formal charge on as many elements as possible as well as the most electronegative atom having the negative formal charge.

Recall that we can calculate formal charge by the following trick:

$$\text{valence electrons} - \text{number of dots} - \text{number of lines}$$

Let's do this for structure and then decide which one is a better representation of the OPF_3 molecule.

For Structure 1:

- P: $5 - 0 - 5 = 0$
- F: $7 - 6 - 1 = 0$
- O: $6 - 4 - 2 = 0$

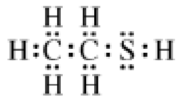
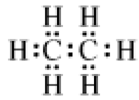
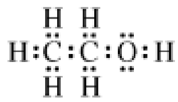
For Structure 2:

- P: $5 - 0 - 4 = 1$
- F: $7 - 6 - 1 = 0$
- O: $6 - 6 - 1 = -1$

After comparing the formal charges on the atoms for each structure, we can conclude that $\boxed{\text{Structure 1}}$ best represents a molecule of OPF_3, because all of its atoms have a formal charge of zero.

Problem 2.8.2 — 2010 AP Chemistry FRQ (Excerpt)

Use the information in the table below to respond to the statements and questions that follow. Your answers should be in terms of principles of molecular structure.

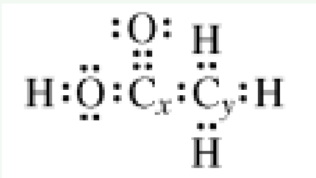
Compound	Formula	Lewis Electron-Dot Diagram
Ethanethiol	CH_3CH_2SH	
Ethane	CH_3CH_3	
Ethanol	CH_3CH_2OH	
Ethyne	C_2H_2	

(a) Draw the complete Lewis electron-dot diagram for ethyne in the appropriate cell in the table above.

(b) Which of the four molecules contains the shortest C − C bond? Explain.

(c) A Lewis electron-dot diagram of a molecule of ethanoic acid is given below. The carbon atoms in the molecule are labeled x and y, respectively.

Identify the geometry of the arrangement of atoms bonded to each of the following.



(i) Carbon x
(ii) Carbon y

Solution to part a: Ethyne, C_2H_2 contains $2 \cdot 4 + 2 \cdot 1 = 10$ valence electrons in total. Since carbon generally goes in the center, but we have two of them, our Lewis diagram will begin with something like this: H − C − C − H, and adjust as needed.

When the Lewis diagram is in the form H − C − C − H, we have already used up

6 valence electrons (2 electrons for each of 3 bonded pairs, represented by a dash), so we only have four electrons left. Hydrogen has its octets filled completely; it only requires 2 electrons. However, each of the carbon atoms require 8, so we will need to add lone pairs to satisfy this. On the left carbon atom, we can complete its octet by adding two lone pairs of electrons (each pair = two dots), but we have run out of electrons now! How will we fill the octet for the other carbon atom? In order to do this, we can have carbon share two pairs of electrons with each hydrogen, leading to the formation of triple bonds. Once this is done, we can be sure that the constraints for number of valence electrons have been satisfied.

$$\boxed{\mathrm{H} - \mathrm{C} \equiv \mathrm{C} - \mathrm{H}}$$

Solution to part b: Since we are given the Lewis diagrams for each molecule and our task at hand is to pick the molecule with the shortest C − C bond, we should think about bond order, as it has a direct correlation with bond length. In fact, as bond order increases, so does bond energy, so the electrons are pulled inward to each other with greater intensity, causing a shorter bond length. Therefore, the shortest C − C bond should be associated with the molecule with the largest C − C bond order. If you're thinking about $\boxed{\text{ethyne}}$, this is the correct answer. It has the shortest C − C bond because it is a triple bond. The other molecules have single C − C bonds, and triple bonds are shorter than single bonds.

Solution to part c(i): Many students get confused on these types of questions because in this case, a C_x atom is bonded to two oxygen atoms as well as one C_y atom. This causes students to question whether this arrangement of atoms is polar or nonpolar. However, it actually does not matter whatsoever. You only need basic knowledge of VSEPR theory to answer this question. Notice how in each of the $C_x = O$, $C_x - O$, and $C_x - C_y$ bonds, there are only shared pairs of electrons, i.e. no lone pairs. More specifically, this arrangement of atoms contains 3 bonded pairs and 0 non-bonded pairs of electrons. This is consistent with $\boxed{\text{trigonal planar}}$ geometry, which is the answer.

Solution to part c(ii): The C_y atom is bonded to four different atoms, specifically three hydrogen atoms as well as one C_x atom. Four electron domains refers to $\boxed{\text{tetrahedral}}$ geometry by VSEPR theory, and you could write this and earn full credit. However, you could also state that this arrangement of atoms has $\boxed{\text{trigonal pyramidal}}$ structure, if you were to account for potential electron repulsions in space.

Problem 2.8.3 — 2014 AP Chemistry FRQ

Nonmetal	C	N	O	Ne	Si	P	S	Ar
Formula	CF_4	NF_3	OF_2	None	SiF_4	PF_3	SF_2	None

Some binary compounds that form between fluorine and various nonmetals are listed in the table above. A student examines the data in the table and poses the following hypothesis: the number of F atoms that will bond to a nonmetal is always equal to 8 minus the number of valence electrons in the nonmetal atom.

(a) Based on the student's hypothesis, what should be the formula of the compound that forms between chlorine and fluorine?

(b) In an attempt to verify the hypothesis, the student researches the fluoride compounds of the other halogens and finds the formula ClF_3. In the box below, draw a complete Lewis electron-dot diagram for a molecule of ClF_3.

(c) Two possible geometric shapes for the ClF_3 molecule are trigonal planar and T-shaped. The student does some research and learns that the molecule has a dipole moment. Which of the two shapes is consistent with the fact that the ClF_3 molecule has a dipole moment? Justify your answer in terms of bond polarity and molecular structure.

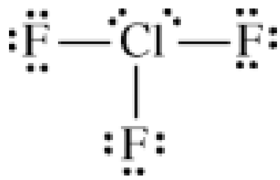
In an attempt to resolve the existence of the ClF_3 molecule with the hypothesis stated above, the student researches the compounds that form between halogens and fluorine, and assembles the following list:

Halogen	Formula of Compound
F	F_2
Cl	
Br	BrF, BrF_3, BrF_5
I	IF, IF_3, IF_5, IF_7

(d) Based on concepts of atomic structure and periodicity, propose a modification to the student's previous hypothesis to account for the compounds that form between halogens and fluorine.

Solution to part a: According to the student's hypothesis, 1 F atom will bond with chlorine because Cl contains 7 valence electrons and $8 - 7 = 1$.
Thus, the formula of the compound that forms between chlorine and fluorine is $\boxed{\text{ClF}}$.

Solution to part b: Fluorine can never be in the center of a Lewis diagram because it is the most electronegative element. Additionally, there are 3 F atoms and 1 Cl atom in the ClF_3 molecule, so it only makes sense to place Cl in the center. It should be surrounded by three bonding pairs with F atoms. F must have three three lone pairs each to fill up their octets. Note that electron pairs can be represented as either dots or line segments.



Solution to part c: This question requires our knowledge of VSEPR theory. We need to consider the electron domains for trigonal planar as well as T-shaped geometry. This will allow us to determine which of these shapes is consistent with the fact that ClF_3 has a dipole moment.

Trigonal planar geometry is associated with 3 bonding pairs and 0 lone pairs of electrons on the central atom. If ClF_3 was trigonal planar, then the dipoles formed by the three $Cl-F$ bonds will cancel, resulting in a nonpolar molecule (symmetric charge distribution) with net dipole moment of zero.

Meanwhile, T-shaped geometry is associated with 3 bonding pairs and 2 lone pairs of electrons on the central atom. If ClF_3 was T-shaped, then the dipoles formed by the three bonding pairs will cancel. However, the two dipoles caused by the lone pairs would not cancel, resulting in a polar molecule (asymmetric charge distribution) with a nonzero net dipole moment. Therefore, ClF_3 being $\boxed{\text{T-shaped}}$ would be consistent with the observation that it has a dipole moment.

Solution to part d: Note that for each halogen including fluorine itself, there is an odd number of F atoms bonded to it. This observation fits the criteria of atomic structure. To meet the criteria for periodicity, we need to describe a pattern between these halogens and the number of surrounding F atoms. If you look at your periodic table, you will notice that the halogens in increasing atomic number are given by $F < Cl < Br < I$. Additionally, we see a general trend of the number of F atoms bonded to halogens increasing as we travel further down this group on the periodic table. Therefore, the periodicity aspect of our explanation can include that as the atomic number of the central halogen atom *increases*, the number of bonded F atoms *increases*.

Problem 2.8.4 — 2015 AP Chemistry FRQ (Excerpt)

Compound	**Melting Point** (°C)
LiI	449
KI	686
LiF	845
NaF	993

A student learns that ionic compounds have significant covalent character when a cation has a polarizing effect on a large anion. As a result, the student hypothesizes that salts composed of small cations and large anions should have relatively low melting points.

(a) Select two compounds from the table and explain how the data support the student's hypothesis.

Solution: For any ionic compound that is chosen, we can compare the relative sizes of the other anion or cation component and thus explain why the overall size of the compound is related to its melting point.

We have three possibilities (in pairs): LiI and KI, LiI and LiF, and LiI and NaF. I will pick the third pair since it is more complex than the first two. I encourage you to analyze them for yourself.

LiI is composed of Li^+ and I^- ions, held together by electrostatic forces. Similarly, NaF consists of Na^+ and F^-. Let's compare the sizes of the cations and anions. The Li^+ ion is smaller than the Na^+ ion, because it has fewer occupied electron shells. Also, the I^- ion is larger than the F^- ion. This is consistent with the student's hypothesis: LiI has a small cation and a large anion while NaF has a relatively small cation and a small anion. As a result, LiI consists of much weaker ionic bonds than NaF, and therefore has the <u>lower</u> melting point.

3 Intermolecular Forces and Properties

Let's talk about matter for a bit. You probably know that liquids and solids are incompressible and have a fixed density (does not change with temperature). The reason for all these similarities are caused by molecules existing in close proximity, unlike gases. Now, you're probably wondering, "What keeps these molecules close together or far apart?" The answer is intermolecular forces! The concepts in this unit represent $18-22\%$ of the AP Chemistry exam, so let's dive right in.

§3.1 Intermolecular Forces

Definition 3.1.1

Intermolecular forces are interactions between two different molecules.

Recall from Unit 2 that we discussed *intramolecular* forces.

Question: How can we avoid confusing the two?
Answer: The best way to remember the difference is to know that *inter* means *between*, while *intra* means *within*.

The following image should clear things up.

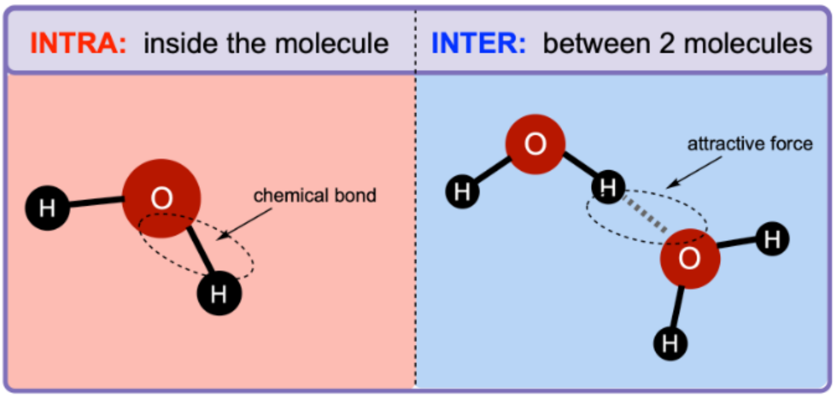


Image Courtesy of Clutch Prep

In conclusion, intermolecular forces hold **molecules** together, while intramolecular forces hold **atoms within a molecule** together.

Now that we know what intermolecular forces (IMFs) are, we can classify them into set categories. The College Board requires us to know *four* types of IMFs and understand their relative strengths.

- London Dispersion Forces (LDFs)
- Dipole-Dipole Interactions
- Hydrogen Bonding

- Ion-Dipole Interactions

Now that you know how to describe IMFs in a molecule, we'll cover the different types.

London Dispersion Forces

- ALL covalent compounds experience LDFs between their molecules.
- These forces represent the weakest form of intermolecular attraction between molecules.

Although LDFs are present in all covalent compounds, it is best used to explain various differences in chemical properties between *nonpolar molecules*, especially diatomic elements. For example, some nonpolar molecules are liquids at room temperature, while others are solids or gases. Even noble gases can be liquefied or solidified at low temperatures, high pressures, or both.

German physicist Fritz London proposed the defining idea in 1930: temporary fluctuations in the electron distributions within atoms and nonpolar molecules could result in the formation of *short-lived instantaneous dipole moments*, which produce attractive forces.

Named after him, these are called London dispersion forces.

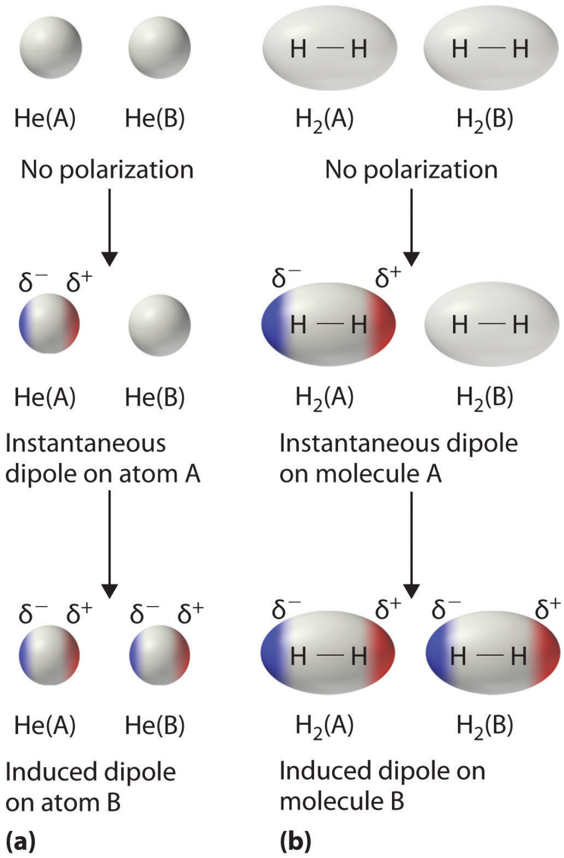


Image Courtesy of Chemistry LibreTexts

The strength of LDFs increases as the size of a molecule increases. This is because more electrons increase the probability of stronger instantaneous dipoles in a **more polarizable electron cloud**.

> **Definition 3.1.2**
> **Polarizability** is the ease by which an electron cloud can be distorted to produce an uneven charge distribution or dipole moment.

The concept discussed in the last paragraph is a very important piece of information that is typically asked on the AP exam. The more electrons there are, the greater the size of the electron cloud, and the more polarizable it is! This makes it more likely for there to be a temporary dipole.

Dipole-Dipole Interactions

While LDFs are significant in nonpolar molecules and atoms due to temporarily induced dipoles, **dipole-dipole attractions** occur between the opposite *partial charges* that exist on opposite ends of a dipole. Additionally, these forces result from permanent dipoles. As a result, dipole-dipole attractions only occur in a sample of *polar* molecules and are slightly stronger than LDFs.

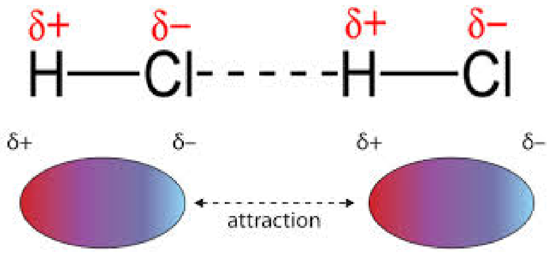


Image Courtesy of EMedicalPrep

As you decrease the distance between two dipoles, you strengthen the interaction (Coulomb's Law, once again). It's also important to remember that with **polar molecules**, the more electronegative element is assigned the partial negative charge, and vice versa. This also means that the more polar the molecules, the greater the attraction.

Hydrogen Bonding

Hydrogen bonding is probably the most popular type of intermolecular forces, and most students just love it! Usually, it's the easiest to identify and the strongest in pure substances, so it tends to stick with many students.

Definition 3.1.3

Hydrogen bonding is NOT actual bonding. It's actually a very strong type of dipole-dipole attraction that occurs when hydrogen is directly bonded to F, O, or N in a molecule.

It occurs between these molecules because of the *high polarity caused by large difference in electronegativity* and small sizes, leading to very strong attractions.

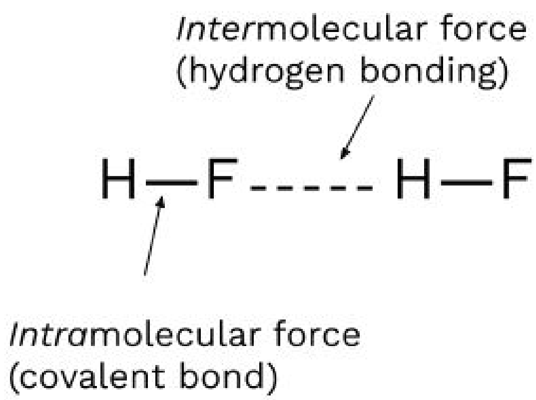
Note 3.1.4

Remember that hydrogen bonding occurs ONLY among polar molecules, since it is a special case of dipole-dipole attraction.

The hydrogen bonded to the F, O, or N is partially positively charged and is attracted to the neighboring unshared, or lone, electrons on the F, O, or N.

An example of a molecule that has hydrogen bonding is water, which explains why it takes so long for it to boil (We will talk about boiling points, melting points, and vapor pressure soon!). The energy input for breaking the intermolecular forces between water molecules when boiling is relatively high.

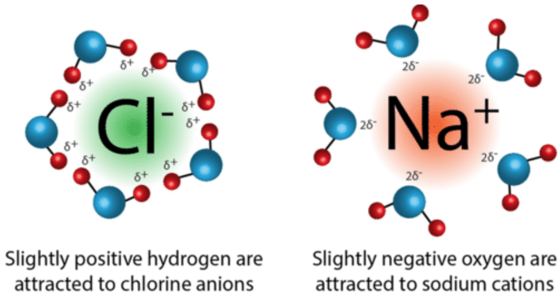
Before we move on to the next (and final) category of IMFs, let us clear up the misconception between intramolecular and intermolecular forces one last time. The image below should do just fine.



Ion-Dipole Interactions

Ion-dipole attractions only occur in a mixture of an ionic compound and polar molecules. These attractions occur when the cations (positively charged) and anions (negatively charged) are (respectively) attracted to the negative and positive ends of a dipole.

Important! Overall, this type of intermolecular attraction is stronger than both dipole-dipole and hydrogen bonding. Many students often assume that hydrogen bonding is the strongest and forget about ion-dipole interactions.



Consider a sample of NaCl dissolved in distilled water. Once the NaCl dissolves, it separates into its cation Na^+ and anion Cl^-. Meanwhile, the partial positive end of the water molecule (hydrogen) is attracted to the negatively charged chloride ion, while the partial negative end (oxygen) is attracted to the positively charged sodium ion.

Breaking it down further, this unequal distribution of electrons in water (a polar molecule) results in partial positive and negative charges, or a dipole. The charges produced in this dipole can then attract the Na^+ and Cl^- once the ionic compound dissolves.

Physical Properties and IMF Strength

The phase of a substance is directly related to the strength of its intermolecular forces. Solids have highly ordered structures where the atoms are tightly packed together, whereas gases have atoms spread so far apart that most of the volume consists of free space.

In terms of this unit, substances that exhibit weak intermolecular forces (such as London dispersion forces) tend to be gases at room temperature. Common examples are nitrogen (N_2) and oxygen (O_2). Meanwhile, substances that exhibit strong intermolecular forces (such as hydrogen bonds) tend to be liquids at room temperature, and the epitome of this concept is water.

An exception, ionic substances do not experience intermolecular forces. Instead, their phase is determined by the ionic bond holding the ions together in the lattice. Because the ionic bonds are significantly stronger than intermolecular forces in covalent molecules (in most cases), ionic substances are generally solid at temperature.

The most important physical properties related to the strength of intermolecular forces for a substance are melting/boiling point and vapor pressure.

Ionic substances are generally solids at room temperature, and melting them into liquid form requires the bonds holding the lattice together to be broken. The amount of energy needed for this to occur is based on the Coulombic attraction between the molecules.

Meanwhile, covalent substances, generally liquid at room temperature, will boil when the intermolecular forces between them are broken. For molecules with similar sizes, use the following ranking of intermolecular forces (from strongest to weakest). This will help you determine the relative strength of the IMFs (and thus relative boiling points) for the molecules.

1. **Hydrogen bonds**
2. Non-hydrogen bond permanent dipoles (**dipole-dipole interactions**)
3. **London dispersion forces** (instantaneous dipoles)
   - Larger molecules are more polarizable and have stronger LDFs because their electron cloud is more expanded.

Also, the melting and boiling points of covalent substances are almost always lower than those of ionic ones. There are some exceptions, but you don't need to worry about them. Finally, metallic bonding tends to be very strong and thus metals (particularly the transition metals) tend to have very high melting points. Network covalent bonding is the strongest type of bonding to exist, and it is very difficult to cause substances governed by this chemical bonding to melt.

Beyond the relative melting and boiling points of covalent substances, the relative IMF strength can also indicate other properties, of which we will focus on **vapor pressure**. This concept arises from the fact that the molecules inside a liquid are in constant motion. If they coincide with the surface of the liquid with sufficient kinetic energy, then they can overcome the intermolecular forces that hold them to the other molecules and *vaporize*, or enter the gas phase. Be very careful that you do **not** confuse vaporization with boiling: when a liquid boils, heat energy is added, increasing the kinetic energy of all molecules in the liquid until the intermolecular forces are fully overcome. In the case of vaporization, no external input of heat energy is required. Also, there is a direct correlation between temperature and vapor pressure: at high temperatures, molecules are moving *faster* and are *more* likely to escape the liquid phase and enter the gas phase.

If two liquids are in the same temperature, then the vapor pressures can be compared by observing the primary intermolecular forces present within each liquid. The stronger the intermolecular forces in a liquid, the *less* likely it is that molecules will escape the liquid phase, and the *lower* the vapor pressure will be.

§3.2 Properties of Solids

In elementary school, you learn that the 3 states of matter are solid, liquid, and gas. But what exactly do these three terms mean? We will discuss solids for this section, and we will study about liquids and gases in section 3.3.

Definition 3.2.1

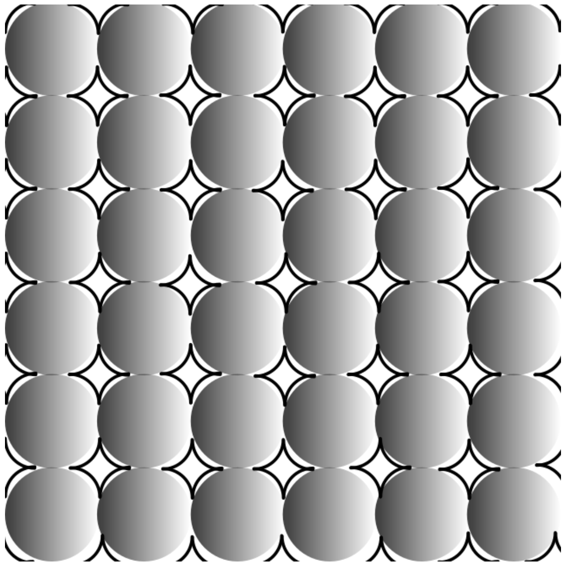
A **solid** is a *state* of matter that is nearly impossible to compress, containing well-defined shapes.

Generally, we must know the following properties of solids:

- Strong interactions between individual particles, holding them in a crystalline structure. This is why you can't walk through a wall!
- Defined shape and volume, e.g. we can classify the shape of ice cubes.
- Regular and crystalline structure, e.g. diamond and graphite are pure carbon solids.

- Fixed arrangement of particles.
- Vibrational (very little) degree of freedom; particles have very little space to move.

Here is a picture that demonstrate the properties of solids:



There are four main types of solids that we will discuss.

- Ionic solids, e.g. table salt (NaCl).
- Molecular solids, e.g. ice, solid H_2O
- Metallic solids, e.g. wire or metal bricks, literally.
- Covalent network solids, e.g. diamond or graphite.

Ionic Solids

These solids are formed by cations (+ charged) and anions (− charged) surrounding each other (opposite charges attract). Ionic solids have varying shapes, and these shapes are held together by lattice energy. Because these interactions are quite strong, ionic solids tend to have higher melting points.

Note 3.2.2

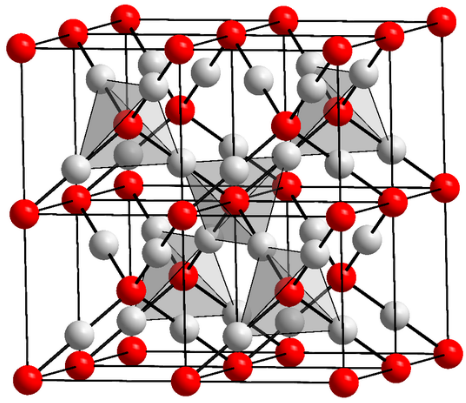
If we think in terms of Coulomb's law, the key trend to note here is that *attractions become stronger as the charges increase and/or the ionic sizes decrease.*

Finally, you are required to know these properties.

1. The presence of both attractive and repulsive interactions helps to explain why ionic compounds are **brittle**.
2. Ionic solids can be thought of as a **crystal lattice** of ions that interact through attractive and repulsive forces.

3. When ionic solids are melted or placed in a solution (liquid and aqueous phases, respectively), they are **great conductors of electricity**. This is because the ions are mobile and can facilitate the flow of electrical charge.

4. Ionic solids possess ions at the **lattice points** of the solid structure.



Molecular Solids

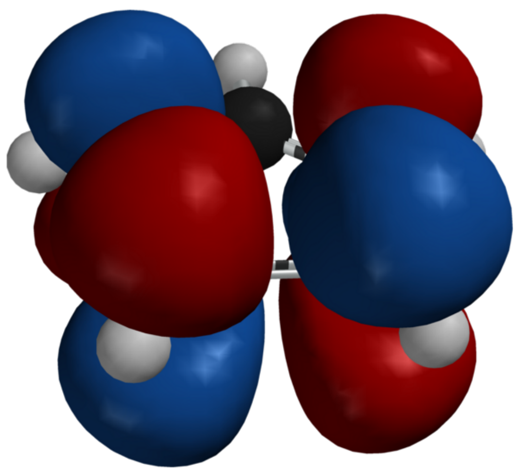
Molecular solids are held together by weak *intermolecular* forces. For example, the dipole-dipole forces in solid H_2O are relatively weak compared to other forms of IMFs. However, they are held together by strong *intramolecular* forces.

Here are some of the most important properties of molecular solids.

1. **Low melting and boiling points** - The intermolecular forces that hold molecular solids together are weak, so they have relatively low melting and boiling points. Some examples of molecular solids are ice (solid H_2O) and glucose (a monosaccharide).

2. **Brittle and hard** - Molecular solids tend to be brittle (easily broken) and hard, because their weak intermolecular forces can be easily overcome.

3. **Poor conductors of heat and electricity** - Molecular solids do not have a metallic structure with free electrons that can flow through the solid. Their valence electrons are held very tightly by the covalent bonds.

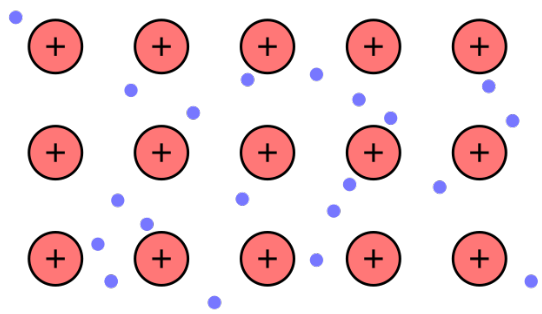


Metallic Solids

Metallic solids, e.g. aluminum foil, are held together by strong bonds between metal ions. This leads to a "sea of electrons" (delocalized) in which they are free to permeate across the entire metal.

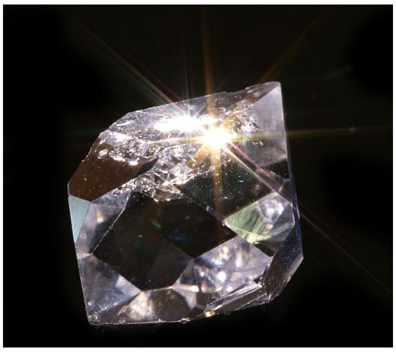
Because of the delocalization of valence electrons, metallic substances have very unique properties.

1. **Good conductors of electricity** - In the "sea," the valence electrons are mobile, capable of moving electric charge across the metal. This leads to them being good conductors of electricity.
2. **High melting and boiling points** - The metal ions and the delocalized electrons interact through very strong metal bonds, so these solids are very difficult to break.
3. **Shiny appearances** - The delocalized electrons in metallic solids have a tendency to reflect off light.
4. **Malleability and ductility** - *Malleability* is the property of metal associated with the ability to be hammered into a thin sheet without breaking. Meanwhile, *ductility* is the property associated with being stretched into a wire without breaking. The fact that metallic solids have high melting/boiling points and are good conductors of electricity provides the reasons for these properties.



Covalent Network Solids

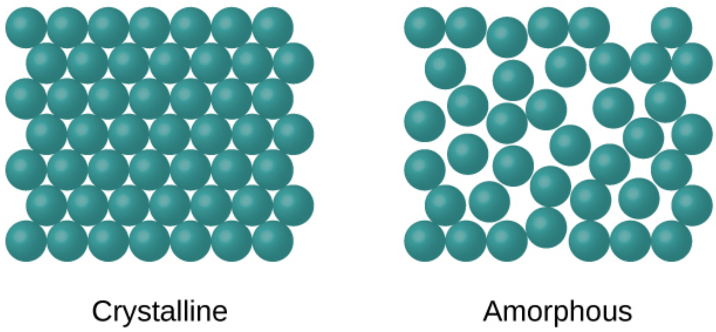
Covalent network solids, e.g. diamond and silica, are composed of atoms covalently bonded together into a three-dimensional network or layers of two-dimensional networks. Although they experience weak IMFs, their strong covalent bonds (high electronegativity difference between atoms) allow for higher melting points.



Crystalline vs. Amorphous Solids

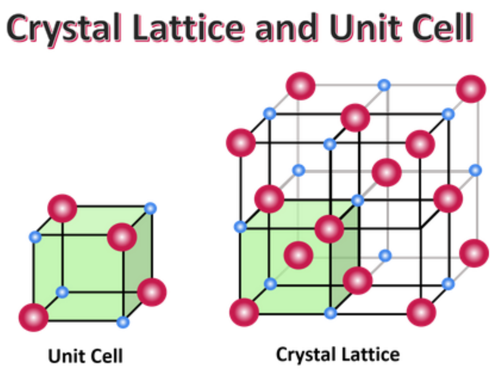
Generally, solids contain diverse arrangements and geometric patterns. They can be placed into two major categories: **crystalline** and **amorphous**.

Crystalline solids include all of the different solids that the College Board requires us to know: ionic solids, covalent network solids, molecular solids, and metallic solids. In crystalline solids, particles are arranged in regular repeating patterns. They also have a fixed melting point and are typically more ductile/less brittle than amorphous solids.



Structure of Crystalline Solids

The geometric arrangement of particles in a crystalline solid is referred to as a **crystal lattice**. These are composed of **unit cells**, or the smallest repeating units that define a crystalline solid.



Note: You don't need to know what a unit cell means, but the above image represents the "hierarchy" of structures in a crystalline solid.

Amorphous solids, however, do not have a long-range, periodic crystal structure. In simple terms, they are irregular, with considerable disorder in their arrangements. This is because they tend to cool very quickly.

These solids represent their own category and *will not* be studied in-depth in AP Chemistry. However, some examples of amorphous solids are gum, glass, and rubber.

This concludes our discussion on solids. In the next section, we will focus more on liquids and gases, the other two important states of matter.

§3.3 Solids, Liquids, and Gases

Recall that **matter** is any physical object that has mass and occupies space. Matter can be classified by its *state*, or its composition (the atoms and/or molecules that compose it. Let's look over the characteristic properties of the states of matter:

Solids

In section 3.2, we learned that **solids** can be either crystalline or amorphous: crystalline solids have a defined structure and 3D order, while amorphous solids have considerable disorder within their structure.

Regardless of the type, all solids retain their own unique shape and volume. They cannot expand and fill up a container holding them because the particles are packed closely and cannot move, due to the high intermolecular forces between them.

In other words, solids are virtually incompressible, cannot flow, and are extremely slow in the diffusion process. **Compressibility** is the measure of how much a material can be squeezed, or the change in volume that occurs when pressure is applied.

Liquids

Liquids are substances that assume the shape of a portion of the container that occupies them. However, they DO NOT expand to fill the container.

Unlike solids, liquid particles are not packed tightly together, so they can flow (this property is known as **fluidity**). The intermolecular forces are strong enough to keep the particles in close proximity, but not strong enough to hold them in place.

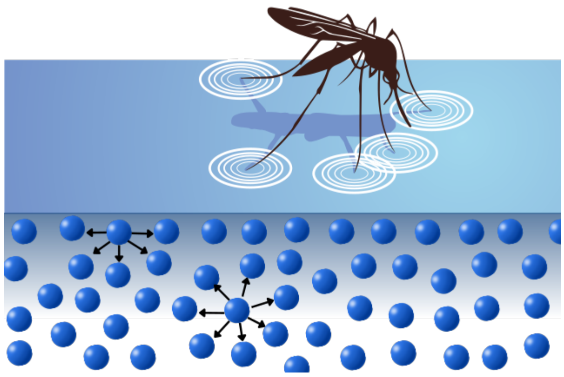
However, liquids are also virtually incompressible, just like solids, and the diffusion process occurs slowly. The only difference is that they flow more easily.

Note 3.3.1

The solid and liquid phases of a substance typically have similar molar masses as the particles are held together. This fact can come in handy when we get to calculations and applying the law of conservation of matter.

Surface Tension

In chemistry, liquids prefer environments where they can minimize their surface area. This is because of an imbalance of intermolecular forces that is caused by an inward force experienced by molecules on the surface of a liquid.



The important idea is that the interior liquid molecules are attracted to particles in all cardinal directions, i.e. the intermolecular forces against particles "cancel" out. However, the molecules at the surface of the liquid experience attraction in lateral and downward directions. This causes the surface molecules to be less stable, so liquids strive to arrange in ways that effectively reduce their surface area.

Example 3.3.2

Whenever you turn on a faucet at low pressure, water particles form a spherical shape to minimize their surface area.

Image Courtesy of Gizmodo

There are two trends related to surface tension that you should be aware of:

- The stronger the intermolecular forces experienced by the molecules, the higher the surface tension. This is because surface molecules resist penetration (or mixing with the interior molecules), and as a result surface area increases.
- The higher the temperature, the lower the surface tension. This is because, at high temperatures, the surfaces of liquid particles are easier to stretch.

Capillary Action

Capillary action is the spontaneous rising of a liquid against gravity. This is most common in polar liquids with strong IMFs (dipole-dipole interactions, hydrogen bonding). For example, if you put a piece of paper in water, you will see that the water will slowly rise up the paper due to capillary action.

There are two classes of forces involved in capillary action:

- **Cohesive forces**: forces between liquid molecules that hold the liquid in shape.
- **Adhesive forces**: forces between liquid molecules and the container.

Capillary action works due to a combination of these two forces! Adhesive forces pull the surface molecules up while cohesive forces pull the bulk, or interior molecules, along with it.

On the other hand, the **meniscus** is created due to the competition between these two forces. When performing experiments, you will become more familiar with the meniscus. For example, the meniscus of water is *concave* because the adhesive forces are **stronger** than the cohesive forces, so water is more strongly attracted to the container than itself. Meanwhile, mercury in a glass container leads to an upside-down meniscus, which is called a *convex* meniscus. This happens because the forces between mercury molecules are stronger than the forces between them and the glass.

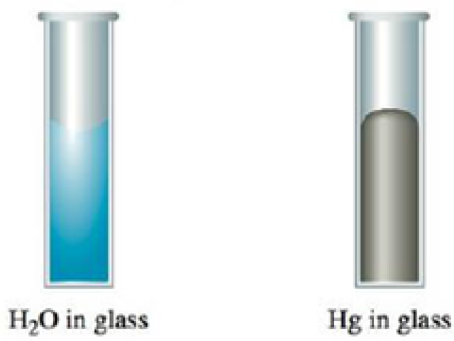


Image Courtesy of Bartelby

Viscosity

Viscosity is a measure of a liquid's resistance to flow.

The general trend you need to know is that the higher the viscosity, the thicker the liquid. Additionally, the higher the temperature, the lower its viscosity. You will be able to understand this more easily if you think of temperature in terms of motion and a means to overcome intermolecular forces.

Gases

Gases assume the shape and volume of their container. They move rapidly in straight lines. We will talk more about their behavior in later sections of this unit.

For now, just know that gas molecules have enough kinetic energy to overcome any intermolecular forces that exist, therefore allowing them to move freely. Unlike solids and liquids, they are compressible, and they flow readily and expand to fill the container. Diffusion within a gas occurs almost spontaneously (quite rapidly).

Density

Density measures how compact a substance is. It is the ratio of the substance's mass to volume.

$$\boxed{D = \frac{m}{V}}$$

Since solid particles are tightly packed, their overall particle volume is smaller, and gas particles move freely and occupy much more volume, solids are the most dense and gases are the least dense of all three phases of matter.

Let's try an AP-style practice problem.

Problem 3.3.3 — Density Practice

A student measured the mass of a sealed 644 mL flash that contained air. The student then flushed the flask with an unknown gas, resealed it, then measured the mass again. Both the air and the unknown gas were at STP. Calculate the mass of the unknown gas. At STP, the density of air is 1.29 g/L.

$$\text{Volume of sealed flask} = 644\,\text{mL}$$

$$\text{Mass of sealed flask and air} = 121.03\,\text{g}$$

$$\text{Mass of sealed flask and unknown gas} = 122.60\,\text{g}$$

Solution: For now, don't worry about STP. We will learn what that is in the next section.

The first step in solving this problem is to determine the mass of the air. Since we are given the density of air and the flask's volume, we can determine the said mass. However, the problem has given the density in g/L, and our volume is in mL, so we will have to convert units accordingly.

$$V = 644\,\cancel{\text{mL}} \cdot \frac{1\,\text{L}}{1000\,\cancel{\text{mL}}} = 0.644\,\text{L}$$

Now, we can use $D = \frac{m}{V}$ and solve for the mass of air:

$$m = D \cdot V = 1.29 \text{ g}/\cancel{\text{L}} \cdot 0.644 \cancel{\text{L}} = 0.831 \text{ g}$$

Next, we need to find the mass of the flask. Since we now know the mass of both the air and the flask, we can subtract the mass of air to find the mass of just the sealed flask.

$$121.03 \text{ g} - 0.831 \text{ g} = 120.20 \text{ g}$$

Finally, we can determine the mass of the unknown gas by subtracting the mass of the sealed flask alone from the mass of both the sealed flask and the unknown gas.

$$122.60 \text{ g} - 120.20 \text{ g} = \boxed{2.40 \text{ g}}$$

§3.4 Ideal Gas Law

The Ideal Gas Law relates the macroscopic properties—those that are visible either to the human eye or under a microscope—of a gas. These properties are referred to as pressure, volume, temperature, and amount of gas.

When describing the variables that affect gas behavior, we use the Ideal Gas Law:

$$PV = nRT$$

where:

- P: Pressure, the forces exerted by gas particles on the interior surface area of the container through collisions,
- V: Volume, the amount of space occupied by the gas particles; the volume of the container holding the particles in place,
- n: Number of moles of gas particles,
- R: Ideal Gas Law constant, relates the other four quantities, and
- T: Temperature, measures the average kinetic energy of the gas molecules, in units of Kelvins (K).

From the Ideal Gas Law, we can make a number of generalizations relating some variables given that the others are held constant.

Definition 3.4.1

Boyle's Law states that at constant temperature, the pressure of a gas and the volume it occupies are inversely proportional. That is,

$$PV = k, \text{ for some constant } k$$

For pressures and volumes at times t_1 and t_2,

$$P_1V_1 = P_2V_2$$

Problem 3.4.2 — Boyle's Law

Sulfur dioxide (SO_2), a gas that plays a central role in the formation of acid rain, is found in the exhaust of automobiles and power plants. Consider a 1.34-L sample of gaseous SO_2 at a pressure of $4.3 \cdot 10^3$ Pa. If the pressure is changed to $8.6 \cdot 10^3$ Pa at constant temperature, what will the new volume of SO_2 be?

Solution: Since the temperature remains constant during the change, the pressure and volume of SO_2 must be inversely proportional, with respect to the Ideal Gas Law.
We proceed with Boyle's Law.

$$P_1V_1 = P_2V_2$$

Rearranging, we have

$$V_2 = \frac{P_1V_1}{P_2} = \frac{(4.3 \cdot 10^3\,\cancel{\text{Pa}})(1.34\,\text{L})}{(8.6 \cdot 10^3\,\cancel{\text{Pa}})} = \boxed{0.67\,\text{L}}$$

Definition 3.4.3

Charles's Law states that gases tend to expand linearly relative to their Kelvin temperature as they are heated at constant pressure. That is,

$$V = kT, \text{ for some constant } k$$

For volumes and temperatures at times t_1 and t_2,

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

Problem 3.4.4 — Charles's Law

A sample of gas at 14°C and 1 atm has a volume of 1.94 L. What volume will this gas occupy at 43°C and 1 atm?

Solution: Since pressure remains constant as the gas is heated, the volume changes with temperature linearly.

Watch Out! T represents the temperature in KELVINS. However, we are given the CELSIUS temperature. We must add 273 to convert from °C to K or else we will get an incorrect result.

$$T_1 = 14°\text{C} + 273 = 287\,\text{K} \quad \text{and} \quad T_2 = 43°\text{C} + 273 = 316\,\text{K}$$

Now that we are in Kelvins, we can proceed by the following.

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

Rearranging, we have

$$V_2 = \frac{V_1T_2}{T_1} = \frac{(1.94\,\text{L})(316\,\cancel{\text{K}})}{(287\,\cancel{\text{K}})} = \boxed{2.14\,\text{L}}$$

Definition 3.4.5

Gay-Lussac's Law states that the pressure of a given amount of gas held at constant volume is directly proportional to the Kelvin temperature. The relevant equation for this law is

$$P = kT, \text{ for some constant } k$$

At times t_1 and t_2, the representation is

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

Note 3.4.6

Gay-Lussac's Law isn't really that important for the AP exam, but it is important for the last generalization of the Ideal Gas Law that follows.

Definition 3.4.7

The gas laws of Boyle, Charles, and Gay-Lussac can be put together to form the **Combined Gas Law**, where the only constant is the number of moles and pressure, volume, and temperature are all variables.

$$\frac{PV}{T} = k, \text{ for some constant } k$$

At times t_1 and t_2, we have

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

Problem 3.4.8 — Combined Gas Law

A gas has a volume of 800.0 mL at −23.0°C and 300.0 torr. What would the volume of the gas be at 227.0°C and 600.0 torr of pressure?

Solution: Since we are given measurements of pressure, volume, and temperature, but the amount of gas stays constant, we apply the combined gas law.

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

In the context of this problem, we are solving for V_2. Rearranging the equation to isolate for V_2, we have

$$V_2 = \frac{P_1V_1T_2}{T_1P_1}$$

P_1 and P_2 are 300.0 torr and 600.0 torr, respectively. For temperature, we must add 273 to each value to account for the change in °C to K. Thus, T_1 and T_2 are 250. K and 500. K, respectively. Finally, our initial volume is $V_1 = 800.0$ mL.

Plugging in our values, we have

$$V_2 = \frac{(300.0\,\cancel{\text{torr}})(800.0\,\text{mL})(500.0\,\cancel{\text{K}})}{(250.0\,\cancel{\text{K}})(600.0\,\cancel{\text{torr}})} = \boxed{800.0\,\text{mL}}$$

Definition 3.4.9

Avogadro's Law states that at constant temperature and pressure, equal volumes of gas contain the same number of moles. This observation is represented by the equation

$$V = kn, \text{ for some constant } k$$

At times t_1 and t_2, the representation is

$$\frac{V_1}{n_1} = \frac{V_2}{n_2}$$

Problem 3.4.10 — Avogadro's Law

Suppose we have a 10.4-L sample containing 0.32 mol dinitrogen tetroxide at a pressure of 1 atm and a temperature of 25°C. If all this dinitrogen tetroxide was converted to nitrogen dioxide at the same temperature and pressure, what would be the volume of the nitrogen dioxide?

Solution: The balanced chemical equation is

$$N_2O_4(g) \rightarrow 2NO_2(g)$$

To calculate the moles of NO_2 produced, we must use the appropriate mole ratio:

$$0.32\,\cancel{\text{mol N}_2\text{O}_4} \cdot \frac{2\,\text{mol NO}_2}{1\,\cancel{\text{mol N}_2\text{O}_4}} = 0.64\,\text{mol NO}_2$$

Let's identify our variables:

$$V_1 = 10.4 \quad V_2 = ?$$
$$n_1 = 0.32\,\text{mol} \quad n_2 = 0.64\,\text{mol}$$

We proceed by the following.

$$\frac{V_1}{n_1} = \frac{V_2}{n_2}$$

Rearranging, we have

$$V_2 = V_1 \cdot \frac{n_2}{n_1} = \frac{(10.4\,\text{L})(0.64\,\cancel{\text{mol}})}{(0.32\,\cancel{\text{mol}})} = \boxed{20.8\,\text{L}}$$

The gas laws of Boyle, Charles, and Avogadro are generalizations of a broader definition of the Ideal Gas Law. In fact, when we isolate for the volume V of a gas for all three cases, we can combine them into the equation for the Ideal Gas Law.

$$\text{Boyle's Law:} \quad V = \frac{k}{P} \text{ (at constant } T \text{ and } P)$$

$$\text{Charles's Law:} \quad V = kT \text{ (at constant } P \text{ and } n\text{)}$$

$$\text{Avogadro's Law:} \quad V = kn \text{ (at constant } T \text{ and } P\text{)}$$

When combined, we have $V = R\,(\frac{Tn}{P})$, where R is the combined proportionality constant, referred to as the universal gas constant. When the pressure is expressed in atmospheres (atm) and the volume in liters (L), this constant has a value of $R = 0.08206\,\text{L atm mol}^{-1}\,\text{K}^{-1}$.

When we rearrange the previous equation, we get the formula for the Ideal Gas Law:

$$\boxed{PV = nRT}$$

Here are some practice problems before we move on to the next topic.

Problem 3.4.11 — Ideal Gas Law I

A sample of hydrogen gas (H_2) has a volume of 3.71 L at a temperature of 10°C and a pressure of 1.3 atm. Calculate the number of moles of H_2 molecules present in this gas sample.

Solution: We proceed using the Ideal Gas Law:

$$PV = nRT$$

Rearranging to solve for n gives

$$n = \frac{PV}{RT}$$

We substitute the values of pressure, volume, and temperature as given in the problem. Thus, the number of moles of H_2 is equal to

$$n = \frac{(1.3\,\cancel{\text{atm}})(3.71\,\cancel{\text{L}})}{(0.08206\,\cancel{\text{L}}\,\cancel{\text{atm}}\,\text{mol}^{-1}\,\cancel{\text{K}^{-1}})(283\,\cancel{\text{K}})} = \boxed{0.21\text{ mol}}$$

Note 3.4.12

In some problems, you will be asked to perform calculations under STP. STP stands for "standard temperature and pressure." This refers to 1 atm of pressure and 0°C (273 K) temperature. Additionally, at STP, one mole of an ideal gas occupies a volume of 22.4 L.

Problem 3.4.13 — Ideal Gas Law II

Calculate the volume occupied by 2.34 grams of carbon dioxide gas at STP.

Solution: Since we are at STP, we already have two variables: pressure $P = 1.0$ atm and temperature $T = 273$ K.

Our goal is to determine the volume occupied by the gas, so the last measurement we need is the number of moles.

We can convert from grams of carbon dioxide to moles using the molar mass.

$$2.34\,\text{g}\,\cancel{\text{CO}_2} \cdot \frac{1\,\text{mol CO}_2}{44.01\,\text{g}\,\cancel{\text{CO}_2}} = 0.0532\,\text{mol CO}_2$$

Now, we can solve for V in the Ideal Gas Law equation:

$$V = \frac{nRT}{P} = \frac{(0.0532\,\cancel{\text{mol}})(0.08206\,\text{L}\,\cancel{\text{atm}}\,\cancel{\text{mol}^{-1}}\,\cancel{\text{K}^{-1}})(273\,\cancel{\text{K}})}{1.0\,\cancel{\text{atm}}} = \boxed{1.19\,\text{L}}$$

Alternatively, we could use the fact that one mole of an ideal gas occupies a volume of 22.4 L. Assuming that the carbon dioxide gas is under ideal conditions, we proceed with the following:

$$2.34\,\text{g}\,\cancel{\text{CO}_2} \cdot \frac{1\,\text{mol CO}_2}{44.01\,\text{g}\,\cancel{\text{CO}_2}} = 0.0532\,\text{mol CO}_2$$

and using our conversion factor, we have

$$0.0532\,\cancel{\text{mol}} \cdot \frac{22.4\,\text{L}}{1\,\cancel{\text{mol}}} = \boxed{1.19\,\text{L}}$$

Dalton's Law of Partial Pressures

In 1803, chemist John Dalton summarized his observations related to mixtures of gases in the following statement:
For a mixture of gases in a container, the total pressure exerted is the sum of the pressures that each gas would exert if it were alone.

Definition 3.4.14

The above statement, known as **Dalton's Law of Partial Pressures**, can be expressed as:

$$P_{total} = P_1 + P_2 + P_3 + \dots$$

where the subscripts refer to individual gases (gas 1, gas 2, and so on). The symbols P_1, P_2, P_3, and so on represent the *partial pressures*, the pressure that a gas would exert if it were alone, for each of the individual gases.

Assuming that gases behave ideally, we can represent the partial pressure of each gas in the form:

$$P_1 = \frac{n_1RT}{V} \qquad P_2 = \frac{n_2RT}{V} \qquad P_3 = \frac{n_3RT}{V} \qquad \dots$$

Therefore, the total pressure of the mixture P_{total} can be written as follows:

$$P_{total} = P_1 + P_2 + P_3 + \dots = \frac{n_1RT}{V} + \frac{n_2RT}{V} + \frac{n_3RT}{V} + \dots$$

$$P_{total} = (n_1 + n_2 + n_3 + \dots)\left(\frac{RT}{V}\right) = \boxed{n_{total}\left(\frac{RT}{V}\right)}$$

where n_{total} is the total number of moles of the various gases.

Note 3.4.15

Dalton's Law actually operates on two assumptions made for ideal gases:

1. The volume of the individual gas particle must not be significant.
2. Any forces of interaction among the particles must also not be significant.

These observations are very important for the model that we will eventually construct in the next section to explain ideal gas behavior!

For now, let's conclude this section with some problems involving Dalton's Law.

Problem 3.4.16 — Dalton's Law I

Mixtures of helium and oxygen gases can be used in scuba diving tanks to help prevent "the bends." For a particular dive, 38 L He at 25°C and 1.0 atm and 12 L O_2 at 25°C and 1.0 atm were pumped into a tank with a volume of 5.0 L. Calculate the partial pressure of each gas and the total pressure in the tank at 25°C.

Solution: By intuition, the first step should be to use the Ideal Gas Law to calculate the number of moles of each substance.

$$n = \frac{PV}{RT}$$

$$n_{\text{He}} = \frac{(1.0\,\cancel{\text{atm}})(38\,\cancel{\text{L}})}{(0.08206\,\cancel{\text{L}}\cdot\cancel{\text{atm}}/\cancel{\text{K}}\cdot\text{mol})(298\,\cancel{\text{K}})} = 1.6\,\text{mol}$$

$$n_{\text{O}_2} = \frac{(1.0\,\cancel{\text{atm}})(12\,\cancel{\text{L}})}{(0.08206\,\cancel{\text{L}}\cdot\cancel{\text{atm}}/\cancel{\text{K}}\cdot\text{mol})(298\,\cancel{\text{K}})} = 0.49\,\text{mol}$$

Since the tank containing the mixture has a volume of 5.0 L and the temperature is 25°C, we can use this information and the Ideal Gas Law to calculate the partial pressures of each gas:

$$P = \frac{nRT}{V}$$

$$P_{\text{He}} = \frac{(1.6\,\cancel{\text{mol}})(0.08206\,\cancel{\text{L}}\cdot\text{atm}/\cancel{\text{K}}\cdot\cancel{\text{mol}})(298\,\cancel{\text{K}})}{5.0\,\cancel{\text{L}}} = \boxed{7.8\,\text{atm}}$$

$$P_{\text{O}_2} = \frac{(0.49\,\cancel{\text{mol}})(0.08206\,\cancel{\text{L}}\cdot\text{atm}/\cancel{\text{K}}\cdot\cancel{\text{mol}})(298\,\cancel{\text{K}})}{5.0\,\cancel{\text{L}}} = \boxed{2.4\,\text{atm}}$$

Via Dalton's Law, the total pressure is the sum of the partial pressures:

$$\text{P}_{\text{total}} = P_{\text{He}} + P_{\text{O}_2} = 7.8\,\text{atm} + 2.4\,\text{atm} = \boxed{10.2\,\text{atm}}$$

At this point, we need to define the **mole fraction**: *the ratio of the number of moles of* *a given component in a mixture to the total number of moles in the mixture.*

This measurement is denoted by the lowercase Greek letter chi (χ).

For example, the mole fraction of the i-th component in a mixture is given by the equation below.

$$\chi_i = \frac{n_i}{n_{\text{total}}}$$

Note that χ has no units.

From the ideal gas equation we know that the number of moles of a gas is directly proportional to its pressure (at constant volume and temperature), i.e. $P = \frac{nRT}{V}$.

In fact, the mole fraction of each component in a mixture of ideal gases is directly related to its partial pressure (assuming a rigid container and fixed temperature):

$$\boxed{\chi_i = \frac{n_i}{n_{\text{total}}} = \frac{P_i}{P_{\text{total}}}}$$

Problem 3.4.17 — Dalton's Law II

The partial pressure of oxygen was observed to be 102 torr in air with a total atmospheric pressure of 743 torr. Calculate the mole fraction of O_2 present.

Solution: We can calculate the mole fraction of O_2 from the following equation.

$$\chi_{O_2} = \frac{n_{O_2}}{n_{\text{total}}} = \frac{P_{O_2}}{P_{\text{total}}} = \frac{102\,\cancel{\text{torr}}}{743\,\cancel{\text{torr}}} = \boxed{0.137}$$

Problem 3.4.18 — Dalton's Law III

The mole fraction of nitrogen in the air is 0.7808. Calculate the partial pressure of N_2 in air when the atmospheric pressure is 760. torr.

Solution: We can relate mole fraction with partial pressure using the following equation.

$$\chi_{N_2} = \frac{P_{N_2}}{P_{\text{total}}}$$

We can rearrange this equation to solve for P_{N_2}:

$$P_{N_2} = \chi_{N_2} \cdot P_{\text{total}} = 0.7808 \cdot 760.\text{ torr} = \boxed{593 \text{ torr}}$$

§3.5 Kinetic Molecular Theory

The Kinetic Molecular Theory (KMT) for Gases is a classic thermodynamic model to describe the behavior of ideal gases. This model allows us to gauge the motion of gas particles, and how they govern the macroscopic (what we can observe) properties of gases. We will also learn about Maxwell-Boltzmann distribution curves and how they depict the energies and velocities of gas particles.

Here are the postulates of the kinetic molecular theory as they relate to ideal gases:

- Gas particles are so small compared to the distances between them that *their individual volumes can be assumed to be negligible.*
- The particles are in a state of *continuous, random* motion. Any collisions with the wall by the particles are elastic (kinetic energy is conserved) and result in the pressure exerted by the gas.
- The particles are assumed to exert no forces (neither attractive nor repulsive) on each other.
- The average kinetic energy of a collection of gas particles is assumed to be *directly* proportional to the **Kelvin** temperature of the gas.

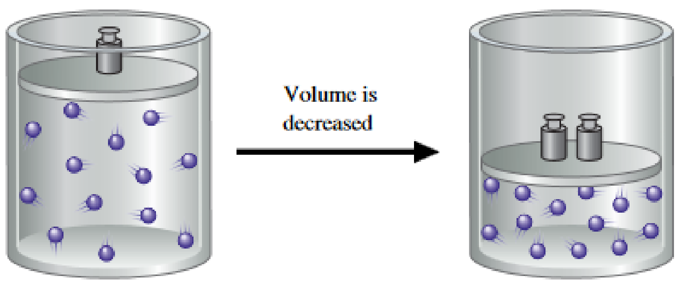
Note 3.5.1

Let's think about something. In the practical world, it is obvious that gas particles have volume, and of course they exert forces on each other. Thus, only *ideal* gases, not *real* gases conform to the Kinetic Molecular Theory. Nevertheless, we will see how these postulates explain ideal gas behavior.

- **Pressure and Volume (Boyle's Law)**
  We know that for a given sample of gas at given temperature (n and T are constant) that if the volume of a gas is decreased, the pressure increases:

  $$P = (nRT)\frac{1}{V}$$

  This makes sense because with less space to move around, the gas particles will hit the wall of a container more often, thus increasing pressure.

- **Pressure and Temperature**
  From the ideal gas law, we can also predict that for a given sample of gas at

constant volume, the pressure will be directly proportional to its temperature:

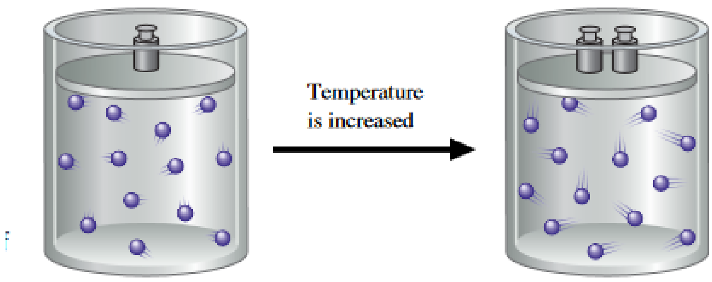
$$P = \left(\frac{nR}{V}\right) T$$

The Kinetic Molecular Theory explains this behavior because as the temperature increases, the speed of the gas particles increases, thus colliding with the container wall to a greater extent, and increasing pressure.

- **Volume and Temperature (Charles's Law)**
  The ideal gas law indicates that for a given sample of gas at a constant pressure, the volume of the gas is directly proportional to the temperature in Kelvins:

  $$V = \left(\frac{nR}{P}\right) T$$

  When the gas particles are heated to a higher temperature, they will move more rapidly and collide with the wall with greater frequency. However, if the pressure must remain constant, the volume has to increase, to compensate for the increased particle speeds.



- **Volume and Number of Moles (Avogadro's Law)**
  Finally, the ideal gas law predicts that at a constant pressure and temperature, equal volumes of gas will occupy an equal number of particles:

  $$V = \left(\frac{RT}{P}\right) n$$

  In terms of the Kinetic Molecular Theory, an increase in the number of gas particles at the same temperature would cause the pressure to increase, as more collisions with the wall will occur. The only way to return the pressure to its original value is to increase the volume by the same factor.

Images Courtesy of Chemistry, Seventh Edition (Zumdahl)

Maxwell-Boltzmann Distributions

Maxwell-Boltzmann distributions, sometimes called Boltzmann distributions, for short, display the distribution of kinetic energy (and subsequent molecular velocity) at specific temperatures for a gas.

Boltzmann diagrams are tricky at first glance, because they can be extremely misleading for students who are new to them. For example, observing a very high peak on the distribution does NOT indicate that, at that temperature, particles have the most energy, rather it means the highest FRACTION of particles have that energy.

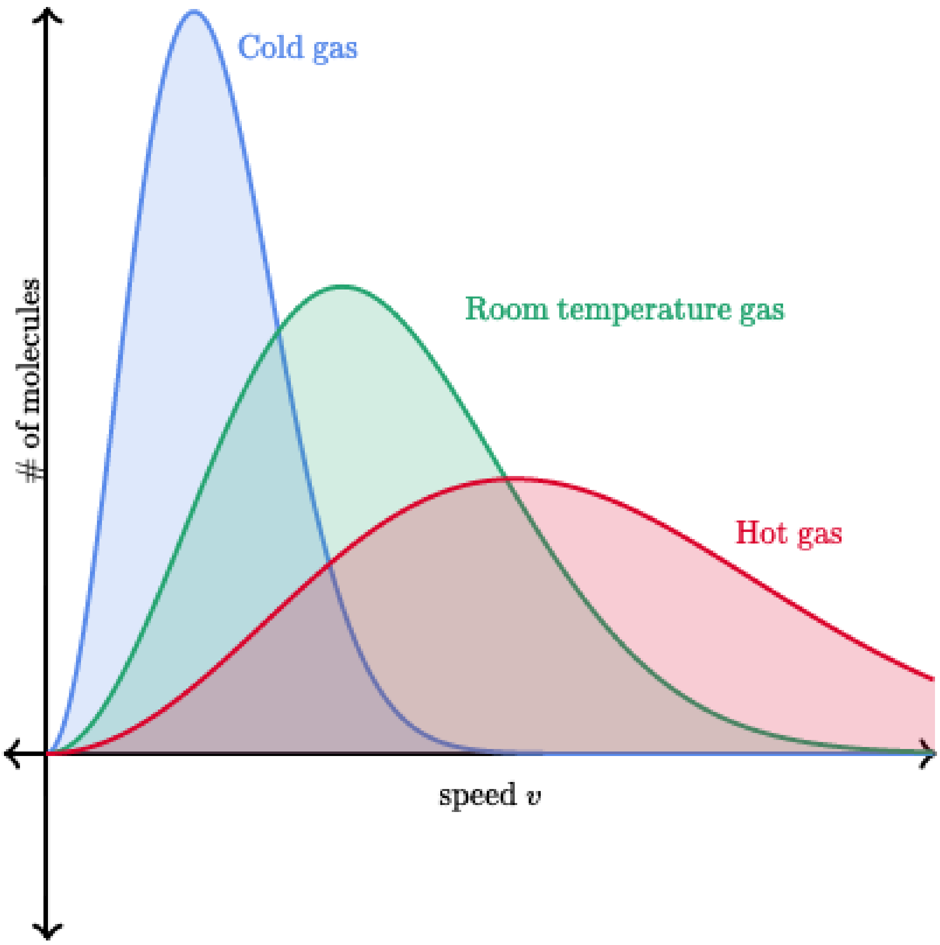


Image Courtesy of DeepAI

Consider three gases: one that is cold, one at room temperature, and one that is hot. The default assumption is that the cold gas must have the higher speed, but if you look closely at the axes, you'll see that this is wrong.

On the x-axis, we have molecular velocity v (also implies kinetic energy, since $\text{KE} = \frac{1}{2}mv^2$) and on the y-axis shows the fraction of molecules. We can interpret the high peak for the cold gas that a large number of gas particles actually have a slower speed. Looking at the hotter gases, more molecules have a faster speed, and therefore more energy.

Note 3.5.2

The Maxwell-Boltzmann distributions show that as the temperatures of gas particles increase, the *range of velocities* becomes larger and therefore particles move at higher speeds. **If the distributions represent different gases instead of temperatures, you would use this trend:** *as the molecule becomes lighter, the range of velocities becomes larger.*

Maxwell-Boltzmann distributions are more aligned with the AP Physics 2: Algebra-Based curriculum. Therefore, this marks the end of the lesson for purposes of AP Chemistry. Just remember these simple facts, be able to interpret the charts, and you're set.

Let's try a short free-response question to wrap up this section.

Problem 3.5.3 — Short FRQ Practice

A student is doing experiments with CO_2(g). Originally, a sample of gas is in a rigid container at 299 K and 0.70 atm. The student increases the temperature of the CO_2(g) in the container to 425 K.

(a) Describe the effect of raising the temperature on the motion of the CO_2(g) molecules.
(b) Calculate the pressure of the CO_2(g) in the container at 425 K.
(c) In terms of the kinetic molecular theory, briefly explain why the pressure of the CO_2(g) changes as it is heated to 425 K.

Solution to part a: As we can recall, raising the temperature of a gas sample increases the molecules' speeds. Therefore, our answer should **always** include the phrase "average kinetic energy."

Increasing the temperature leads to a greater average kinetic energy of the CO_2(g) molecules, which causes their speeds to increase.

Solution to part b: For this problem, we will use the combined gas law.

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

In this case, we have a rigid container, so the volume does not change, i.e. $V_1 = V_2$.

Therefore, we can simplify this equation to the form

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

Isolating for P_2, we have

$$P_2 = P_1 \cdot \frac{T_2}{T_1}$$

and plugging in,

$$P_2 = 0.70\,\text{atm} \cdot \frac{425\,\cancel{K}}{299\,\cancel{K}} = \boxed{0.99\,\text{atm}}$$

Solution to part c: Based on our answer to part (b), we know that $P_2 > P_1$, so the pressure of the CO_2(g) increased as it was heated to 425 K. The kinetic molecular theory states that the average kinetic energy of gas molecules is directly proportional to their Kelvin temperature; therefore since the CO_2(g) was heated, the average kinetic energy of the molecules (and therefore their speeds) increased. The increased speed will cause the gas molecules to collide with the container wall more often, thus increasing the pressure.

§3.6 Deviation from Ideal Gas Law

The Kinetic Molecular Theory (KMT) for Gases is the foundation for the Ideal Gas Law.

The KMT guarantees the following three statements:

- Collisions between gas molecules are perfectly elastic.
- There are no attractive or repulsive forces between gas particles.
- Particle volume is negligible compared to that of the containerparticles are like points in space.

If all these are true, then the Ideal Gas Law is confirmed:

$$PV = nRT$$

However, to what extent are these statements fully true? This is the key question that we will answer in this section.

The Concept of "Real" Gases

The term "real gas" describes a gas that does not function as an ideal gas. In fact, **no** gas can neatly fit into the arbitrary categories of ideal gases: *gaseous particles do interact with each other through intermolecular forces and they do occupy a considerable volume.*

Therefore, all gases deviate from ideal gas behavior, but to different degrees. We will talk about at what conditions will gases exhibit ideal or non-ideal behavior.

Example 3.6.1
Consider the two gases methane and ammonia (CH_4 and NH_3, respectively). Which gas deviates the most from ideal behavior?

Let's stop and think for a minute. Since real gases interact with each other through intermolecular forces (attraction), the gas that experiences the greater IMF strength will deviate the most.

Methane, CH_4 is a nonpolar molecule, so it is only associated with relatively weak

London-dispersion forces.

Ammonia, NH_3, on the other hand, is associated with London dispersion forces, dipole-dipole interactions, as well as hydrogen bonding (due to the lone electron pair on the N atom which attracts nearby H atoms). Hydrogen bonding is the strongest of all IMFs, so NH_3 has much greater IMF strength than CH_4. Thus, $\boxed{\text{ammonia}}$ will deviate the most from ideal behavior.

When do Gases Deviate from Ideal Gas Behavior and Why?

At conditions of *low temperatures* and *high pressures*, gases will deviate from ideal behavior for the following reasons:

1. **Gas particles can become attracted to each other**.
    - At low temperatures, gas particles move slowly and tend to be close to each other due to a large number of particles. This causes the likelihood for more attractive forces, which violates the Kinetic Molecular Theory.
    - Polar and larger molecules generally deviate from ideal behavior more than nonpolar molecules. The stronger IMFs between polar and larger molecules can cause these gas particles to exert attractive forces on one another.
    - **Important:** To simply put it, the pressure of real gases is usually lower than that of ideal gases. When attractive forces are present, IMFs become significant and the gas particles do not hit the container wall as frequently anymore.

2. **Gas particles can make up a significant portion of a gas sample's total volume**.
    - Remember Boyle's Law. At high pressures, the volume of a gas sample decreases. When this happens, the volume of individual gas particles becomes more significant. This can be shown visually.

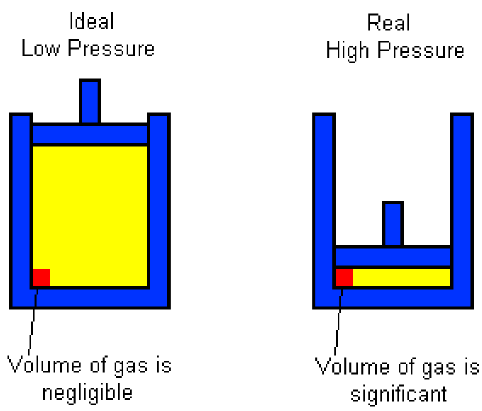


Image Courtesy of AskIITians

Important: The volume of real gases is higher than that of ideal gases.

The Van der Waals Equation

Since the traditional ideal gas law has been shown to have certain exceptions, chemists have created a new equations to account for intermolecular forces and volumes when they become significant.

This is called the **Van der Waals equation**:

$$\left[P + \frac{an^2}{V^2}\right][V - nb] = nRT$$

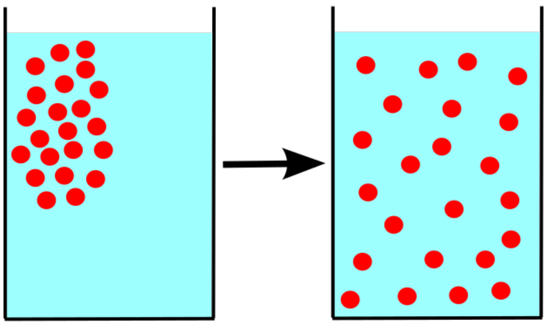
Wow! That looks pretty scary, but here's the good news:

- You will NEVER need to perform any calculations with this equation. Don't even bother memorizing it.
- All you need to know is that it makes corrections to the pressure and volume aspects of the Ideal Gas Law to account for high pressures and/or low volumes. The $+a$ term is used to correct the pressure since the pressure is lower in real gases, while the $-b$ term corrects the volume because it is higher than what it would be in an ideal gas.

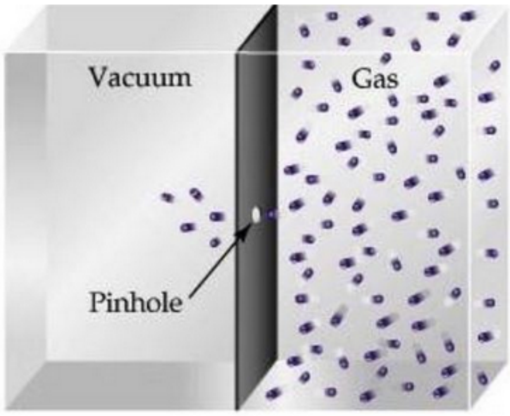
Diffusion and Effusion

Diffusion describes the mixing of gases. There are a few rules you should memorize:

- The process of diffusion occurs faster as the temperature increases, because the particles are moving faster on average.
- Larger molecules tend to diffuse more slowly, because they contain more mass and require more energy to change their positions.



Effusion is similar to diffusion, but it describes the movement of a gas from a tiny space to a vacuum (large) space. The gas particles are moving from a space with higher pressure to a space with lower pressure through a pinhole.



The same rules apply for effusion: the rate of effusion increases with temperature while a higher molar mass decreases the rate of effusion. The distinguishing factor is that the rate of effusion is the speed at which gas particles are transferred into the vacuum.

Graham's Law of Effusion

There is a cool formula, called **Graham's Law of Effusion**, which states that the rate at which a gas escapes is inversely proportional to the square root of its molar mass:

$$\frac{r_1}{r_2} = \frac{\sqrt{M_2}}{\sqrt{M_1}}$$

where r_1 and r_2 are the rates of effusion for gases 1 and 2, respectively, and M_1 and M_2 are the molecular weights of gases 1 and 2, respectively. Note that both gases are at identical temperature.

PRO TIP: It is best to call the denote the lighter substance as gas 1, so when solving a problem, you can state that the rate of effusion of gas 1 is k times as fast as gas 2, for some factor $k > 1$.

Let's end this section with some practice problems.

Problem 3.6.2 — Graham's Law I

Explain why the rates of diffusion of nitrogen gas (N_2) and carbon monoxide (CO) are almost identical at the same temperature.

Solution: We know that Graham's Law states the following:

$$\frac{r_1}{r_2} = \frac{\sqrt{M_2}}{\sqrt{M_1}}$$

Therefore, if the rates of diffusion are almost identical, then we have $r_{CO_2} \approx r_{N_2}$ or $\frac{r_{CO_2}}{r_{N_2}} \approx 1$. For this to be true, then ratio $\frac{\sqrt{M_{N_2}}}{\sqrt{M_{CO}}}$ should be approximately equal to 1. This occurs because the $\boxed{\text{molar masses of CO and N}_2\text{ are essentially equal}}$.

Reality Check: If you do the math, you'll find that both gases have molar masses of approximately 28.0 g/mol.

Problem 3.6.3 — Graham's Law II

What is the rate of effusion for a gas that has a molar mass twice that of a gas that effuses at a rate of 3.62 mol/min?

Solution: Let x and $2x$ represent the molar masses of the lighter and heavier gas molecules, respectively. Additionally, let r represent the rate of effusion for the gas that we are trying to determine.

Therefore, we have

$$\frac{r}{3.62\ \text{mol/min}} = \frac{\sqrt{x}}{\sqrt{2x}}$$

$$\frac{r}{3.62\ \text{mol/min}} = \frac{\sqrt{2}}{2}$$

Solving, we find that $r = \boxed{2.56\ \text{mol/min}}$.

Reality Check: This gas is heavier than the one whose rate is given, so we would expect its rate of effusion to be lower.

Problem 3.6.4 — Graham's Law III

Some gas diffuses 25% as fast as helium (He). What is its molar mass?

Solution: First, we look at the periodic table and find that the molar mass of helium is 4.003 g/mol. Let's call the rates of effusion for helium and the unknown gas as r_{He} and $0.25r_{\text{He}}$, respectively. Since the rate of effusion is inversely proportional to the square root of molar mass, we have the following:

$$\frac{r_{\text{He}}}{0.25r_{\text{He}}} = \frac{\sqrt{M_{\text{gas}}}}{\sqrt{M_{\text{He}}}}$$

Simplifying and plugging in,

$$4 = \frac{\sqrt{M_{\text{gas}}}}{\sqrt{4.003\ \text{g/mol}}}$$

Finally, we find that the molar mass of the gas, M_{gas}, is equal to $\boxed{64.05\ \text{g/mol}}$. Again, it effuses only 25% as fast as helium, so we should expect its molar mass to be larger.

§3.7 Solutions and Mixtures

In this section, we will learn about solutions and mixtures, their properties, similarities and differences, and how to quantitatively describe them in real-life settings.

Definition 3.7.1

A **solution** is a *homogeneous* mixture in which all the particles are evenly mixed: the macroscopic properties don't vary. A classic example of a solution is sugar water. When stirred correctly, the sweet taste is equally felt throughout the entire mixture.

Meanwhile, *heterogeneous* mixtures DO have varying properties depending on location in the mixture. A good example of a heterogeneous mixture is breakfast cereal, like raisin bran. The raisins and flakes could be concentrated in different locations when you pour the cereal into a bowl.

Definition 3.7.2

A solution is formed by two substances, a **solute** and a **solvent**.

The process of **solvation** refers to the mixing of a solute and a solvent. The particles are spread out evenly (as with a homogeneous mixture) and they orient themselves based off intermolecular forces.

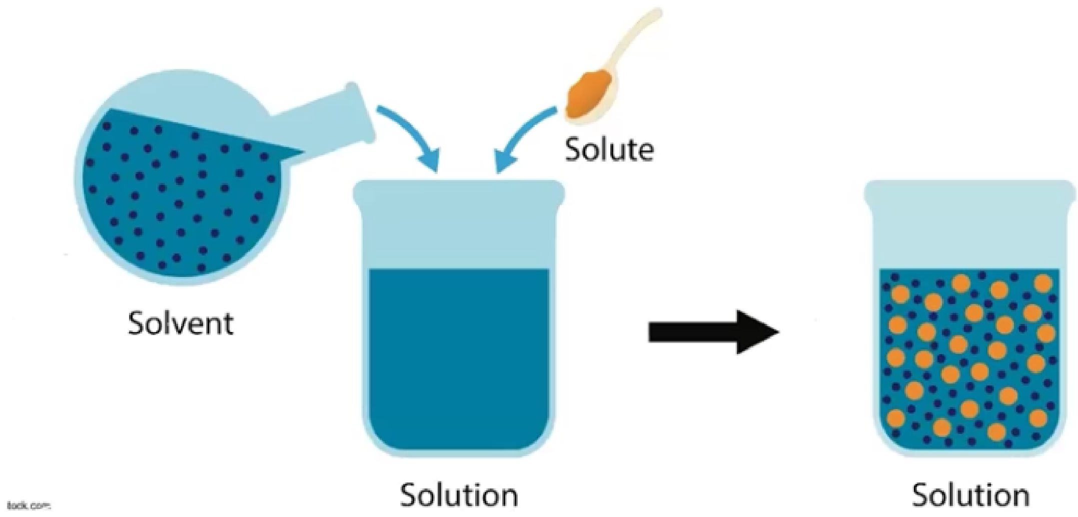


Image Courtesy of Nasky/Shutterstock.com

Quantitative Description of Solutions

In the laboratory setting, the most common method used to express the concentration of a solution is called the **molarity**.

$$\text{Molarity} = \frac{\text{moles of solute}}{\text{liters of solution}}$$

The units for molarity are given in moles per liter ($\mathrm{mol\,L^{-1}}$) or molar (M).

Let's walk through a few problems.

Problem 3.7.3 — Composition of Solutions I

If 100. mL of 0.40 M $MgCl_2$ is added to 200. mL of distilled water, what is the concentration of Mg^{2+}(aq) in the resulting solution? (Assume that volumes are additive.)

Solution: First, let's find the number of moles of $MgCl_2$.
Molarity is equal to moles per liter, so that means the number of moles is equal to the molarity times the volume, or $n = MV$.

$$n = 0.40\,M \cdot 0.100\,\mathrm{L} = 0.04\,\mathrm{mol\ MgCl_2}$$

Since we are adding a 0.04 mol $MgCl_2$ sample to distilled water, we are diluting it, i.e. the volume of the solution has increased.

$$\text{total volume} = 0.100\,\mathrm{L} + 0.200\,\mathrm{L} = 0.300\,\mathrm{L}$$

The molarity of $MgCl_2$ after the dilution is equal to

$$[\mathrm{MgCl_2}] = \frac{0.04\,\mathrm{mol}}{0.300\,\mathrm{L}} = 0.13\,M$$

Finally, there is 1 Mg^{2+} and 2 Cl^- in one molecule of $MgCl_2$ (an ionic compound), so the concentration of Mg^{2+}(aq) is equal to the molarity of $MgCl_2$ solution after it is diluted:

$$[\mathrm{Mg^{2+}}] = \boxed{0.13\,M}$$

Problem 3.7.4 — Composition of Solutions II

Approximately what mass of $CuSO_4 \cdot 5H_2O$ (molar mass 250 g/mol) is required to prepare 250 mL of 0.10 M copper(II) sulfate solution?

Solution: The 5 molecules of water attached to $CuSO_4$ simply means that this is a **hydrated** sample of $CuSO_4$(aq) solution.
Let's find the number of moles of copper(II) sulfate solution using $n = MV$.

$$n = 0.10\,M \cdot 0.25\,\mathrm{L} = 0.025\,\mathrm{mol\ CuSO_4{\cdot}5H_2O}$$

To find the requested mass, multiply by the molar mass given.

$$0.025\,\cancel{\mathrm{mol\ CuSO_4 \cdot 5H_2O}} \cdot \frac{250\,\mathrm{g}}{1\,\cancel{\mathrm{mol\ CuSO_4 \cdot 5H_2O}}} = \boxed{6.25\,\mathrm{g}}$$

Let's recap this section.

- Solutions, or homogeneous mixtures, can exist in any state of matter. The defining characteristic of a solution is that the macroscopic properties do not vary by location of the sample. In the heterogeneous, there are differences in macroscopic properties based on the location.
- There are many ways to describe the composition of a solution. In the laboratory setting, molarity is the most common method, as it represents how many solute particles occupy one liter of solution.

§3.8 Representations of Solutions

In the previous section, we learned the theoretical aspect of solutions and their composition. In this section, we will explore more into the visual representation of solutions, i.e. particle/molecular diagrams. We will need to refresh our understanding of two terms: solute and solvent.

Definition 3.8.1

The **solute** is the substance that is dissolved to form a solution.

Definition 3.8.2

The **solvent** is the substance that ”performs” the dissolving of the solute.

Before visually interpreting solutions, we first explore how a solution is actually formed.

Steps in Solution Formation

There are three steps that make dissolving of a solute to form a solution possible:

- **Step 1**. Expanding the solute: the solute sample is ”pulled apart.” If the solute is ionic, ”expanding” it refers to breaking the ionic bonds. In the case of a covalent solute, it refers to the breaking of intramolecular forces.
- **Step 2**. Expanding the solvent: the solvent particles have to physically ”spread out” in order to make room for the solute particles.
- **Step 3**. (This is the most important!) The *interaction* between solute and solvent particles. If the solute and solvent are strongly attracted to each other, then the solute will readily dissolve in the solvent and whether a solution will form. Similarly, weak attractions between the solute and solvent mean that it the process of solvation is very unlikely. This has connections with the concept of solubility in section 3.10!

The below image represents a visual description of the three steps outlined above.

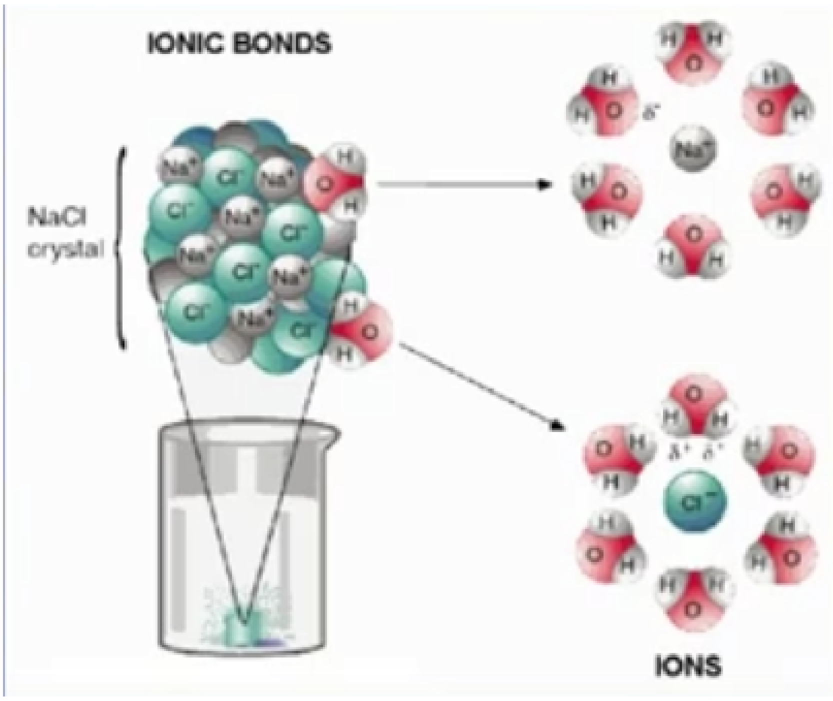


Image Courtesy of Abigail Giordano

Consider a crystal of NaCl that is placed in water. As it is dissolving in water, it is being separated into its constituent Na^+ and Cl^- ions. Meanwhile, the solvent (water) expands, where the partial positive end (hydrogen atoms) surrounds the negatively charged Cl^- ion and the partial negative end (oxygen atoms) surrounds the positively charged Na^+ ion. Finally, the size of the ions matter. Recall your periodic trends for ionic radii, because the size of your ions in a particulate diagram are also important.

Note 3.8.3

Important: On free-response questions, the AP graders will NOT award credit for particulate diagrams if the relative sizes of your species are incorrect.

Now, let's consider what happens when a solution does NOT form, i.e. the attractions between solute and solvent particles are too weak for solvation to occur.

Many of you know that oil is NOT soluble in water. This is because water is a polar molecule, while oil is a lipid (fat), consisting of chains of nonpolar C-H bonds. But why is this the case?

Definition 3.8.4

"Like dissolves like": a simple device that predicts which compounds will dissolve in other compounds. Polar and ionic solutes tend to readily dissolve in polar solvents, while nonpolar solutes tend to dissolve in nonpolar solvents.

Back to our initial question: **Why Doesn't Oil Dissolve In Water?**

The answer is NOT "because like dissolves like, and that these aren't 'like.'"

Watch Out! ***This explanation will be worth NOTHING on either a class test or the AP exam. It's super important to note that "like dissolves like" serves as a convenient tool to understand which solutes are soluble in certain solvents, but it is NOT a valid justification whatsoever on its own.***

Instead, the answer lies in the ATTRACTIONS between the molecules.

Correct Answer: The oil-oil attractions and the water-water attractions are much greater than the oil-water attractions. Therefore, oil and water will be separated from each in other in a mixture, and thus no solution formation will occur.

Particle Diagrams: Whole Number Ratios

The last thing that needs to be emphasized when drawing particulate diagrams is that you must pay attention to the relative number of MOLES of ions in your ionic compound.

For example, if we wanted to represent a solution of copper (II) nitrate, $Cu(NO_3)_2$, we need to use this strategy:

- **Step 1**. Represent the copper (II) nitrate as its ions. One molecule $Cu(NO_3)_2$ consists of Cu^{2+} and NO_3^-.
- **Step 2**. It's important that you note that there are TWO nitrate ions, since the net charge on the compound is 0. When you are instructed to draw species in particle diagrams, not only do you need the correct charges on your ions, but you also need the correct RATIO of them. This means, that, for every one Cu^{2+} ions that is drawn, there must be TWO NO_3^- ions.
- **Step 3**. Draw the particle diagram. (Omit water molecules, for the sake of simplicity).

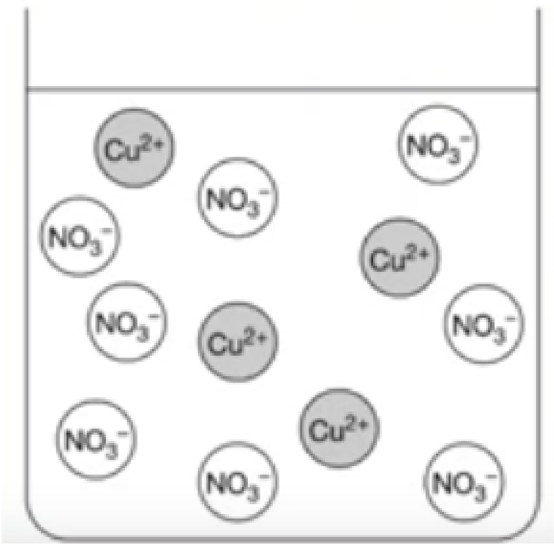
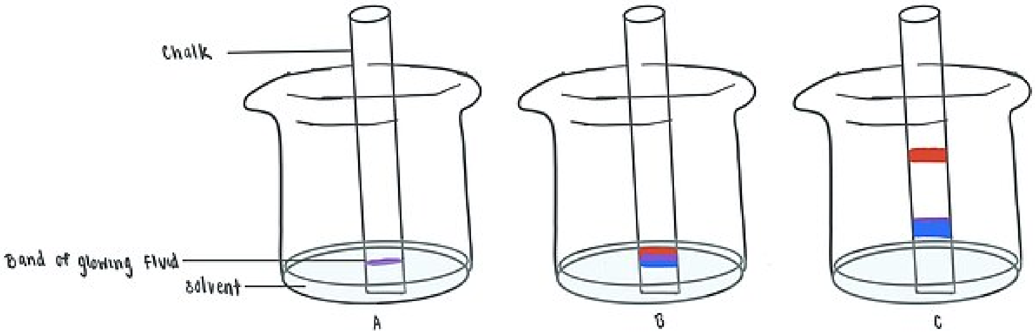


Image Courtesy of Abigail Giordano

§3.9 Separation of Solutions and Mixtures Chromatography

Many times in a chemistry lab, you may be dealing with multiple solutions at once. Therefore, it is useful to be able to *separate* them clearly. In doing so, you can obtain desired components from the resulting mixture and better understand how each individual component contributes to the overall physical and chemical properties.



There are many methods used to separate solutes from their solvents based on physical properties as well as differences in their intermolecular forces. We will study each of them in depth.

Evaporation

Evaporation is the process by which a solvent is boiled and thus evaporated in order to separate out the solute. For example, if you boil salt water for a really long time, all the water will evaporate, leaving you with a small amount of salt at the bottom of your pot.

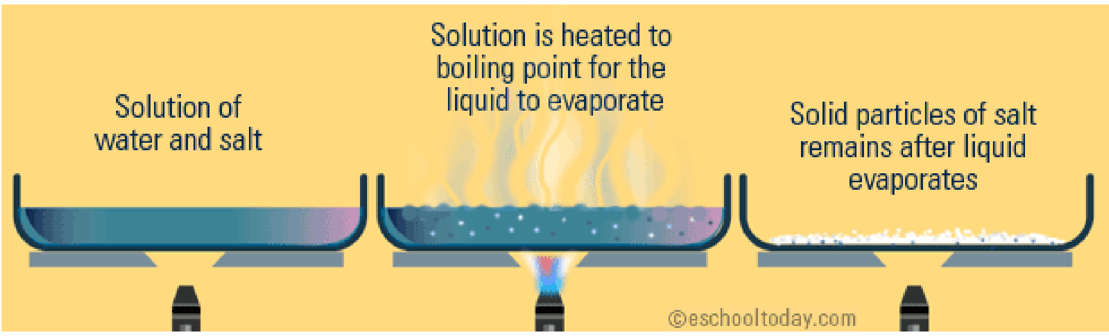
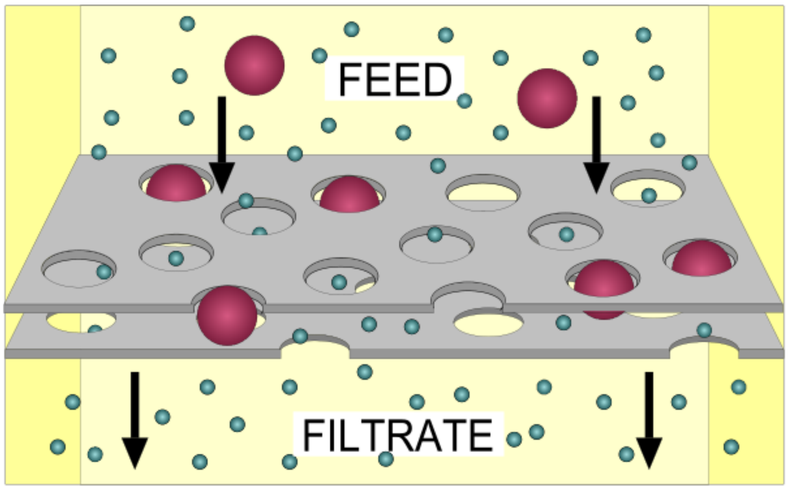


Image Courtesy of eschooltoday.com

The same idea works for virtually any solution with a solid, soluble solute. Evaporation is the simplest method of separation and it is often the one most people have the most experience with. Essentially, just boil the solvent away.

Filtration

Filtration is also a simple method for separation. When you filter a mixture, you run it through a **porous barrier**. With this barrier, the solvent passes through, but the solid gets trapped inside.



A practical application of filtration is making coffee. You pour the mixture of coffee beans and hot water through a coffee filter, in order for the coffee to run through to your mug, but the ground coffee beans are left behind.

Critical Thinking: Even during summer holidays, you enjoy performing experiments. Suppose you are at the beach and you are filtering a solution consisting of salt, water, and sand. Can you guess which component will get caught up in the filter paper?

Answer: ONLY the sand will. This is because the salt will dissolve in water, while the sand will not. Only *insoluble* substances will be filtered by this process, i.e. the filtrate would be both salt and water, or salt water. Therefore, filtration was not very effective for our situation because we did not fully separate all three components in the solution. That is, after filtering the sand, you would have to evaporate the salt water solution to separate the salt from the water.

Chromatography

Chromatography is a technique that can separate chemical species based on their interaction with a *stationary phase*, usually a solid surface or liquid. These interactions are usually governed by relative intermolecular force strengths among the species. Several types of chromatography exist, such as *paper chromatography*, *thin-layer chromatography*, and *column chromatography*, with their specific sets of advantages and disadvantages depending on the characteristics of the sample being analyzed.

Paper Chromatography

Paper chromatography is one of the simplest and most cost-effective forms of mixtures chromatography. Therefore, this is the most likely procedure that you will encounter in your classroom laboratory assignments. A small amount of a chemical sample is first applied to a strip of chromatography paper. The solvent moves up the paper by way of **capillary action**, and the compounds in the sample are carried with it. The most important thing to note here is that different compounds interact differently with the paper, resulting in different rates of movement. Therefore, the compounds can be separated based on their affinity for the paper strip.

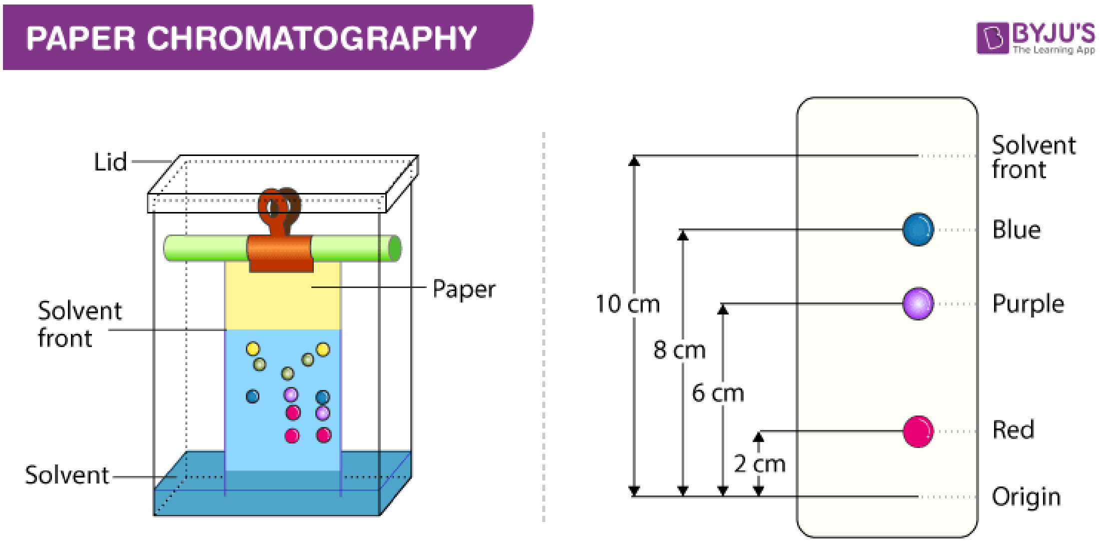


Image Courtesy of BYJU'S

Essentially, the solvent travels up the paper and essentially "drags" each component of the solution away from itself due to differences in intermolecular forces and **polarity**.

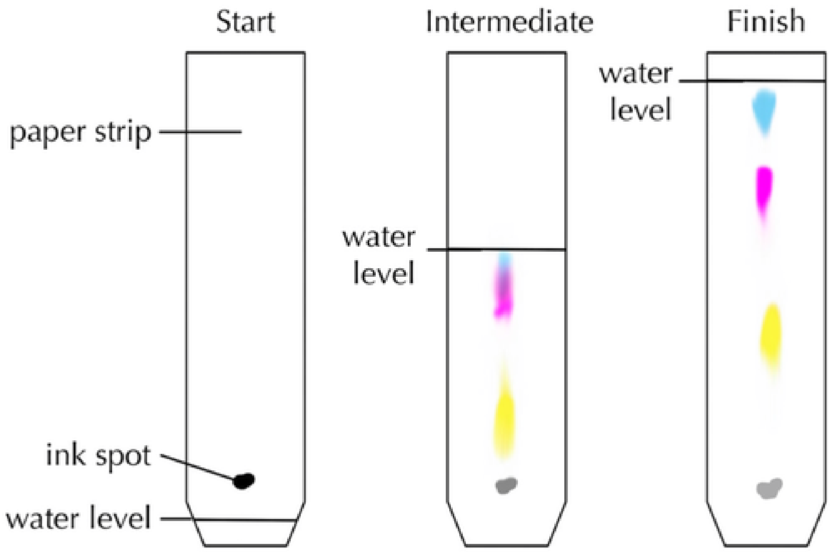
In paper chromatography, the stationary phase is usually a **cellulose** material, which is polar in nature. As a result, polar compounds in the sample will have a greater affinity for the cellulose paper, while nonpolar compounds will have a weaker affinity. However, note that the stationary phase can also be associated with a *nonpolar* solvent, so always make sure you pay attention to the polarity in the context of a question.

Rf Values and Their Meanings

The **retention factor** (R_f) is used to compare and help identify compounds.

Key Idea: Many chemical solutions, such as the ink contained in pens, are a mixture of a number of covalent substances. Each of them have different polarities, and therefore have different affinity depending on the solvent. One of the most common paper chromatography experiments involves the separation of pigments in black ink. Black ink is usually composed of materials with several different colors, which when combined create black.

In paper chromatography, a piece of filter paper is suspended above a solvent so that the very bottom of the paper touches the solvent. The ink in question is dotted onto a line at the bottom of the filter paper that starts out just above the solvent level. As the solvent climbs the paper (via capillary action), the various substances inside the ink will be attracted to the polar water molecules. The more polar the substance is, the greater affinity it has for the water molecules, and the further it will travel. Usually, you would end up with something like this:



Looking at the strip, you can conclude that the ink was composed of three different substances. The one that traveled the farthest with the water experienced the strongest attractions and was the most polar, whereas the one that didn't travel very far from the original starting point was the least polar. This is why paper chromatography is the most useful form of solution separation with colored substances, hence the ink. However, if no components of the ink had a visible color, you would not be able to see them on the filter paper, which is the major limitation of paper chromatography.

The distance the ink travels along the paper is measured via the retention factor, or the R_f value, which is calculated as such:

$$R_f = \frac{\text{Distance traveled by solute}}{\text{Distance traveled by solvent front}}$$

The stronger the attraction between the solute and the solvent front, the larger the R_f value for that component of the mixture.

Note 3.9.1

Water is not the only solvent that can be used in polar chromatography. There are many nonpolar solvents (such as the hexane groups) that can be used instead. In the case of a nonpolar solvent, the position of the various ink components in the above diagram would have been reversed, where the most nonpolar substance would travel the farthest and the most polar substance would travel the least.

In the classroom, you will most likely perform the same black-ink paper chromatography experiment outlined above. Consider this lesson as a start!

Thin-Layer Chromatography

Thin-layer chromatography, or TLC, is a technique that separates compounds in a sample using a stationary phase that is coated onto a thin layer of glass, plastic, or aluminum foil. Similarly to paper chromatography, TLC is based on the differences in the affinity of the compounds for the stationary phase to separate them on the basis of polarity. However, the advantages of TLC over paper chromatography include faster separation times, the ability to use multiple solvents, and the ability to visualize the separated compounds using different techniques.

Most TLC plates are made up of polar **silica**, which is considered the stationary phase. Meanwhile, the solvent in the TLC chamber is referred to as the **mobile phase**. Usually, polar compounds are more strongly attracted to the stationary phase and will travel less, while nonpolar compounds are more readily separated with the solvent. TLC is very similar to paper chromatography, but here the stationary phase is silica glass, rather than a cellulose material.

Column Chromatography

Compared to TLC and paper chromatography, column chromatography is much less tested on the AP exam. However, it is still included in the AP Chemistry Course and Exam Description, so we will do a quick rundown.

As with other types of chromatography, column chromatography is a technique that separates chemical species based on their interactions with a stationary phase. The only difference is that the stationary phase is packed into a **column**, hence the name!

With column chromatography, the stationary phase can be silica or *alumina*, but small solid materials. As the compounds pass through the column, they interact with the stationary phase, resulting in different rates of movement. As in TLC and paper chromatography, this allows the compounds to be separated on the basis of their relative affinity for the stationary phase.

This technique is more complex and time intensive than the other two, but it allows for separating large amounts of a sample, as well as an increased likelihood of preserving the purity of each component (see image below).

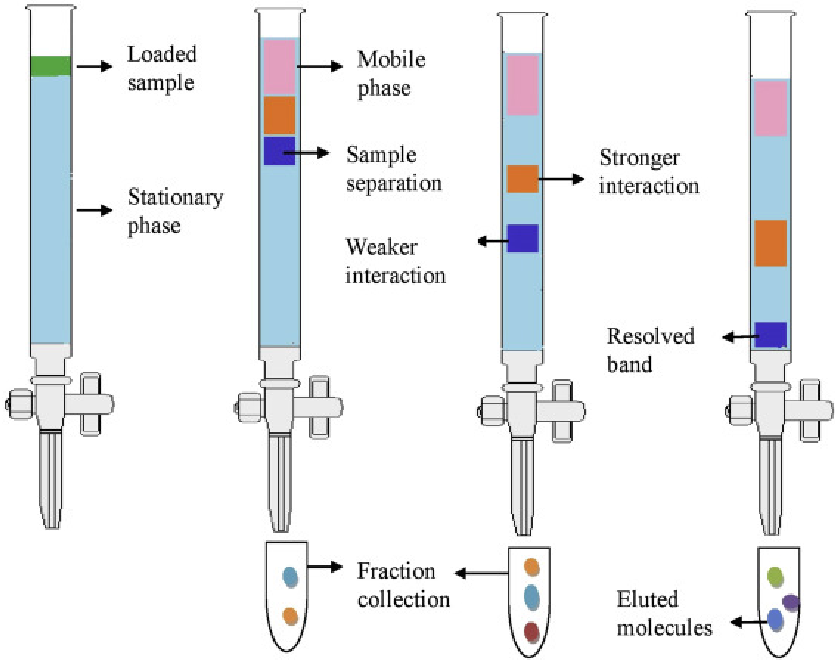


Image Courtesy of Science Direct

Distillation

Finally, you can separate the solutions using **distillation**. This technique involves taking advantage of the different boiling points of substances in order to separate them. For example, if you have a mixture of water and methanol and then heat the mixture to 70°C, methanol will boil, but water will not. This is because the boiling point for methanol (60°C) is lower than 70°C but the boiling point for water (100°C) is higher than 70°C.

For the distillation apparatus, a **condenser** is a piece of glassware that consists of a smaller tube running through a larger tube. The latter has hose connections on it, allowing water to diffuse, effectively cooling the inner tube. At this point, the vapor diffusing through the inner tube will cool and condense into a liquid and then accumulate on the other side of the condenser.

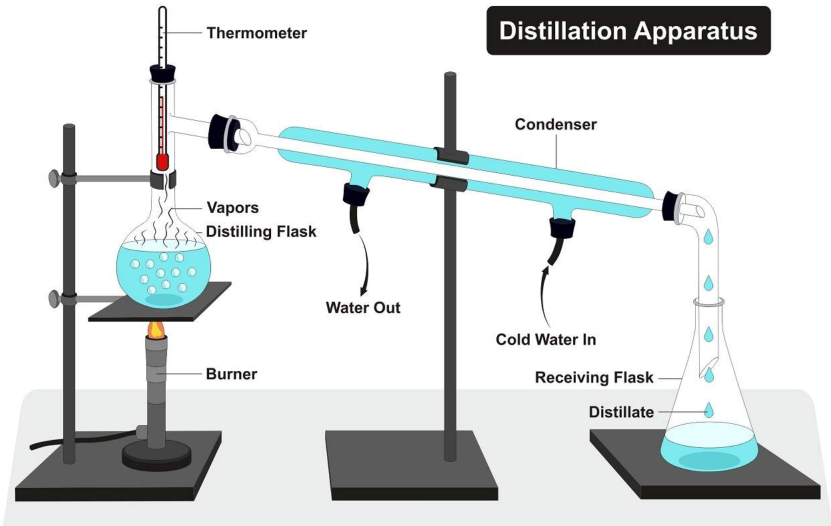


Image Courtesy of Scientific Glass Services

The biggest advantage to distillation is that the solutions need not be colored to effectively separate them. However, maintaining a constant temperature in the flask is difficult, so it must be closely monitored. Otherwise, you could inadvertently boil more than one component of the mixture at a time. Unfortunately, distillation cannot be used to separate a mixture containing substances with extremely similar boiling points.

§3.10 Solubility

In this rather short section, we explore the effects of certain substances having different intermolecular force strengths on their effective solubilities in other substances.

Definition 3.10.1

Solubility is a term that describes how well certain substances called **solutes** dissolve in other substances in more significant amounts, called **solvents**.

Substances with similar intermolecular interactions tend to be *miscible*, or soluble, with one another.

Note 3.10.2

The term *miscible* is generally used to describe a liquid solute that is mixed with a liquid solvent, while *soluble* usually describes a solid solute that is dissolved in a liquid solvent.

***THE KEY DETERMINING FACTOR FOR SOLUBILITY**

Interactions between the solute and the solvent are the primary indicators of whether a substance will dissolve or not.

Solubility Review

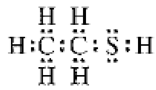
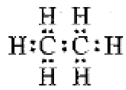
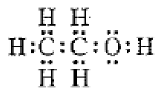
In chemistry, the miscibility of substances can be predicted using a simple trick: **"like dissolves like"**. This means compounds with similar polarities will be more miscible with each other compared to those with markedly different polarities. The relative polarities of molecules can be predicted by observing the relative strength of intermolecular forces that govern them.

- Ionic solutes tend to dissolve in polar solvents. Salt, NaCl, and many other ionic compounds dissolve in water almost spontaneously.
- Polar molecular solutes tend to be soluble in polar solvents. For example, ethanol is very soluble in water, because both molecules have the ability to form *hydrogen bonds*, the strongest form of intermolecular attraction. Therefore, they mix with each other very well.
- Nonpolar molecular solvents tend to dissolve in nonpolar solvents. However, this attraction will not be as strong as with polar solutes and solvents since the former pair will operate through relatively weak London-dispersion forces.

This concludes the conceptual portion of this section. Now, we will solve an AP-style problem to enforce our understanding of the material.

Problem 3.10.3 — Solubility Practice
Source: 2010 AP Chemistry FRQ

Use the information in the table below to respond to the statements and questions below. Your answers should be in terms of principles of molecular structure and intermolecular forces.

Compound	Formula	Lewis Electron-Dot Diagram
Ethanethiol	CH_3CH_2SH	
Ethane	CH_3CH_3	
Ethanol	CH_3CH_2OH	
Ethyne	C_2H_2	H:C⋮⋮C:H or H−C≡C−H

(a) Identify a compound from the table that is nonpolar. Justify your answer.
(b) Ethanol is completely soluble in water, whereas ethanethiol has limited solubility in water. Account for the difference in solubilities between the two compounds in terms of intermolecular forces.

Solution to part a: We can determine if a compound is polar or nonpolar by analyzing their Lewis diagrams. If they have a symmetrical structure, the net dipole moments on the central atom(s) will reduce to 0, characteristic of a nonpolar molecule. We see this occurring in both ethane, CH_3CH_3 and ethyne, C_2H_2, containing CH bonds that travel in opposite cardinal directions, canceling out individual dipole moments and creating an overall symmetric Lewis structure. Thus, either $\boxed{\text{ethane or ethyne}}$ would be correct.

Solution to part b: We know that the solubility of certain solutes is directly correlated with the strength of their intermolecular forces with respect to the solvent. In this case, the solvent is water, which we know contains hydrogen bonding: the strongest category of IMFs. Therefore, the solute that dissolves more in water should be governed by IMFs similar to those of water. Ethanol, CH_3CH_2OH, is a polar molecule and its polar $-OH$ group allows it to interact through hydrogen bonding. Meanwhile, ethanethiol, CH_3CH_2SH, while a polar molecule, does not have a lone pair attached to any of the elements F, O, or N. Therefore, the strongest IMFs that govern it are dipole-dipole interactions. These forces are weaker than hydrogen bonding, so ethanethiol molecules will not interact with water molecules as strongly as those of ethanol will. Thus, the solubility of ethanol in water is significantly greater than that of ethanethiol.

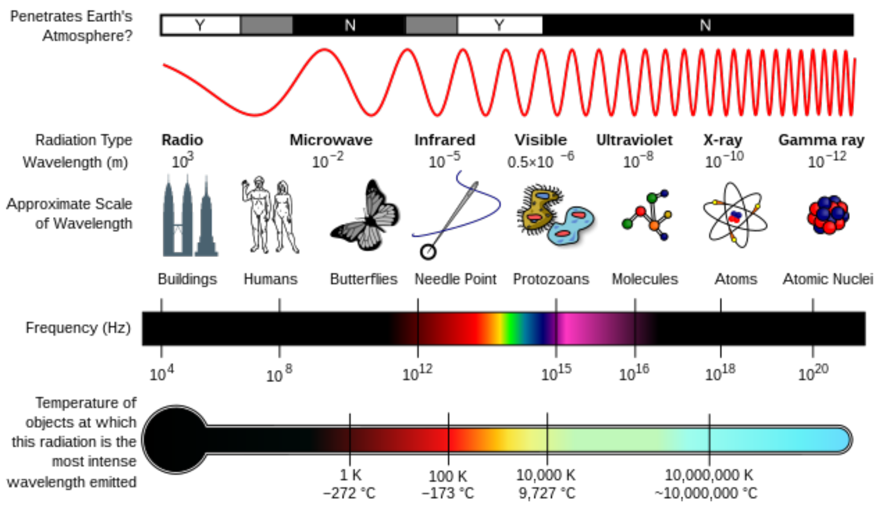
§3.11 Spectroscopy and the Electromagnetic Spectrum

Spectroscopy is the study of the interactions between light and matter. In this context, *light* refers to **electromagnetic radiation** in general.

Spectroscopy also measures the spectra produced when light interacts with matter or electromagnetic radiation is emitted.
The electromagnetic radiation is emitted as light, and it is absorbed, emitted, or scattered. It can be used to identify specific substances.

The key concept to take away from this section is that there are specific wavelengths of radiation in what's known as the electromagnetic **spectrum**, and that different *ranges* of wavelengths correspond to the absorption or emission of different forms of electromagnetic radiation.

The Electromagnetic Spectrum



More specifically,

- **Microwave** radiation is associated with transitions in molecular rotation levels.
- **Infrared** radiation is associated with transitions in molecular vibrational levels.
- Vibrational states of chemical bonds require more energy than molecular rotations; infrared radiation has a higher energy per photon (and thus a higher frequency and shorter wavelength) than microwave radiation.
- **Ultraviolet** radiation is associated with transitions in electronic energy levels.

Finally, the energy given off by electromagnetic radiation is *quantized*, occurring only in discrete quantities. These quantities are referred as **photons**, which are absorbed or emitted as light. We will introduce the mathematical relationships between energy of a photon, wavelength, and frequency in the next section.

§3.12 Photoelectric Effect

The **photoelectric effect** refers to the discharge of electrons from a material resulting from exposure to electromagnetic radiation (in the form of light).

The wavelength of a photon is related to the frequency of the electromagnetic radiation according to the following equation:

$$\boxed{c = \lambda\nu}$$

where:

- c is the speed of light, with a value of $3.0 \cdot 10^8$ m/s
- λ is the wavelength (in m or nm)
- ν is the frequency (in Hz or s^{-1})

Since c, the speed of light is a constant, the wavelength of a photon is **inversely** proportional to the frequency of radiation that is emitted.

Note 3.12.1

Remember to watch out for units! Meters (m) and nanometers (nm) differ by nine powers of 10!

When a photon is absorbed or emitted by an atom or molecule, the change in energy is equal to the amount of energy of the photon.

The energy of a photon is related to the frequency of the wave by Planck's equation:

$$\boxed{E_{\text{photon}} = h\nu}$$

where:

- h is Planck's constant, with a value of $6.626 \cdot 10^{-34}$ J $\cdot$ s
- ν is the frequency (in Hz or s^{-1})

Since h is a constant, the energy of a photon is directly proportional to the frequency of radiation that is emitted.

Let's wrap up with an AP-style problem.

Problem 3.12.2 — Ozone and Radiation

In the upper atmosphere, ozone molecules decompose as they absorb ultraviolet (UV) radiation, as shown by the equation below. Ozone serves to block harmful ultraviolet radiation that comes from the Sun.

$$O_3(g) \rightarrow O_2(g) + O(g)$$

(a) A molecule of $O_3(g)$ absorbs a photon with frequency of $1.00 \cdot 10^{15}\ s^{-1}$. How much energy, in joules, does the $O_3(g)$ molecule absorb per photon?

(b) The minimum energy needed to break an oxygen-oxygen bond in ozone is $387\ kJ\ mol^{-1}$. Does a photon with a frequency of $1.00 \cdot 10^{15}\ s^{-1}$ have enough energy to break this bond? Support your answer with a calculation.

Solution to part a: We proceed using Planck's equation:

$$E_{photon} = h\nu$$

Plugging in our values, we have

$$E_{photon} = (6.626 \cdot 10^{-34}\ \mathrm{J} \cdot \cancel{\mathrm{s}})(1.00 \cdot 10^{15}\ \cancel{\mathrm{s}^{-1}}) = \boxed{6.62 \cdot 10^{-19}\ \mathrm{J}}$$

Solution to part b: We already calculated the energy of the photon with a frequency of $1.00 \cdot 10^{15}\ s^{-1}$ in part (a). We need to compare this value to the minimum energy needed to break an oxygen-oxygen bond in ozone.
First, we need to convert our value in part (a) to kJ.

$$\frac{6.62 \cdot 10^{-19}\ \cancel{\mathrm{J}}}{1\ \text{photons}} \cdot \frac{\mathrm{kJ}}{1000\ \cancel{\mathrm{J}}} = \frac{6.62 \cdot 10^{-22}\ \mathrm{kJ}}{\text{photons}}$$

Next, we need our answer to have units of $kJ\ mol^{-1}$.

This is because the minimum energy is given in per moles of photons. Recall Avogadro's number, $6.022 \cdot 10^{23}$, from Unit 1: one *mole* of a substance contains $6.022 \cdot 10^{23}$ formula units of that substance. In this case, our formula unit is *photons*.
Converting to $kJ\ mol^{-1}$, we have

$$\frac{6.62 \cdot 10^{-22}\ \mathrm{kJ}}{\cancel{\text{photons}}} \cdot \frac{6.022 \cdot 10^{23}\ \cancel{\text{photons}}}{\text{mol}} = 399\ \mathrm{kJ\ mol^{-1}}$$

Clearly, 399 is a larger number than 387. Therefore, the energy of this photon exceeds the minimum energy required to break an oxygen-oxygen bond in ozone. Thus, a photon with this frequency does have enough energy to break the bond.

§3.13 Beer-Lambert Law

Spectrophotometry is a technique that uses the absorption of light to determine the concentration of a solution. A device called a **spectrophotomer** measures the amount of light at a given wavelength that is absorbed by a solution. If the solution changes color as the reaction progresses, the amount of light that is absorbed will change. Absorbance can be calculated the **Beer-Lambert Law**, or Beer's Law for short.

According to the Beer-Lambert Law,

$$\boxed{A = \varepsilon bc}$$

where:

- A measures the absorbance (dimensionless quantity),
- ε is the molar absorptivity (usually in units of $M^{-1}\,\text{cm}^{-1}$),
- b represents path length traveled by the light (cm), and
- c is the molar concentration of analyte solution (M)

As molar absorptivity and path length are constants when using a spectrophotometer, the Beer-Lambert Law is often understood as a *direct* correlation between absorbance and the concentration of the solution. This mathematical relationship is most useful when dealing with solutions that visibly change color over the course of a reaction, but if a spectrophotometer that emits light in the UV region of the electromagnetic spectrum is used, Beer's Law can be used to determine reactant concentrations in solutions that are not visible to the human eye.

Sometimes, Beer's Law is also studied using a device called a **colorimeter**. A colorimeter is a special type of spectrophotometer that can emit only discrete frequency intervals, whereas a spectrophotometer can emit light at any frequency within a set range.

Let's practice!

Problem 3.13.1 — Beer's Law I

A $3.50 \cdot 10^{-6}\,M$ solution of a red pigment has an absorbance of 0.602 at 502 nm in a 1.00 cm cuvette.

Calculate the molar absorptivity, ε, of the pigment at 502 nm.

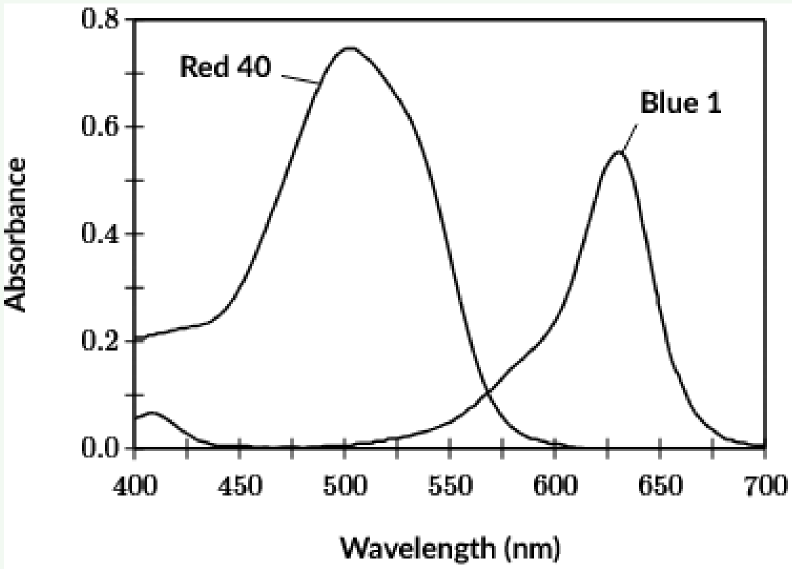
Solution: We use the formula in accordance with Beer's Law.

$$A = \varepsilon bc \therefore \varepsilon = \frac{A}{bc} = \frac{0.602}{1.00\,\text{cm} \cdot 3.50 \cdot 10^{-6}\,M} = \boxed{1.72 \cdot 10^{5}\,M^{-1}\,\text{cm}^{-1}}$$

Note that the wavelength of light was not needed to solve this problem.

Problem 3.13.2 — Beer's Law II

A student wants to use spectrophotometry to determine the concentration of Red 40, a food dye, in aqueous solution. The solution also contains a small amount of Blue 1, another food dye. In order to select the optimal wavelength for analysis, the student references the following diagram which shows the absorbance spectra of both dyes in water.



Based on the diagram, which wavelength should the student use to most accurately determine the concentration of Red 40 in the solution?

Example Courtesy of Khan Academy

Solution: To most accurately determine the concentration of Red 40 in the solution, the student should be looking for absorbance data for the dye *alone*, that is, data with minimal interference from the Blue 1 dye. To do so, they should select a wavelength at which Red 40 absorbs strongly but Blue 1 does not.

According to the diagram, Red 40 absorbs the most strongly at 500 nm, while Blue 1 displays virtually no absorbance at this wavelength.

Thus, the optimal wavelength is $\boxed{500\,\text{nm}}$

That's all there is to Beer's Law.

§3.14 Practice Problems

Problem 3.14.1 — Free-Response Question

Equal molar quantities of two gases, O_2 and H_2O, are confined in a closed vessel at constant temperature.

(a) Which gas, if either, has the greater partial pressure?
(b) Which gas, if either, has the greater density?
(c) Which gas, if either, has the greater concentration?
(d) Which gas, if either, has the greater average kinetic energy?
(e) Which gas, if either, will show the greater deviation from ideal behavior?

Solution to part a: Since equal molar quantities of both gases are confined in a rigid vessel, the partial pressures of both gases are equal. Think of representing the ideal gas law as $P \propto n$, when V and T are held constant, where these constraints are satisfied by the problem statement.

Solution to part b: Density is determined by mass divided by volume. Since both gases are confined in the same container, their occupied volumes are the same. Now, we need to consider their relative masses. Since there are equal number of moles for O_2 and H_2O, the gas with more molar mass will have the greater mass in grams. O_2 has a molar mass of 32.00 g/mol, while H_2O has a molar mass of 18.02 g/mol. Therefore, we should expect $\boxed{O_2}$ to have the greater density.

Solution to part c: Concentration is given by moles per liter of solution, or $M = \frac{n}{V}$. Both gases occupy the same volume, so V does not change. Additionally, since they are in equal molar quantities, n is the same for both. Therefore, both gases have equal concentrations.

Solution to part d: Average kinetic energy depends solely upon the temperature of a gas. Since both O_2 and H_2O are confined at the same, constant temperature, they both have the same average kinetic energy.

Solution to part e: Gases governed by stronger intermolecular forces will deviate from ideal behavior the most, because the Kinetic Molecular Theory states that all forces (attractive or repulsive) between gas particles are negligible, so any significant intermolecular forces would violate this postulate. Oxygen, O_2, is a nonpolar molecule which contains weak London dispersion forces while water H_2O is highly polar and its molecules can interact through strong hydrogen bonding. Therefore, H_2O molecules display the stronger IMFs than those of O_2, so $\boxed{H_2O}$ will demonstrate greater deviation from ideal behavior.

Problem 3.14.2 — 2003 AP Chemistry FRQ

A rigid 5.00-L cylinder contains 24.5 g of $N_2(g)$ and 28.0 g of $O_2(g)$.

(a) Calculate the total pressure (atm) of the gas mixture in the cylinder at 298 K.

(b) The temperature of the gas mixture is decreased to 280 K. Calculate each of the following.

(i) The mole fraction of $N_2(g)$ in the cylinder.
(ii) The partial pressure, in atm, of $N_2(g)$ in the cylinder.

(c) If the cylinder develops a pinhole-sized leak and some of the gaseous mixture escapes, would the ratio $\frac{\text{moles of } N_2}{\text{moles of } O_2}$ in the cylinder increase, decrease, or remain the same? Justify your answer.

A different rigid 5.00 L cylinder contains 0.176 mol of NO(g) at 298 K. A 0.176 mol sample of $O_2(g)$ is added to the cylinder, where a reaction occurs to produce $NO_2(g)$.

(d) Write the balanced equation for the reaction.

(e) Calculate the total pressure in the cylinder at 298 K after the reaction is complete.

Solution to part a: The total pressure in the cylinder is equal to the sum of the (partial) pressures for each gas enclosed in the cylinder.

Dalton's Law of Partial Pressures states that

$$P_{\text{total}} = P_{N_2} + P_{O_2}$$

We can calculate both of these values using the Ideal Gas Law. But first, let's convert from grams to moles for both substances.

$$24.5\,\cancel{\text{g}\,N_2} \cdot \frac{1\,\text{mol}\,N_2}{28.0\,\cancel{\text{g}\,N_2}} = 0.875\,\text{mol}\,N_2$$

$$28.0\,\cancel{\text{g}\,O_2} \cdot \frac{1\,\text{mol}\,O_2}{32.00\,\cancel{\text{g}\,O_2}} = 0.875\,\text{mol}\,O_2$$

Now, using the Ideal Gas Law, we have

$$P_{N_2} = \frac{n_{N_2}RT}{V} = \frac{(0.875\,\cancel{\text{mol}})(0.08206\,\cancel{\text{L}}\,\text{atm}\,\cancel{\text{mol}^{-1}}\,\cancel{\text{K}^{-1}})(298\,\cancel{\text{K}})}{5.00\,\cancel{\text{L}}} = 4.28\,\text{atm}$$

$$P_{O_2} = \frac{n_{O_2}RT}{V} = \frac{(0.875\,\cancel{\text{mol}})(0.08206\,\cancel{\text{L}}\,\text{atm}\,\cancel{\text{mol}^{-1}}\,\cancel{\text{K}^{-1}})(298\,\cancel{\text{K}})}{5.00\,\cancel{\text{L}}} = 4.28\,\text{atm}$$

Taking the sum of these values, we end up with $4.28\,\text{atm} + 4.28\,\text{atm} = \boxed{8.56\,\text{atm}}$.

Solution to part b(i): There is no reaction actually occurring in this cylinder, so decreasing the temperature of the gas mixture will **not** have an effect on the relative amounts of N_2 and O_2. Therefore, we can calculate the mole fraction of N_2 using values consistent with the ones in obtained in part (a).

$$\chi_{N_2} = \frac{\text{mol } N_2}{\text{mol } N_2 + \text{mol } O_2} = \frac{0.875\text{ mol}}{0.875\text{ mol} + 0.875\text{ mol}} = \boxed{0.500}$$

Solution to part b(ii): As temperature decreases, we should also expect a decrease in the total pressure of the gas mixture.

We can use the Ideal Gas Law to calculate the total pressure of the gas mixture at the new temperature:

$$P_{\text{total}} = \frac{(n_{N_2} + n_{O_2})RT}{V} = \frac{(0.875 + 0.875)\cancel{\text{mol}} \cdot 0.08206\,\cancel{\text{L}}\,\text{atm}\,\cancel{\text{mol}^{-1}}\,\cancel{\text{K}^{-1}} \cdot 280\,\cancel{\text{K}}}{5.00\,\cancel{\text{L}}}$$

$$\therefore P_{\text{total}} = \boxed{8.0\text{ atm}}$$

Additionally, pressure is proportional to number of moles (with constant volume), so

$$P_{N_2} = \chi_{N_2} \cdot P_{\text{total}} = 0.500 \cdot 8.0\text{ atm} = \boxed{4.0\text{ atm}}$$

Solution to part c: In order to predict what happens to the ratio $\frac{\text{moles of } N_2(g)}{\text{moles of } O_2(g)}$, we need to determine which gas effuses, or escapes, the cylinder at a faster rate. For this, we will use Graham's Law.

Recall that Graham's Law states that the rate of effusion for a gas is inversely proportional to the square root of its molar mass. Therefore, the gas with a lower molar mass will effuse faster (think about it, lighter objects should be easier to spread out at the same rate).

The molar mass of N_2 is 28.0 g/mol, and the molar mass of O_2 is 32.00 g/mol. Clearly, $N_2(g)$ has the lower molar mass so it will effuse faster than $O_2(g)$. Therefore, the number of moles of $N_2(g)$ will decrease faster than the number of moles of $O_2(g)$, causing the ratio $\frac{\text{moles of } N_2(g)}{\text{moles of } O_2(g)}$ to $\boxed{\text{decrease}}$.

Solution to part d: First, let's write the skeleton equation for the reaction:

$$NO + O_2 \rightarrow NO_2$$

To *balance* a chemical equation means to manipulate coefficients on certain species until both the reactant and product sides contain the same number of atoms for each element.

We see that there are equal number of N atoms on both sides of the reaction, so our focus should be on balancing oxygen. The reactants side contains 3 atoms of O, while the product side contains 2. Via trial and error, it makes sense to attach a 2 in front of both NO as well as NO_2, so that the N atoms are still balanced, and we have $2 + 2 = 4$ O atoms on both sides as well.

Thus, the balanced chemical equation is

$$\boxed{2\text{NO(g)} + \text{O}_2\text{(g)} \rightarrow 2\text{NO}_2\text{(g)}}$$

Solution to part e: Because we have 0.176 mol of both NO and O_2, we will need to use stoichiometry to determine the amounts of both O_2 and NO_2 remaining after the reaction is complete. Only then can we plug these values into the Ideal Gas Law and solve for the total pressure.

$$2\text{NO(g)} + \text{O}_2\text{(g)} \rightarrow 2\text{NO}_2\text{(g)}$$

Note that there is a coefficient of 2 on NO(g), but only a coefficient of 1 on O_2(g). This means that NO(g) is consumed twice as fast by the reaction as O_2, so it will deplete FIRST, making it our limiting reactant. Therefore, not all of the O_2(g) will react because the overall yield of the reaction is limited by the amount of NO(g). We will use NO(g) to determine the amount of O_2(g) that reacted, as well as the amount of NO_2(g) that was formed.

$$0.176\,\cancel{\text{mol NO}} \cdot \frac{1\text{ mol O}_2}{2\,\cancel{\text{mol NO}}} = 0.088\text{ mol O}_2$$

$$0.176\,\cancel{\text{mol NO}} \cdot \frac{2\text{ mol NO}_2}{2\,\cancel{\text{mol NO}}} = 0.176\text{ mol NO}_2$$

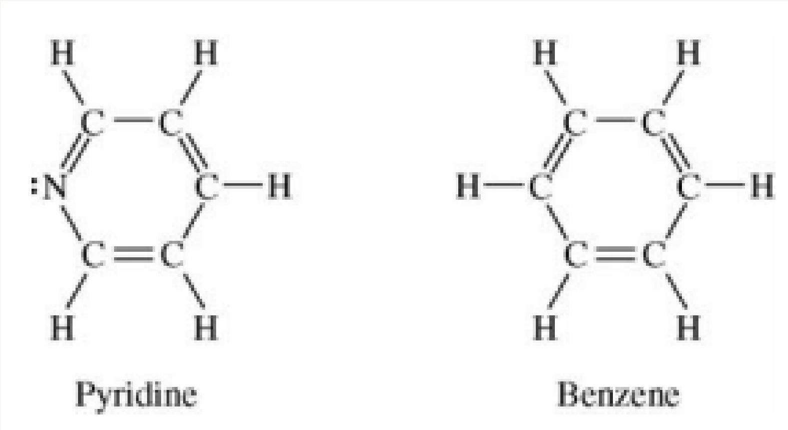
Now, we can determine the total pressure by the following:

$$P_{\text{total}} = \frac{(n_{\text{O}_2} + n_{\text{NO}_2})RT}{V} = \frac{(0.264\,\cancel{\text{mol}})(0.08206\,\cancel{\text{L}}\text{ atm}\,\cancel{\text{mol}^{-1}}\,\cancel{\text{K}^{-1}})(298\,\cancel{\text{K}})}{5.00\,\cancel{\text{L}}} = \boxed{1.29\text{ atm}}$$

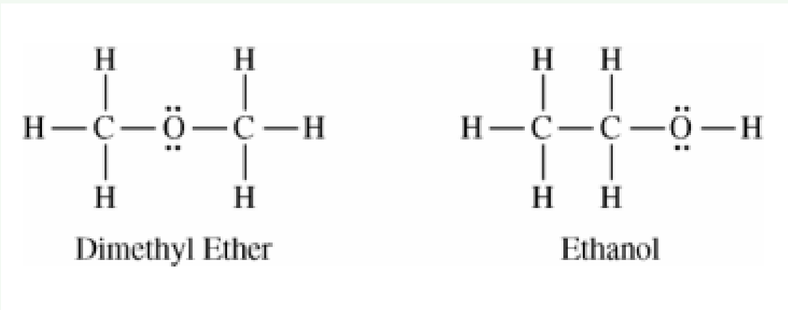
Problem 3.14.3 — 2008 AP Chemistry FRQ

Answer the following questions by using principles of molecular structure and intermolecular forces.

(a) Structures of the pyridine molecule and the benzene molecule are shown below. Pyridine is soluble in water, whereas benzene is not soluble in water. Account for the difference in solubility. You must discuss <u>both</u> of the substances in your answer.



(b) Structures of the dimethyl ether molecule and the ethanol molecule are shown below. The normal boiling point of dimethyl ether is 250 K, whereas the normal point of ethanol is 351 K. Account for the difference in boiling points. You must discuss <u>both</u> of the substances in your answer.



(c) SO_2 melts at 201 K, whereas SiO_2 melts at 1883 K. Account for the difference in melting points. You must discuss <u>both</u> of the substances in your answer.

(d) The normal boiling point of $Cl_2(l)$ (238 K) is <u>higher</u> than the normal boiling point of $HCl(l)$ (188 K). Account for the difference in normal boiling points based on the types of intermolecular forces in the substances. You must discuss <u>both</u> of the substances in your answer.

Solution to part a: The molecular structure of pyridine is asymmetrical, indicating that it is polar. Additionally, there is a lone electron pair on the nitrogen atom, making it capable of strong hydrogen bonding with the solvent water molecules and dissolving in water. In contrast, benzene is symmetrical, so it is a nonpolar molecule. Therefore, it interacts with the solvent water molecules through relatively weak London dispersion forces. Since no strong intermolecular attraction exists between benzene and water, it follows that benzene will be insoluble in water.

Solution to part b: The intermolecular forces in dimethyl ether are London dispersion forces and weak dipole-dipole forces. In addition to London dispersion and dipole-dipole forces, ethanol can also form hydrogen bonds between the hydrogen atom of a nearby molecule and the oxygen atom of a nearby ethanol molecule. Hydrogen bonds are the strongest form of intermolecular forces, so they require the most energy (in the form of heat) to overcome during the boiling process. As a result, a higher temperature is required to boil ethanol than is needed to boil dimethyl ether.

Solution to part c: In the solid phase, SO_2 consists of molecules that interact through dipole-dipole and London dispersion forces. These are the weakest types of intermolecular forces, so they are more easily overcome at low temperatures. This is consistent with the low melting point of SO_2.
On the other hand, solid SiO_2 consists of a network of strong covalent bonds between Si and O atoms. Furthermore, these covalent bonds are stronger than general intermolecular forces, so they can only be broken at relatively high temperatures. This phenomenon is consistent with the high melting point of SiO_2.

Solution to part d: $Cl_2(l)$ is diatomic, a nonpolar molecule. Therefore, its only intermolecular forces are London dispersion forces. HCl(l) is an ionic compound, consisting of both London dispersion forces and dipole-dipole forces. Since the boiling point of $Cl_2(l)$ is higher than the boiling point of HCl(l), the London dispersion forces in $Cl_2(l)$ alone are stronger than the combined London dispersion and dipole-dipole forces in HCl(l). This phenomenon is explained by the former containing a larger number of electrons, as the strength of London dispersion forces is directly proportional to the total number of electrons.

Problem 3.14.4 — 2012 AP Chemistry FRQ (Excerpt)

A sample of a pure, gaseous hydrocarbon is introduced into a previously evacuated rigid 1.00 L vessel. The pressure of the gas is 0.200 atm at a temperature of 127°C.

(a) Calculate the number of moles of the hydrocarbon in the vessel.

(b) $O_2(g)$ is introduced into the same vessel containing the hydrocarbon. After the addition of the $O_2(g)$, the total pressure of the gas mixture in the vessel is 1.40 atm at 127°C. Calculate the partial pressure of $O_2(g)$ in the vessel.

The mixture of the hydrocarbon and the oxygen is sparked so that a complete combustion reaction occurs, producing $CO_2(g)$ and $H_2O(g)$. The partial pressures of these gases at 127°C are 0.600 atm and 0.800 atm, respectively. There is $O_2(g)$ remaining in the container after the reaction is complete.

(c) Use the partial pressures of $CO_2(g)$ and $H_2O(g)$ to calculate the partial pressure of $O_2(g)$ consumed in the combustion.

(d) On the basis of your answers above, write the balanced chemical equation for the combustion reaction and determine the formula of the hydrocarbon.

(e) Calculate the mass of the hydrocarbon that was combusted.

Solution to part a: We know the pressure of the gas, the volume of the container, as well as the temperature. Therefore, we can use the Ideal Gas Law.

$$PV = nRT$$

Rearranging to solve for n, we have

$$n = \frac{PV}{RT}$$

Remember that T is the temperature in Kelvins, so $T = 127°\text{C} + 273 = 400.\text{ K}$.

$$n = \frac{(0.200\,\cancel{\text{atm}})(1.00\,\cancel{\text{L}})}{(0.0821\,\cancel{\text{L}}\,\cancel{\text{atm}}\,\text{mol}^{-1}\,\cancel{\text{K}^{-1}})(400.\,\cancel{\text{K}})} = \boxed{6.09 \cdot 10^{-3}\text{ mol}}$$

Solution to part b: This problem involves Dalton's Law of Partial Pressures.

$$P_{\text{total}} = P_1 + P_2 + ...$$

For this question, we have

$$P_{\text{total}} = P_{O_2} + P_{gas}$$

Rearranging to solve for P_{O_2}, we find

$$P_{O_2} = P_{\text{total}} - P_{gas} = 1.40\text{ atm} - 0.200\text{ atm} = \boxed{1.20\text{ atm}}$$

Solution to part c: We can use $PV = nRT$ to solve for the number of moles of each gas and then use ratios to convert them to moles of O_2. Then, we will use $PV = nRT$ again to solve for P_{O_2} in total.

Setting up the Ideal Gas Law for both CO_2(g) and H_2O(g), we have:

$$n_{H_2O} = \frac{P_{H_2O}V}{RT} = \frac{(0.800\,\cancel{\text{atm}})(1.00\,\cancel{\text{L}})}{(0.08206\,\cancel{\text{L}}\,\cancel{\text{atm}}\,\text{mol}^{-1}\,\cancel{\text{K}^{-1}})(400\,\cancel{\text{L}})} = 0.0244\,\text{mol H}_2\text{O}$$

$$n_{CO_2} = \frac{P_{CO_2}V}{RT} = \frac{(0.600\,\cancel{\text{atm}})(1.00\,\cancel{\text{L}})}{(0.08206\,\cancel{\text{L}}\,\cancel{\text{atm}}\,\text{mol}^{-1}\,\cancel{\text{K}^{-1}})(400\,\cancel{\text{K}})} = 0.0813\,\text{mol CO}_2$$

Now, we need to convert these values to moles of O_2. For this, we need to use the appropriate mole ratio. For every one mole of O_2, there is one mole of CO_2, because both of them contain the same number of oxygen atoms. However, every one mole of O_2 is associated with TWO moles of H_2O because water contains only one oxygen atom per molecule.

Thus, we have

$$0.0244\,\cancel{\text{mol H}_2\text{O}} \cdot \frac{1\text{ mol O}_2}{2\,\cancel{\text{mol H}_2\text{O}}} = 0.0122\,\text{mol O}_2$$

$$0.0183\,\cancel{\text{mol CO}_2} \cdot \frac{1\text{ mol O}_2}{1\,\cancel{\text{mol CO}_2}} = 0.0183\,\text{mol O}_2$$

Adding these up, the total number of moles of O_2 is $n_{O_2} = 0.0305\,\text{mol}$. Now, we can plug everything into the Ideal Gas Law equation for P:

$$P = \frac{n_{O_2}RT}{V} = \frac{(0.0305\,\cancel{\text{mol}})(0.08206\,\cancel{\text{L}}\,\text{atm}\,\cancel{\text{mol}^{-1}}\,\cancel{\text{K}^{-1}})(400\,\cancel{\text{K}})}{1.00\,\cancel{\text{L}}} = \boxed{1.00\text{ atm O}_2}$$

Solution to part d: We can calculate the number of moles of H_2O and CO_2 by using their partial pressures and convert both to moles of H and C by using mole ratios associated with combustion analysis (all the carbon is converted into CO_2 and all the hydrogen is converted into H_2O).

$$n_{H_2O} = \frac{P_{O_2}V}{RT} = \frac{(0.80\,\cancel{\text{atm}})(1.00\,\cancel{\text{L}})}{(0.0821\,\cancel{\text{L}}\,\cancel{\text{atm}}\,\text{mol}^{-1}\,\cancel{\text{K}^{-1}})(400.\,\cancel{\text{K}})} = 0.0244\,\text{mol H}_2\text{O}$$

$$0.0244\,\cancel{\text{mol H}_2\text{O}} \cdot \frac{2\text{ mol H}}{1\,\cancel{\text{mol H}_2\text{O}}} = 0.0487\,\text{mol H}$$

$$n_{H_2O} = \frac{P_{H_2O}V}{RT} = \frac{(0.600\,\cancel{\text{atm}})(1.00\,\cancel{\text{L}})}{(0.0821\,\cancel{\text{L}}\,\cancel{\text{atm}}\,\text{mol}^{-1}\,\cancel{\text{K}^{-1}})(400.\,\cancel{\text{K}})} = 0.0183\,\text{mol CO}_2$$

$$0.0183\,\cancel{\text{mol CO}_2} \cdot \frac{1\text{ mol C}}{1\,\cancel{\text{mol CO}_2}} = 0.0183\,\text{mol C}$$

When determining the empirical formula, we divide by the smallest number of moles to determine the ratio of the number of atoms for each atom.

$$\frac{0.0487\text{ mol H}}{0.0183\text{ mol C}} = \frac{2.\overline{6}\text{ mol H}}{1\text{ mol C}} \cdot \frac{3}{3} = \frac{8\text{ mol H}}{3\text{ mol C}}$$

Since there are 8 H for every 3 C, the chemical formula for the hydrocarbon is $\boxed{C_3H_8}$.

At this point, we need to write the balanced chemical equation describing the combustion of our hydrocarbon.

We can set up the following relationships:

$$P_{\text{hydrocarbon}} \quad : \quad P_{O_2} \quad : \quad P_{CO_2} \quad : \quad P_{H_2O}$$

Recall that when determining the empirical formula of a compound, we would convert all masses to moles, and then divide by the smallest number of moles to determine the ratio of each element's number of atoms. Here, we are not given moles, but pressure (in atm). The Ideal Gas Law states that for constant temperature and volume, $P \propto n$. Thus, we can divide by the smallest amount of pressure to determine the relative coefficients for each species in the balanced chemical equation.

$$0.200\,\text{atm} \quad : \quad 1.00\,\text{atm} \quad : \quad 0.600\,\text{atm} \quad : \quad 0.800\,\text{atm}$$

$$1 \quad : \quad 5 \quad : \quad 3 \quad : \quad 4$$

Now that we have determined the relative number of moles for all species, these numbers become the coefficients in our balanced chemical equation:

$$\boxed{C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O}$$

Solution to part e: We will apply the formula

$$\text{molar mass} = \frac{\text{mass}}{\text{number of moles}}$$

Rearranging for mass, we have

$$\text{mass} = (\text{number of moles})(\text{molar mass})$$

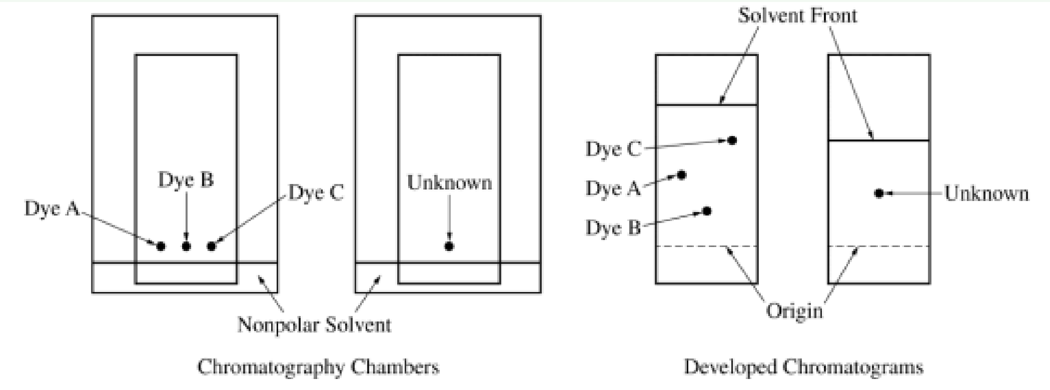
Since we know from part (d) that the formula for the hydrocarbon is C_3H_8, we can determine its molar mass.

$$\text{molar mass } C_3H_8 = 3 \cdot 12.01\text{ g/mol} + 8 \cdot 1.008\text{ g/mol} = 44.1\text{ g/mol}$$

Since we know from part (a) that there are $6.09 \cdot 10^{-3}$ mol of C_3H_8, we can plug this value into the mass calculation:

$$\text{mass} = (6.09 \cdot 10^{-3}\text{ mol})(44.1\text{ g/mol}) = \boxed{0.269\text{ g}}$$

Problem 3.14.5 — 2017 AP Chemistry FRQ



A student investigates various dyes using paper chromatography. The student has samples of three pure dyes, labeled A, B, and C, and an unknown sample that contains one of the three dyes. The student prepares the chromatography chambers shown above on the left by putting a drop of each dye at the indicated position on the chromatography paper (a polar material) and standing the paper in a nonpolar solvent. The developed chromatograms are shown above the right.

(a) Which dye (A, B, or C) is the least polar? Justify your answer in terms of the interactions between the dyes and the solvent or between the dyes and the paper.

(b) Which dye is present in the unknown sample? Justify your answer.

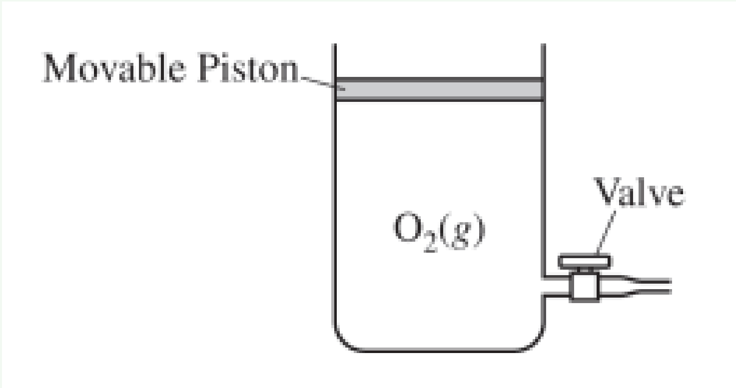
Solution to part a: We will need to consider the relative polarities of the three dyes (A, B, and C) and the polarity of the solvent to solve this problem. We are told that the solvent front is nonpolar. Note that substances with similar polarity tend to be strongly attracted to one another compared to those with very different polarities. This implies that the dye that travels the most along the solvent should be the *least* polar, and vice versa.

Therefore, we conclude that $\boxed{\text{Dye C}}$ is the least polar because it moved the farthest. This is because nonpolar dyes are more strongly attracted to the nonpolar solvent.

Solution to part b: To answer this question, we need to determine which dye travels across the paper to a similar extent as the dye we want to find in the unknown sample.

Observing the diagram, we see that the dye representing the unknown sample moves roughly halfway across the path connecting the origin and solvent front. Therefore, we need to determine which of dyes A, B, and C display a similar progression across the chromatography paper. By inspection, it is clear that $\boxed{\text{Dye A}}$ most nearly moves to a position midway relative to the origin and the solvent front.

Problem 3.14.6 — 2021 AP Chemistry FRQ



A student investigates gas behavior using a rigid cylinder with a movable piston of negligible mass, as shown in the diagram above. The cylinder contains 0.325 mol of O_2(g).

(a) The cylinder has a volume of 7.95 L at 25°C and 1.00 atm. Calculate the density of the O_2(g), in g/L, under these conditions.

(b) Attempting to change the density of the O_2(g), the student opens the valve on the side of the cylinder, pushes down on the piston to release some of the gas, and closes the valve again. The temperature of the gas remains constant at 25°C. Will this action change the density of the gas remaining in the cylinder? Justify your answer.

(c) The student tries to change the density of the O_2(g) by cooling the cylinder to −55°C, which causes the volume of the gas to decrease. Using principles of kinetic molecular theory, explain why the volume of the O_2(g) decreases when the temperature decreases to −55°C.

(d) The student further cools the cylinder to −180°C and observes that the measured volume of the O_2(g) is substantially smaller than the volume that is calculated using the ideal gas law. Assume all equipment is functioning properly. Explain why the measured volume of the O_2(g) is smaller than the calculated volume. (The boiling point of O_2(l) is −183°C.)

Solution to part a: Since density is in units of grams per liter, we should convert the correct units accordingly.

For example, we were given the number of moles of O_2(g), but we want the number of grams of O_2(g). We will convert to grams using the molar mass of O_2(g) - 32.00 g/mol.

$$0.325\,\cancel{\text{mol O}_2} \cdot \frac{32.00\text{ g}}{1\,\cancel{\text{mol O}_2}} = 10.4\text{ g O}_2$$

Using $D = \frac{m}{V}$, we have

$$D = \frac{10.4\text{ g}}{7.95\text{ L}} = \boxed{1.31\text{ g/L}}$$

Solution to part b: We can represent density in terms of other variables from the Ideal Gas Law equation.

For example, we can represent mass as the number of moles (n) in a substance multiplied by its molar mass (MM), i.e. the mass that is occupied in one mole of that substance.

Therefore, we can rewrite $D = \frac{m}{V}$ as

$$D = \frac{n \cdot \text{MM}}{\frac{nRT}{P}} = \frac{P \cdot \text{MM}}{RT}$$

Consider these variables. Molar mass of O_2(g) is always 32.00 g/mol, P, R, and T are held constant, and most importantly, mass and volume decrease *proportionately*, so the density of O_2(g) does <u>not</u> change.

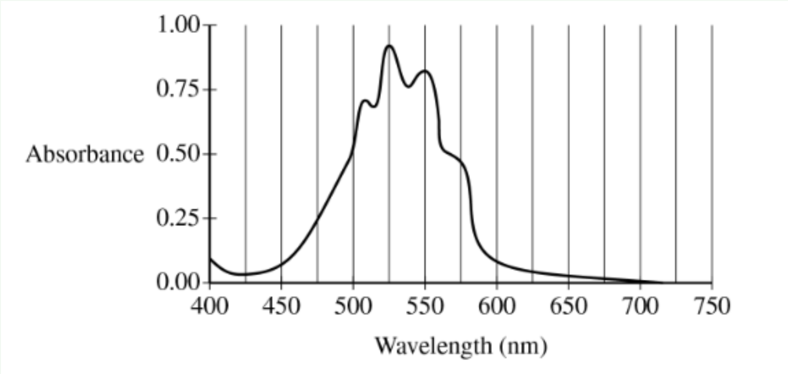
Solution to part c: One of the major postulates of Kinetic Molecular Theory is that the average kinetic energy of gas particles is proportional to the temperature (if given in Kelvins, this relationship is *directly* proportional).

Essentially, as the gas cools, the average kinetic energy (and thus speed) of the O_2(g) molecules decreases. This causes the molecules to rebound against the cylinder and among the other molecules with less energy. Therefore, the overall spacing between individual gas particles decreases, and this causes their occupied volume to decrease, by definition.

Solution to part d: The ideal gas law (which is derived from the kinetic molecular theory) assumes that any attractive or repulsive forces between gas particles are negligible. However, as a *real* gas cools further, the intermolecular forces are more significant regarding the decrease in average speed of the molecules. The only way to maintain constant pressure at 1 atm with stable collisions is for volume to decrease. This will allow the system to accommodate more collisions with less energy.

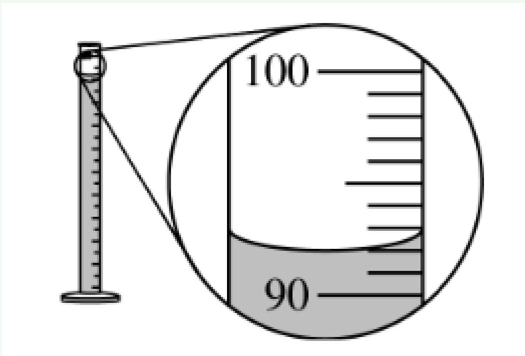
Problem 3.14.7 — 2022 AP Chemistry FRQ

A student wants to determine the concentration of permanganate, $MnO_4^-(aq)$, in a solution. The student plans to use colorimetric analysis because solutions containing $MnO_4^-(aq)$ have a purple color.



(a) To determine the optimum wavelength for an experiment that measures the concentration of $MnO_4^-(aq)$, the student takes a sample of the solution and measures the amount of light absorbed by the sample over a range of wavelengths. The data are plotted in the graph shown. Identify the optimum wavelength that the student should use for the experimental procedure.

(b) The student uses a stock solution of $2.40 \cdot 10^{-3}$ M $KMnO_4(aq)$ to prepare the standard solutions of $MnO_4^-(aq)$ that are needed to construct a calibration curve.



(i) The student uses a 100.0 mL graduated cylinder to measure a certain volume of $KMnO_4(aq)$ stock solution, as shown in the diagram given. What volume should the student record?

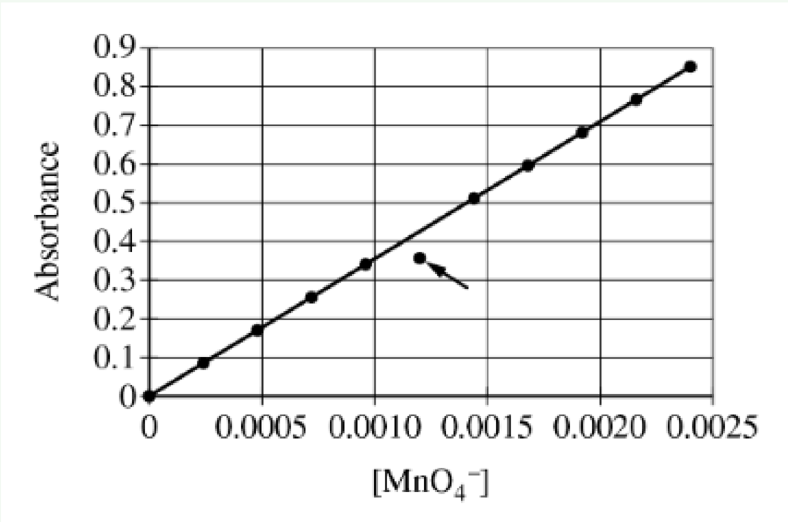
Problem 3.14.8 — 2022 AP Chemistry FRQ (Continued)

(b)(ii) Calculate the volume, in mL, of $2.40 \cdot 10^{-3}$ M $KMnO_4$(aq) that is required to produce 100.0 mL of a standard $1.68 \cdot 10^{-3}$ M MnO_4^-(aq) solution.

The student designs the following procedure to produce a calibration curve.

1. Prepare several standard solutions that have known MnO_4^-(aq) concentrations by dilution of the stock solution.
2. Rinse the cuvette with distilled water.
3. Rinse the cuvette with the standard solution and fill the cuvette with the standard solution.
4. Measure the absorbance of the standard solution with the colorimeter.
5. Repeat steps 2 − 4 for each of the standard solutions.

The data are plotted on the calibration curve shown. One of the data points (indicated with an arrow) on the calibration curve is below the line of best fit.



(c) Assuming that all lab equipment is functioning properly, identify which one of the procedural steps the student could have executed incorrectly that would explain why the marked data point is below the line of best fit. Justify your answer.

Solution to part a: We want to choose a wavelength such that the absorbance of MnO_4^- is maximized. Specifically, we want to find the wavelength that corresponds to the highest point on the y-axis. This occurs at the halfway point of the interval [500 nm, 550 nm], so the optimum wavelength must be $\boxed{525 \text{ nm}}$.

Solution to part b(i): This question tests our knowledge of reading measurements on laboratory instruments. For any instrument involving a liquid, e.g. graduated cylinder, volumetric flask, etc., we read the *lower* meniscus, or from the line that is tangent to the curved liquid that is concave up. Let's look at the graduated cylinder measurement.

We notice that the $KMnO_4$(aq) stock solution begins to curve at 92.0 mL, leading to a concave up shape. Since we read the volume with respect to the lower meniscus, we know that the student should record a volume of $\boxed{92.0\,\text{mL}}$.

Solution to part b(ii): There is a very important concept that will be introduced here, since it is most important when you are actually solving problems involving concentration and volume.

If water is added/removed to/from a solution, the amount of solute does not change, rather, it is only the concentration of the substance that changes. Molarity (M), which is defined as moles of solute per liter of solution, will change because the total volume of the solution changes, not the number of moles in the solute.

$$\#\text{ moles of solute before dilution} = \#\text{ moles of solute after dilution}$$

To generalize this, denote the sets M_1 and V_1 and M_2 and V_2 the concentration and volume of the solution before and after it is diluted, respectively.

$$M_1V_1 = M_2V_2$$

This problem calls for us to determine the initial volume of 70.0 mL $KMnO_4$(aq) stock solution so that we can dilute it into a 100.0 mL solution with final concentration of $1.68 \cdot 10^{-3}\,M$. We can proceed with the formula:

$$M_1V_1 = M_2V_2$$

$$V_1 = \frac{M_2V_2}{M_1} = \frac{(1.68 \cdot 10^{-3}\,\cancel{M})(100.0\,\text{mL})}{(2.40 \cdot 10^{-3}\,\cancel{M})} = \boxed{70.0\,\text{mL}}$$

Solution to part c: A marked data point located below the best-fit line suggests that the absorbance of the solution was *underestimated.* Recall that absorbance is directly proportional to concentration, according to the Beer-Lambert Law. If the problem asks us to identify an error that resulted in a lower calculated absorbance, we essentially need to determine where a student incorrectly executed a step of the procedure that caused the calculated $[MnO_4^-]$ to be underestimated.

The most likely error that occurred here was if the student improperly executed $\boxed{\text{step 3}}$. Specifically, if they forgot to rinse the cuvette with distilled water before filling it to measure absorbance, then the standard solution would be diluted by the remaining distilled water, resulting in a calculated absorbance value that is lower than what it should be (dilution → less concentration → less absorbance).

4 Chemical Reactions

Chemical reactions! They occur all around us, constantly transforming matter in revolutionary ways. This unit explores net ionic equations, stoichiometry, an introduction to titration, types of chemical reactions, and more.

§4.1 Introduction for Reactions

Virtually everything in the world runs on chemical reactions, whether it is the latest technology or fizzy drinks. In a more technical definition, specific interactions with molecules result in the rearrangement of atoms, forming new molecules.

What is a Chemical Reaction?

Generally when discussing matter, there are two types of changes: physical changes and chemical changes.

A **physical change** is one that changes an object but does not change its chemical structure. For example, you can boil water into steam or freeze it into ice, but H_2O remains as H_2O in both processes. Similarly, a piece of paper can be shredded to the point where you can barely see it, but the material is still "paper."

The most common physical changes refer to changes in the state of matter for a substance (phase changes) or the formation/separation of substances in nature.

However, **chemical changes** lead to the formation of new products. There must be some change on the molecular level in order for atoms in an original compound to rearrange and form a new molecule. For example, if you leave iron outside for too long, it rusts due to oxidation. Rusting is the chemical reaction between iron metal (Fe) and oxygen in the air (O_2) to form iron oxide (Fe_2O_3).

Chemical changes are the foundation for this course and are described using **chemical reactions**. That being said, here are some evidences for a chemical change, and therefore implies a chemical reaction that is taking place:

- Evolution of heat or light - **combustion reactions**, as we discuss later, are evident with fire.
- Formation of a gas, or odor - you may see bubbles forming in an experiment.
- Precipitation - this refers to the formation of a solid when two substances mix.
- Color change - using indicators, or chemicals that undergo changes in color based on the pH of the environment.

Important: You only need one of these evidences to determine a chemical change, but you will usually see 2 or 3 in most situations.

Representing Chemical Reactions

For this course, chemical reactions are represented by **chemical equations**. These are written representations of substances involved in the reaction and the changes that they undergo.

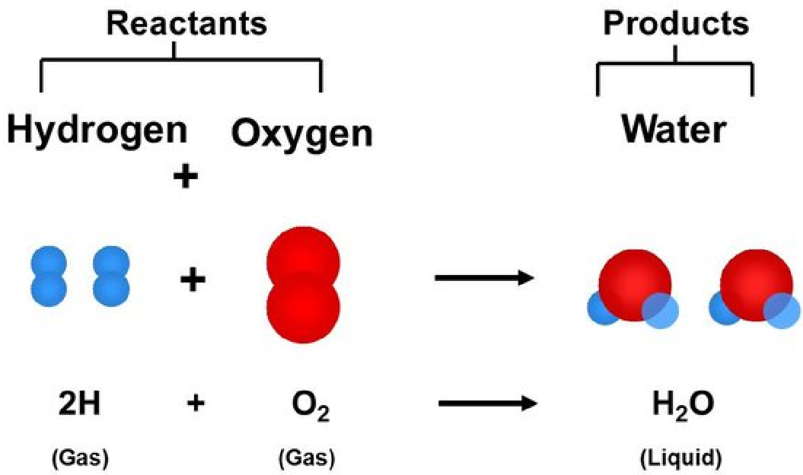


Image Courtesy of Quora

- The **reactants**, or the substances that are reacting with each other, are listed on the left side.
- The **products**, or the substances that are produced, are listed on the right side.
- The arrow (→) indicates the direction of the reaction, from left to right.
- The **coefficients**, the numbers in front of each species, indicate the relative amounts of each substance in the reaction.
- The **chemical formulas** of the reactants and products represent the composition of the substances involved. The formulas are made up of symbols for the elements present in the substances, with subscripts indicating the number of atoms of each element.

There are **five** main types of chemical reactions, namely, synthesis, decomposition, combustion, single replacement, and double replacement. For now, we will have a brief overview for each of them.

Synthesis Reactions

These reactions are the most intuitive to understand. Essentially, **synthesis reactions** consist of two reactants *fusing* together to form products in the following manner:

$$\mathrm{A} + \mathrm{B} \rightarrow \mathrm{AB}$$

where the molecules A, B, and AB are arbitrary.

An example of a synthesis reaction is the formation of solid sodium chloride from sodium metal and chlorine gas:

$$\mathrm{Na(s)} + \frac{1}{2}\mathrm{Cl_2(g)} \rightarrow \mathrm{NaCl(s)}$$

Decomposition Reactions

These are the complete opposite of synthesis reactions. Here, one reactant breaks down into two or more products. This is usually achieved via heat energy breaking the chemical bonds within the reactant.

$$\mathrm{XY} \rightarrow \mathrm{X} + \mathrm{Y}$$

Again, the molecules X, Y, and XY are arbitrarily designated.

For example, **hydrogen peroxide** decomposes into oxygen gas and water when heated.

$$\mathrm{2H_2O_2(aq)} \rightarrow \mathrm{2H_2O(l)} + \mathrm{O_2(g)}$$

Combustion Reactions

These reactions are a special type of decomposition reactions involving **organic molecules**, which are carbon-based. For the scope of AP Chemistry, the important class of organic molecules is the **hydrocarbons**, only composed of carbon and hydrogen atoms.

At high temperatures or in the presence of atmospheric oxygen, hydrocarbons **combust**, or burn, and heat energy is released from the chemical reaction. Therefore, the general reaction sees a hydrocarbon being combusted into carbon dioxide and water in the presence of oxygen.

For example, the combustion of methane, CH_4, is represented by the balanced equation:

$$\mathrm{CH_4(g)} + \mathrm{2O_2(g)} \rightarrow \mathrm{CO_2(g)} + \mathrm{2H_2O(g)}$$

The key definition of combustion is why oxygen gas is necessary in order to start a fire!

Single Replacement Reactions

Single replacement reactions occur when a compound reacts with a single element. The general form of the equation is described by

$$\mathrm{AB} + \mathrm{C} \rightarrow \mathrm{AC} + \mathrm{B}$$

where all these molecules are arbitrary, for simplicity.

The most common type of single replacement reactions is **redox reactions**, where electrons are transferred between atoms. (We will discuss these in section 4.9.)

Double Replacement Reactions

The most common type of reaction in this course is a **double replacement** reaction, with the general form

$$AB + CD \rightarrow AD + CB$$

For example, if you react an acid with a base in equal amounts, they will neutralize each other, forming water and a salt (ionic compound).

$$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$$

HCl and NaOH are hydrochloric acid and sodium hydroxide, which are a strong acid and strong base, respectively.

These reactions involve the exchange of ions between two compounds to form new compounds. Here, *two* switches take place, whereas only one occurs in single replacement reactions.

Let's do some practice to conclude this section.

Problem 4.1.1 — Identifying Type of Reaction

For each chemical reaction, classify which type it represents.

1. $Zn + HCl \rightarrow ZnCl_2 + H_2$
2. $2C_8H_{18} + 25O_2 \rightarrow 16CO_2 + 18H_2O$
3. $2H_2O \rightarrow 2H_2 + O_2$
4. $BaCl_2 + Na_2SO_4 \rightarrow BaSO_4 + 2NaCl$

Solution to part 1: Zinc replaces hydrogen in HCl, forming $ZnCl_2$ instead. Additionally, only one "switch" takes place, so the reaction is $\boxed{\text{single replacement}}$.

Solution to part 2: We have C_8H_{18}, a hydrocarbon, reacting with oxygen (in air) (O_2) to form carbon dioxide and water. This is a $\boxed{\text{combustion}}$ reaction.

Solution to part 3: Here, a water molecule breaks apart into its constituent elements, hydrogen and oxygen. This is a $\boxed{\text{decomposition}}$ reaction.

Solution to part 4: Two ionic compounds react with each other, and an exchange of ions occurs. In other words, there are two "switches" between the ions in both compounds, so we have a $\boxed{\text{double replacement}}$ reaction.

§4.2 Net Ionic Equations

When dealing with chemical reactions, in this course, most of them are taking place in **aqueous environments**, where species are dissolved in water. For example, if you dissolve table salt (NaCl) in water, the water molecules will separate it into its constituent ions, Na^+ and Cl^-. Additionally, water is a **polar** molecule so its negative and positive ends orient themselves to wrap around the sodium and chloride ions.

The terminology follows: ionic compounds **dissociate** into their ions when dissolved in water. Going back to intermolecular forces from the previous unit, when you dissolve an ionic compound, you will recognizes **ion-dipole interactions**.

Therefore, we can write the dissociation of NaCl in water as

$$\mathrm{NaCl(s)} \rightarrow \mathrm{Na^+(aq)} + \mathrm{Cl^-(aq)}$$

When representing the reaction between aqueous solutions, we can write out the ionic components that dissolve rather than the entire compound itself.

Precipitation Reactions

In some cases, when two ionic compounds react, one of the products is **insoluble**. This means that it will not be separated into its ions and will therefore *precipitate out* as a solid and does *not* dissolve in water.

For example, if aqueous solutions of KI(aq) and $Pb(NO_3)_2$(aq) are mixed together, the following reaction occurs:

$$\mathrm{2KI(aq)} + \mathrm{Pb(NO_3)_2(aq)} \rightarrow \mathrm{2KNO_3(aq)} + \mathrm{PbI_2(s)}$$

If we break apart each ionic compound that dissolves into constituent ions, we get the **complete ionic equation**:

$$\mathrm{2K^+(aq)} + \mathrm{2I^-(aq)} + \mathrm{Pb^{2+}(aq)} + \mathrm{2NO_3^-(aq)} \rightarrow \mathrm{2K^+(aq)} + \mathrm{2NO_3^-(aq)} + \mathrm{PbI_2(s)}$$

Note: PbI_2 does NOT dissociate into its ions, because it is insoluble. Make sure to be on the lookout for these cases. ONLY dissociate **soluble** ionic compounds in the complete ionic equation. Additionally, don't dissociate **weak acids** and **weak bases**, but we'll get to that a little later.

Writing Net Ionic Equations

A net ionic equation is a chemical equation that shows only the species that *actively* participate in the chemical reaction. Therefore, **spectator ions** are omitted. These are ions that appear on both sides of the arrow in a chemical equation in equal amounts but do not actually participate in the reaction. In **precipitation reactions**, spectator ions are those that did not facilitate the formation of the precipitate (solid product).

Going back, let's identify the spectator ions that we can remove to determine the net ionic equation. When looking at the complete ionic equation, we notice that K^+ and

NO_3^- are both present in equal amounts on the reactants and products sides. Therefore, these are the spectator ions.

Once we eliminate them, we are left with the following equation:

$$\boxed{2I^-(aq) + Pb^{2+}(aq) \rightarrow PbI_2(s)}$$

This is the **net ionic equation** that describes our reaction, and it represents what actually occurred when these two solutions were mixed. Although K^+ and NO_3^- are freely floating in the flask, they didn't really assist in forming the solid PbI_2 precipitate. There could've been any other pair of aqueous cation and anion and the reaction would have the same outcome.

In order to fully understand these reactions, you must be aware of the solubility rules.

1. All Group 1 ions (Li^+, Na^+, etc.) form soluble salts in water.
2. All ammonium (NH_4^+) salts are soluble in water.
3. All nitrates (NO_3^-), chlorates (ClO_3^-), and hydrogen carbonates (HCO_3^-) are soluble.
4. All halides (Cl^-, Br^-, I^-, etc.) are soluble with the exception of those combined with Ag^+, Hg_2^{2+}, and Pb^{2+}.
5. All sulfates (SO_4^2-) are soluble except for those combined with Ag^+, Ca^{2+}, Sr^{2+}, Ba^{2+}, or Pb^{2+}.
6. All sulfides are insoluble except for those containing NH_4^+, the alkali metal ions, and Ca^{2+}, Sr^{2+}, and Ba^{2+}.
7. All carbonates (CO_3^{2-}) and phosphates (PO_4^{3-}) are insoluble except for those containing NH_4^+ and the alkali metal ions.
8. All hydroxides (OH^-) are insoluble except for those of the alkali metal ions, and Ca^{2+}, Sr^{2+}, and Ba^{2+}.

These can be handy at times, but you don't need to memorize all of them. College Board has stated that only the following solubility rule will be assessed on the AP Exam: **"all sodium, potassium, ammonium, and nitrate salts are soluble in water."**

General Steps

Let's describe a problem-solving strategy that will work every time you have to write a net ionic equation for a chemical reaction.

It will take practice, but if you follow these steps repeatedly, writing net ionic equations will become very easy for you.

1. Use solubility rules to identify soluble and insoluble compounds.
2. If needed, balance the chemical equation (they are usually done for you, but it doesn't hurt to check).

3. Construct the complete ionic equation by dissociating soluble compounds into constituent ions.

4. Omit the spectator ions to get the final net ionic equation for the given reaction. Make sure to include the phases of matter, e.g. (aq) means aqueous, soluble (s) means solid, insoluble.

§4.3 Representations of Reactions

In the first section, we briefly discussed how physical changes and chemical reactions can be tracked by **chemical equations**. Chemical equations will be extremely important for not only Unit 4, but for the entire course. However, before we can examine these reactions to observe and quantify the changes in matter, we need to learn how to properly set them up. In other words, we need to learn how to **balance** a chemical reaction. If the equations are not balanced, we will get incorrect results.

Consider the combustion of propane shown by the reaction below.

$$C_3H_8(g) + O_2(g) \rightarrow CO_2(g) + H_2O(g)$$

Count the number of atoms of each element on the reactant and product sides.

$$\begin{array}{ll} C:3 & C:1 \\ H:8 & H:2 \\ O:2 & O:3 \end{array}$$

Ask yourself, "Is the chemical reaction balanced or not, and why does it matter?"

Reason for Balancing Chemical Reactions

There is a fundamental principle in chemistry that explains why we must balance chemical reactions before we can use them to perform analysis for changes in chemical reactions.

The **law of conservation of mass** states that the amount of matter stays constant in a closed system. In other words, matter cannot be created or destroyed (in thin air).

We can consider a chemical reaction as a closed system. Since the amount of matter in that system must be conserved, the number of atoms that are produced for each element must match the number of atoms that are put in. However, the atoms can still rearrange themselves (by definition of a chemical reaction), but we need to make sure that the number of atoms for all elements in the reactants is the same as those in the products, even if the products are chemically different from the species that we started with.

We will go through a couple examples to make sense of this concept.

Example 4.3.1

The following chemical equation represents the synthesis of carbon dioxide:

$$CO(g) + O_2(g) \rightarrow CO_2(g)$$

The first thing we should ask ourselves is, "Is the reaction balanced or not?" For this, the step is to take a look at the reactants and products.

In this case, the reactant side contains 1 carbon atom and 3 oxygen atoms, while the product side has 1 carbon atom and 2 oxygen atoms. Although we have the same number of carbon atoms, we do not have the same number of oxygen atoms. Therefore, we conclude that the equation is unbalanced.

Since the carbon atoms are already balanced, we know that the compounds containing carbon will have to have the same coefficient. For now, we can leave the coefficients of CO and CO_2 as 1 for now.

Note 4.3.2

This brings me to an important point. We can only change the **coefficients** of the molecules, but not the **subscripts**. If we do so, then we create completely different molecules. For example, $2NO_2$ represents two molecules of **nitrogen dioxide**, but N_2O_4 represents one molecule of **dinitrogen tetroxide**. Additionally, coefficients should generally be whole numbers.

Now, look for elements that appear in multiple compounds on one side. In our equation, that element is oxygen. Since the products side contains less oxygen, we can increase the coefficient of CO_2 from 1 to 2.

Note that CO and CO_2 must have the same coefficient, so we will increase the coefficient of CO to 2 as well.

$$2CO(g) + O_2(g) \rightarrow 2CO_2(g)$$

At this point, we can check to see if our reaction is balanced.

$$\begin{array}{cc} C:2 & C:2 \\ O:4 & O:4 \end{array}$$

Awesome! Both reactants and products have an equal number of atoms for each element. Therefore, we have obeyed the law of conservation of mass, and the equation is balanced.

Example 4.3.3

Consider the chemical equation shown below:

$$Li(s) + N_2(g) \rightarrow Li_3N(s)$$

As always, the first step is to check the number of atoms for each element. There is one atom of lithium on the reactant side and three on the product side. Additionally, there are two nitrogen atoms on the reactant side and one on the product side. Therefore, neither lithium nor nitrogen is balanced, so our solution will be slightly more rigorous than the one in the previous example.

Although the best approach may be to "guess and check," we can still go about balancing the equation strategically.

Since there are three lithium atoms on the right and only one on the left, we can increase the coefficient of Li to 3.

$$3\mathrm{Li(s)} + \mathrm{N_2(g)} \rightarrow \mathrm{Li_3N(s)}$$

Looking at nitrogen, there are 2 atoms on the left and only 1 on the right. Therefore, we will increase the coefficient of Li_3N from 1 to 2.

$$3\mathrm{Li(s)} + \mathrm{N_2(g)} \rightarrow 2\mathrm{Li_3N(s)}$$

However, lithium is no longer balanced! Fortunately, we are allowed to keep manipulating the coefficients until the chemical equation is balanced. Since there are now 6 atoms of lithium on the right, we can increase the coefficient of Li(s) from 3 to 6.

$$6\mathrm{Li(s)} + \mathrm{N_2(g)} \rightarrow 2\mathrm{Li_3N(s)}$$

Finally, we will double check our work. If time allows, try to always do this. It is possible that you may have "unbalanced" one element when trying to balance one or more others.

$$\mathrm{Li}: 6 \qquad \mathrm{Li}: 6$$

$$\mathrm{N}: 2 \qquad \mathrm{N}: 2$$

Sure enough, we have obeyed the law of mass conservation, and the chemical equation representing the reaction is balanced.

$$\boxed{6\mathrm{Li(s)} + \mathrm{N_2(g)} \rightarrow 2\mathrm{Li_3N(s)}}$$

General Steps to Balancing Chemical Equations

Balancing chemical equations is possibly the least concept-heavy topic in AP Chemistry. Therefore, mastering it only takes some practice. Be sure to keep these steps in mind:

1. Check if the equation is already balanced. Unless AP specifies that the reaction is balanced, you should always initially assume that it is not, because missing this can lead to answers that are extremely off.

2. Identify elements that appear only in one compound on both the reactant and product sides and generate the same number of atoms on each side. This should tell you that these species must have the same coefficient.

3. Determine which elements occur only in one compound on both sides and have different numbers of atoms on both sides. You will need to balance these.

4. Look at the elements that exist in more than one compound and balance them accordingly.

5. Finally, double-check your work to ensure that you still have the same number of atoms for each element on both the reactant and product sides. The key to this is satisfying the law of mass conservation.

For more review and practice, try the following drill.

Problem 4.3.4 — Balancing Chemical Equations Drill

Balance each of the following chemical equations.

1. $Mg(OH)_2 + HCl \to MgCl_2 + H_2O$
2. $SiO_2 + HF \to SiF_4 + H_2O$
3. $Cr_2O_3 + Mg \to Cr + MgO$
4. $N_2H_4 + O_2 \to NO_2 + H_2O$

Solution to part 1: There is one atom of Mg on both the left and right, so magnesium is already balanced. Next, there are 2 Cl atoms on the right and only 1 on the left, so we can increase the coefficient of HCl to 2.

$$Mg(OH)_2 + 2HCl \to MgCl_2 + H_2O$$

At this point, there are 4 H atoms on the left and only 2 on the right, so we increase the coefficient of H_2O to 2.

$$Mg(OH)_2 + 2HCl \to MgCl_2 + 2H_2O$$

Finally, O is balanced, so the balanced equation is:

$$\boxed{Mg(OH)_2 + 2HCl \to MgCl_2 + 2H_2O}$$

Solution to part 2: There is 1 atom of Si on both left and right sides of the equation, so Si is already balanced. Next, there are 4 atoms of F on the right and only 1 on the left, so we can increase the coefficient of HF to 4.

$$SiO_2 + 4HF \to SiF_4 + H_2O$$

At this point, there are 4 H atoms on the left and only 2 on the right, so we increase the coefficient of H_2O to 2.

$$SiO_2 + 4HF \to SiF_4 + 2H_2O$$

Additionally, O is balanced, with 2 atoms on both the left and right sides, so the balanced equation is:

$$\boxed{SiO_2 + 4HF \to SiF_4 + 2H_2O}$$

Solution to part 3: First, there are 2 atoms of Cr on the left and only 1 on the right, so increase the coefficient of Cr to 2.

$$Cr_2O_3 + Mg \to 2Cr + MgO$$

There are 3 O atoms on the left and only 1 on the right, so we increase the coefficient of MgO to 3.

$$\mathrm{Cr_2O_3 + Mg \rightarrow 2Cr + 3MgO}$$

To account for the previous change, we multiply Mg by 3, and the balanced equation is:

$$\boxed{\mathrm{Cr_2O_3 + 3Mg \rightarrow 2Cr + 3MgO}}$$

Solution to part 4: There are 2 N atoms on the left and only 1 on the right, so we increase the coefficient of NO_2 to 2.

$$\mathrm{N_2H_4 + O_2 \rightarrow NO_2 + H_2O}$$

There are 4 H atoms on the left and only 2 on the right, so increase the coefficient of H_2O to 2.

$$\mathrm{N_2H_4 + O_2 \rightarrow 2NO_2 + 2H_2O}$$

This change results in 6 O atoms on the right and only 2 on the left, so we will multiply O_2 by 3. This was very easy because oxygen was alone on the left side, so giving it a coefficient would not affect other elements. Therefore, we are done, and the balanced equation is:

$$\boxed{\mathrm{N_2H_4 + 3O_2 \rightarrow 2NO_2 + 2H_2O}}$$

§4.4 Physical and Chemical Changes

In the last section, we learned that **chemical equations** show the products that are formed by a certain combination of reactants. However, they do not show *how* these new substances are actually formed. There are certain underlying chemical and **physical changes** that allow reactant molecules to rearrange to change properties and create new substances, the products.

Chemical Changes

Generally, **chemical changes** involve *intramolecular* (within the molecule) bonds. For example, the breaking and/or forming of ionic or covalent bonds between elements during a chemical reaction. This is easier to visualize using Lewis dot diagrams.

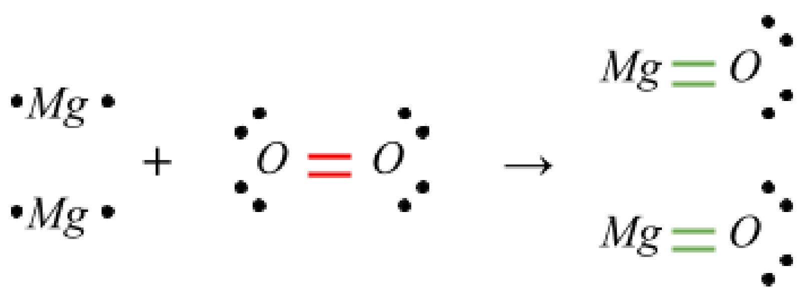


Image Courtesy of Fiveable

The reaction above (synthesis) shows an interaction between two magnesium atoms and a molecule of diatomic oxygen. The bonds that are broken are color-coded as red, and the bonds formed are green. Here, we can see that the covalent bonds within O_2 must have broken, resulting in a new bond between the magnesium and oxygen to form two molecules of MgO, an ionic compound.

Important Note: The above image is only a simplification. Ionic bonds are not actually represented by the lines as shown in the above diagram. Rather, they are expressed with brackets and charges around the brackets to demonstrate their ionized state (whether a neutral atom gained or lost electrons to form the ion).

Chemical changes are usually accompanied by chemical reactions to demonstrate the breaking and forming of bonds. Examples of chemical changes include, but are not limited to:

- Burning: The chemical reaction that occurs when a substance reacts with oxygen gas in order to produce heat and light. For organic molecules, this usually falls in the category of **combustion reactions**.
- Rusting: The chemical reaction that occurs when iron reacts with water and oxygen to produce iron oxide (commonly called "rust").
- Digestion: In our digestive system, several reactions are occurring to break down the food into nutrients that cells can absorb for short-term and long-term use.

Physical Changes

Physical changes are usually associated with *intermolecular* (between two or more molecules) changes, such as **phase changes**. Some examples include freezing water and tearing a paper in pieces.

Specifically, when water freezes to form ice, the molecules maintain the same atomic structure (H_2O), but more **hydrogen bonds** between each water molecule are formed. Conversely, when paper is cut into smaller pieces, the interaction between the molecules is altered (or broken).

Note 4.4.1

The most important aspect of physical changes is that they change a substance's properties without altering atomic structure, so they are reversible.

However, there are some exceptions. Reactions can proceed in either direction and sometimes physical processes can involve the breaking of chemical bonds. For example, when salt (NaCl) dissolves in water, bonds between the Na^+ and Cl^- ions are broken, but this also creates **ion-dipole interactions** between the ions and water molecules.

The easiest way to distinguish between a chemical and physical bond is to think about what **types of forces/bonds** are breaking or forming. If intramolecular bonds, such as covalent and ionic bonds, are being broken and formed, there must be a change at a molecular level. However, if intermolecular forces are involved and changing, it is only a physical change.

Review Activity

Problem 4.4.2 — Physical vs. Chemical Change

Name whether each scenario represents a chemical or physical change.

1. A solid is crushed into a powder.
2. Mixing salt with pepper.
3. A bicycle changes color as it rusts.
4. Burning a match.
5. You blow dry your wet hair.

Solution to part 1: Crushing a solid into powder is a $\boxed{\text{physical change}}$. The substance's chemical identity remains the same; only its physical form has changed from solid to powder. Additionally, it can be brought back to solid form.

Solution to part 2: Mixing salt with pepper is a $\boxed{\text{physical change}}$, because the salt and pepper powders can be separated (very exhausting but it is still possible!). Therefore, each of the powders retain their chemical properties during this change.

Solution to part 3: The color change of the bicycle indicates a $\boxed{\text{chemical change}}$ since two substances, the metal and oxygen gas, are reacting together to form a new substance, rust. Since the metal molecules do not remain pure through the change, this process is not physical.

Solution to part 4: Burning a match is a $\boxed{\text{chemical change}}$ since it indicates combustion. The burning of matchstick involves the reaction with oxygen in the air to form carbon dioxide and water vapor.

Solution to part 5: When you blow dry your hair, the heat energy supplied evaporates the water in your hair, effectively changing the state of matter from liquid to gas. Additionally, no new substance is formed and the process can be reversed. Finally, there was no change in the chemical properties of either your hair or the water, so this is a $\boxed{\text{physical change}}$.

§4.5 Stoichiometry

Earlier, we learned that we can represent chemical reactions by using chemical equations. In this section, we will learn how to quantitatively approach chemical reactions using **stoichiometry**. As a "math-heavy" topic in AP Chemistry, it can appear daunting but with more practice, you will build your confidence and this will feel as simple as your ABCs and 123s!

Prerequisites for Stoichiometry - Review

In earlier sections, we learned about concepts such as moles, molar mass, molarity, and Avogadro's number. Stoichiometry is about using **mole ratios** and dimensional analysis to manipulate a series of measurements to get our desired unit. First, let's recap many key concepts used in stoichiometry:

1. **Balanced chemical equation**: This is a written representation of a chemical that shows the reactants on the left side and the products on the right side, with the number of atoms of each element balanced on both sides of the equation.

2. **Mole**: The mole is a unit of measurement that represents the amount of formula units in a substance. One mole of a substance is equal to Avogadro's number, $6.022 \cdot 10^{23}$ formula units (atoms, molecules, etc.), of that substance.

3. **Stoichiometric coefficients**: The coefficients of the balanced chemical equation represent the relative amounts of the reactants and products in a chemical reaction. The coefficients can be used to create mole ratios and calculate the amount of reactants and products that are required or are produced in a reaction.

4. **Stoichiometric calculations**: These involving using the balanced chemical equation and the mole concept to predict the amount of reactants and products that are required or produced in a chemical reaction. These calculations are valid due to the Law of Conservation of Mass, which states that the total mass of the reactants must be equal to the total mass of the products. In this manner, stoichiometry is used to quantify the amount of all species in a chemical reaction. This becomes especially significant in the laboratory and it therefore becomes a piece of cake for chemists.

Mole Ratios

A **mole ratio** is a ratio of the amounts of two or more substances in a chemical reaction, expressed in moles. These ratios make stoichiometry a very easy process to quantify values in the laboratory.

The following balanced chemical equation represents the combustion of propane:

$$\mathrm{C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)}$$

This equation means that 1 mole of C_3H_8 reacts with 5 moles of O_2 to produce 3 moles of CO_2 and 4 moles of H_2O.

We can use this equation to answer questions such as: *"How many moles of propane* *are present in 96.1 grams of propane?*" The molar mass of propane, to three significant digits, is 44.1 g/mol. We can calculate the number of moles of propane as follows:

$$96.1\,\cancel{\text{g C}_3\text{H}_8} \cdot \frac{1\text{ mol C}_3\text{H}_8}{44.1\,\cancel{\text{g C}_3\text{H}_8}} = \boxed{2.18\text{ mol C}_3\text{H}_8}$$

Next, suppose we also wanted to determine the number of moles of oxygen needed to react with the propane. We must take into account that each mole of propane reacts with 5 moles of oxygen gas. Using the balanced equation, the appropriate mole ratio is:

$$\frac{5\text{ mol O}_2}{1\text{ mol C}_3\text{H}_8}$$

If we multiply the number of moles of C_3H_8 by this factor, we get the number of moles of O_2 required.

$$2.18\,\cancel{\text{mol C}_3\text{H}_8} \cdot \frac{5\text{ mol O}_2}{1\,\cancel{\text{mol C}_3\text{H}_8}} = \boxed{10.9\text{ mol O}_2}$$

Notice that we set up the mole ratio so that the units for number of moles of C_3H_8 would cancel out, leaving us with the units for moles of O_2.

Additionally, these questions can be extended to the point where we use multiple factors and mole ratios to reach our desired answer.

It's important to internalize the relationships between certain units as we perform mole ratios. They are summarized below.

- At STP, one mole of an ideal gas occupies 22.4 L of volume. This is also known as **molar volume** can this value can be found on the AP Chemistry equations and formulas sheet.
- As discussed above, one mole $= 6.022 \cdot 10^{23}$ formula units. This is Avogadro's number and it is also on the reference sheet for the exam.
- One mole of a substance is defined by the molar mass (number of grams in one mole). Each element's molar mass is listed on the periodic table. For example, hydrogen has a molar mass of 1.008 g/mol. For a molecule, you can find the molar mass by summing the molar masses of all atoms of each element.

The following problems illustrate the concepts of using mole ratios to determine amounts of reactants and products for a chemical reaction.

Problem 4.5.1 — Mole Ratios I

How many moles of potassium are required to fully react with 11.6 moles of water?

$$2\text{K(s)} + 2\text{H}_2\text{O(l)} \rightarrow 2\text{KOH(aq)} + \text{H}_2\text{(g)}$$

Solution: First, we check if the chemical reaction is balanced. If we count the number of atoms of K, H, and O, we realize that it is indeed balanced. At this point, we need to identify the value that is given to us. We know that there are 11.6 moles of water.

Additionally, our objective is to determine the number of moles of potassium required to fully react with it. Our target answer is also in units of moles, so we use the mole ratio between K and H_2O to find our answer.

We want a mole ratio that can cancel the units of our known measurement and leave us with the units for our desired value. Looking at the chemical equation, we know that for every 2 moles of H_2O, we need 2 moles of K metal.

Thus, our calculation should look like the following:

$$11.6\ \cancel{\text{mol H}_2\text{O}} \cdot \frac{2\ \text{mol K}}{2\ \cancel{\text{mol H}_2\text{O}}} = \boxed{11.6\ \text{mol K}}$$

Notice how the units for moles of H_2O canceled out, leaving us with our desired answer in moles of potassium metal.

Problem 4.5.2 — Mole Ratios II

The combustion of liquid ethanol in air is given by the following balanced chemical equation.

$$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$$

If a sample of ethanol weighs 105.2 g, what is the maximum volume of carbon dioxide that can form at STP?

Solution: We convert the given mass of C_2H_5OH to moles, using the molar mass of C_2H_5OH:

$$105.2\ \cancel{\text{g C}_2\text{H}_5\text{OH}} \cdot \frac{1\ \text{mol C}_2\text{H}_5\text{OH}}{46.07\ \cancel{\text{g C}_2\text{H}_5\text{OH}}} = 2.283\ \text{mol C}_2\text{H}_5\text{OH}$$

Since we want to determine the amount of CO_2 that reacts with the given mass of C_2H_5OH, we will use the following mole ratio:

$$\frac{2\ \text{mol CO}_2}{1\ \text{mol C}_2\text{H}_5\text{OH}}$$

We calculate the number of moles of CO_2 needed to react with the given mass of C_2H_5OH using this mole ratio:

$$2.283\ \cancel{\text{mol C}_2\text{H}_5\text{OH}} \cdot \frac{2\ \text{mol CO}_2}{1\ \cancel{\text{mol C}_2\text{H}_5\text{OH}}} = 4.566\ \text{mol CO}_2$$

Finally, we will use the fact that one mole of an ideal gas occupies 22.4 L at STP:

$$4.566\ \cancel{\text{mol CO}_2} \cdot \frac{22.4\ \text{L}}{1\ \cancel{\text{mol CO}_2}} = \boxed{102.3\ \text{L}}$$

Calculations Involving a Limiting Reactant

When chemicals are mixed together to undergo a chemical reaction, they are often mixed in *stoichiometric quantities*, that is, in the amounts that all the reactants are fully consumed at the same time.

Example 4.5.3

Hydrogen gas can be obtained from the reaction of methane with water vapor:

$$CH_4(g) + H_2O(g) \to 3H_2(g) + CO(g)$$

Since this reaction involves one molecule of methane reacting with one molecule of water, to have stoichiometric amounts of methane and water we must have equal numbers of them (in moles).

Suppose we want to calculate the mass of water required to react *exactly* with $1.25 \cdot 10^3$ kg of methane. That is, how much water will exactly consume all $1.25 \cdot 10^3$ kg of methane, leaving no remaining methane or water?

First, we determine the number of moles of methane molecules in the $1.25 \cdot 10^3$ kg sample ($1.25 \cdot 10^6$ g):

$$1.25 \cdot 10^6 \cancel{\text{g CH}_4} \cdot \frac{1 \text{ mol CH}_4}{16.04 \cancel{\text{g CH}_4}} = 7.8 \cdot 10^4 \text{ mol CH}_4$$

This same number of water molecules has a mass determined as follows:

$$7.8 \cdot 10^4 \cancel{\text{mol H}_2\text{O}} \cdot \frac{18.02 \text{ g}}{\cancel{\text{mol H}_2\text{O}}} = 1.41 \cdot 10^6 \text{ g H}_2\text{O} = 1.41 \cdot 10^3 \text{ kg H}_2\text{O}$$

Therefore, if $1.25 \cdot 10^3$ kg of methane is mixed with $1.41 \cdot 10^3$ kg of water, then both reactants will deplete at the same time (because they have the same coefficient in the balanced chemical equation). Therefore, the reactants have been mixed in stoichiometric quantities.

This time, suppose the original $1.25 \cdot 10^3$ kg methane sample is mixed with $3.00 \cdot 10^3$ kg of water. The methane will be consumed before the water runs out. The water will be in *excess*; that is, there will be more water molecules than methane molecules in the reaction mixture. What is the result of this in terms of formation of products?

To answer this question, consider the problem on a simpler scale.
Suppose we place 10 CH_4 molecules and 17 H_2O molecules in a container and allow them to react. How many H_2 and CO molecules can form?

The image below represents our scenario.

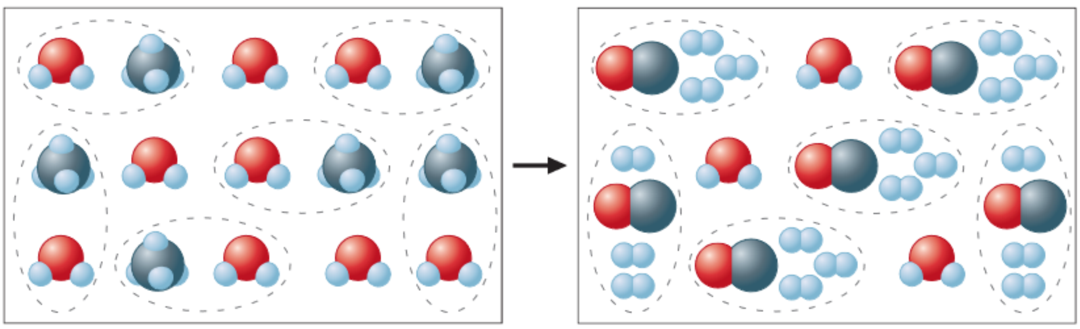


Image Courtesy of Chemistry, Seventh Edition (Zumdahl)

According to the stoichiometric coefficients of our chemical reaction, we can form a "group" consisting of one CH_4 molecule and one H_2O molecule that react to form three H_2 molecules and one CO molecule.

Note that products can only form when both CH_4 and H_2O are available to react. Once the 10 molecules of CH_4 are consumed by reacting with the 10 H_2O molecules, the 7 remaining water molecules cannot react. They are in excess. Thus, the number of products that can form is *limited* by the methane. This brings us to the concept of the **limiting reactant** (or limiting reagent), which is the reactant that is fully consumed first, effectively limiting the amount of products that can be formed.

To illustrate this concept, let us consider the synthesis of ammonia.

Example 4.5.4

25.0 kilograms of nitrogen and 5.00 kilograms of hydrogen are mixed and reacted to form ammonia. How do we calculate the mass of ammonia produced once the reaction is complete (when one of the reactants is fully consumed)?

The balanced chemical equation is

$$\mathrm{N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)}$$

In order to determine which reactant is limiting, we will first calculate the moles of reactants present using their molar masses:

$$25.0\,\cancel{\mathrm{kg\,N_2}} \cdot \frac{1000\,\cancel{\mathrm{g\,N_2}}}{1\,\cancel{\mathrm{kg\,N_2}}} \cdot \frac{1\,\mathrm{mol\,N_2}}{28.0\,\cancel{\mathrm{g\,N_2}}} = 8.93 \cdot 10^2\,\mathrm{mol\,N_2}$$

$$5.00\,\cancel{\mathrm{kg\,H_2}} \cdot \frac{1000\,\cancel{\mathrm{g\,H_2}}}{1\,\cancel{\mathrm{g\,H_2}}} \cdot \frac{1\,\mathrm{mol\,H_2}}{2.016\,\cancel{\mathrm{g\,H_2}}} = 2.48 \cdot 10^3\,\mathrm{mol\,H_2}$$

Since 1 mol N_2 reacts with 3 mol H_2, the number of moles of H_2 that will react exactly with $8.93 \cdot 10^2$ mol N_2 is equal to

$$8.93 \cdot 10^2\,\cancel{\mathrm{mol\,N_2}} \cdot \frac{3\,\mathrm{mol\,H_2}}{1\,\cancel{\mathrm{mol\,N_2}}} = 2.68 \cdot 10^3\,\mathrm{mol\,H_2}$$

However, in this case, only $2.48 \cdot 10^3$ mol H_2 is present. This means that the hydrogen depleted before the nitrogen. Therefore, hydrogen is the limiting reactant in this particular situation, and we must use its amount to determine the quantity of ammonia formed:

$$2.48 \cdot 10^3\,\cancel{\mathrm{mol\,H_2}} \cdot \frac{2\,\mathrm{mol\,NH_3}}{3\,\cancel{\mathrm{mol\,H_2}}} = 1.65 \cdot 10^3\,\mathrm{mol\,NH_3}$$

Finally, converting moles of ammonia to kilograms gives us the following:

$$1.65 \cdot 10^3\,\cancel{\mathrm{mol\,NH_3}} \cdot \frac{17.0\,\mathrm{g\,NH_3}}{1\,\cancel{\mathrm{mol\,NH_3}}} = 2.80 \cdot 10^4\,\mathrm{g\,NH_3} = \boxed{28.0\,\mathrm{kg\,NH_3}}$$

Reaction Yield

The amount of a product formed when the limiting reactant is completely consumed is called the **theoretical yield** of that product. In other words, it represents the *maximum* amount of a product that can be produced from the quantities of reactants used. Actually, the amount of product predicted by the theoretical yield is rarely obtained because of side reactions (other naturally-occurring reactions that involve one or more reactants and products), impurities in certain substances, and other complications. The *actual yield* is often given as a percentage of the theoretical yield. This gives us a metric called the **percent yield**:

$$\boxed{\frac{\text{actual yield}}{\text{theoretical yield}} \cdot 100\% = \text{percent yield}}$$

We will end this section with a problem that asks us to calculate the percent yield.

Problem 4.5.5 — Percent Yield

Methanol (CH_3OH), also called *methyl alcohol*, is the simplest alcohol. It is used as fuel by race cars and is a potential replacement for gasoline. Methanol can be manufactured by combination of gaseous carbon monoxide and hydrogen. Suppose 68.5 kg CO(g) reacts with 8.60 kg H_2(g). Calculate the theoretical yield of methanol. If $3.57 \cdot 10^4$ g CH_3OH is actually produced, what is the percent yield of methanol?

Solution: The first step will be to determine the limiting reactant. The balanced equation is

$$2H_2(g) + CO(g) \rightarrow CH_3OH(l)$$

Next we must calculate the moles of each reactant:

$$68.5\,\cancel{\text{kg CO}} \cdot \frac{1000\,\cancel{\text{g CO}}}{1\,\cancel{\text{kg CO}}} \cdot \frac{1\text{ mol CO}}{28.02\,\cancel{\text{g CO}}} = 2.44 \cdot 10^3 \text{ mol CO}$$

$$8.60\,\cancel{\text{kg H}_2} \cdot \frac{1000\,\cancel{\text{g H}_2}}{1\,\cancel{\text{kg H}_2}} \cdot \frac{1\text{ mol H}_2}{2.016\,\cancel{\text{g H}_2}} = 4.27 \cdot 10^3 \text{ mol H}_2$$

At this point, I will introduce a trick for determining the limiting reactant, we can compare the required mole ratio of the reactants (according to the balanced chemical equation) against the actual mole ratio (based on the above calculation).

$$\frac{\text{mol H}_2}{\text{mol CO}}\text{(required)} = \frac{2}{1} = 2$$
$$\frac{\text{mol H}_2}{\text{mol CO}}\text{(actual)} = \frac{4.27 \cdot 10^3}{2.44 \cdot 10^3} = 1.75$$

Since the actual mole ratio of H_2 to CO is smaller than the required ratio, H_2 is the limiting reactant. We therefore use the amount of H_2 to determine the maximum amount of methanol that can be produced (theoretical yield):

$$4.27 \cdot 10^3\,\cancel{\text{mol H}_2} \cdot \frac{1\text{ mol CH}_3\text{OH}}{2\,\cancel{\text{mol H}_2}} = 2.14 \cdot 10^3 \text{ mol CH}_3\text{OH}$$

Using the molar mass of methanol, we can convert the theoretical yield to grams:

$$2.14 \cdot 10^3\,\cancel{\text{mol CH}_3\text{OH}} \cdot \frac{32.04\text{ g CH}_3\text{OH}}{1\,\cancel{\text{mol CH}_3\text{OH}}} = \boxed{6.86 \cdot 10^4 \text{ g CH}_3\text{OH}}$$

Finally, we can calculate our percent yield. The problem states that the actual yield of methanol was $3.57 \cdot 10^4$ g, so our answer is

$$\frac{3.57 \cdot 10^4 \cancel{\text{g}}}{6.86 \cdot 10^4 \cancel{\text{g}}} \cdot 100\% = \boxed{52.0\%}$$

§4.6 Introduction to Titration

Titration is a lab procedure that allows you to determine the unknown concentration of one solution by titrating it with a solution of known concentration.

- The **titrant** is the solution of known concentration which is used to determine the concentration of the unknown solution in a titration. It is usually dispensed using a *buret*, a long, narrow tube with a stop clock. In this way, chemists can accurately control the volume of titrant solution that they add to the unknown solution.
- The **analyte** is the unknown solution whose concentration is determined via titration. Usually, it is kept in an *Erlenmeyer flask* directly below the buret.

The image below shows a setup of the apparatus which chemists (and also you guys!) use to conduct a titration.

Image Courtesy of Chemistry LibreTexts

Titrations: Types

There are many different types of titrations in chemistry, but this course specifically focuses on **acid-base titrations**. Here is a quick rundown of them as well as the others.

1. Acid-base titrations: These involve determining the concentration of an acid or base in a solution. The point where the pH drastically changes is referred to as the **endpoint** of the titration. This can be detected by using a pH meter or an indicator. Don't worry too much about these new terms; they will be covered with more depth in Unit 8.

2. **Redox titrations**: These titrations are used to determine the concentration of an oxidizing or reducing agent in a solution. The endpoint in a redox titration is usually indicated by a color change, which again, can be detected by an indicator or a meter.

3. **Precipitation titrations**: Precipitation titrations are used to determine the concentration of a substance that can form a precipitate with another substance. To detect this, chemists often use the naked eye or a device that measures light transmittance of the solution.

4. **Complexation titrations**: Complexation titrations are a form of analysis in which the formation of a colored complex is used to indicate the end point of a titration. They are particularly useful for identifying a mixture of different metal ions in solution.

Acid-Base Titrations

Don't worry about the other three titrations. If you learn them, they will be just for fun. From now, let's dig deeper into acid-base titrations.

The titrant solution in the buret is usually a strong acid or base, and the most important thing is that we know its concentration. Meanwhile, the analyte of unknown solution is in the Erlenmeyer flask beneath and is usually a weak acid or base.

Both these containers contain tick marks that are accurate to some number of significant figures, so we know the initial volumes for both solutions. Therefore, we can perform the necessary calculations to find the molarity of the analyte solution.

Along with the analyte solution, the Erlenmeyer flask also has one or two drops of an **indicator solution**. These result in a change in the solution's color when it reaches a certain pH range.

Note 4.6.1

Don't worry about indicators much for this unit. They are covered in more detail in Unit 8. Just take the above information as it is given.

Additionally, remember that molarity (M) is a measure of concentration that is calculated by dividing the number of moles of the substance by the volume in liters. That is why it is so important to record how much solution is used in a titration (your teacher will emphasize this in class!).

Acid-Base Titration: Procedure

When you are performing an acid-base titration, you will always follow these steps (don't forget your safety goggles!):

1. Fill the buret with the titrant of known concentration. Record the concentration and initial volume of titrant in the buret in a notebook before you begin the titration.

2. Measure out the desired volume of the analyte and place it in the Erlenmeyer flask. It is highly recommended that you measure out the analyte solution using a **volumetric flask**, because their shape minimizes the effect of a meniscus. If the desired volume cannot be dispensed by a volumetric flask, then you can used a **graduated cylinder**.

3. Add a few drops of indicator to the analyte solution. Now, you are ready to begin the titration.

4. Gradually add the titrant solution from the buret into the flask, stirring constantly (but gently!), until the indicator changes the color of the solution. At this point, you will need to be mindful of one thing: any added titrant after the color change can lead to inaccurate results, so make sure to be adept with your equipment and thoroughly understand the procedure.

Additionally, there are two critical points during a titration that are kept note of:

- **Equivalence point** is the point where the titrant and analyte are in equimolar quantities. Additionally, the reactants are fully consumed and the products are present in stoichiometric amounts. This indicates the end of the reaction.

- The **endpoint** is the point where this is a visible change in color or pH in the Erlenmeyer flask. Optimally, the endpoint should occur at the equivalence point, where the moles of titrant equals the moles of analyte.

The most common indicator that you will encounter is **phenolphthalein**, which creates a light pink solution at the equivalence point of an acid-base titration. If the analyte and titrant are weak acid and strong base, respectively, then the pH of the resulting solution is less than 7 prior to the titration. Therefore, the solution is initially colorless. As the strong base is added, the pH of the solution gradually increases. Finally, at the endpoint, once just enough base is added, the solution exhibits a noticeable color change.

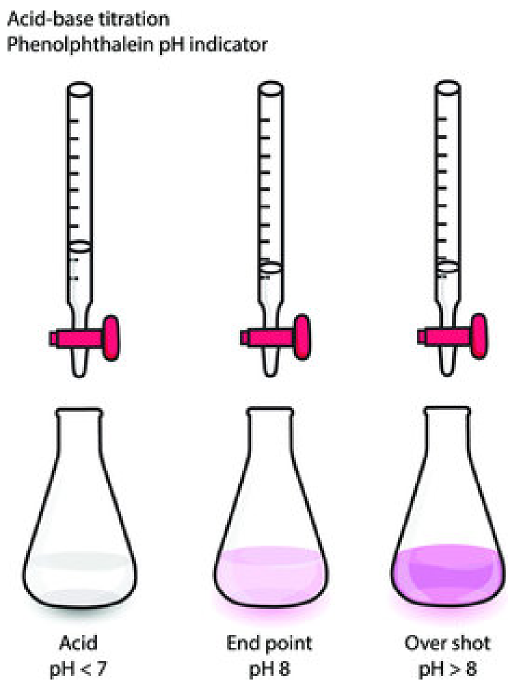
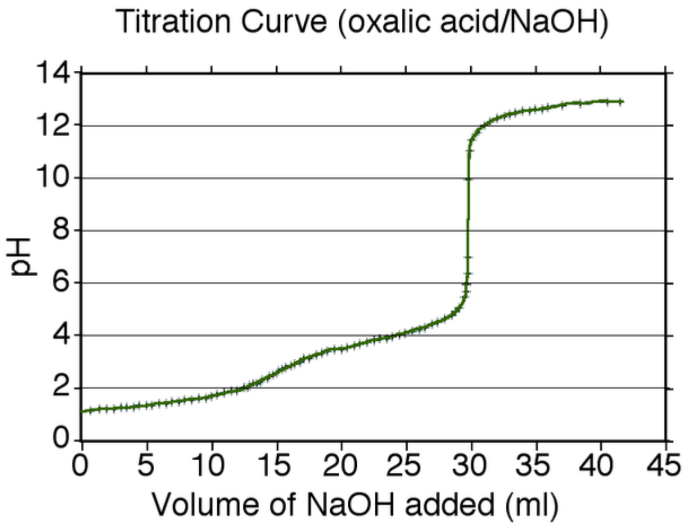


Image Courtesy of Adobe Stock

Titrations: A Graphical Representation

At the end of a titration, you will be asked to plot your data and create what is referred to as a **titration curve**, or a pH curve. This is a graph that represents the relationship between volume of titrant added and the corresponding pH of the resulting solution.

Below is a sample graph of the curve:



There are two important regions on a titration curve:

1. The **linear region** is the portion of the curve where the pH of the analyte solution is pretty constant as more titrant is added.

2. The **inflection point** is where the slope changes significantly. It indicates the equivalence point, which is shown when the number of moles of titrant is equal to the number of moles of analyte. In the graph above, it is the point (30.0 mL volume of NaOH) where the pH is 8.

Basic Titration Calculations

For now, our calculations will solely focus on the equivalence point.

Since this is the point where the number of moles of acid and base are equal, we can make an equation involving molarity ($\mathrm{mol\,L^{-1}}$) and volume (L):

$$\text{moles of acid} = \text{moles of base}$$

Since $n = MV$, we conclude that the volume of the titrant multiplied by the molarity of the titrant equals the volume of the analyte multiplied by the molarity of the analyte.

$$M_a V_a = M_b V_b$$

If the analyte is a weak acid and the titrant is a strong base, our unknown concentration is denoted by M_a, so we can rearrange the equation and solve for the following:

$$M_a = \frac{M_b V_b}{V_a}$$

Note 4.6.2

It is important to note that mole ratios make a big difference! For example, if the acid and base react in a 1 : 2 ratio, then the equation would be written as $M_a V_a = 2M_b V_b$, to account for the stoichiometry.

We'll go through the following problem before we move on to the next section.

Problem 4.6.3 — Titration Calculations

A solution of vinegar contains an unknown amount of acetic acid, $HC_2H_3O_2$. A 25.0 mL sample of vinegar is titrated with 0.650 M NaOH according to the chemical reaction below. If it requires 32.04 mL of the titrant to reach the equivalence point, what is the concentration of $HC_2H_3O_2$ in the vinegar?

$$HC_2H_3O_2(aq) + NaOH(aq) \rightarrow NaC_2H_3O_2(aq) + H_2O(l)$$

Solution: According to the chemical reaction above, acetic acid and sodium hydroxide react in a 1 : 1 ratio, so this problem warrants a simple use of

$$M_a V_a = M_b V_b$$

Plugging in, we have

$$(M_a)(25.0\,\text{mL}) = (0.650\,M)(32.04\,\text{mL})$$

so the molar concentration of $HC_2H_3O_2$ is equal to

$$M_a = \frac{(0.650\,M)(32.04\,\cancel{\text{mL}})}{(25.0\,\cancel{\text{mL}})} = \boxed{0.833\,M}$$

§4.7 Types of Chemical Reactions

The learning objective of this section in AP Chemistry is to "identify a reaction as acid-base, oxidation-reduction, or precipitation."

Types of Chemical Reactions

This chapter will focus more on precipitation, acid-base, and oxidation-reduction (redox) reactions. Here is a quick overview of these three reactions:

1. **Acid-base reactions** are chemical reactions that involve the transfer of a proton from one molecule to another. Usually, this proton transfer happens between a strong acid and strong base, which leads to the formation of a salt and water.

2. **Oxidation-reduction reactions**, also called **redox reactions**, are chemical reactions in which the atoms of some elements are oxidized (they lose electrons) and reduced (they gain electrons). Overall, the reaction undergoes a transfer of electrons from the *reducing agent* to the *oxidizing* agent. For example, combustion reactions are a type of redox reaction and we have already discussed them in previous sections. Meanwhile, the specific and more complex information of redox reactions will be covered in section 4.9.

3. **Precipitation reactions** are chemical reactions in which two or more soluble reactants combine to form an insoluble product, which is known as a precipitate. The bulk of this section will focus on precipitation reactions.

Precipitation Reactions Explained

When ions in an aqueous solution react, there is a possibility of them producing an insoluble, or marginally soluble ionic compound. This substance is called a **precipitate**.

All sodium, potassium, ammonium, and nitrate salts are soluble as guidelines given by College Board, so they cannot be precipitates. As far as the AP exam is concerned, you do not need to know any other solubility rules. However, it wouldn't hurt to be familiar with common soluble and insoluble compounds. Below shows a table of solubility for common ions in water. The AP exam will tell you if compounds are soluble and in which solution, if they are not one of Na^+, K^+, NH_4^+, or NO_3^-.

TABLE 4.1 Solubility Guidelines for Common Ionic Compounds in Water

Soluble Compounds		Important Exceptions
Compounds containing	NO_3^-	None
	$C_2H_3O_2^-$	None
	Cl^-	Compounds of Ag^+, Hg_2^{2+}, and Pb^{2+}
	Br^-	Compounds of Ag^+, Hg_2^{2+}, and Pb^{2+}
	I^-	Compounds of Ag^+, Hg_2^{2+}, and Pb^{2+}
	SO_4^{2-}	Compounds of Sr^{2+}, Ba^{2+}, Hg_2^{2+}, and Pb^{2+}
Insoluble Compounds		**Important Exceptions**
Compounds containing	S^{2-}	Compounds of NH_4^+, the alkali metal cations, and Ca^{2+}, Sr^{2+}, and Ba^{2+}
	CO_3^{2-}	Compounds of NH_4^+ and the alkali metal cations
	PO_4^{3-}	Compounds of NH_4^+ and the alkali metal cations
	OH^-	Compounds of the alkali metal cations, and Ca^{2+}, Sr^{2+}, and Ba^{2+}

Net Ionic Equations - Review

These were covered in section 4.2, but it's such an important topic in this course that it wouldn't hurt to review them again.

Generally, the best steps to follow when writing a net ionic equation are:

1. Figure out which compounds are soluble and insoluble using your knowledge of solubility rules.
2. The question writers are (usually) nice, so the chemical reaction will be (mostly) balanced. However, it may not, so be sure to quickly check.
3. Write the complete ionic equation by breaking apart soluble compounds into ions, and leaving insoluble compounds as single units.
4. Omit the spectator ions and write the final net ionic equation for the given reaction. Be sure to also include the phase of matter for each reactant and product.

College Board likes to ask questions that require you to use multiple concepts simultaneously. For precipitation reactions, in particular, they love to incorporate stoichiometry as well as solubility rules.

Let's see how this is tested in the problem that follows.

Problem 4.7.1 — Concentration of Ions

If 20.0 mL of 0.100 M NaCl is mixed with 30.0 mL of 0.0400 M $Pb(C_2H_3O_2)_2$, determine the following.

(a) The mass of solid $PbCl_2$ formed.
(b) The concentrations of all ions once the reaction is complete.

Solution to part a: This will be needed for both parts of this problem. They did not give us the equation, we will write it ourselves.

$$\mathrm{NaCl(aq)} + \mathrm{Pb(C_2H_3O_2)_2(aq)} \rightarrow \mathrm{NaC_2H_3O_2(aq)} + \mathrm{PbCl_2(aq)}$$

This equation is not balanced.

When you are balancing double displacement reactions, polyatomic ions are treated as *single* units. You don't need to worry about each of the individual elements in these cases.

After balancing, the chemical equation is

$$2\mathrm{NaCl(aq)} + \mathrm{Pb(C_2H_3O_2)_2(aq)} \rightarrow 2\mathrm{NaC_2H_3O_2(aq)} + \mathrm{PbCl_2(s)}$$

Note: we know that $NaC_2H_3O_2$ is soluble because of the Na^+ ion, so it is represented as (aq). Meanwhile, the problem states that $PbCl_2$ is our precipitate.

Now, we will start to use the math. The problem gave us the molar concentrations and volumes of each of the aqueous solutions. We can find the number of moles of NaCl and $Pb(C_2H_3O_2)_2$ by using the formula $n = MV$.

The volume V is in liters, but the volumes that we are given are in milliliters, so we need to convert by dividing by 1000.

$$\text{mol NaCl} = 0.100\,M \cdot 0.020\,\text{L} = 0.00200\,\text{mol NaCl}$$

$$\text{mol Pb(C}_2\text{H}_3\text{O}_2)_2 = 0.0400\,M \cdot 0.030\,\text{L} = 0.00120\,\text{mol Pb(C}_2\text{H}_3\text{O}_2)_2$$

At this point, we can use stoichiometry to determine the mass of $PbCl_2$(s) that was produced. However, since we are given the number of moles for both reactants, we will need to determine which one is limiting.

We will have to convert each reactant into the amount of precipitate.

$$0.00200\,\cancel{\text{mol NaCl}} \cdot \frac{1\text{ mol PbCl}_2}{2\,\cancel{\text{mol PbCl}_2}} = 0.00100\text{ mol PbCl}_2$$

$$0.00120\,\cancel{\text{mol Pb(C}_2\text{H}_3\text{O}_2)_2} \cdot \frac{1\text{ mol PbCl}_2}{1\,\cancel{\text{mol Pb(C}_2\text{H}_3\text{O}_2)_2}} = 0.00120\text{ mol PbCl}_2$$

Since there are less moles of $PbCl_2$ from NaCl as a reactant, we know that it is limiting, and that $Pb(C_2H_3O_2)_2$ is in excess.

Finally, we can convert from moles to mass by using the molar mass of $PbCl_2$.

$$0.0010\,\cancel{\text{mol PbCl}_2} \cdot \frac{278.2\text{ g}}{1\,\cancel{\text{mol PbCl}_2}} = \boxed{0.278\text{ g PbCl}_2}$$

Solution to part b: In order to find the concentration of each ion, we need to know the number of moles as well as the volume of each.

Thinking about it conceptually, once solid $PbCl_2$ forms, what is left in the solution?

Since NaCl was the limiting reactant, either Na^+ or Cl^- must have a final concentration of 0 since one of them will be completely consumed. $PbCl_2$ consists of Cl^- ion, so it is the ion that has a final concentration of $\boxed{0\,M}$.

Note 4.7.2

The ion that is part of the limiting reactant and precipitate **always** has a final concentration of 0, since all of it in solution was consumed to form as much precipitate as possible.

Next, we can solve for the concentrations of our two spectator ions: Na^+ and $C_2H_3O_2^-$. We gave to use the number of moles of $PbCl_2$ from NaCl and $Pb(C_2H_3O_2)_2$, respectively.

$$\text{mol Na}^+ = 0.00100\,\cancel{\text{mol PbCl}_2} \cdot \frac{2\text{ mol NaCl}}{1\,\cancel{\text{mol PbCl}_2}} \cdot \frac{1\text{ mol Na}^+}{1\,\cancel{\text{mol NaCl}}} = 0.00200\text{ mol Na}^+$$

The volume that we are going to divide this value by is the sum of 0.020 L and 0.030 L, or 0.050 L.

Thus, the concentration of Na^+ is

$$[\mathrm{Na^+}] = \frac{0.0020\,\mathrm{mol}}{0.050\,\mathrm{L}} = \boxed{0.0400\,M}$$

Similarly, for $C_2H_3O_2^-$:

$$0.00120\,\cancel{\mathrm{mol\,PbCl_2}} \cdot \frac{2\,\cancel{\mathrm{mol\,Na_2C_2H_3O_2}}}{1\,\cancel{\mathrm{mol\,PbCl_2}}} \cdot \frac{1\,\mathrm{mol\,C_2H_3O_2^-}}{1\,\cancel{\mathrm{mol\,Na_2C_2H_3O_2}}} = 0.00240\,\mathrm{mol\,C_2H_3O_2^-}$$

and the final concentration is

$$[\mathrm{C_2H_3O_2^-}] = \frac{0.00240\,\mathrm{mol}}{0.050\,\mathrm{L}} = \boxed{0.0480\,M}$$

We have one more ion whose final concentration is unknown Pb^{2+}. For this, we need to determine the number of moles of $Pb(C_2H_3O_2)_2$ that are in excess, and then divide by the total volume (0.050 L).

First, convert the amount of limiting reactant to the excess reactant. This value represents the amount of $Pb(C_2H_3O_2)_2$ that was consumed. Using stoichiometry, 0.00120 mol of $Pb(C_2H_3O_2)_2$ reacted. Then, we subtract this from the number of moles that were initially present, which is 0.00120.

$$0.00120 - 0.00100 = 0.00020\,\mathrm{mol\,Pb^{2+}}$$

and dividing by the total volume, we have

$$[\mathrm{Pb^{2+}}] = \frac{0.00020\,\mathrm{mol}}{0.050\,\mathrm{L}} = \boxed{0.0040\,M}$$

§4.8 Introduction to Acid-Base Reactions

Now that we've got precipitation reactions down, the other type of aqueous reaction we need to know for stoichiometry purposes is the **acid-base neutralization reaction**. This section will lay the foundation for the entirety of Unit 8, which comprises a significant portion of the AP exam.

Defining Acids and Bases

Different subfields of chemistry have their unique descriptions of acids and bases, but our course curriculum will focus on the **Brønsted-Lowry** definition. When you see "Brønsted-Lowry," you should think of protons or hydrogen ions, as well as how they are transferred.

But first, how is a proton equivalent to a hydrogen ion?

Recall from Unit 1 that a proton is a subatomic particle that is located in the nucleus of an atom. Additionally, it has a positive electric charge.

Remember that an ion is an atom or molecule that has gained or lost a number of electrons, resulting in a net charge. A hydrogen ion, H^+, is a hydrogen atom that has been stripped of its electron, resulting a net charge of +1. Therefore, the terms "proton" and "hydrogen ion" mean the same thing, and are used interchangeably in chemistry. Sometimes, you might even see H_3O^+, the **hydronium** ion, used in place of H^+.

Definition 4.8.1

A Brønsted-Lowry **acid** serves as a proton donor, while a Brønsted-Lowry **base** serves as a proton acceptor.

Since acid-base reactions are simply transfers of protons or hydrogen ions, they can take place in both directions. However, this will be covered in more detail in Unit 8, when we discuss *equilibrium*, taught in Unit 7.

If acid-base reactions can occur both back and forth, there must be an acid and base on both the reactant and product sides. This is where the concept of **conjugate acid-base pairs** comes into play. The next learning objective is for you to look at a chemical equation and be able to identify the acid-base pairs and the conjugates.

Let's consider the following example:

$$H_2Se(aq) + H_2O(l) \rightarrow H_3O^+(aq) + HSe^-(aq)$$

The above equation represents the reaction between hydroselenic acid (H_2Se) and water.

First, we will identify the acid-base pairs. Remember that a Brønsted-Lowry acid donates a H^+, and a Brønsted-Lowry base accepts it. Therefore, the species in a pair should differ by exactly one H^+ ion.

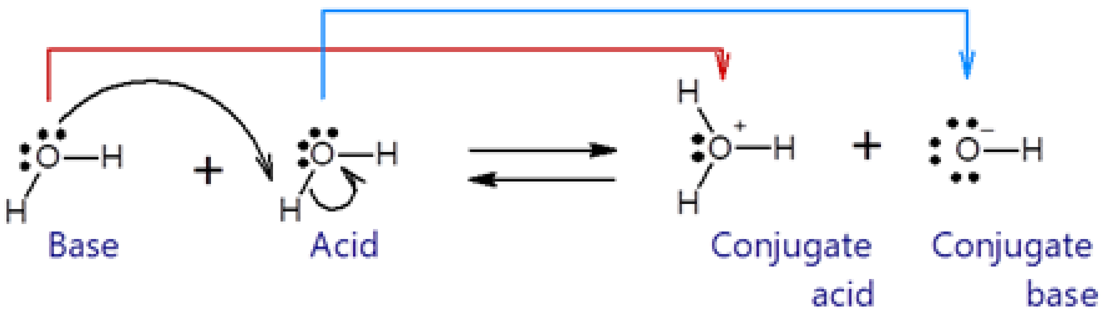
Thus, the first pair is H_2O and H_3O^+ and the second pair is H_2Se and HSe^-.

Additionally, we need to identify the acid, base, conjugate acid, and conjugate base. A quick way would be to figure out which species in the pair has the additional hydrogen. Since H_3O^+ contains one more H^+ ion than H_2O, it is the conjugate acid. This makes H_2O the base. From here, it is trivial to determine that HSe^- is the conjugate base of hydroselenic acid, since it contains one less H^+.

Amphiprotic Substances

Some special agents can function as both an acid and a base. These are referred to as **amphiprotic** or **amphoteric** substances. The only example of these you need to know for this course is water, H_2O.

The reason why some amphoteric substances function in this manner is that they possess both a lone pair of electrons that can accept and bond with a proton as well as a proton that they can donate.



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Acid-Base Neutralization

A **neutralization reaction** occurs when an acid and base react to form an ionic compound and water. For example, if $HNO_3(aq)$ reacts with NaOH(aq), the general form of the reaction is

$$HNO_3(aq) + NaOH(aq) \rightarrow NaNO_3(aq) + H_2O(l)$$

Using solubility rules, we know that KNO_3 is in the aqueous state (aq), since any salt containing NO_3^- is soluble.

At this point, we need to revisit **net ionic equations**. So far, we have written them for precipitation reactions, where soluble salts were dissociated into ions, while insoluble salts were kept in their original form. This time, we will write them for acid-base reactions and also learn about distinguishing weak from strong electrolytes (acids or bases).

Here, in neutralization reactions, we have to be very particular about not dissociating weak acids and bases. This is because they do not readily accept or donate protons to species and thus only partially ionize into their constituent ions.

In order to do this, we need to memorize the strong acids and strong bases!

The strong acids are as follows:

- Hydrochloric acid, HCl
- Hydrobromic acid, HBr
- Hydroiodic acid, HI
- Nitric acid, HNO_3
- Sulfuric acid, H_2SO_4
- Chloric acid, $HClO_3$
- Perchloric acid, $HClO_4$

For the purposes of the AP exam, any acid that is not one of those listed above can be assumed to be *weak*.

The strong bases are as follows:

- Calcium hydroxide, $Ca(OH)_2$
- Strontium hydroxide, $Sr(OH)_2$
- Barium hydroxide, $Ba(OH)_2$
- All Group 1 (alkali metal) hydroxides are soluble, and therefore fully ionize into their constituent ions, metal cation and hydroxide anion.

Similarly, any base that is not one of those listed above can be assumed as *weak*.

You will need to memorize these lists, in order to be able to distinguish strong vs. weak acids and bases. This will be especially important for both writing the correct reactions and solving stoichiometry problems involving aqueous species.

Back to the initial example: luckily, HNO_3 is a strong acid and NaOH is a strong base, so we can separate both of them into their constituent ions in the chemical equation.

The complete ionic equation for the reaction is:

$$\mathrm{H^+(aq) + NO_3^-(aq) + Na^+(aq) + OH^-(aq) + OH^-(aq) \rightarrow Na^+(aq) + NO_3^-(aq) + H_2O(l)}$$

Finally, we eliminate the spectator ions, Na^+ and NO_3^-, and the net ionic equation is

$$\boxed{\mathrm{H^+(aq) + OH^-(aq) \rightarrow H_2O(l)}}$$

Try these problems on your own.

Problem 4.8.2 — Net Ionic Equations I

What is the balanced, net ionic equation for the reaction between hydrofluoric acid, HF, and potassium hydroxide, KOH?

Solution: HF is a weak acid, while potassium hydroxide is a strong base.

We begin with the basic reaction

$$\mathrm{HF(aq) + KOH(aq) \rightarrow KF(aq) + H_2O(l)}$$

Now, let's use our solubility rules to dissociate the soluble ionic compounds.

KOH is a strong base, so it will completely dissociate into its ions, and KF is a Group 1 ionic salt, which will also completely dissociate. However, HF is a weak acid so it will NOT be broken apart. Therefore, the complete ionic equation reads

$$\mathrm{HF(aq) + K^+(aq) + OH^-(aq) \rightarrow K^+(aq) + F^-(aq) + H_2O(l)}$$

There is one spectator ion that we can omit, which is K^+. Finally, the net ionic equation that describes the reaction is

$$\boxed{HF(aq) + OH^-(aq) \to F^-(aq) + H_2O(l)}$$

Problem 4.8.3 — Net Ionic Equations II

What is the balanced, net ionic equation for the reaction between hydrobromic acid, HBr, and aluminum hydroxide, $Al(OH)_3$?

Solution: As always, we need to identify the species involved. HBr is a strong acid, but $Al(OH)_3$ is marginally soluble in water.

Next, write the basic reaction

$$HBr(aq) + Al(OH)_3(s) \to AlBr_3(aq) + H_2O(l)$$

Note that because aluminum hydroxide is insoluble according to our solubility rules, we will denote it with (s). Additionally, $AlBr_3$ is soluble in water according to our solubility rules, so it is also shown as (aq).

But we have a bit of a problem here: our equation is not balanced! There are three hydroxides on the left and only one on the right (from one water molecule). We should find that the balanced chemical reaction is

$$3HBr(aq) + Al(OH)_3(s) \to AlBr_3(aq) + 3H_2O(l)$$

Now, we can dissociate our soluble components into their constituent ions, omit the spectator ions, and generate our net ionic equation.

$$3H^+(aq) + 3Br^-(aq) + Al(OH)_3(s) \to Al^{3+}(aq) + 3Br^-(aq) + 3H_2O(l)$$

We have only one spectator ion, Br^-, and since there are three on both sides, we can cross them off to yield the net ionic equation as

$$\boxed{3H^+(aq) + Al(OH)_3(s) \to Al^{3+}(aq) + 3H_2O(l)}$$

Acid-Base Reaction Stoichiometry

Many times, you will be asked to solve for concentrations of certain ions (especially H^+ and OH^-) in problems involving acid and base neutralization reactions.

Example 4.8.4

Suppose we mixed 28.0 mL of a 0.250 M HNO_3 solution with 53.0 mL of a 0.320 M solution of KOH. What is the concentration of H^+ and OH^- once the reaction is complete?

Solution: The first step is to determine the number of moles of each species present. We will use the formula relating molarity to moles, or $n = MV$, where V is the volume in liters. Make sure to divide by the volume by 1000, as it is initially given in mL.

$$\text{mol HNO}_3 = 0.250\,M \cdot 0.0280\,\text{L} = 0.00700\,\text{mol HNO}_3$$
$$\text{mol KOH} = 0.320\,M \cdot 0.0530\,\text{L} = 0.0170\,\text{mol KOH}$$

Next, we need to determine the limiting reactant, or the reactant that depletes first and limits the amount of product formed. In this case, there is a $1:1$ ratio for all compounds and there is *less of* HNO_3 compared to KOH, so we can quickly identify HNO_3 as the limiting reactant.

Since all of the H^+ is contained in the limiting reactant HNO_3 (no longer present in the solution mixture), its concentration after the two solutions are mixed is $\boxed{0\,M}$.

Now, to determine the concentration of OH^-, we need to determine the amount of KOH that reacted with the HNO_3, and then subtract from the initial number of moles of KOH to calculate the amount that is in excess. Finally, divide by the total volume of the solution mixture to determine the molarity.

HNO_3 and KOH react in a one-to-one ratio, so the amount of KOH that reacted is equal to the amount of HNO_3, the limiting reactant, that depleted.

$$0.0170 - 0.0070 = 0.010\,\text{mol KOH unreacted}$$

The total volume of the solution mixture is $0.028\,\text{L} + 0.053\,\text{L} = 0.081\,\text{L}$.

Finally, the final concentration of hydroxide ions is

$$[\text{OH}^-] = \frac{0.010\,\text{mol KOH unreacted}}{0.081\,\text{L}} = \boxed{0.12\,M}$$

These problems may seem difficult at first, but it's all a matter of practice. Eventually, it all boils down to more stoichiometry, but with one extra step: using the formula $n = MV$.

§4.9 Oxidation-Reduction (Redox) Reactions

This is the last section of Unit 4. Be sure that you have understood the fundamentals and problem-solving techniques from both precipitation and acid-base reactions before reading further.

Redox Reactions

Oxidation-reduction reactions, commonly called **redox reactions**, are chemical reactions that involve a transfer of electrons, which cause molecules to shift oxidation states.

Definition 4.9.1

An **oxidation state** is the hypothetical charge of an atom if all its bonds to other atoms were fully ionic.

It is represented by a positive or negative number that expresses the number of electrons that an atom has gained or lost in a compound relative to its state on the periodic table.

When molecules lose an electron, they are *oxidized*, and when they gain an electron, they are *reduced*. Therefore, oxidation involves an increase in oxidation number, while reduction involves a decrease in oxidation number.

Important: In redox reactions, electrons travel from *oxidized species to reduced species.*

We can make the following analogy to relate redox reactions with acid-base reactions: Acids donate protons (H^+ ions) to bases, but here, the substance that is oxidized "donates" electrons to the substance that is reduced.

Writing out the chemical equation of redox reactions will reveal which species are oxidized and which are reduced by representing the transfer of electrons between the molecules.

Here are some fun mnemonic devices that can help you distinguish between the electron transfers in oxidation and reduction processes:

1. **OIL RIG**: "oxidation is loss" and "reduction is gain"
2. **LEO the lion says GER**: "loss of electrons is oxidation" and "gain of electrons is reduction."

Use whichever one that works better for you!

Assigning Oxidation Numbers

Assigning oxidation states to atoms is important because, for chemical reactions, it helps determining which species are oxidized and which are reduced. Consequently, you can predict the direction of electron flow for a set of compounds in the reaction.

Here are the rules for oxidation states that you should familiarize yourself with:

1. **Free elements**, e.g. Br_2, Na, S_8, have an oxidation number of 0.
2. **Neutral molecules** also have oxidation numbers of 0, so the oxidation numbers of their elements must sum to 0. For example, consider the molecule IF_3: if x is the oxidation number of I and y is the oxidation number of F, then the following must be true since IF_3 is a neutral molecule:

   $$x + 3y = 0$$

   Additionally, for *charged* **polyatomic ions**, the sum of the oxidation numbers on their elements must sum to the overall charge on the ion. For example, the phosphate ion, PO_4^{3-} has a net charge of -3. If x and y denote the oxidation numbers of P and O, respectively, then the following holds true:

   $$x + 4y = -3$$

3. **Monoatomic ions** have an oxidation number equal to their charge. For example, the oxidation numbers of Na^+, Cl^-, and Al^{3+} are $+1$, -1, and $+3$, respectively.

4. The oxidation number of oxygen is -2 in all compounds, except for **peroxides** (those containing O_2^{2-}), where it is -1.
5. Hydrogen has a $+1$ oxidation number in its compounds, except for **metal hydrides** (e.g. LiH, NaH, etc.), where it's -1.
6. Fluorine is -1 in all compounds. Other halogens are also usually -1 (there are rare exceptions, but you don't need to worry about them).
7. Oxidation numbers can be fractions, but it's **extremely rare** in general, and will likely never be tested on the AP exam.

Here are some practice exercises that involve assigning the correct oxidation number to elements in various compounds. It is highly recommended that you work through these independently before moving on in this section.

Problem 4.9.2 — Oxidation States Drill

For each of the following, give the oxidation number of the indicated species.

1. N in N_2O_3
2. O_2
3. C in CO_3^{2-}
4. Zn^{2+}
5. Mn in MnO_2

Solution to part 1: N_2O_3 is a neutral covalent compound, so the oxidation numbers for all atoms must total to 0. Let x and y denote the oxidation numbers of nitrogen and oxygen, respectively.

$$2x + 3y = 0$$

Using our rules, we know that oxygen has a charge of -2, since, in this case, N_2O_3 is not a peroxide.

Substituting and solving, we get

$$2x + 3(-2) = 0 \therefore x = 3$$

Therefore, the oxidation number of N in N_2O_3 is $\boxed{+3}$.

Solution to part 2: O_2 is diatomic oxygen, a free element. We know that all free elements have an oxidation number of zero, so the oxidation number of O_2 is $\boxed{0}$.

Solution to part 3: CO_3^{2-} is a polyatomic ion, with a net charge of -2. This is not too different from problem 1, so we proceed similarly.

Call x and y the oxidation numbers of C and O. We wish to solve for x.

$$x + 3y = -2$$

This ion does not contain peroxide, so the oxidation number on oxygen is -2, or $y = -2$.

Plugging in and solving for x yields

$$x + 3(-2) = -2 \therefore x = 4$$

Therefore, the oxidation number of C in CO_3^{2-} is $\boxed{+4}$.

Solution to part 4: Zn^{2+} is a monoatomic ion, it only consists of a zinc atom that has been ionized to a 2+ charge. The oxidation number of a monoatomic ion is simply its charge, so our answer is $\boxed{+2}$.

Solution to part 5:

$$x + 2y = 0$$

where x and y denote the oxidation numbers of manganese and oxygen.

Oxygen is not in the form of a peroxide, so its oxidation number is -2, or $y = -2$.

Substituting and solving for x,

$$x + 2(-2) = 0 \therefore x = 4$$

Therefore, the oxidation number of Mn in MnO_2 is $\boxed{+4}$.

Balancing Redox Reactions - Part 1: Acidic Solution

Consider the redox reaction described below. For this example, we will learn how to balance redox reactions in an acidic solution.

Solid magnesium oxide can be synthesized from magnesium metal and oxygen gas:

$$2Mg(s) + O_2(g) \rightarrow 2MgO(s)$$

Step 1

We begin by assigning oxidation numbers to all atoms participating in the reaction. Mg(s) and O_2(g) are free elements, so they have oxidation states of 0. Additionally, MgO is formed by an ionic bond between Mg^{2+} and O^{2-}, and their oxidation states sum to zero in this neutral compound. Since oxygen has an oxidation number of -2 (MgO is not a peroxide), Mg^{2+} will have to have an oxidation number of +2.

Using this information, we can write **half-reactions** for each reactant to demonstrate the transfer of charge for each specific molecule.

Step 2

Neutral magnesium metal is oxidized into magnesium ion, and neutral oxygen gas is oxidized into oxide ion.

$$2Mg(s) \rightarrow 2Mg^{2+}(aq)$$

$$O_2(g) \rightarrow 2O^{2-}(aq)$$

We need to balance the half reactions, but we are not only using the **law of conservation of mass**, like we did for basic chemical equations. We also need to conserve charge, so the number of electrons lost in oxidation is the same as the number of electrons gained in reduction.

Step 3

We can conserve charge by adding electrons or subatomic particles to the appropriate side, when necessary.

In the first half-reaction equation, the reactants have a charge of 0, but the products have a charge of +4 (2 Mg^{2+} ions). We need a −4 (or 4 electrons) charge to be added on the products to conserve charge in the half-reaction equation.

$$2Mg(s) \rightarrow 2Mg^{2+}(aq) + 4e^-$$

In the second equation, the reactants have a charge of 0, but the products have a charge of −4. Therefore, we need to add four electrons on the neutral side to produce a negative charge equal to that of the products.

$$O_2(g) + 4e^- \rightarrow 2O^{2-}$$

Step 4

Since both half-reactions conserve mass and charge, we can add them up to get the **overall reaction**.

$$2Mg(s) \rightarrow 2Mg^{2+}(aq) + 4e^-$$

$$O_2(g) + 4e^- \rightarrow 2O^{2-}(aq)$$

$$2Mg(s) + O_2(g) + 4e^- \rightarrow 2Mg^{2+}(aq) + 2O^{2-}(aq) + 4e^-$$

Notice that there are four electrons on both sides of the equation. When we have like terms, we can cancel them out, like we do in algebra.

The overall balanced redox reaction is thus

$$\boxed{2Mg(s) + O_2(g) \rightarrow 2Mg^{2+}(aq) + 2O^{2-}(aq)}$$

> **Note 4.9.3**
> In ionic bonds, electrons are transferred *completely* from one element to another. MgO is an example of an ionic bond. In covalent bonds, electrons are *shared* between molecules.

For redox reactions involving covalent compounds, scientists have developed a method of assigning oxidation states rather than traditional ionic charges. These numbers reflect the maximum number of electrons a molecule could gain or lose if they were (hypothetically) in an ionic bond.

PRO TIP: Don't get confused by this concept. You still only need to remember the rules for assigning oxidation states to elements in general.

Balancing Redox Reactions - Part 2: Basic Solution

In the example above, we balanced a very easy equation in acidic solution. Sometimes, you may be asked to balance redox reactions in a **basic solution**. This procedure follows the same exact steps of an acidic solution, but there is one additional step at the end. In a basic solution, OH^- ions are present, so that extra step is to form H_2O with the present H^+ and oxygen atoms, and then balance the equation by adding the extra mass on the other side with any OH^- ions leftover.

Review of Balancing Redox Reactions

Here are the general rules for balancing redox reactions. This will work for all possible questions that could be asked on the AP exam.

1. Assign oxidation states to each element, and determine which species are being oxidized and reduced.
2. Write the half-reactions for the oxidation and reduction processes.
3. Balance elements in the half-reactions other than oxygen and hydrogen.
4. Add appropriate number of water molecules to balance the oxygen atoms.
5. Add protons (H^+) to balance the hydrogen atoms.
6. Balance the half-reactions for charge by adding electrons as necessary. Usually, electrons are added to the side containing H^+.
7. Combine the half-reactions by adding them up and cancel any species that appear on both sides of the equation.
8. If the problem indicates a basic solution, add the appropriate number of OH^- ions to neutralize hydrogen ions and convert them to H_2O. Remember, what is added to one side must be added to the other as well.
9. Check to ensure that the number of atoms of each element is balanced on both sides of the equation, and that the total charge on the reactant side is equal to the total charge on the product side.

Here is one practice problem before we move on to the cumulative problems.

Problem 4.9.4 — Balancing Redox Reaction

Balance the redox reaction below in basic solution.

$$\mathrm{N_2O_4 + TeO_3^{2-} \rightarrow NO_3^- + Te}$$

Solution: First, let's identify our half-reactions, oxidation or reduction.

Nitrogen is oxidized from +4 to +5, as represented by the half reaction

$$\mathrm{N_2O_4 \rightarrow NO_3^-}$$

Additionally, Te is reduced from +4 to 0, as represented by the half reaction

$$\mathrm{TeO_3^{2-} \rightarrow Te}$$

Now that we have our half reactions set up, we can balance all other elements except for hydrogen and oxygen.

$$\mathrm{N_2O_4 \rightarrow 2NO_3^-}$$
$$\mathrm{TeO_3^{2-} \rightarrow Te}$$

We can balance oxygen by adding water molecules:

$$\mathrm{2H_2O + N_2O_4 \rightarrow 2NO_3^-}$$

$$\mathrm{TeO_3^- \rightarrow Te + 3H_2O}$$

Now, we will balance hydrogen by adding protons ($\mathrm{H^+}$):

$$\mathrm{2H_2O + N_2O_4 \rightarrow 2NO_3^- + 4H^+}$$

$$\mathrm{6H^+ + TeO_3^{2-} \rightarrow Te + 3H_2O}$$

We will balance the charges by adding electrons as needed:

$$\mathrm{2H_2O + N_2O_4 \rightarrow 2NO_3^- + 4H^+} + 2e^-$$

$$4e^- + \mathrm{6H^+ + TeO_3^{2-} \rightarrow Te + 3H_2O}$$

Now, we multiply the half reactions in order to balance electrons and add them together.

$$2 \cdot [\mathrm{2H_2O + N_2O_4 \rightarrow 2NO_3^- + 4H^+} + 2e^-]$$

$$4e^- + \mathrm{6H^+ + TeO_3^{2-} \rightarrow Te + 3H_2O}$$

When left with this, cancel common species:

$$\cancel{4e^-} + \cancel{\mathrm{6H^+}} + \mathrm{TeO_3^{2-}} + \overset{1}{\cancel{4}}\mathrm{H_2O} + \mathrm{2N_2O_4} \rightarrow \mathrm{4NO_3^-} + \overset{2}{\cancel{8}}\mathrm{H^+} + \cancel{4e^-} + \mathrm{Te} + \cancel{\mathrm{3H_2O}}$$

$$TeO_3^{2-} + H_2O + 2N_2O_4 \to 4NO_3^- + 2H^+ + Te$$

If we were asked to balance the equation in acidic solution, we would have stopped here. However, we are in a basic solution, so we need to add as many OH^- ions as possible to both sides of the equation:

$$2OH^- + TeO_3^{2-} + H_2O + 2N_2O_4 \to 4NO_3^- + 2H^+ + Te + 2OH^-$$

Since H^+ and OH^- neutralize each other and form water, we have

$$2OH^- + TeO_3^{2-} + H_2O + 2N_2O_4 \to 4NO_3^- + Te + 2H_2O$$

Finally (thought we'd never get there, huh?), cancel out the common species, and ensure that both the relative number of atoms and charges are balanced, giving us a final answer

$$\boxed{2OH^- + TeO_3^{2-} + 2N_2O_4 \to 4NO_3^- + Te + H_2O}$$

§4.10 Practice Problems

Problem 4.10.1 — 2000 AP Chemistry FRQ

Answer the following questions about $BeC_2O_4(s)$ and its hydrate.

(a) Calculate the mass percent of carbon in the hydrated form of the solid that has the formula $BeC_2O_4 \cdot 3H_2O$

(b) When heated to 220.°C, $BeC_2O_4 \cdot 3H_2O(s)$ dehydrates completely as represented below.

$$BeC_2O_4 \cdot 3H_2O(s) \rightarrow BeC_2O_4(s) + 3H_2O(g)$$

If 3.21 g of $BeC_2O_4 \cdot 3H_2O(s)$ is heated to 220.°C, calculate

(i) the mass of $BeC_2O_4(s)$ formed, and,
(ii) The volume of the $H_2O(g)$ released, measured at 220.°C and 735 mm Hg.

(c) A 0.345 g sample of anhydrous BeC_2O_4, which contains an inert impurity, was dissolved in sufficient water to produce 100. mL of solution. A 20.0 mL portion of the solution was titrated with $KMnO_4(aq)$. The balanced equation for the reaction that occurred is as follows.

$$16H^+(aq) + 2MnO_4^-(aq) + 5C_2O_4^{2-}(aq) \rightarrow 2Mn^{2+}(aq) + 10CO_2(g) + 8H_2O(l)$$

The volume of 0.0150 M $KMnO_4(aq)$ required to reach the equivalence point was 17.80 mL.

(i) Identify the species that was oxidized in the titration reaction.
(ii) For the titration at the equivalence point, calculate the number of moles of each of the following that reacted.

- $MnO_4^-(aq)$
- $C_2O_4^{2-}(aq)$

(iii) Calculate the total number of moles of $C_2O_4^{2-}(aq)$ that were present in the 100. mL of prepared solution.
(iv) Calculate the mass percent of $BeC_2O_4(s)$ in the impure 0.345 g sample.

Solution to part a: First, we need to find the total mass of the hydrated BeC_2O_4. Then, we find the total mass of carbon in this sample and divide, multiplying by 100.

$$\text{molar mass} = [9.012 + 2(12.01) + 4(16.00) + 3(16.00 + 2(1.008))] = 151.08\,\text{g mol}^{-1}$$

We see that BeC_2O_4 contains 2 atoms of carbon, so the mass percent is equal to

$$\%\,\text{carbon} = \frac{2(12.01)}{151.08} \cdot 100\% = \boxed{15.90\%}$$

Solution to part b(i): This problem can be solved by using a series of stoichiometric calculations. First, we convert from grams of $BeC_2O_4 \cdot 3H_2O(s)$ to moles of $BeC_2O_4 \cdot 3H_2O(s)$, then from moles of $BeC_2O_4 \cdot 3H_2O(s)$ to moles of $BeC_2O_4(s)$, and finally from moles of $BeC_2O_4(s)$ to grams of $BeC_2O_4(s)$.

Using dimensional analysis, we have

$$\frac{3.21\ \text{g BeC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}}{151.08\ \text{g mol}^{-1}} = 0.02124\ \text{mol BeC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$$

$$0.02124\ \cancel{\text{mol BeC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}} \cdot \frac{1\ \text{mol BeC}_2\text{O}_4}{1\ \cancel{\text{mol BeC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}}} = 0.02124\ \text{mol BeC}_2\text{O}_4$$

$$0.02124\ \cancel{\text{mol BeC}_2\text{O}_4} \cdot \frac{97.034\ \text{g BeC}_2\text{O}_4}{1\ \cancel{\text{mol BeC}_2\text{O}_4}} = \boxed{2.06\ \text{g BeC}_2\text{O}_4}$$

Solution to part b(ii): Since we are given the pressure and temperature and are asked to calculate volume, this is a clue to use the Ideal Gas Law. However, an important measurement is missing: the number of moles of $H_2O(g)$ produced in the reaction.

To find the number of moles of $H_2O(g)$ produced in the reaction, we use the molar ratio between the hydrated solid and water:

$$0.0124\ \cancel{\text{mol BeC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}} \cdot \frac{3\ \text{mol H}_2\text{O}}{1\ \cancel{\text{mol BeC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}}} = 0.0637\ \text{mol H}_2\text{O}$$

Now that we have the number of moles of water produced, we can find the volume that was released. Note: 1 atm = 760 mm Hg and K =° C + 273.

$$V = \frac{nRT}{P} = \frac{(0.0637\ \cancel{\text{mol}})(0.0821\ \text{L}\ \cancel{\text{atm}}\ \cancel{\text{mol}^{-1}}\ \cancel{\text{K}^{-1}})(493\ \cancel{\text{K}})}{(735\ \cancel{\text{mm Hg}} \cdot \frac{1\ \cancel{\text{atm}}}{760\ \cancel{\text{mm Hg}}})} = \boxed{2.67\ \text{L H}_2\text{O}}$$

Solution to part c(i): In a redox reaction, oxidizing a species involves an increase in the oxidation number of a constituent atom. Clearly, H^+ did not undergo any change, as it has an oxidation of +1 throughout (in H_2O, H has a oxidation number of +1, and O is −2). In MnO_4^-, the oxidation number of Mn is +7, because it is not a peroxide (O is −2, not −1) and the net charge is −1. On the products side, Mn appears as Mn^{2+}, which indicates a *decrease* in oxidation number (+7 to +2). This means that MnO_4^- was *reduced*, not oxidized. However, $\boxed{C_2O_4^{2-}}$ is oxidized, because the oxidation number of carbon increases from +3 to +4 in CO_2.

Solution to part c(ii): For MnO_4^-, we know its molar concentration as well as its volume, so we simply apply the equation $n = MV$:

$$n_{\text{MnO}_4^-} = \left(0.0150\ \text{mol}\ \cancel{\text{L}^{-1}}\right) \cdot (0.01780\ \cancel{\text{L}}) = \boxed{2.67 \cdot 10^{-4}\ \text{mol MnO}_4^-}$$

According to the balanced chemical equation, 5 moles of $C_2O_4^{2-}$ react for every 2 moles of MnO_4^-, so the stoichiometry yields

$$n_{\text{C}_2\text{O}_4^{2-}} = \frac{5}{2} n_{\text{MnO}_4^{2-}} = \frac{5}{2}\left(2.67 \cdot 10^{-4}\right) = \boxed{6.68 \cdot 10^{-4}\ \text{mol C}_2\text{O}_4^{2-}}$$

Solution to part c(iii): Our answer of $6.68 \cdot 10^{-4}$ mol $C_2O_4^{2-}$ in part c(ii) refers to the number of moles of C_2O_4 in a 20 mL portion of the solution that was titrated. We need to find the total number of moles of $C_2O_4^{2-}$ in the entire 100. mL of solution. In both cases, the concentration of $C_2O_4^{2-}$ must be equal, so we will have to multiply the answer in part c(ii) by 5 to account for this change, yielding an answer of

$$\text{total } n_{C_2O_4^{2-}} = \frac{100.\text{ mL}}{20.0\text{ mL}} \cdot 6.68 \cdot 10^{-4}\text{ mol} = \boxed{3.34 \cdot 10^{-3}\text{ mol } C_2O_4^{2-}}$$

Solution to part c(iv): BeC_2O_4 is an ionic compound that completely dissociates into Be^{2+} and $C_2O_4^{2-}$ ions in water, and all of these species are in a equivalent molar amounts. Therefore, we have the following:

$$\text{mol } BeC_2O_4 = \text{mol } C_2O_4^{2-} = 3.34 \cdot 10^{-3}\text{ mol } BeC_2O_4$$

We can find the mass of BeC_2O_4 by multiplying the number of moles with its molar mass. Finally, we will take its mass, divide by the total mass of the sample, and multiply by 100 to calculate the mass percent.

$$\text{mass } BeC_2O_4 = (3.34 \cdot 10^{-3}\text{ mol } BeC_2O_4)(97.034\text{ g mol}^{-}) = 0.32385\text{ g}$$

$$\%\ BeC_2O_4 = \frac{0.32385\text{ g } BeC_2O_4}{0.345\text{ g sample}} \cdot 100\% = \boxed{93.9\%}$$

Problem 4.10.2 — (Modified) 2003 AP Chemistry FRQ

Answer the following questions that relate to chemical reactions.

(a) Iron(III) oxide can be reduced with carbon monoxide according to the following equation.

$$Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(s) + 3CO_2(g)$$

A 16.2 L sample of CO(g) at 1.50 atm and 200.°C is combined with 15.39 g of $Fe_2O_3(s)$

(i) How many moles of CO(g) are available for the reaction?
(ii) What is the limiting reactant for the reaction? Justify your answer.
(iii) How many moles of Fe(s) are formed in the reaction?

(b) In a reaction vessel, 0.600 mol of $Ba(NO_3)_2(s)$ and 0.300 mol of $H_3PO_4(aq)$ are combined with deionized water to a final volume of 2.00 L. The reaction represented below occurs.

$$3Ba(NO_3)_2(aq) + 2H_3PO_4(aq) \rightarrow Ba(PO_4)_2(s) + 6HNO_3(aq)$$

(i) Calculate the mass of $Ba_3(PO_4)_2(s)$ formed.
(ii) If pH is defined as the negative base-10 logarithm of the H^+ ion concentration, calculate the pH of the resulting solution.
(ii) What is the concentration, in mol L^{-1}, of the nitrate ion, $NO_3^-(aq)$, after the reaction reaches completion?

Solution to part a(i): We are given the pressure and volume amount of CO(g) as well as the temperature. Therefore, we can use the Ideal Gas Law to solve for the number of moles of CO(g) that are available to react.

$$PV = nRT$$

$$n_{CO} = \frac{(1.50\,\cancel{\text{atm}})(16.2\,\cancel{\text{L}})}{(0.0821\,\cancel{\text{L}}\,\cancel{\text{atm}}\,\text{mol}^{-1}\,\cancel{\text{K}^{-1}})(473\,\cancel{\text{K}})} = \boxed{0.626\text{ mol CO}}$$

Solution to part a(ii): Let's find the number of moles of Fe_2O_3 and CO required for the reaction.

The number of moles of Fe_2O_3 we have can be determined by converting grams to moles via the molar mass:

$$n_{Fe_2O_3} = 15.39\,\cancel{\text{g Fe}_2\text{O}_3} \cdot \frac{1\text{ mol Fe}_2\text{O}_3}{159.7\,\cancel{\text{g Fe}_2\text{O}_3}} = 0.0964\text{ mol Fe}_2\text{O}_3$$

Next, we use the mole ratio between CO and Fe_2O_3 to calculate the number of moles of CO required to completely react with 0.0964 mol Fe_2O_3

$$n_{\text{CO required}} = 0.0964\,\cancel{\text{mol Fe}_2\text{O}_3} \cdot \frac{3\text{ mol CO}}{1\,\cancel{\text{mol Fe}_2\text{O}_3}} = 0.298\text{ mol CO}$$

We know that there are 0.626 mol CO available, but only 0.298 mol are actually needed for the reaction. Therefore, CO is in excess and $\boxed{Fe_2O_3}$ is the limiting reactant.

Solution to part a(iii): We will use stoichiometric coefficients to convert from moles of Fe_2O_3 to moles of Fe. According to the balanced chemical equation, 2 moles of Fe(s) are produced for every 1 mole of Fe_2O_3(s) that is consumed. Note that we must use Fe_2O_3 for the stoichiometry and not CO, because it is the limiting reactant and will limit the amount of products formed.

$$0.0964\,\cancel{\text{mol Fe}_2\text{O}_3} \cdot \frac{2\,\text{mol Fe}}{1\,\cancel{\text{mol Fe}_2\text{O}_3}} = \boxed{0.193\,\text{mol Fe produced}}$$

Solution to part b(i): Since we are given molar amounts of both reactants, we need to determine which one is limiting. Remember that the limiting reactant will determine the amount of products formed.

We will use mole ratios to calculate the number of moles of H_3PO_4 needed to completely react with $0.600\,\text{mol Ba(NO}_3)_2$.

$$0.600\,\cancel{\text{mol Ba(NO}_3)_2} \cdot \frac{2\,\text{mol H}_3\text{PO}_4}{3\,\cancel{\text{mol Ba(NO}_3)_2}} = 0.400\,\text{mol H}_3\text{PO}_4$$

However, there is only 0.300 mol H_3PO_4 available, according to the problem statement. Therefore, H_3PO_4 is the limiting reactant.

We must use the limiting reactant to calculate the mass of $Ba(PO_4)_2$ produced.

$$0.300\,\cancel{\text{mol H}_3\text{PO}_4} \cdot \frac{1\,\cancel{\text{mol Ba}_3(\text{PO}_4)_2}}{2\,\cancel{\text{mol H}_3\text{PO}_4}} \cdot \frac{602\,\text{g Ba}_3(\text{PO}_4)_2}{1\,\cancel{\text{mol Ba}_3(\text{PO}_4)_2}} = \boxed{90.3\,\text{g Ba}_3(\text{PO}_4)_2}$$

Solution to part b(ii): First, we need to determine the number of moles of HNO_3 that are produced in this reaction. Using our initial amount of H_3PO_4, we have

$$0.300\,\cancel{\text{mol H}_3\text{PO}_4} \cdot \frac{6\,\text{mol HNO}_3}{2\,\cancel{\text{mol H}_3\text{PO}_4}} = \boxed{0.900\,\text{mol HNO}_3}$$

Additionally, the final volume of the solution is 2.00 L, so the concentration of HNO_3 is

$$[\text{HNO}_3] = \frac{0.900\,\text{mol HNO}_3}{2.0\,\text{L}} = 0.45\,M$$

Finally, all the H_3PO_4 has been fully consumed (as it is limiting), so the only species left in the solution that contributes to the amount of H^+ ions is HNO_3. Moreover, HNO_3 is a strong acid, and will fully dissociate into H^+ ions, so $[H^+] = 0.45\,M$.

The pH of the resulting solution is equal to

$$\text{pH} = -\log(0.45) = \boxed{0.35}$$

Solution to part b(iii): It's important to note that the final concentration of NO_3^- must be the same as the initial concentration. Additionally, molarity is moles per liter, so we will find the number of moles of NO_3^- ion and divide by the final volume.

$Ba(NO_3)_2$ is an ionic compound, which fully dissociates in water as Ba^{2+} and NO_3^- ions. However, for every one mole of $Ba(NO_3)_2$ that dissociates, two moles of NO_3^- ions are formed.

$$n_{NO_3^-} = 0.600\,\cancel{\text{mol Ba(NO}_3)_2} \cdot \frac{2\,\text{mol NO}_3^-}{1\,\cancel{\text{mol Ba(NO}_3)_2}} = 1.2\,\text{mol NO}_3^-$$

Finally, molarity is defined as moles per liter, so

$$[NO_3^-] = \frac{1.2\,\text{mol NO}_3^-}{2.0\,\text{L}} = \boxed{0.60\,M}$$

Problem 4.10.3 — 2004 AP Chemistry FRQ (Excerpt)

Write the formulas to show the reactants and products for the following laboratory situations described below. Assume that a chemical reaction occurs in all cases. Additionally, assume that all solutions are aqueous unless otherwise stated.

(a) A solution of copper(II) sulfate is spilled onto a sheet of freshly polished aluminum metal.

(b) A 0.1 M nitrous acid (HNO_2) is added to the same volume of a 0.1 M sodium hydroxide solution.

(c) A solution of sodium phosphate is added to a solution of aluminum nitrate.

(d) Concentrated hydrochloric acid is added to a solution of sodium bisulfide, NaHS.

Solution to part a: Copper(II) sulfate has chemical formula $CuSO_4$. It is an ionic compound, composed of Cu^{2+} and SO_4^{2-} ions.

The chemical equation that we are interested in is

$$2Al(s) + 3CuSO_4(aq) \rightarrow Al_2(SO_4)_3(aq) + 3Cu(s)$$

This is a single replacement reaction because the Al(s) replaces Cu^{2+} in $CuSO_4$, forming $Al_2(SO_4)_3$.

We see that the sulfate ion, SO_4^{2-}, does not directly participate in the reaction, so we can cancel it. Our chemical equation is

$$Al + Cu^{2+} \rightarrow Al^{3+} + Cu$$

and balancing, we have

$$\boxed{2Al + 3Cu^{2+} \rightarrow 2Al^{3+} + 3Cu}$$

Solution to part b: By definition, acids and bases neutralize each other. When they react (in equimolar quantities), formation of a salt (ionic compound) and water is observed.

The chemical equation we are interested in is

$$HNO_2(aq) + NaOH(aq) \rightarrow NaNO_2(aq) + H_2O(l)$$

However, this doesn't tell us what actually happens. Let's write the complete ionic equation.

$$HNO_2(aq) + Na^+(aq) + OH^-(aq) \rightarrow Na^+(aq) + NO_2^-(aq) + H_2O(l)$$

Note that we did not dissociate nitrous acid into its ions because it is a weak acid. You must memorize the strong acids for the AP exam. Anything else is assumed to be weak, unless the question states otherwise.

We have one spectator ion, Na^+. If we cancel it, we are left with the net ionic equation:

$$\boxed{HNO_2(aq) + OH^-(aq) \rightarrow NO_2^-(aq) + H_2O(l)}$$

Solution to part c: When you see a reaction occurring between two ionic compounds, you should think of double replacement reactions. The cations and anions of both compounds exchange, leading to the formation of another ionic compound as well as a precipitate (insoluble substance).

Na_3PO_4 is an alkali metal salt and $Al(NO_3)$ is a nitrate salt. According to solubility rules, both these substances are soluble in water. When they react, they produce sodium nitrate which, for the same reasons, is very soluble in water, as well as aluminum phosphate. Because a chemical reaction occurs, there must be a precipitate and because sodium nitrate is soluble, aluminum phosphate must be the substance that is insoluble.

Therefore, the balanced chemical equation is

$$Na_3PO_4(aq) + Al(NO_3)_3(aq) \rightarrow 3NaNO_3(aq) + AlPO_4(s)$$

Breaking apart our soluble components and canceling off spectator ions, we have

$$\cancel{3Na^+(aq)} + PO_4^{3-}(aq) + Al^{3+}(aq) + \cancel{3NO_3^-(aq)} \rightarrow \cancel{3Na^+(aq)} + \cancel{3NO_3^-(aq)} + AlPO_4(s)$$

and the net ionic equation is

$$\boxed{PO_4^{3-}(aq) + Al^{3+}(aq) \rightarrow AlPO_4(s)}$$

Solution to part d: Hydrochloric acid, HCl(aq), is a strong acid that completely dissociates into H^+ and Cl^- ions in aqueous solution. Also, sodium bisulfide, NaHS, is an alkali metal salt so it is soluble in water.

The reaction that occurs is represented by the chemical equation

$$HCl + NaHS \rightarrow NaCl + H_2S$$

We can now proceed with the complete ionic equation. However, be careful with H_2S! You should NOT separate it into $2H^+$ and S^{2-}. This molecule actually consists of two sulfur atoms bonded to hydrogen with stable single bonds. Hence, it is a *covalent* compound, and should be left as a single unit in the complete and net ionic equations.

$$H^+ + Cl^- + Na^+ + HS^- \rightarrow Na^+ + Cl^- + H_2S$$

We have two spectator ions, Na^+ and Cl^-. Therefore, we will remove them when writing the net ionic equation:

$$\boxed{H^+ + HS^- \rightarrow H_2S}$$

Problem 4.10.4 — (Modified) 2007 AP Chemistry FRQ

$$5Fe^{2+}(aq) + MnO_4^-(aq) + 8H^+(aq) \rightarrow 5Fe^{3+}(aq) + Mn^{2+}(aq) + 4H_2O(l)$$

The mass percent of iron in a soluble iron(II) compound is measured using a titration based on the balanced chemical equation above. Note: Fe^{2+} and MnO_4^- are both colored ions, but the intensity of the latter far exceeds that of the former.

(a) What is the oxidation number of manganese in the permanganate ion, $MnO_4^-(aq)$?

(b) Identify the substance that is oxidized in the reaction represented above.

The mass of a sample of the iron(II) compound is carefully measured before the sample is dissolved in distilled water. The resulting solution is acidified with $H_2SO_4(aq)$. The solution is then titrated with $MnO_4^-(aq)$ until the end point is reached.

(c) Explain why the solution color changes at the end point of the titration.

(d) Let the variables g, M, and V be defined as follows:

- g = the mass, in grams, of the sample of the iron(II) compound
- M = the molarity of the $MnO_4^-(aq)$ used as the titrant
- V = the volume, in liters, of $MnO_4^-(aq)$ added to reach the end point

In terms of these variables, the number of moles of $MnO_4^-(aq)$ added to reach the end point of the titration is expressed as $M \cdot V$. Using the variables defined above, the molar mass of iron ($55.85\,\text{g}\,\text{mol}^{-1}$), and the coefficients in the balanced chemical equation, write the expression for each of the following quantities.

(i) The number of moles of iron in the sample.
(ii) The mass of iron in the sample, in grams.
(iii) The mass percent of iron in the compound.

(e) What effect will adding too much titrant have on the experimentally determined value of the mass percent of iron in the compound? Justify your answer.

Solution to part a: The overall charge on the MnO_4^- ion is -1. Therefore, the sum of the oxidation numbers for all constituent atoms in the ion should add up to -1.

Let's call x and y the oxidation numbers of Mn and O, respectively. We wish to solve for x and can set up the following equation:

$$x + 4y = -1$$

Since MnO_4^- is not a peroxide (any species containing the O_2^{2-} ion), the oxidation number of oxygen is -2 so $y = -2$. Substituting these into our equation, we have

$$x + 4(-2) = -1 \therefore x = 7$$

The oxidation number of Mn in the permanganate ion is $\boxed{+7}$.

Solution to part b: The substance that is oxidized in a redox reaction is the one that experiences an increase in oxidation number, i.e. a loss in electrons. By inspecting the chemical equation, the oxidation number of iron is initially +2 but as the reaction progresses, it increases to +3. Thus, $\boxed{Fe^{2+}}$ is the species that is oxidized.

Solution to part c: At the end point of the titration, the Fe^{2+}(aq) and MnO_4^- are in stoichiometric amounts. Since the coefficient on Fe^{2+} is 5 while the coefficient on MnO_4^- is 1, the former is clearly the limiting reactant, because its initial amount reduces five times as quickly as the latter. Therefore, there is no Fe^{2+}(aq) left in the flask to react with the colored MnO_4^-(aq) ion. Therefore, when a small amount of permanganate ion is added after the endpoint of the titration has been reached, the unreacted (excess) MnO_4^- present in the solution will cause a color change.

Solution to part d(i): Since the variables M and V describe the molarity and volume of the MnO_4^-(aq), we know that the number of moles of MnO_4^-(aq) is equal to MV, according to the equation $M = \frac{n}{V}$ for molarity.

We wish to calculate the number of moles of iron (existing as Fe^{2+}) in the sample. To do this, we can use mole ratios. The coefficient on Fe^{2+} is 5 and the coefficient on MnO_4^- is 1. Therefore we can set up a mole ratio:

$$\frac{5\ \mathrm{mol\ Fe^{2+}}}{1\ \mathrm{mol\ MnO_4^-}}$$

since Fe^{2+} is consumed five times as much MnO_4^- is consumed.

The number of moles of iron in the sample is therefore 5 times the number of moles of permanganate ion, or $\boxed{5 \cdot M \cdot V}$

Solution to part d(ii): Since we found the number of moles of iron in the sample in part (d)(i), we can just multiply that value by the molar mass of iron (55.85 g/mol) to determine the mass present in the sample.

Thus, we have

$$5 \cdot M \cdot V\ \cancel{\mathrm{mol\ Fe^{2+}}} \cdot \frac{55.85\ \mathrm{g}}{1\ \cancel{\mathrm{mol\ Fe^{2+}}}} = \boxed{5 \cdot M \cdot V \cdot 55.85}$$

Solution to part d(iii): Mass percent of a certain component in a sample is defined as the mass of that component divided by the total mass of the sample.

Therefore,

$$\text{mass \% Fe} = \frac{\text{mass Fe}}{\mathrm{g}} \cdot 100$$

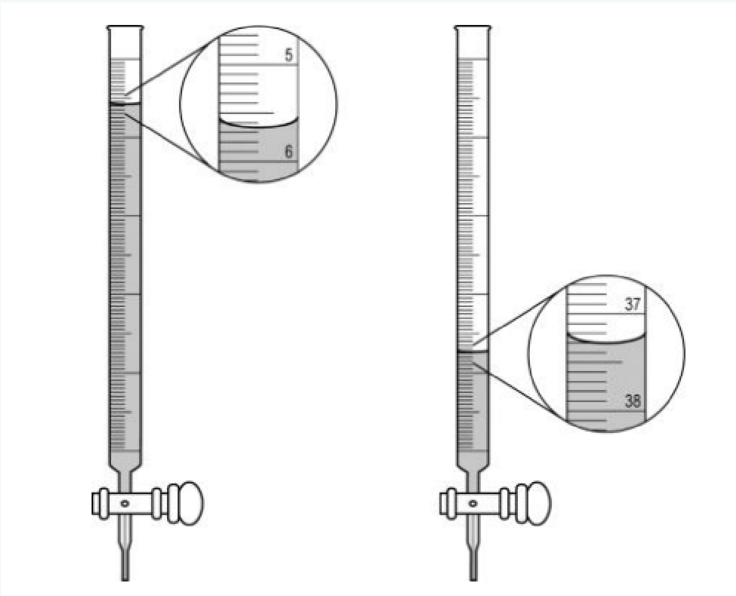
We know the mass of iron in the sample (in grams) from our answer to part (d)(ii), leading to our final answer of $\boxed{\frac{5 \cdot M \cdot V \cdot 55.85}{\mathrm{g}} \cdot 100}$

Solution to part e: Adding too much titrant (MnO_4^-) will result in the overall volume being too large. Note that the mass percent calculation for iron in the compound contains V in the numerator. If V is too large, then the experimentally determined mass percent of iron would also be too large.

Problem 4.10.5 — 2016 AP Chemistry FRQ

A student is given a 25.0 mL sample of a solution of an unknown monoprotic acid and asked to determine the concentration of the acid by titration. The student uses a standardized solution of 0.110 M NaOH(aq), a buret, a flask, an appropriate indicator, and other laboratory equipment necessary for the titration.

(a) The images below show the buret before the titration begins (below left) and at the end point (below right). What should the student record as the volume of NaOH(aq) delivered to the flask?



(b) Based on the given information and your answer to part (a), determine the value of the concentration of the acid that should be recorded in the student's lab report.

(c) In a second trial, the student accidentally added more NaOH(aq) to the flask than was needed to reach the end point, and then recorded the final volume. Would this error increase, decrease, or have no effect on the calculated acid concentration for the second trial? Justify your answer.

Solution to part a: To determine the volume of NaOH(aq) that was delivered to the flask, we need to find the absolute difference between the initial and final buret readings. Remember that we read the level of a liquid by using the *lower* meniscus, so the initial reading is 37.30 mL, rounding as necessary. Similarly, we can observe that the final reading is 5.65 mL. The difference between these two readings is the volume of titrant solution (NaOH) that was added to the flask.

$$37.30\,\text{mL} - 5.65\,\text{mL} = \boxed{31.65\,\text{mL}}$$

Solution to part b: At the equivalence point of an acid-base titration, the acid and base are in equimolar quantities. We will use the formula

$$M_aV_a = M_bV_b$$

where the subscripts a and b indicate acid and base, respectively.

Because we wish to determine the concentration of acid, we should rearrange the equation to solve for M_a:

$$M_a = \frac{M_bV_b}{V_a} = \frac{(0.110\,M)(0.03165\,\cancel{L})}{0.0250\,\cancel{L}} = \boxed{0.139\,M}$$

Note that V_b is equal to the volume of NaOH(aq) that was delivered to the flask. Additionally, the equation for molarity involves volume in liters, so I converted units to demonstrate the correct setup.

Solution to part c: If the student accidentally added more NaOH(aq) to the flask than necessary, this would cause the calculated acid concentration for the second trial to $\boxed{\text{increase}}$. This error will cause V_b to increase, leading to more moles of base (M_bV_b) than moles of acid actually present in the solution. The assumption that the number of moles of acid are equal to the number of moles of base at the end point would lead to a calculated acid concentration that would be higher than the actual concentration.

5 Kinetics

This unit focuses on the rates of change in chemical reactions and the factors that influence them. We will unpack the concepts of rate laws, reaction mechanisms, catalysis, and more.

§5.1 Reaction Rates

Welcome to the first section of unit 5! This unit will cover everything you need to know about kinetics on the AP exam.

Definition 5.1.1

Kinetics is the study of the rate of a reaction.

Essentially, we will learn about the factors causing reactions to occur, as well as their rates. You may notice when performing experiments, some reactions proceed incredibly fast, whereas others go extremely slow. The role of kinetics is to explain why certain reactions occur faster or slower than others.

Measuring Rate of a Reaction

The **rate of a reaction** has a simple definition that is actually very nuanced. The rate of reaction is essentially how fast a reaction produces products. We can determine "how quickly" reactants form products by observing changes in **concentrations** of species.

$$\text{reactants} \rightarrow \text{products}$$

As this generic reaction progresses, the concentration of the **reactants** decreases as they are consumed to form **products**. It follows that the concentration of the products will increase as more of them are created.

Mathematically, the rate of a reaction can be written as

$$rate = \frac{\Delta[\text{reactants}]}{\Delta t}$$

What about the units? The square brackets represent molar concentrations, or molarity values. These are in units of moles per liter ($\mathrm{mol\,L^{-1}}$) or molar (M). Also, time is usually given in seconds (s). Therefore, the units of reaction rate are usually expressed as $M\,\mathrm{s^{-1}}$ or $\mathrm{mol\,L^{-1}\,s^{-1}}$. Remember that you must always watch out for units when doing math!

Reaction Rates - Graphical Representation

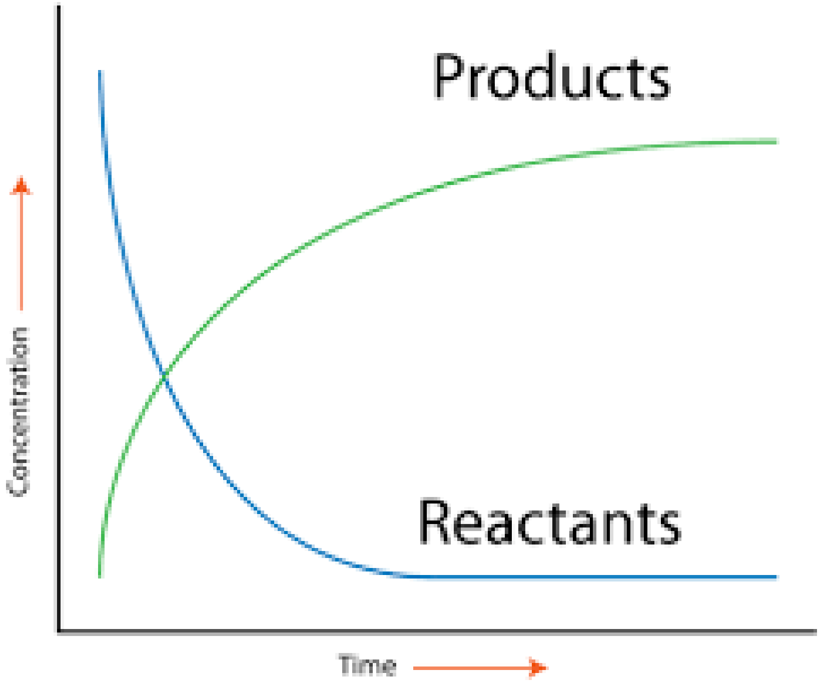


Image Courtesy of CK-12 Learning

Going back to our generic reaction:

$$\text{reactants} \rightarrow \text{products}$$

As this reaction progresses, the [reactants] decreases whereas the [products] increases until the reaction reaches **equilibrium**. At this point, the rate of the reaction going forward is equal to the rate of the reaction going backward, and the concentrations of all species remain stable. You can think of equilibrium the same way as homeostasis works in our bodies. Both involve systems in a state of balance.

Equilibrium is covered in-depth in Unit 7, but it doesn't hurt to have some knowledge to interpret the above graph. Here, the rate of reaction is represented by the *slope* of the line containing two points on either curve. The slope represents the change in concentration over the change in time, which as we saw previously, gives us the rate of reaction.

The **average rate of a reaction** is the change in concentration of a reactant or product over a specific *interval* of time. This wording should serve as a clue that we are using the slope of a line passing through two points. An average rate could vary over time, depending on both the concentrations of species and the conditions of the reaction.

The **instantaneous rate of a reaction**, by contrast, is the rate of the reaction at a very specific point in time. In technical jargon, it is calculated by taking the limit of the average rate as the time interval approaches zero. This is equivalent to calculating the slope of the line tangent to any given point of a graph, and this concept requires calculus (which is beyond the scope of AP Chemistry). For those who understand the math, this can be written as the derivative

$$rate = -\frac{d[\text{reactants}]}{dt} = +\frac{d[\text{products}]}{dt}$$

Overall, the difference between average vs. instantaneous rate is that the former measures concentration changes over a specific time interval, while the latter describes the change in concentration at a specific moment in time.

Using Stoichiometry with Reaction Rates

Consider an arbitrary reaction

$$2\text{A} + \text{B} \rightarrow 5\text{C}$$

Using examples like this are great for simplifying concepts rather than immediately jumping into some intimidating equations.

Suppose that after 2 seconds, the concentration of A decreased by 0.2 M. Therefore, the rate of the reaction with respect to A is

$$\frac{\Delta[\text{A}]}{\Delta t} = \frac{-0.2\,M}{2\,\text{s}} = -0.1\,M^{-1}\,\text{s}^{-1}$$

Using this information, we can use some simple stoichiometry to determine the rate at which substance B is being consumed:

$$-0.1\,\frac{\cancel{\text{mol A}}}{\text{L}\cdot\text{s}} \cdot \frac{1\text{ mol B}}{2\,\cancel{\text{mol A}}} = -0.05\,\frac{\text{mol B}}{\text{L}\cdot\text{s}}$$

The same approach can be used if we wanted to find the rate of production for C. Stoichiometry continues to be an important tool in this course, and we can use it to actually generalize the rate of reaction in terms of its reactants and products.

If we have a general reaction

$$a\text{A} + b\text{B} \rightarrow c\text{C} + d\text{D}$$

where a, b, c, and d are the stoichiometric coefficients of substances A, B, C, and D, respectively, we can represent the rate of reaction as

$$\boxed{rate = -\frac{1}{a}\frac{\Delta[\text{A}]}{\Delta t} = -\frac{1}{b}\frac{\Delta[\text{B}]}{\Delta t} = \frac{1}{c}\frac{\Delta[\text{C}]}{\Delta t} = \frac{1}{d}\frac{\Delta[\text{D}]}{\Delta t}}$$

If you need a review of stoichiometry, check out section 4.5 of this book!

Physical Attributes to Reaction Rates

There are several factors that can influence the rate of a chemical reaction. According to the Course and Exam Description for AP Chemistry, these include:

1. **Concentration**: Increasing the concentration of the reactants is one way to speed up a chemical reaction. This is because there are more reactant molecules present, increasing the probability of successful collisions occurring between them.

2. **Temperature**: The easiest way to increase the rate of reaction is to increase the temperature of the system. This is because reactant molecules have more *kinetic energy*, increasing the probability of successful collisions between them. Always remember that temperature represents *average* kinetic energy—this concept will be priceless for this unit and AP Chemistry in general.

3. **Surface area**: Increasing the surface area of a reactant (e.g. grinding a solid into smaller chunks or even powder) can increase the rate of a reaction. This is because there is more space available for reactant molecules to collide within, increasing the chance of successful collisions.

4. **Presence of a catalyst**: A catalyst is a substance that speeds up a reaction without being consumed in the process. They provide an alternative pathway for the reaction to occur, effectively lowering the activation energy required to bring about the reaction. We will refer back to this concept with more detail in section 5.11.

5. **Pressure (for gaseous systems)**: Increasing the pressure can result in an increase in the rate of reaction. As with increasing concentration, a higher pressure indicates that more gas molecules are present in a given volume, so successful collisions between the reactant molecules are more likely. If you need a refresher on temperature, pressure, or gases in general, feel free to revisit Unit 3!

§5.2 Introduction to Rate Law

Earlier, when we defined *kinetics*, we could infer that an increase in the concentration of reactants causes the reaction rate to increase. This makes sense because if more reactants are present in the same volume, the forward reaction (reactants to products) will clearly occur faster since the system (chemical reaction) strives to achieve stability in the least amount of time.

Key Question: However, how can we quantitatively determine *how* much faster will the rate be? This is where the **rate law** comes in.

Define: What is a Rate Law?

A rate law is an equation that describes the relationship between the rate of a chemical reaction and the concentration of the reactants.

$$rate = k[\text{A}]^m[\text{B}]^n \dots$$

where:

- r is the rate of the chemical reaction (this is sometimes given by $\frac{\Delta[]}{\Delta t}$, but we will study this form in the next section),
- k is the **rate constant**,
- [A], [B], . . . represent the reactant concentrations, and

- m n, ... represent the **reaction orders** for each reactant (A, B, etc). This rate law is in *generalized*, so it is followed by ... because a reaction can consist of any number of reactants. It could have reactants 3, 4, or even 5, but for the AP exam, you probably will not see more than 2. Even in nature, it is very uncommon for a reaction with 3+ reactants to take place since it would require three or more species to interact in a very specific orientation−more on this in section 5.5−but just know this process is very taxing and unlikely to occur under standard conditions.

Reaction Order

In the above generalized equation for the rate law of a chemical reaction, we saw that m and n represent the reaction order for each reactant. This concept ties back into the main question at the beginning of this section: How can we quantitatively determine the effect of **concentration changes** on the **reaction rate**? The reaction order describes how the rate of reaction changes as the concentration of each reactant changes.

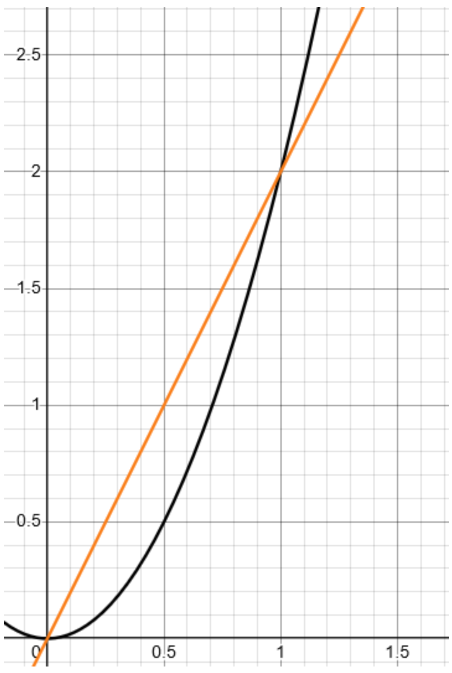
Example 5.2.1

A hypothetical chemical reaction

$$\mathrm{A} + \mathrm{B} \rightarrow \mathrm{C}$$

has the expression of the rate law of $rate = k[\mathrm{A}]^2[\mathrm{B}]$. This can tell us that the reaction rate has a *quadratic relationship* with the concentration of A, because its reaction order is 2. In contrast, it has a *linear relationship* with the concentration of B, which has a reaction order of 1.

If we increase the concentration of A by a factor of 2 (assuming [B] is constant), then the rate of reaction will increase by a factor of 4. Meanwhile, if we double the concentration of B (assuming [A] is constant), the rate of reaction will double.



The above graph shows a quadratic (black curve) vs. linear (orange curve) relationship between the rate of reaction and concentrations of A and B, respectively.

The overall reaction order for the reaction is the sum of the orders for each reactant. In our hypothetical example, the overall reaction order would be 3, since the reaction order of reactant A is 2 and the reaction order of reactant B is 1.

Using Experimental Data to Determine Rate Laws

The most important aspect of rate laws is that **they can only be determined experimentally**. Specifically, a chemist would run several tests in the lab at different reactant concentrations and find the corresponding rates of reaction for each test. With this data, they can determine the order of the reaction with respect with each order for each reactant.

Example 5.2.2

We have a reaction:

$$2NO(g) + 2H_2(g) \to N_2(g) + 2H_2O(g)$$

For the reaction, we will observe three experiments conducted with different concentrations for each reactant.

$2NO_{(g)} + 2H_{2(g)} \longrightarrow N_{2(g)} + 2H_2O_{(g)}$ (at 1280° C)

Experiment	[NO] (M)	$[H_2]$ (M)	Initial Rate (M/s)
1	0.0050	0.0020	1.25×10^{-5}
2	0.0100	0.0020	5.00×10^{-5}
3	0.0100	0.0040	1.00×10^{-4}

We will determine the reaction orders for each reactant by examining how a change in concentration (keeping the other reactant concentrations constant) causes the reaction rate to change.

Example Courtesy of Khan Academy

Let's compare experiments 1 and 2 where [NO] changes but $[H_2]$ is kept constant. We see that the concentration of NO doubles from the first experiment to the second, and the reaction rate increases by a factor of 4.

$$\frac{\text{initial rate of experiment 2}}{\text{initial rate of experiment 1}} = \frac{5.00 \cdot 10^{-5}}{1.25 \cdot 10^{-5}} = 4$$

This means that the reaction is *second* order with respect to NO, because $2^2 = 4$.

Now, we need to determine the order of the reaction with respect to H_2. For this, we will compare experiments 2 and 3, where $[H_2]$ changes but [NO] is held constant.

We see that the concentration of H_2 increases by a factor of 2 from the second experiment to the third, and that the reaction rate increases by a factor of 2.

$$\frac{\text{initial rate of experiment 3}}{\text{initial rate of experiment 2}} = \frac{1.00 \cdot 10^{-4}}{5.00 \cdot 10^{-5}} = 2$$

This means that the reaction is *first* order with respect to H_2, because $2^1 = 2$.

Now, we can put this all together to get the rate law:

$$\boxed{rate = k[\text{NO}]^2[\text{H}_2]}$$

As an exercise, you can pick any one of the experiments and plug in the reactant concentrations, effectively solving for the value of k. Additionally, include the correct units. (You should find that $k = 250\, M^{-2}\,\text{s}^{-1}$).

Note 5.2.3

It's extremely important that you know that the rate law can only be determined through experiment. For the above example, if you simply used the stoichiometric coefficients as the reaction orders, you would get an incorrect rate law of $rate = k[\text{NO}]^2[\text{H}_2]^2$.

The ONLY exception to this is when dealing with elementary steps of a chemical reaction, where you can use the coefficients of the balanced equation to write the rate law for that corresponding step.

We will delve into elementary reactions in section 5.4.

Understanding k, the Rate Constant

The rate constant, k, is an obscure concept to understand. Essentially, the easiest definition is that it is a proportionality constant for a reaction to take place. If you understand the calculus behind its existence (although you are not required to), it makes a little more sense. For simplicity, all you need to know is that k is a constant that quantifies the rate of a given chemical reaction and that it is a **temperature-specific value**. This means that for different temperatures (even for the same reaction), the value of k is different!

Additionally, the units of k change depending on the overall reaction order. We will focus on the zero, first, and second orders. Since we know that rate is in M/s, and concentration is in M, it follows that for certain reactions:

- **Zero Order**
  - The rate law is $rate = k[\text{A}]^0$, which simplifies to $rate = k$.
  - This means k is in units of $M\,\text{s}^{-1}$.
- **First Order**
  - The rate law is $rate = k[\text{A}]$.
  - We can think of this as $M\,\text{s}^{-1} = k \cdot M$, and therefore k is in units of s^{-1}.

- **Second Order**
  - The rate law is $rate = k[\text{A}]^2$.
  - Thinking of this as $M\,\text{s}^{-1} = k \cdot M^2$, and therefore k is in $M^{-1}\,\text{s}^{-1}$.

Problem 5.2.4 — Rate Law I

$$2\text{HgCl}_2(\text{aq}) + \text{C}_2\text{O}_4^{2-}(\text{aq}) \rightarrow 2\text{Cl}^-(\text{aq}) + 2\text{CO}_2(\text{g}) + \text{Hg}_2\text{Cl}_2(\text{aq})$$

A rate study of the reaction represented above yields the following data.

Trial	Initial $[\text{HgCl}_2]$ (M)	Initial $[\text{C}_2\text{O}_4{}^{2-}]$ (M)	Initial reaction rate ($M\,\text{s}^{-1}$)
1	0.020	0.010	3.0×10^{-5}
2	0.020	0.020	1.2×10^{-4}
3	0.010	0.020	6.0×10^{-5}

Based on the data, what is the rate law for the reaction?

Example Courtesy of Khan Academy

Solution: First, we know that the rate law for the reaction has general form

$$rate = k[\text{HgCl}_2]^m[\text{C}_2\text{O}_4^{2-}]^n$$

where m and n are the reaction orders with respect to HgCl_2 and $\text{C}_2\text{O}_4^{2-}$, respectively.

We can determine the values of m and n by studying how changes in reactant concentration affect the rate of reaction.

Comparing trials 2 and 3, when $[\text{HgCl}_2]$ is halved (with $[\text{C}_2\text{O}_4^{2-}]$ constant), the reaction rate is also halved. Therefore, the reaction is first-order with respect to HgCl_2, or $m = 1$.

Next, comparing trials 1 and 2, when $[\text{C}_2\text{O}_4^{2-}]$ is increased by a factor of 2, the reaction rate increases by a factor of 4. Therefore, the reaction is second-order with respect to $\text{C}_2\text{O}_4^{2-}$, or $n = 2$.

Thus, the overall rate law for the reaction is

$$\boxed{rate = k[\text{HgCl}_2][\text{C}_2\text{O}_4^{2-}]^2}$$

Problem 5.2.5 — Rate Law II

The rate law for a particular reaction is $rate = k[\mathrm{X}]^2$. In an experiment, the initial rate of the reaction is determined to be $0.080\,\mathrm{mol/(L\cdot s)}$ when the initial concentration of X is $0.20\,\mathrm{mol/L}$.

What is the value of the rate constant, k, for the reaction?

Solution: To find the value of the rate constant for the reaction, first solve the rate law equation for k:

$$k = \frac{rate}{[\mathrm{X}]^2}$$

Next, let's plug in the initial rate and concentration that is given:

$$k = \frac{0.080\,\mathrm{mol/(L\cdot s)}}{(0.20\,\mathrm{mol/L})^2}$$

and with correct units,

$$\frac{0.080\,\mathrm{mol/(L\cdot s)}}{0.040\,\mathrm{mol^2/L^2}} = \boxed{2.0\,\mathrm{L/(mol\cdot s)}}$$

§5.3 Concentration Changes Over Time

Before we dive into this section, I want to say that it gets a little advanced. Especially if you don't know integral calculus that is used in this section, don't worry!

You will not need to derive anything, just know how to apply the formulas for rate laws and understand them from an algebraic perspective.

Deriving the Rate Law

As mentioned previously, the **reaction order** is described by the value n in a rate law expression $rate = k[\mathrm{A}]^n$. We use n because it denotes an integer in science and mathematics, but it is also possible for reaction orders to be fractions.

One such example is **Michaelis-Menten kinetics**, one of the prevalent kinetic models in the field of biochemistry. For this course, the specifics are not important, but for biology enthusiasts, the general reaction described by this kinetics is

$$\mathrm{E + S \leftrightarrow ES \rightarrow E + P}$$

In this case, E is an **enzyme** (a specific category of catalyst, which we will discuss later in this unit), S is a **substrate**, and P is a general **product**. These reactions typically involve a fractional reaction order in certain cases. Additionally, notice that the enzyme is regenerated in the reaction as if it were never consumed in the first place (E is present in the same amounts on both sides of the reaction).

For the purposes of the AP Chemistry exam, we will only consider the $n = 0$, 1, and 2 cases for reaction order. However, we will also demonstrate an optional problem-solving technique for the general case (such that $n \neq 1$).

To emphasize the overall reaction order, we describes how the concentration of reactants affects the reaction rate. A **rate law** helps us understand this further. Let's consider a simple example: population dynamics. If a population is in *crisis*, then its population as a function of time is modeled as exponential decay:

$$P = P_0 \cdot \left(\frac{1}{2}\right)^{t/t_{1/2}} = P_0 \cdot 2^{-t/t_{1/2}}$$

where:

- P_0 is the initial population,
- t is the time, and
- $t_{1/2}$ is the half-life of the population.

Definition 5.3.1
The **half-life** of a reaction is the duration for a population to reach half its original value.

We can express this exponential as:

$$P = P_0 e^{-kt}$$

This should be intuitive. Consider the case of a disease: as more people die, the number of disease carriers decreases, meaning fewer and fewer people can be affected as time progresses. This leads to a decrease in population and a decrease in the rate of population decay.

An important property of exponential functions is that the rate of change is proportional to itself, and the equation that follows is derived from basic differentiation rules (**PRO TIP**: you do not need to know the calculus for this!):

$$\text{rate of change of } e^{bx} = be^{bx}$$

Going back to our practical application, as the reaction progresses, fewer people are able to interact with one another, so there are fewer disease carriers that are able to further spread the disease.

Connecting Calculus and Chemistry

If we have a simple reaction A $\rightarrow$ B, we can represent the overall rate of reaction as either the rate of appearance for B or the rate of disappearance for A. As mentioned previously, this relationship is visually represented as an exponential decay curve, and we can arrive at the logical conclusion for $rate = k[\mathrm{A}]$. However, this is only true for the

$n = 1$ case. In general, our expression is $rate = k[\text{A}]^n$.

If we invoke some calculus, those students proficient in the subject will recognize this as a separable **ordinary differential equation (ODE)**:

$$-\frac{d[\text{A}]}{dt} = k[\text{A}]^n$$

If you do not know calculus, or are not comfortable with separation of variables, you may disregard this derivation, as it is not needed for the AP Exam. Feel free to skip to the next topic about integrated rate laws. However, for those who are comfortable with the technique, we can solve for [A] as a function of time:

$$\frac{d[A]}{[A]^n} = -kdt \text{ so } \int \frac{1}{[A]^n} d[A] = -\int kdt$$

$$\therefore \int [A]^{-n} d[A] = \frac{[A]^{-n+1}}{-n+1} = -kt + C \text{ for } -n+1 \neq 0$$

To solve for the **constant of integration** C, we will use the condition $[\text{A}] = [\text{A}]_0$, which indicates the concentration of reactant(s) before the reaction begins.

$$\frac{[A]_0^{-n+1}}{-n+1} = C \text{ so } \frac{[A]^{-n+1}}{-n+1} - \frac{[A]_0^{-n+1}}{-n+1} = -kt$$

Because we are working in the $n \neq 1$ case, we analyze the above equation for $n = 2$:

$$\frac{[A]^{-2+1}}{-2+1} - \frac{[A]_0^{-2+1}}{-2+1} = -kt = \frac{[A]^{-1}}{-1} - \frac{[A]_0^{-1}}{-1} = -kt$$

Finally, we can divide both equations by a factor of -1 and rearrange the terms to get the following equation:

$$\boxed{\frac{1}{[\text{A}]} - \frac{1}{[\text{A}]_0} = kt}$$

This equation is written in the official AP formula sheet and is known as the **second-order integrated rate law**, where $[\text{A}]_0$ is the initial concentration, [A] is the final concentration, k is the rate constant, and t is the elapsed time. The **first-order integrated rate law** is given by

$$\boxed{\ln[\text{A}] - \ln[\text{A}]_0 = -kt}$$

and is also in the formula sheet. These equations can be used to calculate the rate law, based on reaction order and the rate constant, which again, is dependent on temperature.

Integrated Rate Laws

An important concept in kinetics is that these complicated, calculus-based equations we just saw can be plotted to produce a linear relationship. This is far more simple, and it's really all you need for the course and exam! Using an established linear relationship, we can easily calculate the value of k for a reaction.

A **linear relationship** between two variables x (independent) and y (dependent) is defined by a familiar algebraic equation:

$$y = mx + b$$

where m and b represent the slope and y-intercept of the line, respectively.

Let's analyze the integrated rate laws for the following three cases:
$n = 0$, $n = 1$, and $n = 2$.

- For a zero-order reaction, with $n = 0$, the integrated rate law is

  $$\boxed{[\mathrm{A}]_t = -kt + [\mathrm{A}]_0}$$

  where y, m, and b correspond to $[\mathrm{A}]_t$, $-k$, and $[\mathrm{A}]_0$, respectively.

- For a first-order reaction, with $n = 1$, the integrated rate law is

  $$\ln[\mathrm{A}]_t - \ln[\mathrm{A}]_0 = -kt$$

  where y, m, and b correspond to $\ln[\mathrm{A}]_t$, $-k$, and $\ln[\mathrm{A}]_0$, respectively.

- For a second-order reaction, with $n = 2$, the integrated rate law is

  $$\frac{1}{[\mathrm{A}]_t} - \frac{1}{[\mathrm{A}]_0} = kt$$

  where y, m, and b correspond to $\frac{1}{[\mathrm{A}]_t}$, k, and $\frac{1}{[\mathrm{A}]_0}$, respectively.

From here, we can logically derive three qualitative cases:

1. For a zero-order reaction, the graph of [A] vs. time is linear with a slope of $-k$. In a zero-order reaction, the reaction rate is constant with changing concentration, so $rate = k$.

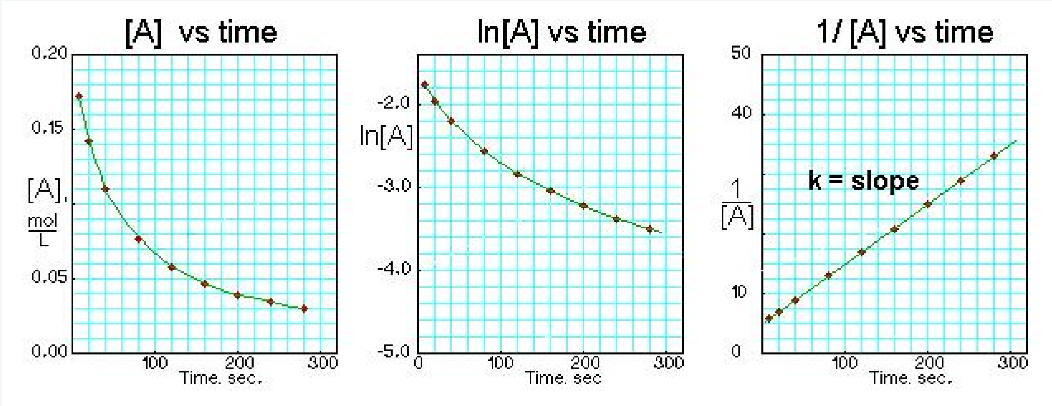
2. For a first-order reaction, the graph of ln[A] vs. time is linear with a slope of $-k$.

3. For a second-order reaction, the graph of $\frac{1}{[\mathrm{A}]}$ vs. time is linear with a slope of k.

This information will likely be necessary to determine the order of a reaction, and the topic has appeared on several free-response questions.

Problem 5.3.2 — Free-Response Practice

For the reaction A → B, the following graphs are shown:



(a) What is the rate law for the reaction? Represent the rate constant as k, not a numerical value. Explain how you arrived at your answer.
(b) Estimate the value of k for this reaction. Show all work.
(c) If the initial concentration of substance A is 0.200 M, what is the concentration remaining after 30 seconds?

Example Courtesy of Fiveable

Solution to part a: We know that the rate law is going to be of the form $rate = k[\text{A}]^n$, where n is the order of the reaction. We can use the information in the graphs shown above to determine the order of the reaction. Since neither [A] vs. time or ln[A] vs. time yield a straight line, the reaction cannot be zeroth or first order. It must be $\boxed{\text{second order}}$ because the graph of $\frac{1}{[\text{A}]}$ vs. time is positive linear, with a slope of k.

Solution to part b: We are given that the value of k is represented by the slope of the line generated by graphing $\frac{1}{[\text{A}]}$ vs. time, so we must estimate the slope of this line to get our answer.

We know that the slope formula is given by

$$m = \frac{y_2 - y_1}{x_2 - x_1}$$

where (x_1, y_1) and (x_2, y_2) represent two points.

Thus, we choose the points $(0, 5)$ and $(200, 25)$, and

$$k = \text{slope} = \frac{(25-5)}{(200-0)} = \boxed{0.1\ M^{-1}\,\text{s}^{-1}}$$

Make sure that you have the correct units for k!

Solution to part c: Since we know the initial concentration of A, the elapsed time of the reaction, as well as the rate constant, we can use the integrated rate law (for second-order reactions) to determine the final concentration.

$$\frac{1}{[\mathrm{A}]_t} - \frac{1}{[\mathrm{A}]_0} = kt$$

$$\frac{1}{[\mathrm{A}]_t} = kt + \frac{1}{[\mathrm{A}]_0}$$

$$\frac{1}{[\mathrm{A}]_t} = (0.1)(30) + \frac{1}{0.200} = 8 \therefore [\mathrm{A}]_t = \boxed{0.125\ M}$$

Half-Life in First-Order Reactions

Half-life is the amount of time it takes for the concentration of a substance to decrease to half of its original value. This concept goes into nuclear chemistry, which is not included in the AP Chemistry curriculum. We only need to understand it for **first-order reactions**.

The half-life, $t_{1/2}$, of a first-order chemical reaction is related to its rate constant, k, according to the equation:

$$\boxed{t_{1/2} = \frac{0.693}{k}}$$

This equation is in your formula sheet and can be used to determine the half-life of a substance if the rate constant is known. Additionally, note that the rate constant is temperature-specific. This means that the value of k will not change if the temperature is constant. Therefore, for first-order reactions, the half-life is *constant* at a specific temperature.

In AP Chemistry, half-life is used exclusively when discussing **radioactive decay**, a first-order process. There are not too many concepts involved at this point, so we will conclude this section with the following practice problem.

Problem 5.3.3 — Radioactive Decay

The radioisotope ^{198}Au decays to ^{198}Hg with a half-life of 2.69 days.

If a sample initially contains 9.10 mg of ^{198}Au, what mass of ^{198}Au remains after 3.50 days?

Solution: To solve this problem, we first need to use the half-life equation to determine the value of the rate constant, k, for the decay of ^{198}Au to ^{198}Hg. Then, because radioactive decay is a first-order process, we can use the corresponding integrated rate law to calculate the mass of ^{198}Au.

First, we calculate the value of k.

$$t_{1/2} = \frac{0.693}{k}$$

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{2.69\text{ days}} = 0.258\text{ days}^{-1}$$

Now, let us use the integrated rate law to determine the final mass of ^{198}Au. The integrated rate law for a first-order process is written as

$$\ln[\text{A}]_t - \ln[\text{A}]_0 = -kt$$

Using algebra, we have

$$\frac{[\text{A}]_t}{[\text{A}]_0} = e^{-kt} \therefore [\text{A}]_t = [\text{A}]_0 e^{-kt}$$

Finally, let's plug in the initial mass of ^{198}Au, the rate constant, and the elapsed time:

$$[\text{A}]_t = (9.10\text{ mg})[e^{-(0.258\,\cancel{\text{days}^{-1}})(3.50\,\cancel{\text{days}})}] = \boxed{3.69\text{ mg}}$$

§5.4 Elementary Reactions

Because they are so important for the remainder of this unit, let us refresh ourselves on rate laws. If we have a general reaction A $\to$ products, the rate law is $rate = k[\text{A}]^n$, where k is the rate constant and n is the order of the reaction with respect to A. The rate law shows that the reaction rate is directly proportional to the concentration of the reactants.

Don't forget that rate laws can **only** be found through an experiment! It is a common mistake for chemistry students to look at the stoichiometric coefficients of the reactants and use those as reaction orders, but you *cannot* do that! For example, the reaction 2A $\to$ B is not necessarily second-order; it could be, but we cannot know for sure until we run an experiment. These experiments involve multiple *trials* of a reaction with different concentrations of each reactant and quantitatively analyzing the effect of concentration changes on the overall reaction rate.

Lastly, these reactions *must* be run at the same temperature. Even minor fluctuations in temperature can lead to major changes in reaction rates, giving incorrect results. This is because k, the rate constant, is **temperature dependent**, and once you find the orders of a reaction, you can substitute values from an experiment to determine k.

Elementary Reactions

Now, we will define **elementary reactions**. An elementary reaction is a chemical reaction that occurs in a single step and involves only a single molecule or a group of atoms. It is the simplest type of chemical reaction and serves as a starting point for understanding more complex reactions. Much of the rest of this unit comprises elementary steps, we will discuss more complex reactions later.

As we have seen in previous sections, elementary reactions can either be first-order or second-order, depending on whether the reaction rate is affected by the concentration of one or two species. Examples of elementary reactions include the reaction of hydrogen and oxygen to produce water, the decomposition of ozone, and the ionization of a gas.

- Formation of water: $2H_2 + O_2 \rightarrow 2H_2O$
- Decomposition of ozone: $O_3 \rightarrow O_2 + O$
- Ionization of an gaseous element: $M(g) \rightarrow M^+(g) + e^-$

Rate Law and Elementary Reactions

The last concept in this section goes back to rate laws. Recall that we can only use experimental data to determine the rate law for a reaction. There is, however, one exception. That is, when we are dealing with elementary step reactions.

Since the series of elementary steps in a reaction (mechanism) represent the scope of sections 5.6 and 5.7, we won't go too deep at this moment.

The most important concept regarding rate laws and elementary reactions is that these are the only type of reactions that do not require experimental data to generate a rate law expression−you can simply use the stoichiometric coefficients of the balanced chemical equation.

Example 5.4.1

The formation of nitrogen dioxide from nitrogen gas and oxygen gas is a complex reaction, that occurs in two elementary steps:

1. $NO + NO \rightarrow N_2O_2$
2. $N_2O_2 + O_2 \rightarrow 2NO_2$

To determine the rate law for each elementary reaction that composes a complex reaction, we need to know the stoichiometric coefficients on the species for each step in the balanced chemical equation.

For Step 1, call the rate constant k_1. Since there are two molecules of NO, we can state that the reaction order with respect to NO is 2, and thus the rate law is

$$rate = k_1[\mathrm{NO}]^2$$

Similarly, for step 2, we will call the rate constant k_2. Since there is a coefficient of 1 on both N_2O_2 and O_2, the rate law will be written as

$$rate = k_2[\mathrm{N_2O_2}][\mathrm{O_2}]$$

However, this is technically not the right answer. For this sequence of elementary steps, N_2O_2 falls into a category of species that are generally excluded from the rate law expression. Additionally, why is it important that we can use stoichiometric coefficients to determine rate laws for elementary step reactions? Both of these concerns will be addressed in the later sections of this unit.

§5.5 Collision Model

In this section, we will focus more on the conceptual aspect of kinetics. We will learn that in order for a reaction to proceed, specific conditions must be satisfied, which we will incorporate in a model.

There exists some interesting math and logic that help derive these concepts, which you are not required to know, but it can help understand the model better.

Collision Model

The **collision model** essentially "fixes" molecules as projectiles moving in random directions with a constant **average speed** dictated by a set temperature. When collisions between projectiles occur, the kinetic energy and momentum of the closed system is conserved. Using this model, students can understand that a chemical reaction is simply two atoms or molecules "slamming" into each other with:

- sufficient energy to cause a reaction (the energy required to cause a reaction is referred to as the **activation energy**).
- the correct orientation to form products. This can be seen in the image below:

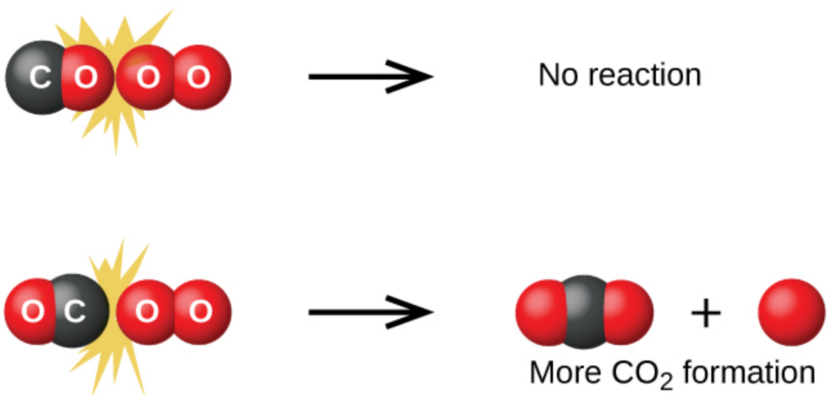


Image Courtesy of UH PressBooks

As we can see in the image, two molecules, carbon monoxide and diatomic oxygen, are the reactants that fuse together to produce carbon dioxide gas. However, in the first collision, no formation of CO_2 occurs while the second collision leads to a significant yield of CO_2. This is because molecules are not in the proper orientation to break old bonds and form new ones, so the collision is **ineffective**. In the second case, the molecules are oriented together so that the bonds in CO_2 can be formed, which is characteristic of an **effective** collision.

Deriving the Collision Model

While you do not need to know the math (specific equations and formulas) behind the collision model, it is worth reading through to better conceptually understand its mechanics.

Firstly, one must realize that these collisions are not random. In physics, when two particles collide with one another, there is a well-defined system of equations that one can use to quantitatively describe their paths. The first equation is the **conservation of kinetic energy**:

$$\frac{1}{2}m_1v_{1i}^2 + \frac{1}{2}m_2v_{2i}^2 = \frac{1}{2}m_1v_{1f}^2 + \frac{1}{2}m_2v_{2f}^2$$

The second equation is the **conservation of momentum**:

$$m_1v_{1i} + m_2v_{2i} = m_1v_{1f} + m_2v_{2f}$$

where in both scenarios:

- m_1 and m_2 are the masses of the first and second particles, respectively,
- v_{1i} and v_{2i} are the initial velocities of particles 1 and 2 prior to the collision, and
- v_{1f} and v_{2f} are the final velocities of particles 1 and 2 after the collision.

Essentially, the total kinetic energy and momentum of the two-particle system are assigned a constant value.

Note 5.5.1

For now, take the term "system" as given. We will talk about systems in more detail in Unit 6: Thermodynamics.

However, a significant change must be made to account for a phenomenon called **reactive collisions**. In these collisions, chemical reactions actually take place because some of the kinetic energy is dissipated in order to break and form new bonds, so the total kinetic energy of the system is variable.

However, these equations alone are not very beneficial on the macroscopic scale; they occur within systems of many (far more than just 2) molecules, and our equations only describe two-particle collisions. At any instant, if we fix each particle's collision with another at the same time, we would need $N/2$ systems of equations to represent the system as a whole, where N is the number of molecules.

This makes sense because if each system of equations is composed of two equations (conservation of kinetic energy and momentum), then we would need $(N/2) \cdot 2 = N$ equations to fully model the situation. The reason why this is not very feasible is that if dealing with a 1.00 mol sample, this value would be $6.022 \cdot 10^{23}$, leading to a nasty algebra bash.

The easiest way to describe the collision theory is by a *statistical* approach (using averages), rather than a survey of *individual* values.

$$K = \frac{1}{2}mv^2 \therefore K_{avg} = \left(\frac{1}{2}mv^2\right)_{avg} = \frac{1}{2}m\left(v^2\right)_{avg}$$

where the $_{avg}$ subscript indicates the average value of a variable. I moved the subscript to solely the v^2 term because assuming a pure sample, the mass m does not vary. However, this equation kinetic energy per ONE particle, so we will multiply the entire term by N, the total number of particles, to obtain the total kinetic energy of the gas:

$$K_{total} = \frac{1}{2}Nm\left(v^2\right)_{avg}$$

Interpretation of Collision Model

The most necessary interpretation of the collision model about the rate of a chemical reaction lies in the fact that the faster a molecule is moving, the more collisions it will make, and therefore the rate of reaction (as well as the probability of it occurring) will be increased.

The easiest way to speed up molecules at constant pressure is by raising the temperature! Recall from Unit 3 that the average kinetic energy of molecules in a gas sample is directly proportional to its temperature (**Don't forget this**! This has shown up on TONS of FRQs). This all goes back to the very definition of **temperature**: it is the average kinetic energy of particles.

Recall that Maxwell-Boltzmann diagrams represent the distribution of kinetic energy (and also particle speeds) of samples at various temperatures. The most obvious trend shown is that as temperatures increase, the range of velocities increases and a fraction of particles travel at a higher speed.

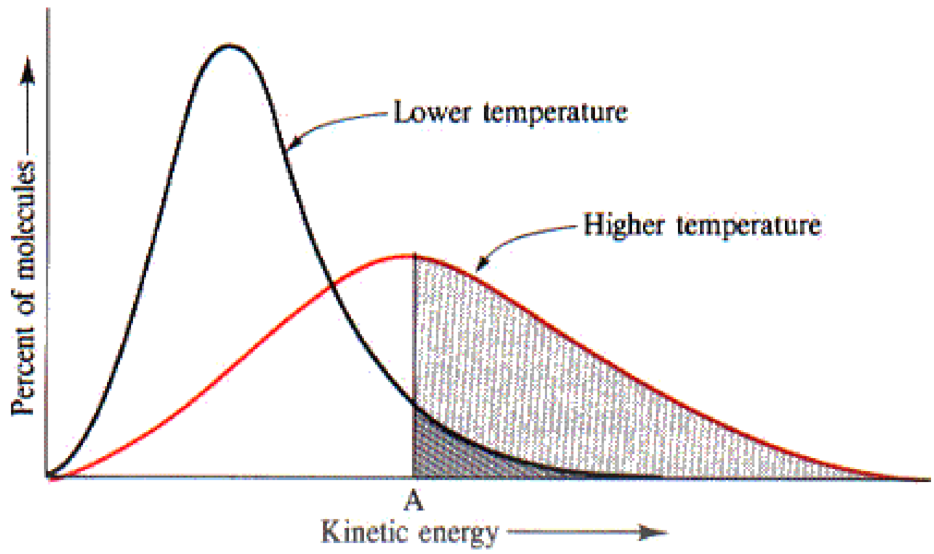


Image Courtesy of the University of Illinois at Urbana-Champaign

We will end this section with a quick discussion on **effective collisions** vs. **ineffective collisions**, which were briefly introduced. This is the major caveat to the collision model; essentially, not EVERY collision results in a chemical reaction. Ineffective collisions can be caused by a lack of sufficient force, very slow molecular speeds, and/or misalignment within the molecules. **This is why particular reactions at different temperatures**

tend to have very different rates.

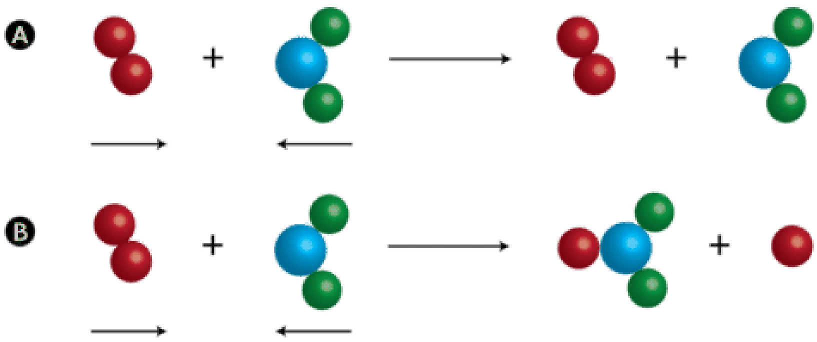


Image Courtesy of Chemistry LibreTexts

Collision (A) is an ineffective collision that does not lead to product formation, while collision (B) displays some chemical bonds being broken and new ones being formed.

Just remember that in **most** reactions, only a small fraction of the collisions are effective and they are responsible for the reaction itself. Additionally, effective collisions occur if and only if particles fulfill both criteria:

- have sufficient energy, and
- arrange themselves in the proper orientation.

§5.6 Reaction Energy Profile

Let's review what we studied in the last section. We discussed the **collision model** that represents molecules as projectiles moving in random directions with a fixed average temperature determined by temperature. Specifically, an "effective" collision involves two conditions that must be satisfied:

1. There must be enough energy to cause the reaction.
2. The **reactant** molecules must be in the proper orientation to form the products.

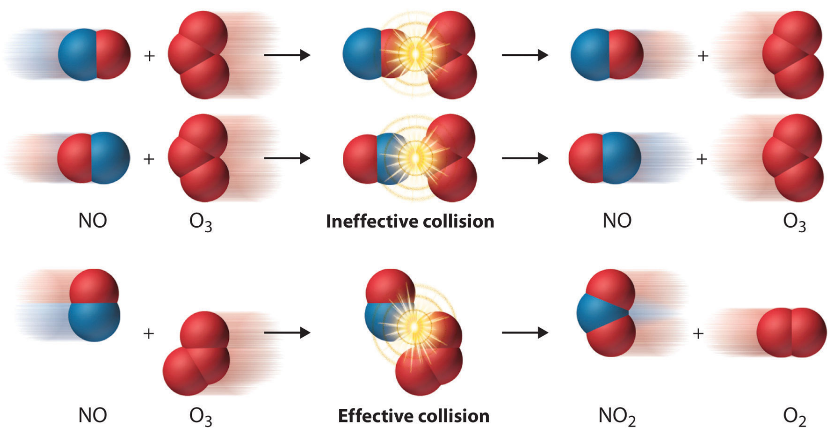


Image Courtesy of Facts.net

In this section, we will study the first condition closely: the energetics of chemical reactions.

Review of Elementary Reactions

Recall that an **elementary reaction** is a chemical reaction that occurs in a single step and involves only a single molecule or a single group of atoms. It serves as a starting point for more complex reactions we will see in this unit. As we have seen, elementary reactions can be either first-order or second-order, depending on the reaction rate's dependence on the concentration of one species or two.

The most important thing to remember about elementary reactions in this section is that they involve the breaking of old bonds and the formation of new bonds. These concepts tie into the energetics associated with a chemical reaction.

Exothermic vs. Endothermic Potential Energy (PE) Diagrams

You may have seen before that potential energy in a chemical reaction can be represented as a curve with an extreme point as the reaction progresses. You can track the changes in energy during the reaction, and this is called a **reaction coordinate** or potential energy diagram.

Typically, these diagrams are used to determine whether a reaction is *exothermic* or *endothermic*. Specifically, is the system (all species in the reaction) *losing* energy or *gaining* energy with respect to its initial and end points? Here are what the plots look like:

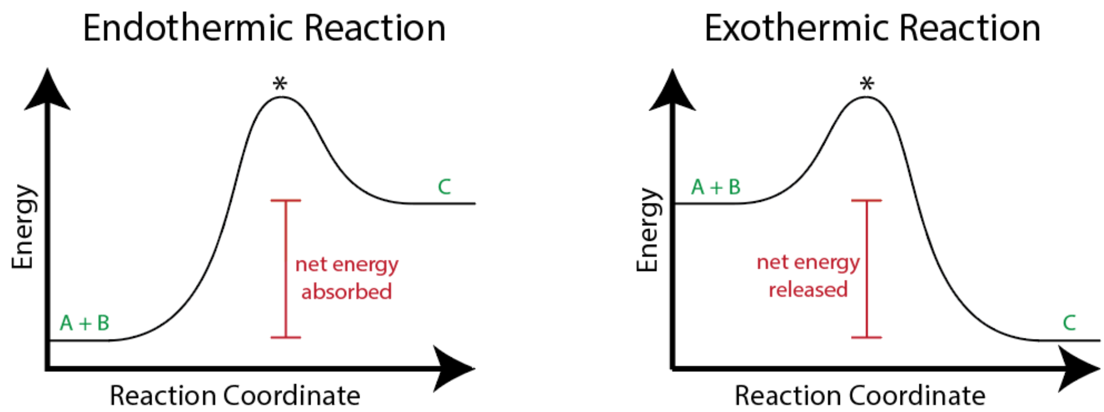


Image Courtesy of ChemTalk

In ALL chemical reactions, energy is either released or absorbed and this will affect the energy involved in starting the reaction.

Differentiating Endothermic and Exothermic Reactions

- In an **endothermic reaction**, the potential energy of the reactants is *less* than the potential energy of the products. This means that energy was absorbed by the reaction to raise the reactant molecules to a higher energy state. Mathematically, you can think of an endothermic reaction as

$$\text{Reactants} + \text{Energy} \rightarrow \text{Products}$$

- In an **exothermic reaction**, the potential energy of the reactants is *greater* than the potential energy of the products. This means that energy was released by the reaction in order to bring the reactant molecules to a lower energy state. Similarly, you can represent an exothermic reaction as

$$\text{Reactants} \rightarrow \text{Products} + \text{Energy}$$

Using the above information, you should be able to recognize whether a reaction is exothermic or endothermic by looking at its PE diagram as a function of reaction progress (a.k.a. reaction coordinate).

Reaction Progress

In a reaction coordinate, three components are shown: the reactants, the **activated complex**, and the products.

1. The **reactants**, as you know, are the species that "go into" the chemical reaction. Since the x-axis of a PE diagram represents the reaction progress, it is always at the far left.

2. The **activated complex**, also known as the **transition state**, is the highest point on the PE diagram. Hence, this complex has the highest energy and is therefore the most unstable point of the reaction. An easier way to think about it is the point where the reaction is transitioning *from* reactants to products. The bonds have not yet been completely broken or formed.

3. The **products** are the species that result from the chemical reaction, and are always present at the far right of the PE graph.

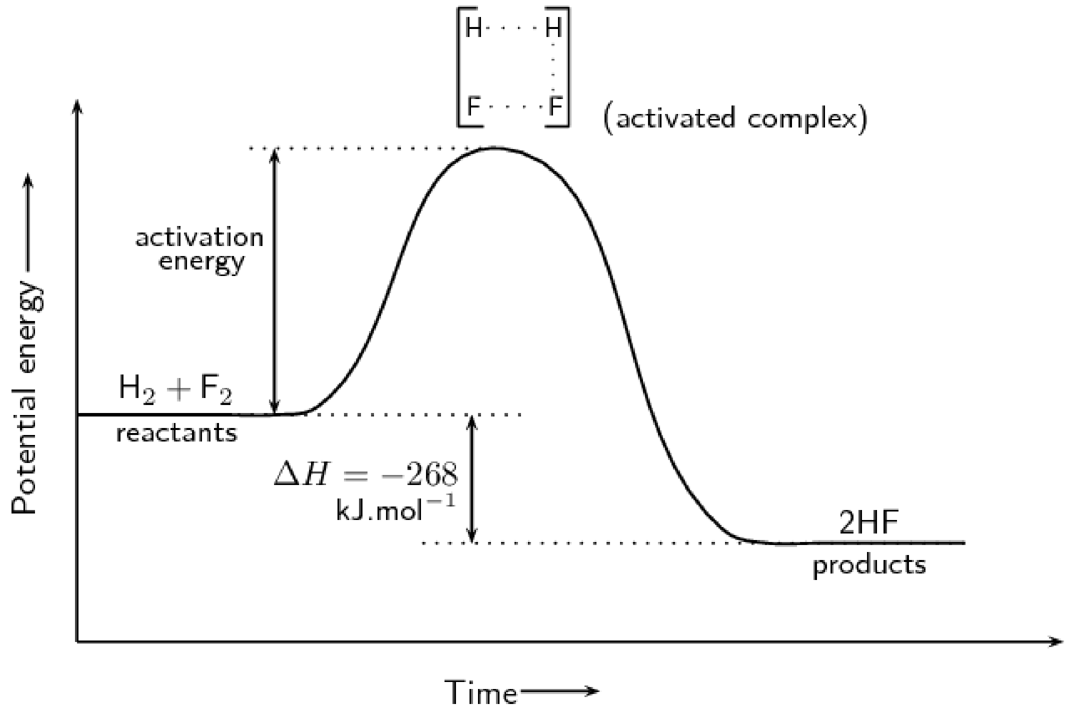


Image Courtesy of Fiveable

Activation Energy

Definition 5.6.1

Activation energy is the energy required to break the bonds in a reaction to transition from the reactants to the activated complex and finally to the products. College Board defines it as "the energy difference between the reactants and the transition state."

On the diagram, it is indicated by an arrow pointing from the reactants towards the peak of the graph, as shown in the previous image.

Alternatively, you could think of it as the minimum amount of energy required to start a chemical reaction; it is a *barrier* that must be overcome for the reactants to reach the activated complex and then proceed to the products.

The activation energy and rate of reaction are inversely related; the *lower* the activation energy, the *faster* a reaction will proceed and vice versa. Also, the more likely the reactants will have sufficient energy to overcome the barrier and reach the transition state and form products.

The Arrhenius Equation

The **Arrhenius equation** is an empirical formula for the temperature dependence of reaction rates. It was proposed by Svante Arrhenius in 1889. More specifically, it describes the temperature dependence of the rate constant on the absolute Kelvin temperature.

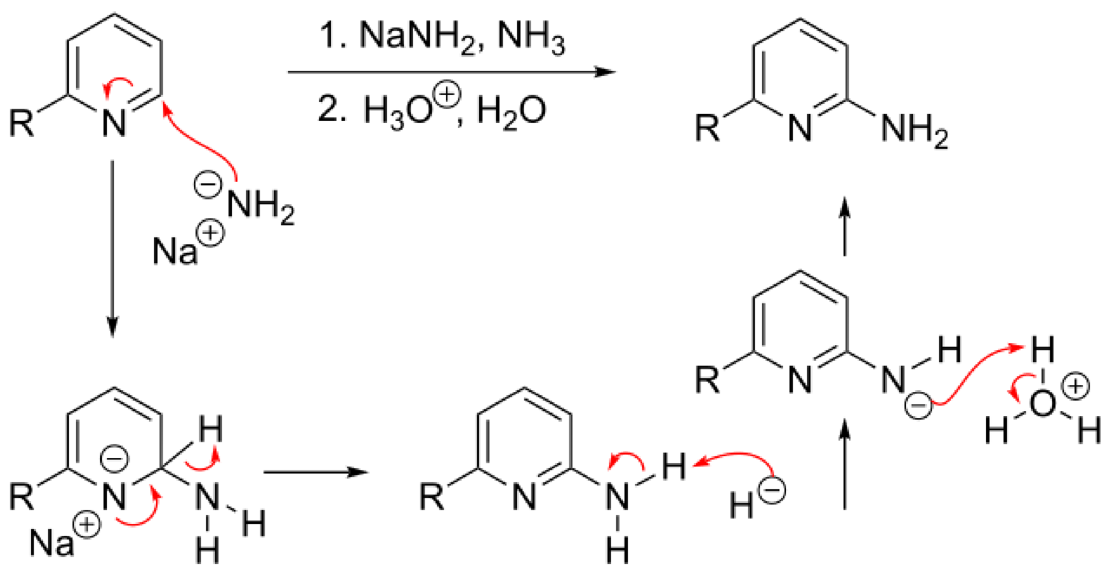
$$\ln\frac{k_2}{k_1} = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Note: you will **NOT** need to use this equation to make calculations on the AP exam. Rather, you should understand it conceptually: As the absolute temperature (in Kelvins) increases, so will the magnitude of the rate constant.

§5.7 Introduction to Reaction Mechanisms

Up until this point, we have discussed the kinetics of only **elementary reactions**, ones that occur in a single step and involve a single molecule or group of atoms.

Generally, they are the most basic types of chemical reaction and represent the foundation for studying more complex reactions (relevant to what happens in real life).



Fortunately, you will not see any of *these* reactions for this course at all!

Defining Mechanisms

A **reaction mechanism** is the sequence of elementary steps by which a chemical reaction occurs. A reaction that occurs in two or more elementary steps is called a **multistep** or **complex** reaction.

For example, an acid and base can only neutralize each other in the presence of water, but water is not considered a reactant. The actual reaction occurs in two steps.

Understanding Elementary Steps

A mechanism essentially takes a complex reaction and splits it into a number of **elementary steps**. These steps tell us about what *actually* happens in a reaction as well as *all* species that are involved.

Example 5.7.1

The decomposition of hydrogen peroxide, H_2O_2, is a multistep reaction consisting of two elementary steps:

1. $H_2O_2 + I^- \rightarrow H_2O + IO^-$
2. $H_2O_2 + IO^- \rightarrow H_2O + O_2 + I^-$

Instead of a surface-level understanding of the reaction by observing its **net equation**, we can break it down to its level of elementary steps. Another way to think of them is as the smallest units of a chemical reaction that can be analyzed, because they are simple and individual steps that make up the reaction and ultimately result in the same products being formed.

When hydrogen peroxide decomposes:

1. In the first step, H_2O_2 reacts with iodide, I^-, forming water molecules and hypoiodite ions. One of the oxygen atoms from hydrogen peroxide reacts with I^- to form the IO^- ion.
2. In the next and final step, hydrogen peroxide reacts with the products of the previous step: hypoiodite ions. In this process, another oxygen atom of H_2O_2 reacts with IO^-, to produce water molecules, oxygen gas, and iodide.

The gist of all this is to try not to think of chemical reactions as mathematical equations, rather, try to observe what is actually occurring at the molecular level. Reaction mechanisms help us reach this understanding, because when all elementary steps are added and the spectators are canceled, we end up with the net equation a.k.a. overall balanced chemical equation.

In response to the previous statement, you may ask, "But if we cancel IO^- and I^- in the net equation, why are these species even present to begin with?" Let's find out!

Catalysts and Intermediates

Since elementary steps represent what occurs at a molecular level, their species may involve **intermediates** and **catalysts** as well as general reactants and products.

In the reaction in Example 5.7.1, iodide ion acts as a **catalyst**. The function of catalysts in chemical reactions will be covered in more detail in section 5.11, but the basics for this section follow as: a catalyst is a substance that increases the rate of a chemical reaction without being consumed in the process.

Additionally, the catalyst is not present in the overall balanced equation, so it does not affect the reaction's products, but rather affects the *mechanism* by introducing an *alternative pathway*, but more on this later. In the lab, the decomposition of H_2O_2 is a slow process, so catalysts will be used frequently to speed up the process.

So, iodide is a catalyst, but what is iodite? This ion that is produced in the first elementary step and is consumed in the next is an **intermediate**. This term describes species that are formed in one elementary step of the reaction and then go on to participate in further steps of the mechanism. They are neither reactants nor products; they are present in the reaction mixture in significant amounts, but ONLY when the actual reaction is taking place.

§5.8 Reaction Mechanism and Rate Law

A **mechanism** describes the steps of a reaction as it occurs from *reactants* to *products*. It's important to know that mechanisms present *exactly* what happens in a reaction, because the vast majority of reactions occur in multiple steps.

To explain this more clearly, consider a reaction

$$\text{reactants} \rightarrow \text{products}$$

There are usually multiple steps that *lead* reactants to yield products. This could mean that the reactants could react with an **intermediate**, or the reaction is **catalyzed**. Nevertheless, each step is known as an **elementary step**, and when all elementary steps are combined, the overall **balanced chemical equation** is generated.

Example 5.8.1
The chemical reaction

$$O_3 + 2I^- + H_2O \rightarrow O_2 + I_2 + 2OH^-$$

occurs in a series of three steps:

1. $O_3 + I^- \rightarrow O_2 + IO^-$, slow
2. $IO^- + H_2O \rightarrow HOI + HO^-$, fast
3. $HOI + I^- \rightarrow I_2 + HO^-$, fast

How do we prove this is the mechanism for the chemical reaction? The answer is simple: if you add up all the steps of a mechanism, it must and always will result in the overall reaction.

This reaction mechanism consists of three elementary steps:

1. Ozone gas and iodide ion slowly react to form diatomic oxygen and hypoiodite ions.
2. The hypoiodite ions produced go on to react with water molecules to form hypoiodous acid and hydroxide ions.
3. Finally, the hypoiodous acid produced in the previous step reacts with iodide ion to form diatomic iodine and more hydroxide ions.

Catalysts and Intermediates

The steps of a reaction mechanism help us identify any possible **intermediates** or **catalysts**. Since no species enter and exit the mechanism without being affected, there are no catalysts.

However, there are two intermediates in this mechanism. Intermediates are species that are produced in one step of a reaction and then participate as reactants in subsequent steps. If we compare the first step to the second, we find that hypoiodite, IO^-, is one of the intermediates. Comparing the second and third steps, we can also see that hypoiodous acid, HOI, is the second intermediate.

If you would like a refresher of catalysts and intermediates in reaction mechanisms, refer back to section 5.7 to understand how to identify the components of a mechanism.

Rate-Determining Steps

Now that we have jogged our memory on mechanisms, we can expand onto rate laws and how we can write their expressions using a mechanism.

We must first identify the **rate-determining step** before writing the rate law of a mechanism. This is the slowest step of a mechanism, which essentially limits the rate of the reaction. You can make an analogy between the rate-determining step and the limiting reactant; as the latter limits the formation of products, no matter how much the other reactants are in excess. Similarly, no matter how fast other elementary step reactions proceed, the overall rate of reaction is limited by the rate-determining step.

For example, if we consider the reaction mechanism in Example 5.8.1, the rate-determining step is step 1, since it occurs more slowly than steps 2 and 3, therefore controlling the overall rate of reaction.

Additionally, with the exception of intermediates, the rate law expression for the mechanism is determined by **stoichiometric coefficients** of the rate-determining step. It is important to note that unless a mechanism is involved, rate laws *must* be determined by using experimental data. In fact, many problems will ask you to *verify* a mechanism given the experimentally determined rate law.

We observe that the rate law for the reaction mechanism in Example 5.8.1 is

$$rate = k[O_3][I^-]$$

because the coefficients on both reactants are 1 and neither O_3 nor I^- is an intermediate of the reaction mechanism.

Note 5.8.2

In the case of intermediates, it is improper to include them in the rate law of a reaction mechanism. Therefore, the steady-state approximation is used for such cases, and this will be the topic of section 5.9.

Before we move on to more complex reaction mechanisms involving intermediates in rate law expressions, we will solidify our understanding of this section with an AP-style problem.

Problem 5.8.3 — Multiple Choice Question

A reaction and its experimental rate law are shown.

$$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$$

$$rate = k[H_2O_2]$$

A chemist proposes a mechanism for the reaction that is consistent with the rate law. The mechanism has two elementary steps, and the first step is slow compared to the second.

Which of the following could be the first step of the proposed mechanism?

(A) $H_2O_2(aq) \rightarrow 2OH(aq)$
(B) $H_2O_2(aq) + OH(aq) \rightarrow H_2O(l) + HO_2(aq)$
(C) $H_2O_2(aq) + HO_2(aq) \rightarrow H_2O(l) + O_2(g) + OH(aq)$
(D) $2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$

Solution: The rate law for a multistep reaction is governed by the slow (rate-determining) step in the mechanism. In this case, the first step is rate-determining. Therefore, we can identify the corresponding elementary step reaction by determining which of the four answer choices has a rate law consistent with that of the overall reaction.

Recall that for elementary step reactions, the rate law can be derived from the stoichiometry of the balanced equation. Therefore, we have

- Choice (A): $H_2O_2(aq) \rightarrow 2OH(aq)$, with rate law given by $rate = k[H_2O_2]$
- Choice (B): $H_2O_2(aq) + OH(aq) \rightarrow H_2O(l) + HO_2(aq)$, with rate law given by $rate = k[H_2O_2][OH]$
- Choice (C): $H_2O_2(aq) + HO_2(aq) \rightarrow H_2O(l) + O_2(g) + OH(aq)$, with rate law given by $rate = k[H_2O_2][HO_2]$
- Choice (D): $2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$, with rate law given by $rate = k[H_2O_2]^2$

Of these, only one of the steps has a rate law that is identical to the rate law for the net reaction, $rate = k[H_2O_2]$. Therefore, the first step in the proposed mechanism could be $H_2O_2(aq) \rightarrow 2OH(aq)$, which is consistent with choice $\boxed{\textbf{(A)}}$.

§5.9 Steady-State Approximation

The **steady-state approximation**, also known as the *pre-equilibrium approximation*, is a method used to determine the rate law for a reaction with a fast and reversible initial step. This is important because there are often intermediates involved in the reaction, which can interfere with constructing the correct rate law expression. Because it is preferred to have no intermediates present in the rate law of the overall reaction, this approximation is used.

Consider the reaction

$$2NO(g) + Br_2(g) \rightarrow 2NOBr_2(g)$$

The reaction mechanism consists of two steps:

$$\text{Step 1: } NO(g) + Br_2(g) \rightleftharpoons NOBr_2(g); \quad \textit{fast, reversible}$$

$$\text{Step 2: } NOBr_2(g) + NO(g) \rightarrow 2NOBr(g); \ \textit{slow}$$

Step 2 is the rate-determining step, so we would expect the rate law for this elementary reaction to match that of the overall reaction:

$$rate = k_2[NOBr_2][NO]$$

However, the above expression is **not** the experimental rate law. $NOBr_2$ is a reaction intermediate, so it is bad practice to include it in our rate expression.

Note 5.9.1

The key idea of the pre-equilibrium approximation method is for the fast and reversible step, we assume that the rates of the forward and reverse reactions are the same. Therefore, we can write rate law expressions and thus substitute reaction intermediate concentrations in terms of reactant and product concentrations.

Since these are elementary reactions, we can simply use the coefficients of reactant molecules. **(remember that we cannot do this for net reactions!)**. Therefore,

$$k_1[NO][Br_2] = k_{-1}[NOBr_2]$$

Dividing both sides by k_{-1},

$$\frac{k_1}{k_{-1}}[NO][Br_2] = [NOBr_2]$$

where:

- k_1 is the rate constant of the first elementary step reaction in the *forward* direction,
- k_{-1} is the rate constant of the first elementary step reaction in the *reverse* direction, and
- k_2 is the rate constant of the second step of the reaction mechanism.

Wait! We just solved for the intermediate concentration in terms of the concentrations of species present in the overall reaction! We can substitute the result back into our rate law expression for the slow step of the mechanism.

$$rate = \frac{k_2 k_1}{k_{-1}}[NO][Br_2][NO]$$

Combining $\frac{k_2 k_1}{k_{-1}}$ into one effective constant k, we have

$$\boxed{rate = k[NO]^2[Br_2]}$$

That is how you can use the steady-state approximation to write rate laws for multistep chemical reactions. Neat, isn't it?

§5.10 Multistep Reaction Energy Profiles

In chemical reactions, the transformation of reactants into products often involves a series of *intermediate* steps, known as **elementary reactions**. These elementary reactions are then combined to describe the overall reaction through a **chemical equation**, which illustrates the reactants and products, as well as their **stoichiometric coefficients**.

Consider the chemical reaction that represents the decomposition of ozone into oxygen:

$$2O_3(g) \to 3O_2(g)$$

The reaction energy profile is shown below. Notice that there are two peaks because O, the intermediate, is formed in the first elementary step and consumed in the second.

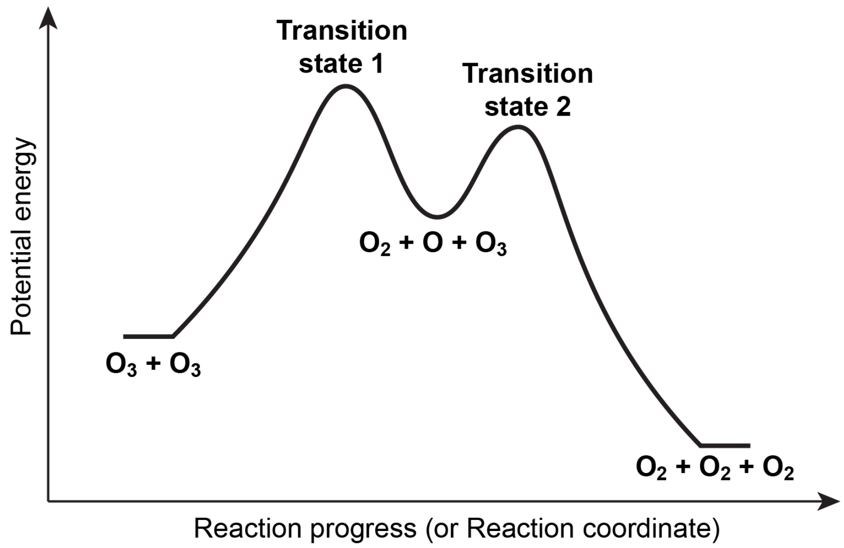


Image Courtesy of University of Wisconsin

The chemical equation provides a compact representation of the reaction and allows you to make predictions about the yield and kinetics based on individual rates of the elementary reactions.

We can also classify elementary reactions by the number of reactants they have.

- **Unimolecular Reaction**: These are of the form
$$\mathrm{A} \to \mathrm{P}$$
- **Bimolecular Reaction**: These are of the forms
$$\mathrm{A} + \mathrm{A} \to \mathrm{P}$$
$$\mathrm{A} + \mathrm{B} \to \mathrm{P}$$
- **Termolecular Reaction**: These are of the forms
$$\mathrm{A} + \mathrm{A} + \mathrm{B} \to \mathrm{P}$$
$$\mathrm{A} + \mathrm{B} + \mathrm{C} \to \mathrm{P}$$
$$\vdots$$

where A, B, and C are reactants and P represents some amount of products.
Note: A, B, C, and P are arbitrary designations.

Constructing Reaction Energy Profiles

We begin with the definition of a **reaction energy profile:** a graphical representation of the *activation energy* and *overall energy change* in a multistep reaction. It typically represents the potential energy of the system (reactants and products) as a function of the reaction coordinate (or reaction progress).

The following steps are taken to represent the activation energy and overall energy change in a multistep reaction:

1. **Plot the reactants and products**: Begin by plotting the potential energy of the reactants and products as the starting and ending points, respectively, of the reaction.

2. **Add transition states**: Next, if the reaction involves a transition state, add a point on the energy profile to represent it. This point demonstrates the highest (most unstable) point along the reaction coordinate, being the strongest energy barrier that reactants must overcome to form the products.

3. **Plot the energy change**: Connect the reactants to the transition state with a curved arrow to represent the activation energy, E_a, and connect the reactants to the products with a straight arrow to represent the overall energy change, ΔE.

4. **Label the activation energy and overall energy change**: You must use appropriate units, such as joules (J) or kilojoules (kJ). The ultimate purpose of a reaction energy profile is to visually represent the energy changes involved in a multistep reaction, as well as analyze the role of activation energy in determining the rate and outcome of the reaction.

Having a comprehensive understanding of the energy changes that occur through each of the elementary reactions in a **mechanism** is important to construct a reaction energy profile for a multistep reaction.

Review of Reactants, Intermediates, and Products

Knowing the energetics of each elementary reaction in a reaction mechanism, one can determine the highest energy barrier or transition state, the activation energy required to overcome this barrier, and the overall change in potential energy between the reactants and products that occurs during the reaction. This information can be labeled into the energy profile, allowing to better understand reaction energetics as well as factors that influence its rate and outcome.

- **Reactants** are the *starting materials* that react with each other to form new substances. In the chemical reaction equation, they are written on the left-hand side.

- **Intermediates** are species that are *formed during the reaction* and then *react further to form the final products*. In other words, these are species that are formed in one elementary step and consumed in a subsequent step. They are not directly involved in the overall reaction and are generally not present at the beginning or end of the reaction.

- **Products** are the *final substances* formed *after* the reaction has taken place. In the chemical reaction equation, they are written on the right-hand side.

Example 5.10.1

The **Haber process** represents the synthesis of ammonia (NH_3) from nitrogen gas (N_2) and hydrogen gas (H_2).

- The reactants are H_2 and N_2.
- The product is NH_3.
- However, there is actually an intermediate species, $N_2H_3^+$.

The H_2 and N_2 react to form the intermediate $N_2H_3^+$, which then reacts further to form the final product of NH_3.

In the next (and last) section of this unit, we will learn about how we can speed up chemical reactions and the effects of these factors on the reaction energy profile.

§5.11 Catalysis

A **catalyst** is a substance that speeds up a chemical reaction without being consumed.

Those who have studied biology should be familiar with this concept, as catalysts serve a similar function as enzymes. From the perspective of a reaction mechanism, catalysts are defined as species that are consumed in one step but **appear again** in later steps. In other words, they enter the mechanism as a reactant and exit as a product while remaining completely *untouched*.

When writing chemical equations that proceed in the presence of a catalyst, we use the notation indicated here:

$$\boxed{2H_2O_2 \xrightarrow{I^-} 2H_2O + O_2}$$

The equation can be read as, "The decomposition of hydrogen peroxide into water and oxygen in the presence of iodide ion as a catalyst." Actually the reaction is performed with potassium iodide, KI, but only the I^- ion contains the catalytic properties.

2 Types of Catalysts

Based on the phase of catalysts compared to those of species in the reaction mixture, we can classify catalysts as either **homogeneous** or **heterogeneous**.

- Homogeneous catalysts are present in the same phase as the reacting molecules.

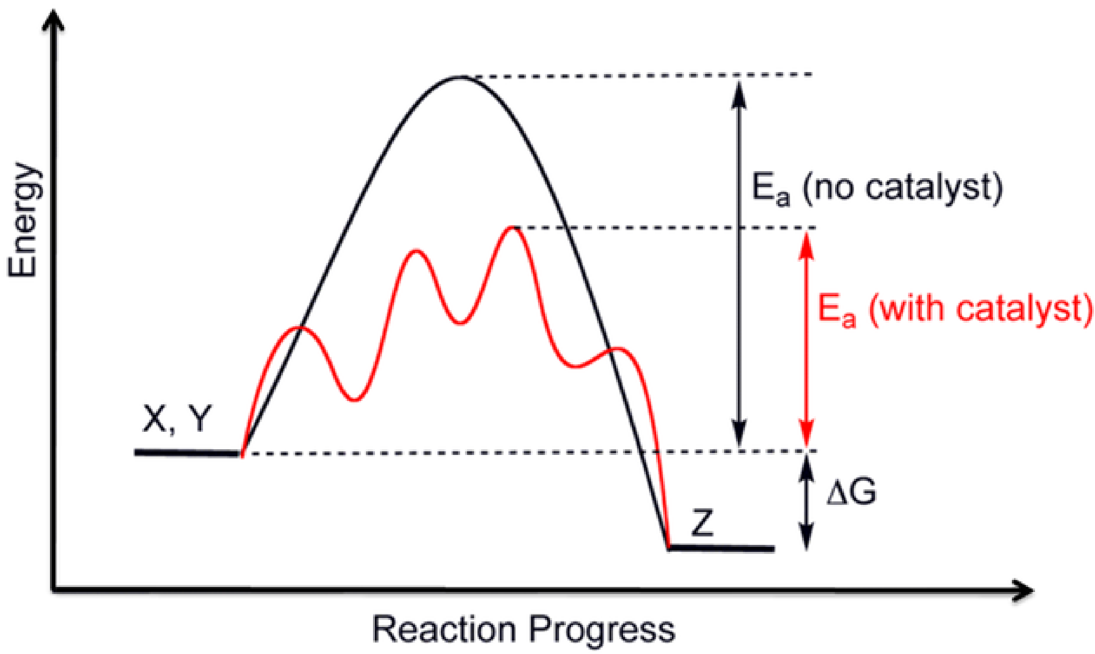
- Heterogeneous catalysts are present in a different phase than the reacting molecules.

How Catalysts Work

Catalysts allow chemical reactions to proceed by a different mechanism, or an **alternative pathway**. This introduced pathway has a lower activation energy, and more molecules will be governed by this new activation energy.

However, note that the total difference in potential energy between the reactants and products will be UNCHANGED, regardless of whether or not the reaction involved a catalyst.

The above information is represented by the image below.



Well, you guys are all curious souls. You must be wondering, "How exactly does a catalyst provide this alternate pathway to a faster reaction?"

Answer: The presence of a catalyst leads to the formation of a more stable activated complex, i.e. the middle peak on the catalyzed reaction energy profile is lower than that of the original reaction. Therefore, reactants can transition into products at a lower energy state. Additionally, catalysts can help arrange the molecules in a way that the breaking and forming of new chemical bonds is more likely, which is in agreement with the collision model.

There are actually many more possible explanations than the two mentioned above, but the main takeaway for catalysts is that they lower the activation energy of a reaction, thus increasing its rate.

Catalysis and Reaction Mechanisms

Catalysts can change reaction mechanisms! The most common example of catalysis in reaction mechanisms is the decomposition of hydrogen peroxide, so we will just stick to that one.

This reaction mechanism for the decomposition of H_2O_2 is uncatalyzed:

$$H_2O_2(g) \rightarrow 2OH(g)$$

$$H_2O_2(g) + OH(g) \rightarrow H_2O(g) + HO_2(g)$$
$$HO_2(g) + OH(g) \rightarrow H_2O(g) + O_2(g)$$

Here is the reaction mechanism that occurs in the presence of iodide ion (catalyst):

$$H_2O_2(aq) + I^-(aq) \rightarrow H_2O(l) + IO^-(aq) \qquad \textit{slow}$$

$$IO^-(aq) + H_2O_2(aq) \rightarrow H_2O(l) + O_2(g) + I^-(aq) \qquad \textit{fast}$$

As we can see, the catalyzed mechanism has **two** elementary steps, whereas the uncatalyzed mechanism has **three**. By eliminating a step, the catalyzed reaction occurs faster.

Catalysts can increase the rate of a reaction because their presence must increase the number of **effective collisions** between reacting molecules (if you need a refresher on collision theory, refer back to section 5.5) and/or introduce an alternate path with a lower activation energy relative to the original reaction.

Physically, catalysts are able to do this by **binding to the reactants**. The addition of a catalyst causes the reactants to orient more favorably or react with less energy, similar to the interactions between an enzyme and substrate (for those proficient in biology). However, other catalysts, such as **acid-base catalysts**, create covalent bonds with the reactants so that a reactant or intermediate donates or accepts a proton. This causes the formation of a new **intermediate** as well as new **elementary reactions**.

Finally, it is important to understand that while catalysts are frequently consumed by the slow, or **rate-determining** step, the net concentration of the catalyst does not change. This means that catalysts are *always* regenerated in reaction mechanisms!

§5.12 Practice Problems

Problem 5.12.1 — 2008 AP Chemistry FRQ

$$A(g) + B(g) \rightarrow C(g) + D(g)$$

For the gas-phase reaction represented above, the following experimental data were obtained.

Experiment	Initial [A] (mol L^{-1})	Initial [B] (mol L^{-1})	Initial Reaction Rate (mol L^{-1} s^{-1})
1	0.033	0.034	6.67×10^{-4}
2	0.034	0.137	1.08×10^{-2}
3	0.136	0.136	1.07×10^{-2}
4	0.202	0.233	?

(a) Determine the order of the reaction with respect to reactant A.
(b) Determine the order of the reaction with respect to reactant B.

(c) Write the rate law for the overall reaction.
(d) Determine the value of the rate constant, k, for the reaction. Include units with your answer.
(e) Calculate the initial reaction rate for experiment 4.

(f) The following mechanism has been proposed for the reaction.

$$\text{Step 1: } B + B \rightarrow E + D; \quad \text{slow}$$

$$\text{Step 2: } E + A \rightleftharpoons B + C; \quad \text{fast, equilibrium}$$

Provide two reasons why the mechanism is acceptable.

(g) In the mechanism in part (f), is species E a catalyst, or is it an intermediate? Justify your answer.

Solution to part a: Let's compare experiments 2 and 3. [B] stays the same and [A] increased by a factor of 4, but the initial reaction rate stays the same. This means the initial reaction rate is independent of [A], so the reaction is $\boxed{\text{zero order}}$ with respect to substance A.

Solution to part b: I determined the answer to part (a) by using proportions. Here, I will justify my answer in a slightly different approach.
Choose experiments 1 and 2 for this problem. Their initial reaction rates are $rate_1$ and $rate_2$, respectively.
The rate laws for experiments 1 and 2 are $rate_1 = k[A]_1^x[B]_1^y$ and $rate_2 = k[A]_2^x[B]_2^y$,

respectively. I will use ratios to solve for the unknown.

$$\frac{rate_2}{rate_1} = \frac{k[\mathrm{A}]_2^x[\mathrm{B}]_2^y}{k[A]_1^x[B]_1^y},$$
$$\frac{1.08 \cdot 10^{-2}}{6.67 \cdot 10^{-4}} = \frac{k(0.034)^x(0.137)^y}{k(0.033)^x(0.034)^y}, \text{ where } x = 0$$
$$16.2 = (4.03)^y \therefore y = 2, \text{ so the reaction is } \boxed{\text{second order}} \text{ with respect to B.}$$

Solution to part c: Since our reaction is zero order with respect to A and second order with respect to B, the rate law for the overall reaction is given by

$$\boxed{rate = k[\mathrm{B}]^2}$$

Solution to part d: Use the data in experiment 1 to solve this problem.

$$rate = k[\mathrm{B}]^2 \therefore k = \frac{rate}{[\mathrm{B}]^2}$$
$$k = \frac{6.67 \cdot 10^{-4}\,\mathrm{mol\,L^{-1}\,s^{-1}}}{\left(0.034\,\mathrm{mol\,L^{-1}}\right)^2} = \boxed{0.577\,M^{-1}\,\mathrm{s}^{-1}}$$

Solution to part e: Since we know the rate constant of the reaction at constant temperature, we can determine the initial reaction rate in experiment 4 by using the overall rate law determined in (c). Note: $M = \mathrm{mol\,L^{-1}}$.

$$rate = k[\mathrm{B}]^2 = \left(0.577\,M^{-1}\,\mathrm{s}^{-1}\right)\left(0.233\,\mathrm{mol\,L^{-1}}\right)^2 = \boxed{3.13 \cdot 10^{-2}\,\mathrm{mol\,L^{-1}\,s^{-1}}}$$

Solution to part f: The elementary step reactions should add up to the overall reaction. We proceed with the following:

$$\text{Step 1: } \mathrm{B + B \rightarrow E + D}$$

$$\text{Step 2: } \mathrm{E + A \rightarrow B + C}$$

$$\text{Overall: } \mathrm{B + B + E + A \rightarrow E + D + B + C}$$

We can "cancel" off species that appear on both sides of the combined reaction.We have an extra B on the reactants side, as well as an A that can be canceled off from both sides. Thus, the final combined reaction is

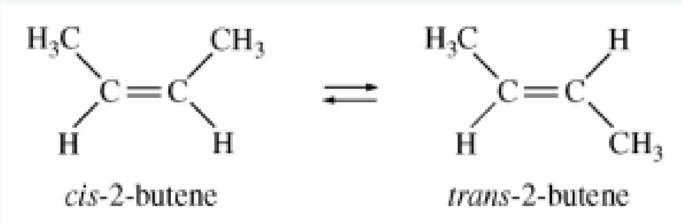
$$\mathrm{A + B \rightarrow C + D}$$

which aligns with the overall chemical reaction equation stated in the problem.
Next, we need to see if the mechanism is consistent with the overall rate law of the

reaction. For this, we look at the rate-determining, or slowest step. It is given that Step 1 is the slow step, so we need to use the reactants' coefficients to determine its rate law. The reaction $\mathrm{B + B \rightarrow E + D}$ can also be written as $\mathrm{2B \rightarrow E + D}$. Because this is the slow step of the reaction, we use the coefficient on the reactant B to find that the rate law is $rate = k[\mathrm{B}]^2$, which is consistent with the rate law for the overall reaction.
Since both requirements have been met, the mechanism is acceptable.

Solution to part g: Species E is not a catalyst. Although it exists as a reactant in an earlier step and is produced in a later step, it is formed in step 1 and consumed in step 2, so E is an $\boxed{\text{intermediate}}$.

Problem 5.12.2 — 2014 AP Chemistry FRQ



The half-life ($t_{1/2}$) of the catalyzed isomerization of *cis*-2-butene gas to produce *trans*-2-butene gas, represented above, was measured under various conditions, as shown in the table below.

Trial Number	Initial $P_{cis\text{-}2\text{-butene}}$ (torr)	V (L)	T (K)	$t_{1/2}$ (s)
1	300.	2.00	350.	100.
2	600.	2.00	350.	100.
3	300.	4.00	350.	100.
4	300.	2.00	365	50.

(a) The reaction is first order. Explain how the data in the table are consistent with a first-order reaction.

(b) Calculate the rate constant, k, for the reaction at 350. K. Include appropriate units with your answer.

(c) Is the initial rate of reaction in trial 1 greater than, less than, or equal to the initial rate in trial 2? Justify your answer.

(d) The half-life of the reaction in trial 4 is less than the half-life in trial 1. Explain why, in terms of activation energy.

Solution to part a: The easiest way to determine whether a reaction is first-order is to observe its half-life. The value of $t_{1/2}$ is independent of reactant concentrations (or partial pressures) at a constant Kelvin temperature T. This phenomenon is shown in trials 1, 2, and 3.

Solution to part b: For each trial at 350 K, the half-life is 100. s.
Use the formula $t_{1/2} = \frac{0.693}{k}$. Rearranging, we have

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{100.\text{ s}} = \boxed{0.00693\,\text{s}^{-1}}$$

Solution to part c: The rate law for both trials is

$$rate = k[cis\text{-2-butene}] \text{ or } rate = kP_{cis\text{-2-butene}}$$

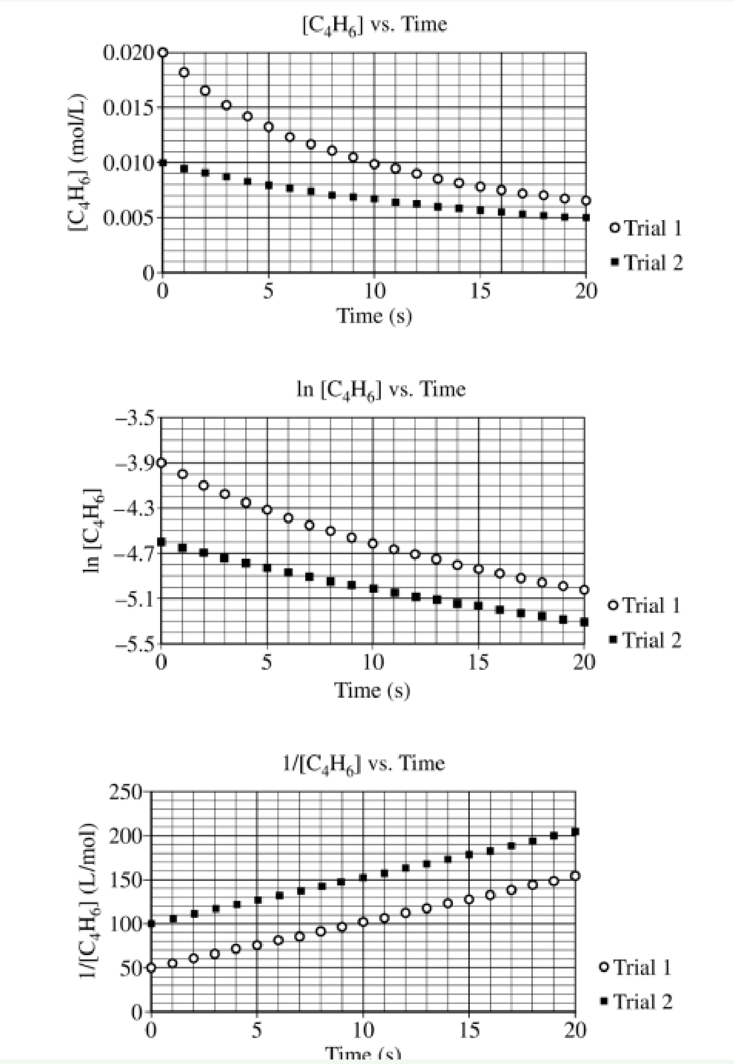
The initial rate depends on the initial amount of *cis*-2-butene gas initially present. Therefore, the initial reaction rate in trial 1 is $\boxed{\text{less than}}$ that of trial 2 because more *cis*-2-butene is initially present in trial 1 than in trial 2 and the value of k is the same due to the constant temperature.

Solution to part d: In trial 4, it takes less time for *cis*-2-butene to decompose, compared to trial 1. According to the data, the temperature in trial 4 is higher than that of trial 1, so the average kinetic energy of the *cis*-2-butene molecules is greater. Consequently, a greater fraction of collisions between the molecules have sufficient energy to overcome the activation energy barrier, so the rate of reaction is higher.

Problem 5.12.3 — 2016 AP Chemistry FRQ

$$2C_4H_6(g) \rightarrow C_8H_{12}(g)$$

At high temperatures the compound C_4H_6 (1,3-butadiene) reacts according to the equation above. The rate of the reaction was studied at 625 K in a rigid reaction vessel. Two different trials, each with a different starting concentration, were carried out. The data were plotted in three different ways, as shown below.



(a) For trial 1, calculate the initial pressure, in atm, in the vessel at 625 K. Assume that initially all the gas present in the vessel is C_4H_6.

(b) Use the data plotted in the graphs to determine the order of the reaction with respect to C_4H_6.

(c) The initial rate of the reaction in trial 1 is $0.0010\,\text{mol}/(\text{L}\cdot\text{s})$. Calculate the rate constant, k, for the reaction at 625 K.

Solution to part a: Because this problem involves kinetics, we can consider pressure and concentration as proportional to each other. More specifically, we see that the initial

$[C_4H_6]$ is equal to 0.020 mol/L, according to the topmost graph. Since the volume of the vessel is not specified but we MUST know the volume to calculate the initial pressure, we can assume that it is 1.0 L, so the number of moles of C_4H_6 initially present is 0.020.

Since we know these two values and the problem specifies the temperature (625 K), we can use the Ideal Gas Law to solve for the pressure:

$$P = \frac{nRT}{V} = \frac{(0.020\,\cancel{\text{mol}})(0.08206\,\cancel{\text{L}}\,\text{atm}\,\cancel{\text{mol}^{-1}}\,\cancel{\text{K}^{-1}})(625\,\cancel{\text{K}})}{1.0\,\cancel{\text{L}}} = \boxed{1.0\,\text{atm}}$$

Solution to part b: To determine the order of a chemical reaction, we need to analyze experimental data. For this problem, we are given three graphs that can be interpreted to determine the order of the reaction with respect to our one reactant, C_4H_6.

Recall the three integrated rate laws and their generalizations:

- If reactant concentration over time produces a straight line with a slope of $-k$, the reaction is zero order.
- If the natural log of the reactant concentration over time produces a straight line with a slope of $-k$, the reaction is first order.
- Finally, if the reciprocal of the reaction concentration over time produces a straight line with a slope of k, the reaction is second order.

From this information as well as the shape of data in the graphs, we conclude that the reaction is $\boxed{\text{second order}}$ with respect to C_4H_6, as the plot of $1/[C_4H_6]$ over time is a straight line with positive slope.

Solution to part c: We established in part (b) that the reaction is second order with respect to C_4H_6, so the rate law expression is given by

$$rate = k[C_4H_6]^2$$

Since we are given the initial concentration of C_4H_6 as well as the initial rate of the reaction, we can solve for the rate constant:

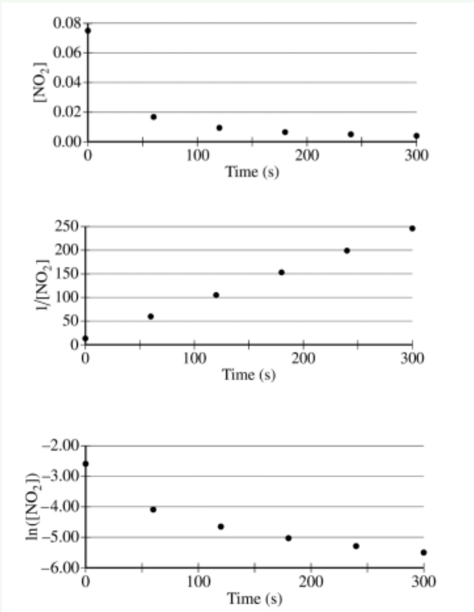
$$k = \frac{rate}{[C_4H_6]^2} = \frac{0.010\,\text{mol}/(\text{L}\cdot\text{s})}{(0.020\,\text{mol/L})^2} = \boxed{2.5\,\text{L}/\,(\text{mol}\cdot\text{s})}$$

Problem 5.12.4 — 2019 AP Chemistry FRQ

Nitrogen dioxide, NO_2(g), is produced as a byproduct of the combustion of fossil fuels in internal combustion engines. At elevated temperatures NO_2(g) decomposes according to the equation below.

$$2NO_2(g) \rightarrow 2NO(g) + O_2(g)$$

The concentration of a sample of NO_2(g) is monitored as it decomposes and is recorded on the graph directly below. The two graphs that follow it are derived from the original data.



(a) Explain how the graphs indicate that the reaction is second-order.

(b) Write the rate law for the decomposition of NO_2(g).

(c) Consider two possible mechanisms for the decomposition reaction.

(i) Is the rate law described by mechanism I shown below consistent with the rate law you wrote in part (b)? Justify your answer.

Mechanism I

Step 1:	$NO_2(g) + NO_2(g) \rightarrow NO(g) + NO_3(g)$	*slow*
Step 2:	$NO_3(g) \rightarrow NO(g) + O_2(g)$	*fast*

(ii) Is the rate law described by mechanism II shown below consistent with the rate law you wrote in part (b)? Justify your answer.

Solution to part a: The integrated rate law for second-order reactions is given by

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$$

which indicates that the reciprocal of the concentration of a substance A over time is represented by an increasing linear relationship. We can see this in the second graph above, where $1/[NO_2]$ as a function of time t is a linear graph with a slope equal to k.

Solution to part b: Since the rate of the reaction is second order with respect to NO_2, the rate law expression is given by

$$\boxed{rate = k[\mathrm{NO_2}]^2}$$

Solution to part c(i): Step 1 of the mechanism is slow, which means it determines the rate of the overall reaction. The rate law for this elementary step can be found using the coefficients of the reactants, so we have

$$rate = k[\mathrm{NO_2}][\mathrm{NO_2}] = k[\mathrm{NO_2}]^2$$

and this is consistent with the second-order rate law we found in part (b). ✓

Solution to part c(ii): Let's identify the slow step in this mechanism. It is step 2, and it is the rate-determining step for the overall reaction. The rate law of this elementary reaction is $rate = k[\mathrm{N_2O_4}]$ but we have a problem here. N_2O_4(g) is an intermediate of the reaction mechanism, so we cannot include it in the overall rate law expression. Therefore, we will use *steady-state approximation* to replace $[\mathrm{N_2O_4}]$ with concentrations of reactants and products that are not intermediates.

For this we will set the rates of the forward and reverse reactions of the fast equilibrium step of the mechanism equal to each other.

$$rate_{forward} = rate_{reverse}$$

$$k_1[\mathrm{NO_2}]^2 = k_{-1}[\mathrm{N_2O_4}]$$

where k_1 and k_{-1} are the rate constants for the forward and reverse reactions, respectively, in step 1 of the mechanism.

Isolating for $[\mathrm{N_2O_4}]$, we have

$$[\mathrm{N_2O_4}] = \frac{k_1[\mathrm{NO_2}]^2}{k_{-1}}$$

Now, let's call the rate constant of the slow step as k_2

The rate law for this elementary reaction is $rate = k_2[\mathrm{N_2O_4}]$, but wait! We solved for our intermediate concentration in terms of the concentrations of other species, so we don't need to include it in our overall rate law!

$$rate = k_2[\mathrm{N_2O_4}] = \frac{k_1 k_2}{k_{-1}}[\mathrm{NO_2}]^2$$

and combining $\frac{k_1 k_2}{k_{-1}}$ all into one effective constant k, we are finally left with

$$rate = k[\mathrm{NO_2}]^2$$

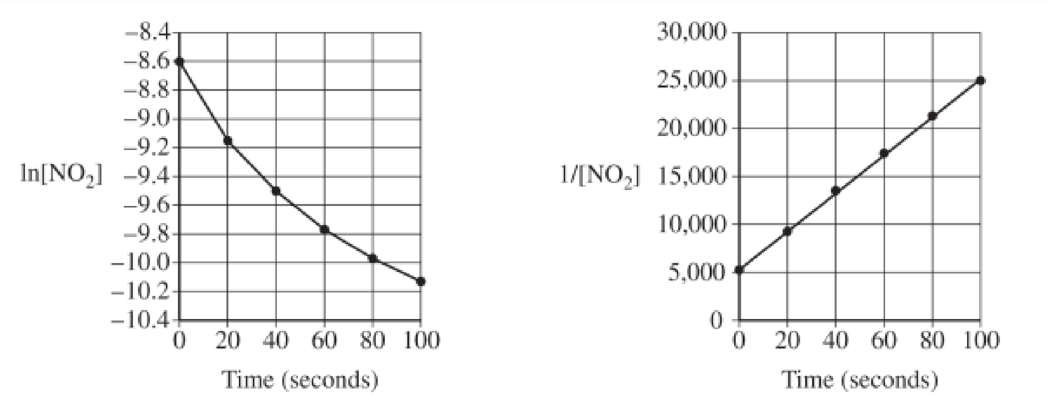
which is consistent with the second-order rate law we found in part (b). ✓

Problem 5.12.5 — 2024 AP Chemistry FRQ (Excerpt)

At elevated temperatures, NO_2 undergoes decomposition in the gas phase, forming NO and O_2 as represented as the following equation.

$$2NO_2 \rightarrow 2NO + O_2$$

A scientists measures the change in $[NO_2]$ over the first 100. s of the reaction at 546°C. The scientist uses the data collected from the experiment to generate the following two graphs.



Based on these data, the scientist makes the claim that the rate law for the reaction is $rate = k[NO_2]^2$.

(a) Explain how the graphs indicate that the reaction is second order with respect to NO_2.

(b) At a certain point in the reaction, the rate of disappearance of NO_2 is determined to be $6.52 \cdot 10^{-7}$ M/s. Determine the rate of appearance, in M/s, of O_2 at this same point in the reaction.

Solution to part a: The graph of $\frac{1}{[NO_2]}$ vs. time is increasing linear. According to the integrated rate laws, this indicates a $\boxed{\text{second-order}}$ reaction.

Solution to part b: The rates of disappearance and appearance for species in a reaction are correlated to their stoichiometric coefficients.
Since the NO_2 and O_2 are in a 2 : 1 mole ratio, the rate of appearance for the O_2 is equal to half the rate of disappearance of the NO_2, or

$$\frac{1}{2} \cdot 6.52 \cdot 10^{-7}\ \text{M/s} = \boxed{3.26 \cdot 10^{-7}\ \text{M/s}}$$

6 Thermodynamics

This unit emphasizes energy and its role in physical and chemical processes. We will discuss heat transfer, enthalpy of reaction, Hess's law, thermal equilibrium, and more.

§6.1 Endothermic vs. Exothermic Processes

Before we begin, we will understand the concept of energy.

> **Definition 6.1.1**
> **Energy** is the capacity to do work or to produce heat.

The units of energy are usually given in *joules* (J) or *kilojoules* (kJ) Additionally, we should internalize the *Law of Conservation of Energy*, also known as the *1st Law of Thermodynamics.*

> **Definition 6.1.2**
> The **Law of Conservation of Energy** states that energy can be converted from one form to another but cannot be created or destroyed.

Two Types of Energy

- **Potential energy**: this energy is due to position or composition of a substance. It is stored and can be converted into work, e.g. water behind a dam or saturated fat that stores energy for later use.

- **Kinetic energy**: this energy is due to the motion of a particle. It depends on both the mass (m) and the velocity (v).

$$\boxed{\mathrm{KE} = \frac{1}{2}mv^2}$$

Temperature vs. Heat

In practice, many students use the terms *temperature* and *heat* interchangeably. However, they DO NOT mean the same thing. Temperature reflects *random motions* of particles governed by the Kinetic Molecular Theory, and is related to the kinetic energy of the system containing those particles. Therefore, a *change in temperature indicates a change in kinetic energy.* On the other hand, **heat** involves an energy transfer *between* 2 objects due to their temperature difference.

Important! Finally, always remember this general rule: heat flows from *hot to cold*, and not cold to hot. If this confuses you, don't worry. Here is a real-life example to help you understand.

Example 6.1.3

Imagine placing your hand on a doorknob. These objects are typically made of metal, so the doorknob will "feel" cold to your hand. Ask yourself, "Is the doorknob actually cold?" The answer is *no.* It is actually at room temperature. However, your body temperature is greater than room temperature, so in simple terms, your hand is hotter than the doorknob. As a result, heat will flow from your hand to the doorknob. Just as your hand feels cold with the touch, the doorknob will feel the warmth coming from your hand.

In this unit, there are two terms that you will hear A LOT. Be sure that you can distinguish them very well.

Definition 6.1.4

A **system** is a set of objects that we are currently studying.

Definition 6.1.5

The **surroundings** represent all other objects in the universe that are not part of the system.

Note 6.1.6

The **universe** is the set of all objects in both the system and the surroundings.

$$\text{Universe} = \text{System} + \text{Surroundings}$$

There are two categories to describe the flow of heat in matter and energy processes.

Endothermic vs. Exothermic Processes

Virtually all matter and energy processes involve an exchange of heat energy. Examples:

1. Heating or cooling of a substance.
2. Phase changes, such as sublimation, condensation, evaporation, etc.
3. Dissolving of a solute, e.g. when solid NaCl is placed in water, the temperature of the water changes.
4. Chemical reactions. Heat can be gained or lost by the reactants and products.

There are two possible directions for heat to flow in universal processes: endothermic and exothermic.

- **Exothermic:** Heat energy flows *out* of the system and *into* the surroundings.
- **Endothermic:** Heat energy flows *into* the system *from* the surroundings.

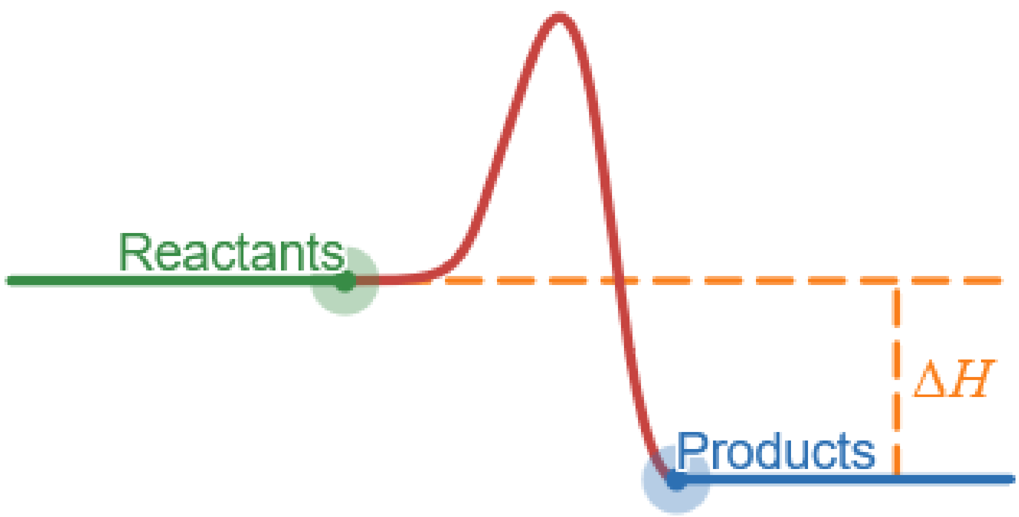
§6.2 Energy Diagrams

In the previous section, we talked about what endothermic and exothermic reactions are, their definitions, and in what situations do they apply. Now, we will explore visual representations of them using something that's called an *energy diagram*.

First, let's consider an exothermic reaction:

$$\text{reactants} \rightarrow \text{products} + \text{heat}$$

The appropriate energy diagram is shown below.



What evidence can we use to justify that this is an exothermic reaction?

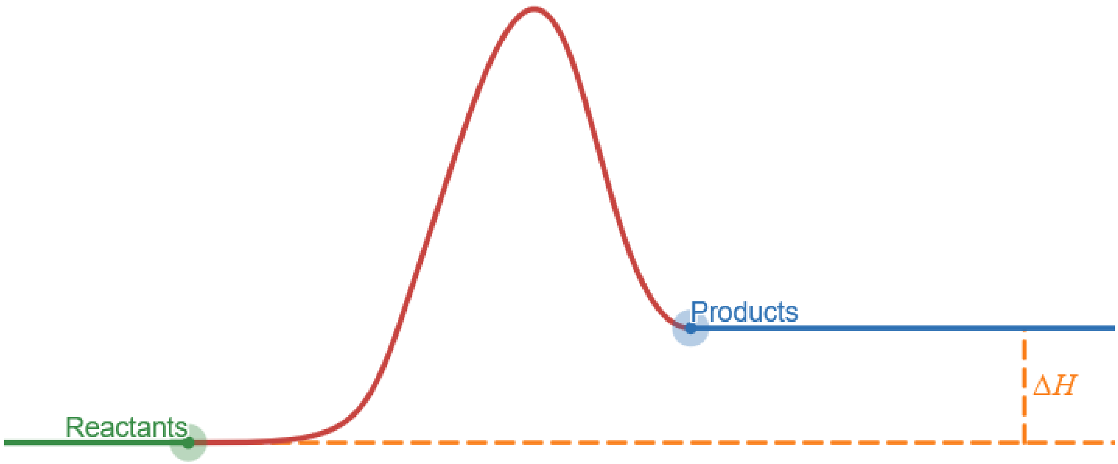
First off, in the chemical reaction, we see that heat energy is generated on the products side. If we considered our reaction as the *system*, then heat is being released from the system into the surroundings as the reaction progresses. Thus, the potential energy of the products is lower than that of the reactants. The change in heat energy (ΔH) for the reaction, represented by the dashed vertical line, is therefore a negative value.

Important Note: Whenever you see chemical reactions in which the equation has "heat", "energy", or a number of kilojoules on the PRODUCTS side, you can confirm that it is an *exothermic* reaction. Similarly, if you see anything along the same lines on the REACTANTS side, you can be sure that the reaction is *endothermic*.

Now, let's consider the endothermic reaction:

$$\text{reactants} + \text{heat} \rightarrow \text{products}$$

The appropriate energy diagram is shown below.



Let's look back on our chemical reaction: we know that the reaction is endothermic because we have a "heat" term on the reactants side. This means the reaction, or *system*, absorbs heat energy as it proceeds, so the potential energy of the products is greater than that of the reactants. Finally, the change in heat energy (ΔH), represented by the dashed vertical line, is a positive value.

Important Properties of an Energy Diagram

Here is a more detailed form of energy diagrams that you may often see in other textbooks as well as questions provided by College Board. We will do a full breakdown of what all these labels on the diagram actually mean, so you will be prepared if you are asked about a specific property of the graph!

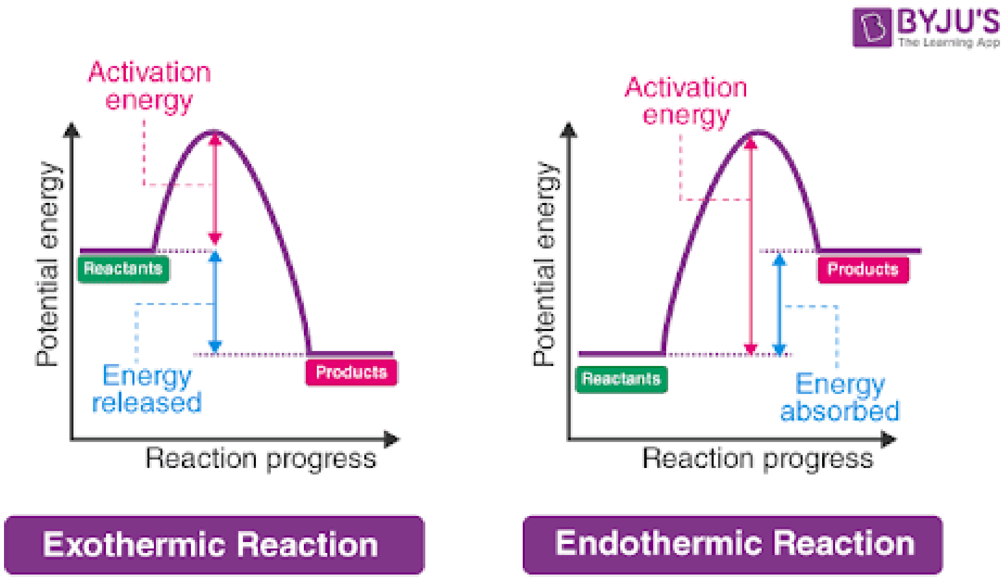


Image Courtesy of BYJU'S

- H_r represents the potential energy of the reactants at the beginning of the reaction before any transfer of energy occurs. Meanwhile, H_p represents the potential energy of the products at the end of the reaction after all of the heat energy has been transferred (either added to or released from the system).
- **Activation energy** is the minimum amount of energy that is required to *initiate* the chemical reaction. A more intuitive definition would be that it is the minimum energy required to overcome the initial barriers that prevent reactant molecules from having effective collisions.
- The **activated complex** is a hypothetical intermediate state that a molecule must pass through before it can react. This is represented by the highest point on the energy diagram, the most unstable state of the reaction, where the energy supplied to the reactants must exceed the activation energy.

What is ΔH?

Earlier, we talked about the change in heat energy, ΔH for the reaction. Most chemistry textbooks and College Board refer to this as the change in enthalpy.

Definition 6.2.1
Enthalpy is the total heat content that is stored in a system.

The value of ΔH can be determined by using the following equation.

$$\boxed{\Delta H = H_p - H_r}$$

where H_r and H_p are the potential energies of the reactants and products, respectively.

The units for ΔH can be given in kJ, kJ/mol, or kJ/mol$_{rxn}$.

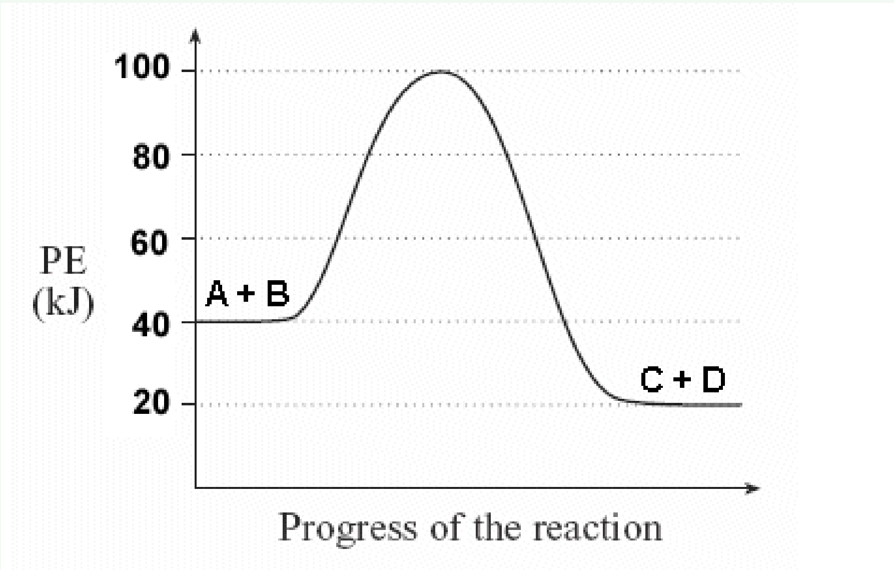
Quick Problem-Solving Strategies Involving ΔH

- When $H_p > H_r$, the potential energy of the products exceeds the potential energy of the reactants. Thus, $\Delta H > 0$ and the reaction is endothermic.
- When $H_p < H_r$, the potential energy of the products is lower than the potential energy of the reactants. Thus, $\Delta H < 0$, and the reaction is exothermic.

Let's practice with an AP-style problem.

Problem 6.2.2 — Free-Response Practice

For the generic reaction $A + B \rightarrow C + D$, use the image below and your knowledge of thermodynamics and kinetics to answer the following questions.



(a) What is the potential energy of the reactants?
(b) What is the potential energy of the products?
(c) What is the value of ΔH for the reaction?
(d) What is the activation energy?
(e) Is this reaction endothermic or exothermic?

Solution to part a: According to the chemical equation, $A + B$ represent both the reactants. Their potential energy is shown on the vertical axis before the reaction proceeds at all. By inspection, we know that it is $\boxed{40\,\text{kJ}}$.

Solution to part b: This question involves the same logic as part (a). The products of the reaction are represented by $C + D$ in the equation, and we can determine their energy by finding the point at which the reaction reaches completion, i.e. the point where all reactants have been converted into products. We see that this occurs at the rightmost section of the graph, with a corresponding vertical axis value of $\boxed{20\,\text{kJ}}$, which is indeed the answer.

Solution to part c: Remember that the change in enthalpy, ΔH, for a reaction can be determined by finding the difference between the potential energies of the products and the reactants.

$$\Delta H = H_p - H_r$$

Using our answers to parts (a)-(b), we can just plug in.

$$\Delta H = 20\,\text{kJ} - 40\,\text{kJ} = \boxed{-20\,\text{kJ}}$$

Solution to part d: To find the activation energy, we need to find the absolute value of the vertical displacement between the initial energy (of the reactants) and the energy of the activated complex, or the maximum point on the graph.

If we scan our graph properly, we should determine that the energy of the activated complex (transition state) is 100 kJ. Additionally, the initial energy of the reactants is already known, it is 40 kJ from part (a). Therefore,

$$E_a = 100\,\text{kJ} - 40\,\text{kJ} = 60\,\text{kJ}$$

It takes $\boxed{60\,\text{kJ}}$ of energy to complete the reaction.

Solution to part e: The question of whether a reaction is endothermic or exothermic can be answered based on the sign of its ΔH value. From part (c), we know that the calculated value of ΔH is negative, so the potential energy of the products is greater than that of the reactants. This indicates an $\boxed{\text{exothermic}}$ reaction.

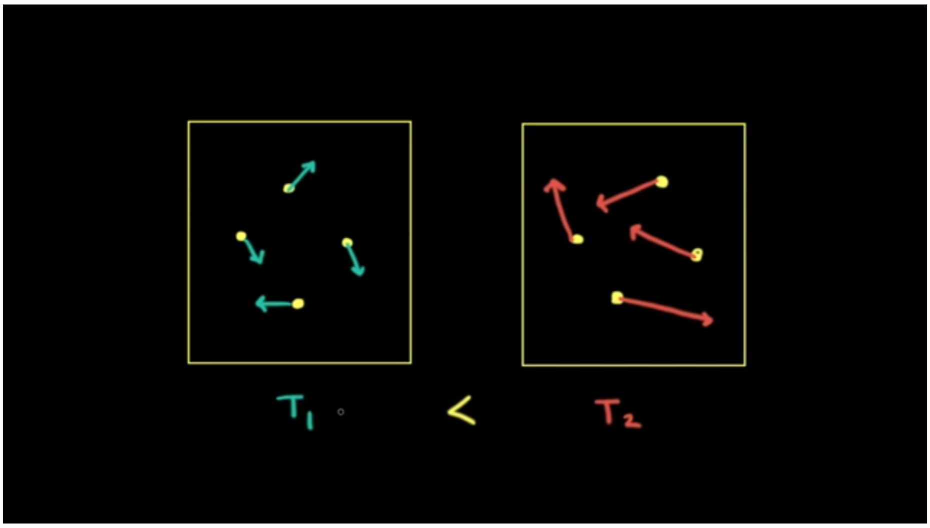
§6.3 Transfer of Heat Energy and Thermal Equilibrium

In section 6.1, we learned that heat flows from a warmer object (with higher temperature) to a cooler object (with lower temperature). Because temperature is proportional to average kinetic energy, we know that the warmer object, on average, has its particles at a higher kinetic energy, while those in the cooler object, on average, have a lower kinetic energy.

Example 6.3.1

Let's say we have two samples of identical gas molecules in two separate containers with equal volume. Also, the containers have temperatures T_1 and T_2, with $T_1 < T_2$.

The below diagram illustrates the scenario.



Example Courtesy of Khan Academy

As we learned in Unit 3, at higher temperatures, gas particles have a higher velocity. Therefore, the gas particles at temperature T_2 are, on average, moving faster than those at temperature T_1. This is evidenced by the relative length of the molecular velocity vectors drawn in both containers.

Definition 6.3.2

The equation for kinetic energy of a particle is

$$\text{KE} = \frac{1}{2}mv^2$$

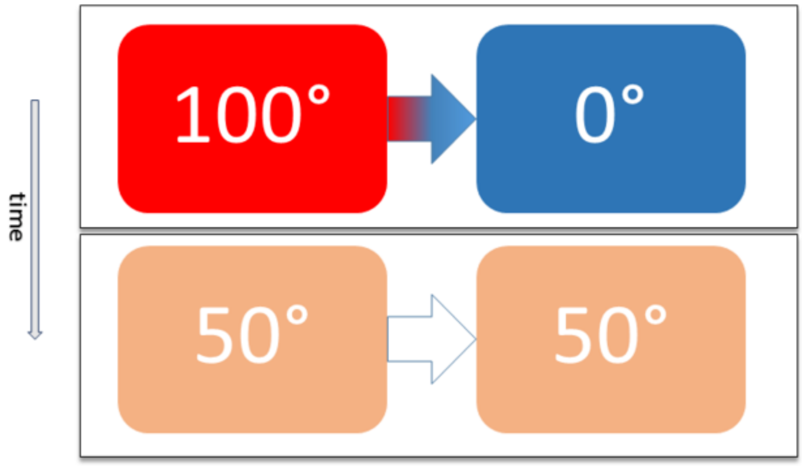
where m is the mass of the particle and v is the velocity of the particle.

According to the equation, the kinetic energy of the gas particles is proportional to their velocity. Therefore, the particles on the right container have a higher average kinetic energy than the particles in the left container.

Thermal Equilibrium

Let's consider what happens when the contents of the two containers come in contact with each other. On a molecular level, the particles at the surface of each particle in the containers will collide, resulting in the transfer of energy as **heat**. These collisions continue as heat keeps being transferred until a state of **thermal equilibrium** is reached, at which point the temperatures of the particles—are equal. The kinetic energy from the warmer object is transferred to the cooler object, and thermal equilibrium is established when both objects have the same average kinetic energy.

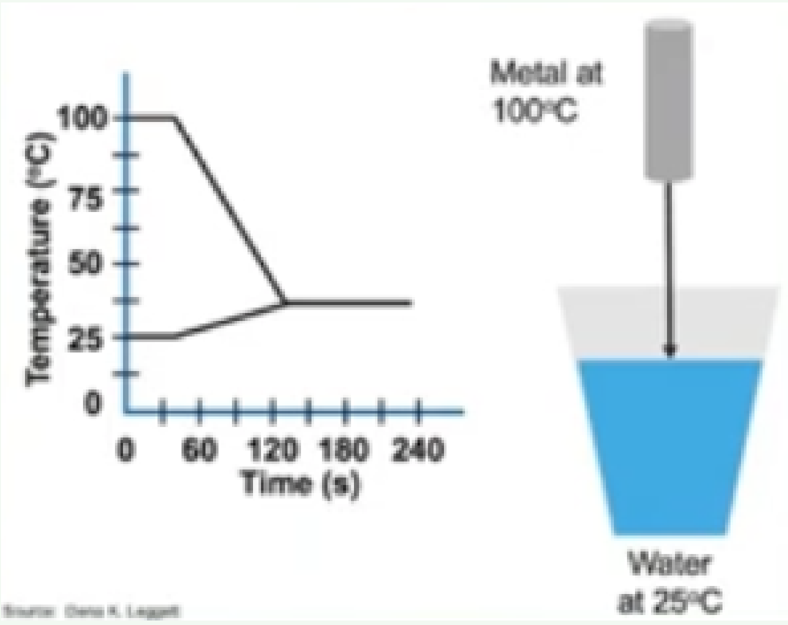
In terms of molecular speed, the warmer particles in the right container move slower while the cooler particles in the left container move faster until both groups of particles move at a constant speed and approach the same temperature T_f.



Here's a short free-response question to conclude this section.

Problem 6.3.3 — Heat Transfer FRQ

A student conducted an experiment where she placed a piece of hot metal inside a beaker of cold water. The change in temperature for both samples was monitored and is shown in the graph below.



(a) What is the change in temperature for the metal?
(b) What time is thermal equilibrium achieved? Justify your answer.
(c) Does the average speed of the metal particles increase or decrease with time? Use particle level reasoning to justify your answer.

Example Courtesy of Abigail Giordano

Solution to part a: Note that the water and metal have the same final temperature, i.e. at this point, thermal equilibrium is reached. The change in temperature for the metal can be calculated by finding the difference between its final and initial temperatures. The diagram tells us that the initial temperature of the metal is 100°C.

Looking at the graph of temperature vs. time for the metal-water system, we see that the temperature of the metal decreases until it reaches 37.5°C.

Therefore, we can calculate ΔT using

$$\Delta T = T_f - T_i = 37.5°\text{C} - 100°\text{C} = \boxed{-62.5°\text{C}}$$

Solution to part b: Recall that when thermal equilibrium is achieved, all substances will no longer transfer heat amongst themselves, i.e. they will have approached the same final temperature. Therefore, we should be looking for the time where both the metal and water stabilizes at the same temperature. Somewhere between the times $\boxed{t = 130 \text{ and } t = 140 \text{ seconds}}$, both the metal and water reach a final temperature of 37.5°C and remain at that temperature, which is consistent with the definition of thermal equilibrium.

Solution to part c: This question tests us on our knowledge of the topics covered in Unit 3. We know that the temperature of the metal decreases, because our calculated ΔT for the metal from part (a) was a negative value. Remember that temperature describes the average kinetic energy of a substance, i.e. at higher temperatures, particles are moving at a greater speed (and thus a greater average kinetic energy). Since the temperature of the metal decreases with time, so does the average kinetic energy of its particles. This causes their average speeds to $\boxed{\text{decrease}}$ with time.

§6.4 Heat Capacity and Calorimetry

Grab your calculators! We're going to be doing a fair amount of math. This section is all about quantitative descriptions of heat energy as well as the techniques to measure heat exchange.

Heat Exchange Terminology

Before we can get to the math, however, we should understand these vocabulary words.

Definition 6.4.1

Specific heat capacity, c, represents the quantity of heat (J) that a 1 g substance must absorb in order to raise its temperature by 1°C (or 1 K). The units for specific heat capacity are given by $\text{J}/(\text{g} \cdot^\circ \text{C})$ or $\text{J}/(\text{g} \cdot \text{K})$.

Definition 6.4.2

Molar heat capacity, also denoted by c, is almost identical to specific heat capacity. The only difference is that this is the quantity of heat required for 1 MOLE of a substance to raise its temperature by 1°C (or 1 K). The units for specific molar capacity are given by $\text{J}/(\text{mol} \cdot^\circ \text{C})$ or $\text{J}/(\text{mol} \cdot \text{K})$.

Another metric that is loosely used by College Board is called "heat capacity."

Definition 6.4.3

Heat capacity, C_p, is the amount of heat absorbed per degree. Its units are given in J/°C or J/K.

The last thing to note here is that all these properties are referred to as *intensive*.

Definition 6.4.4

Intensive properties are properties of matter that only depend on the type of matter in a sample and not the amount. Examples include color, temperature, solubility, and more.

We can use these measures to compare certain properties of different substances.

Example 6.4.5

Gold and silver are two of the precious metals known to exist. Asides from their value in jewelry, they are known to have important applications in engineering, electronics, and medicine.

If the same amount of heat was applied to the same mass of gold and silver metal, which one would display the greater change in temperature? The specific heat capacities of gold and silver are 0.031 J/(g $\cdot ^{\circ}$ C) and 0.057 J/(g $\cdot ^{\circ}$ C), respectively.

Since specific heat capacity represents the quantity of heat that 1 g of a substance will absorb in order to raise its temperature by 1 degree, the substance with a higher specific heat capacity will require more energy to raise its temperature, as opposed to a substance with a lower heat capacity.

Therefore, gold will display the greater change in temperature, because it has the lower specific heat capacity. In other words, less energy is required for 1 g of the substance to raise its temperature by 1°C.

Calculating Heat Transfer for a Chemical Reaction

Recall that the **First Law of Thermodynamics** states that energy cannot be created or destroyed—it can only be transferred or converted from one form to another. This means that the total amount of energy in a closed system remains constant over time.

Mathematically, we can calculate the amount of heat gained or lost by a sample by using the formula

$$\boxed{q = mc\Delta T}$$

where:

- q is the heat in joules (J),
- m is the mass in grams (g),
- c is the specific heat capacity for the substance in J/(g $\cdot ^{\circ}$ C) or J/(g $\cdot$ K), and
- ΔT is the change in temperature in either Celsius (°C) or Kelvin (K).

Note 6.4.6

Since temperatures in both degrees Celsius and Kelvins are on equivalent scales, ΔT will have the same values for both °C and K, e.g. a change in temperature of 2 Kelvins is the same as a change of 2°C.

In the beginning of this section, we established that heat capacity, molar heat capacity, as well as specific heat capacity were all *intensive* properties; their values are not dependent on the amount of substance present. However, the heat energy itself, q, is an *extensive* property, so it DOES depend on the mass of the substance, as we can infer from the equation.

Also, we can connect this equation to the Law of Conservation of Energy, or the 1st Law of Thermodynamics.

In a closed system, the total internal energy is constant, or $\Delta E = 0$. If we generalize this using heat transfer, we can say that for an isolated system, the total change in heat energy is zero. In other words, **the heat gained by one component of the system is equal to the heat lost by the other component of the system**.

Calorimetry

We cannot determine the absolute **enthalpy**, H, of a system, but *changes* in enthalpy (ΔH) for systems can be measured using a technique called **calorimetry**. Calorimetry is the study of heat exchange between a system and surroundings and it can be used to calculate the change in enthalpy by measuring changes in *temperature*, that can represent heat being *lost* or *gained*.

There are several types of calorimeters that can be used to describe the flow of heat in a chemical reaction or physical process:

- In a **bomb calorimeter**, a process occurs in a sealed container (constant-volume) called the bomb, and the heat generated by the reaction is used to raise the temperature of the surrounding water. Therefore, ΔH for the reaction can be calculated by measuring the rise in temperature and knowing its specific heat capacity.

- In a **constant-pressure calorimeter**, the change in enthalpy for a reaction can be determined by measuring the change in temperature of the **reaction mixture** (all reactants and products) at constant pressure. This is because, at constant pressure, the total heat amount is equal to ΔH.

- In a **coffee-cup calorimeter**, also known as a *simple* calorimeter, the heat that is released or absorbed by a reaction is used to change the temperature of the surrounding water. By measuring the change in temperature as well as knowing the specific heat capacity of the water, the overall heat energy change of the reaction can be calculated.

Coffee-cup calorimetry will be our focus for thermodynamics, and we will see how we can use it to observe changes in heat energy for the system as well as surroundings.

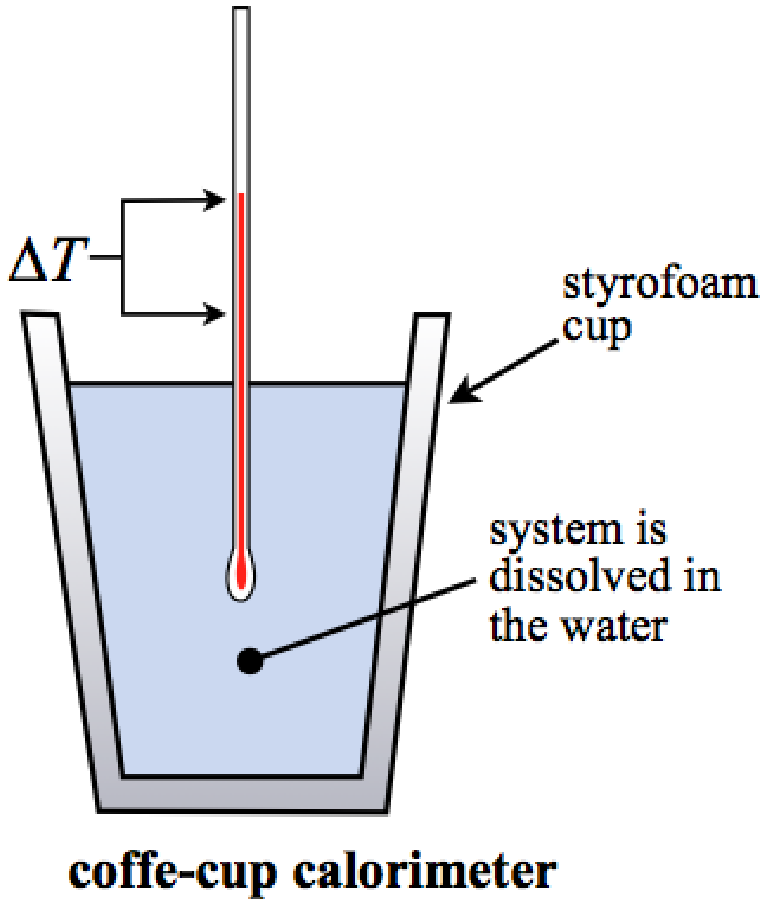


Image Courtesy of University of Texas at Austin

There are several important components for a coffee-cup calorimeter, including:

- A thermometer to measure the change in temperature for the surrounding water,
- The reaction mixture, consisting of all reactants and products,
- The **stirrer** to stir the reaction mixture and allow for more accurate temperature measurements (this becomes more important the sensitivity of your thermometer increases!),
- An insulated container (e.g. styrofoam cup), and
- A **heat-resistant lid** to cover the calorimeter. The calorimeter is designed to insulate the sample, i.e. prevent heat from entering or exiting the system (remember 1st Law of Thermodynamics!). The more insulated the system, the more accurate the measured change in heat energy of the reaction.

To conclude this section, we will walk through some problems involving concepts of heat transfer and calorimetry.

Problem 6.4.7 — Calorimetry Practice I

An insulated cup contains 255.0 grams of water and the temperature changes from 25.4°C to 91.4°C. Calculate the amount of heat released that is released by the system. The specific heat capacity of water is 4.184 J/(g ·° C).

Solution: Since this problem involves an insulated cup containing a sample, we should recognize this as involving calorimetry. Additionally, you are given the initial and final temperatures of water as well as the specific heat, so the equation that comes to mind is

$$q = mc\Delta T$$

Plugging in known values, we determine

$$q = (255.0\,\text{g})(4.184\,\text{J/g}\cdot^\circ\text{C})(91.4^\circ\text{C} - 25.4^\circ\text{C}) = \boxed{70416.72\,\text{J or } 70.4\,\text{kJ}}$$

We will be covering more equations later in this unit, but for now, whenever you see a problem involving change in temperature, always think of the equation $q = mc\Delta T$.

Misconception: q vs. ΔH

When many students look at q and ΔH, they associate both with heat. However, this is a common pitfall. While they can be related, they are not the same thing.
For the purpose of this course, q is always a positive value, for simplicity. It is considered the *magnitude* of heat energy that is transferred in a chemical reaction or physical process. Meanwhile, ΔH could be positive or negative, depending on whether the heat is released or absorbed by the system.

Problem 6.4.8 — Calorimetry Practice II

A laboratory procedure is being performed in a calorimeter involving a strip of copper metal being placed into distilled water.

Once the procedure is complete, the following data is collected.

Mass of Copper	50.00 g
Initial Temperature of Copper	100.0°C
Mass of Water	100.00 g
Initial Temperature of Water	20.0°C
Final Temperature of System (Copper + Water)	23.6°C

(a) What is $|\Delta T|$ for the copper? What is $|\Delta T|$ for the water?
(b) A student claims that, since the magnitude of ΔT for the copper is greater than that of the water, it means that the magnitude of heat (q) lost by the copper is greater than the magnitude of heat (q) gained by the water. Do you agree with this claim?
(c) Find the specific heat of copper.

Example Courtesy of Advanced Placement YT Channel

Solution to part a: The change in temperature, ΔT, is always calculated by finding the difference between final temperature and initial temperature.
Thus, we have

- Copper: $|23.6°\text{C} - 100.0°\text{C}| = \boxed{74.6°\text{C}}$ and
- Water: $|23.6°\text{C} - 20°\text{C}| = \boxed{3.6°\text{C}}$

Solution to part b: You should disagree with this student's claim. While the copper and water have different values of ΔT, this is not sufficient to claim their overall transfer of heat values, q, will be different. This is because q is also dependent on the mass and specific heat of a substance ($q = mc\Delta T$). Additionally, this violates the Law of Conservation of Energy. The combination of copper and water can be treated as a closed system, and thus, the heat lost by the copper should equal the heat gained by the water.

Solution to part c: As established in part (b), the heat gained by the water is equal to the heat lost by the copper, or $-q_{\text{Cu}} = q_{\text{H}_2\text{O}}$. Thus, we can solve for c.

We set up the following calculation:

$$-(m_{\text{Cu}})(c)(\Delta T_{\text{Cu}}) = (m_{\text{H}_2\text{O}})(c_{\text{H}_2\text{O}})(\Delta T_{\text{H}_2\text{O}})$$

Substituting our known values gives

$$-(50.00\text{ g})(c)(-74.6°\text{C}) = (100.00\text{ g})(4.184\text{ J/g}\cdot°\text{ C})(3.6°\text{C})$$

and isolating for c, we find that the specific heat of copper is

$$c = \frac{(100.00\text{ g})(4.184\text{ J/g}\cdot°\text{ C})(3.6°\text{C})}{-(50.00\text{ g})(-74.6°\text{C})} = \boxed{0.404\text{ J/(g}\cdot°\text{ C)}}$$

§6.5 Energy of Phase Changes

Definition 6.5.1

A **phase change** is a physical process in which a substance transitions from one phase of matter to another.

Examples of phase changes include melting (solid to liquid), vaporizing (liquid to gas), freezing (liquid to solid), etc.

Heating Curves

We can visually represent the energetics of phase changes through a **heating curve**:

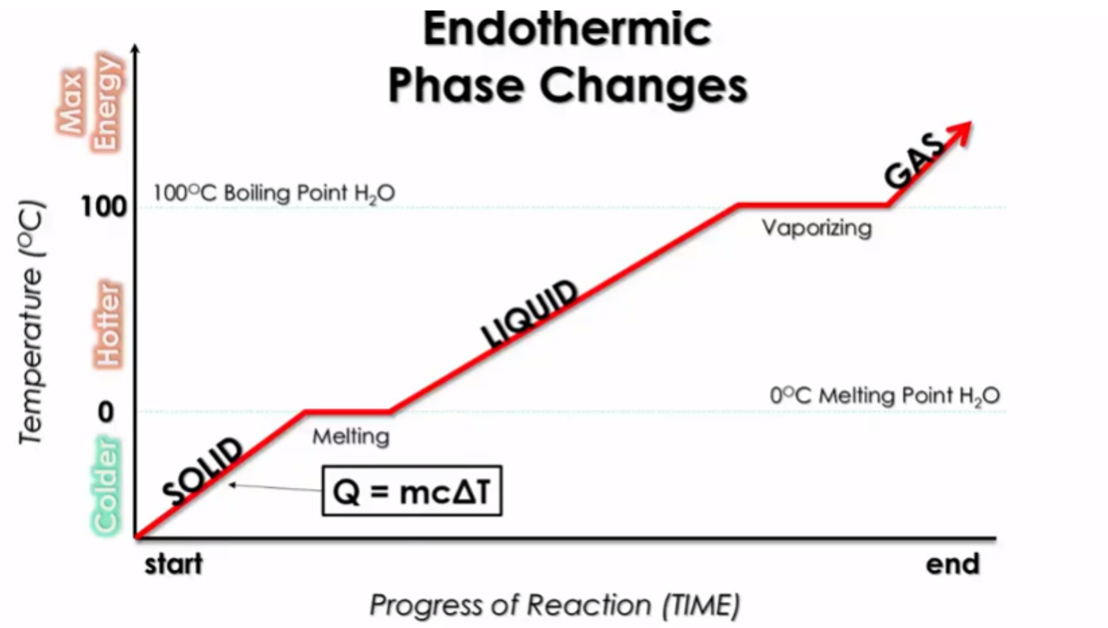


Image Courtesy of Schoenherr & Diamantopoulos Chemistry Videos

For heating curves, the x-axis represents the progress of the reaction (over time) and the y-axis represents the temperature.

According to the equation $q = mc\Delta T$, as the temperature increases, q becomes more positive. This means you are absorbing heat energy, which defines an endothermic phase change. For example, increasing the temperature causes ice to eventually melt into water (solid to liquid phase change). Additionally, increasing the temperature to a greater extent will cause the liquid water to vaporize. These changes are marked by the slant lines where the temperature steadily increases.

But what about the straight line segments, or plateaus, that we see in the graph?

It makes sense that temperature increases as you transition from solid to liquid and liquid to gas, but the plateaus that are marked **melting** and **vaporizing** are where heat energy is used to actually melt or boil the object. The reason that temperature doesn't increase in this process can be confusing for many students. Remember that heat and temperature are **not** the same! Temperature is related to the average kinetic energy, while heat is the flow of thermal energy that is CAUSED BY a temperature difference. During the actual phase change, energy is not inputted to increase the speed of the molecules, but rather, to break the intermolecular forces between them, thus allowing them to transition from one phase to another.

With respect to the given diagram, you not only need to increase the temperature, but you also need to add heat energy to melt/boil the entire substance. These energy values are referred to the enthalpies of fusion and vaporization, or ΔH_{fusion} and $\Delta H_{vaporization}$, respectively.

For example, when ice (initially at a temperature below 0°C, the freezing point of water) melts into water, it remains at 0°C until ALL of it has been fully melted into water, and then the heating curve continues.

You may have noticed that the plateau of vaporization is significantly longer than the one associated with melting. This means that more energy is required for the substance to boil than to melt. This is also the reason as to why $\Delta H_{vaporization}$ is almost *always* greater than ΔH_{fusion}.

You can think about this difference in terms of intermolecular forces. During the melting phase, the majority of, but not all IMFs, effectively break. However, when water boils, **all** IMFs must break (due to the large space between gas particles), and thus requires more heat energy.

Here is a common question type that College Board will ask you involving your knowledge of energy associated with phase changes.

Problem 6.5.2 — Multistep Heat Transfer Practice

How much heat energy is required to convert 30.0 g of ice at −20°C to water vapor at 140°C? Use the following given information:

- The specific heat capacity of ice is 2.108 J/(g ·° C)
- The specific heat capacity of water is 4.18 J/(g ·° C)
- The specific heat capacity of steam is 2.010 J/(g ·° C)
- ΔH_{fusion} for H_2O is 334 J/g
- $\Delta H_{vaporization}$ for H_2O is 2260 J/g

Provide your answer in kilojoules (kJ).

Solution: First, as solid is changing to liquid, the temperature is increasing. Therefore, we will use the initial calculation of $q = mc\Delta T$:

$$q = mc\Delta T = (30.0\,\text{g})(2.108\,\text{J}/(\text{g}\cdot^\circ\text{C})(0^\circ\text{C} - (-20^\circ\text{C})) = 1264.8\,\text{J}$$

Here, ΔT is determined by subtracting the temperature of ice from the melting point of water (0°C).

Now, the temperature will not increase since all the energy being inputted is to break the intermolecular forces and actually melt all of the ice. We will use the enthalpy of fusion to calculate the amount of heat absorbed in this process:

$$q = m \cdot \Delta H^\circ_{fusion} = 30.0\,\text{g} \cdot 334\,\text{J/g} = 10020\,\text{J}$$

In liquid form, the temperature rises so that a portion of water molecules moves as a faster speed. This is a $q = mc\Delta T$ calculation:

$$q = mc\Delta T = (30.0\,\text{g})(4.18\,\text{J}/(\text{g}\cdot^\circ\text{C})(100^\circ\text{C} - 0^\circ\text{C}) = 12540\,\text{J}$$

Here, ΔT is determined by subtracting boiling point (100°C) by the melting point (0°C).

Now, because the liquid needs additional heat energy to completely boil into water vapor, we will use the enthalpy of vaporization:

$$q = m \cdot \Delta H^\circ_{vaporization} = (30.0\,\text{g}) \cdot 2260\,\text{J/g} = 67800\,\text{J}$$

Finally, the amount of heat energy needed to increase the temperature of the gas from 100°C to 140°C can be calculated using $q = mc\Delta T$:

$$q = (30.0\,\text{g})(4.18\,\text{J}/(\text{g}\cdot^\circ\text{C})(140^\circ\text{C} - 100^\circ\text{C}) = 2412\,\text{J}$$

Adding everything up, we get 94036.8 J, and converting to kJ, the final answer is $\boxed{94.0\,\text{kJ}}$

In general, when dealing with heating curves, we should use the formula $q = mc\Delta T$ at the slopes, as temperature is changing, and the enthalpies of fusion and/or vaporization at the plateaus since these involve breaking of IMFs rather than an increase in temperature.

Cooling Curves

Cooling curves represent the opposite of what heating curves show. That is, they represent the *exothermic* processes, such as the freezing and condensation of a substance.

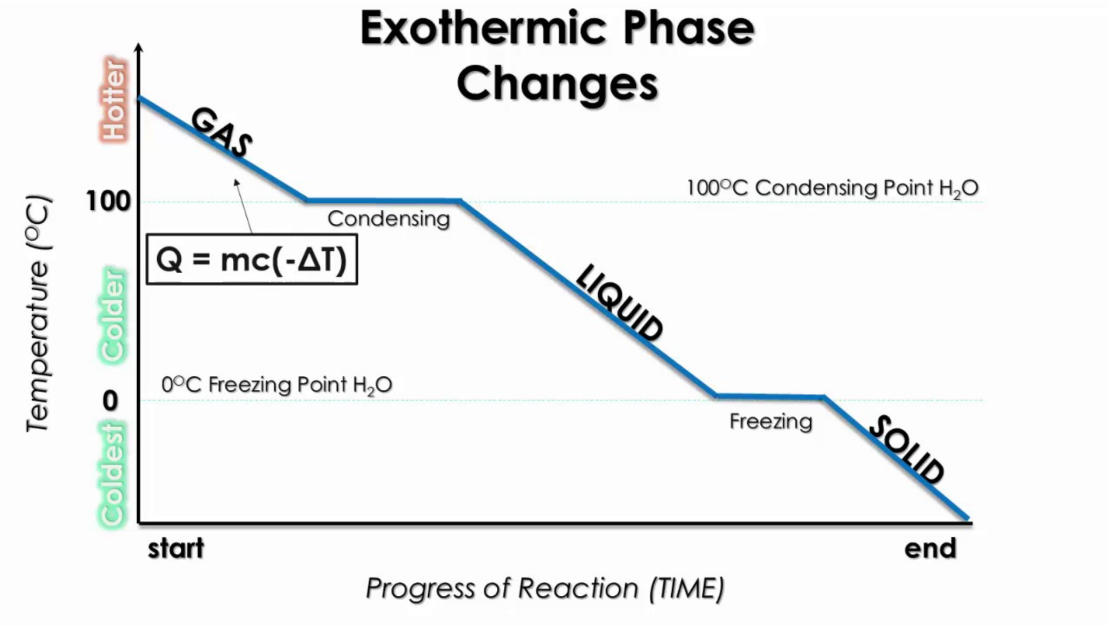


Image Courtesy of Schoenherr & Diamantopoulos Chemistry Videos

Cooling curves are virtually identical to heating curves, but instead of the enthalpies of fusion and vaporization, it has the enthalpies of condensation and freezing, or $\Delta H^{\circ}_{condensation}$ and $\Delta H^{\circ}_{freezing}$, respectively. Also, note that these values are simply the negatives (same magnitude, opposite signs) of the enthalpies of fusion and vaporization, respectively.

Note 6.5.3

Pay close attention to the units that are given to you in problems involving both heating and cooling curves. In the heating curve example we did previously, the enthalpy values for both fusion and vaporization were given in J/g, but they could have also been given in J/mol or kJ/g. Always remember to convert as necessary.

For example, if the molar heat capacity (J/mol · K) was given instead of the specific heat capacity, you would need to convert the mass of the substance from grams to moles before using the $q = mc\Delta T$ formula.

Phase Diagrams

The last important concept of this section covers **phase diagrams**: what are they, why are they important, and how they help us better understand chemistry.

As we know, the three phases of matter are **solid**, **liquid**, and **gas**. Additionally, we already know that substances can transition between the three phases through **melting**,

boiling, **condensation**, or **freezing** (thanks to heating and cooling curves!). Visually, these changes can be represented by a phase diagram:

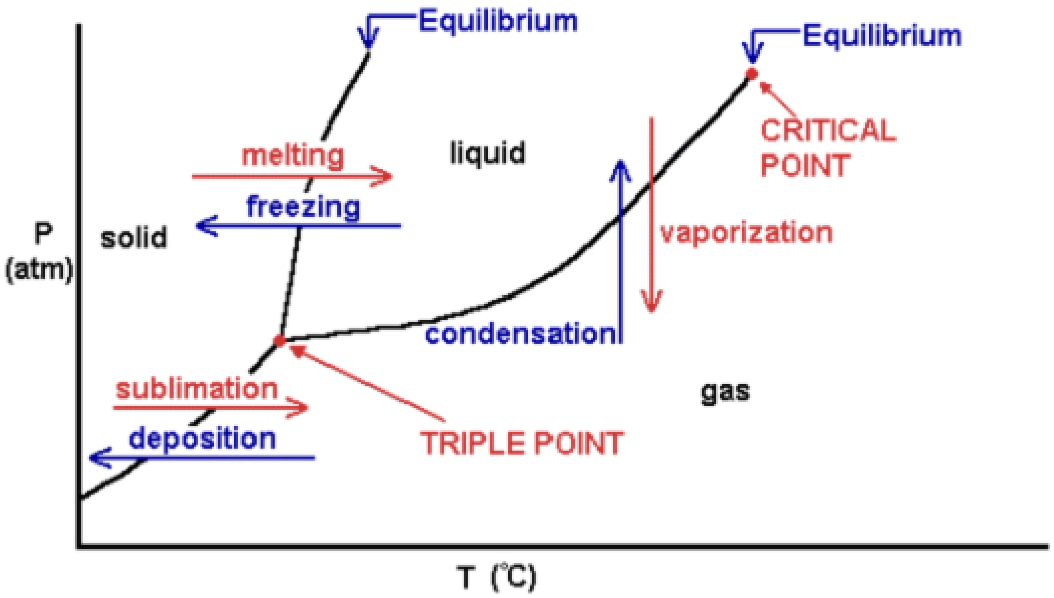


Image Courtesy of Aakash Shah

On the x-axis, we have the temperature in degrees Celsius (°C) and on the y-axis, we have the pressure in atmospheres (atm). This diagram shows how temperature and pressure are related in determining the state of matter for a substance. For example, if we increase the temperature (at a minimum threshold pressure), we can perform sublimation (solid to gas) and vice versa.

The two important points on a phase diagram, the **triple point** and the **critical point**. The triple point is an interesting point where you are somehow in all three states of matter at once. The critical point is the point at which you can no longer have a liquid past it. In this situation, you will either have a **supercritical fluid** or a **gas**.

That's all we need to know about the thermodynamics of phase changes (physical changes)! In the next section, we will talk about the thermodynamics regarding reactions (chemical changes).

§6.6 Introduction to Enthalpy of Reaction

Most, if not all chemical reactions require a transfer of heat energy (change in enthalpy) to proceed. In this section, we will focus on the heat energy that is transferred as species are consumed and produced in chemical reactions.

Definition 6.6.1

More specifically, **enthalpy**, H, is a measure of the total internal energy of a system, including the energy required to change the temperature as well as the pressure.

This change in heat that accompanies the reaction *at constant pressure*, q_p, is also known as the **enthalpy of reaction**, abbreviated as ΔH_{rxn}. In most cases, the units for ΔH_{rxn} are given by kJ/mol$_{rxn}$, but they can also be given in terms of kJ/mol or kJ.

Note 6.6.2

Remember in this course that in thermodynamics, we always take the system's point of view. This will be important when we assign different categories of reactions based on the sign of ΔH_{rxn} for a chemical process.

Let's say we perform a chemical reaction in an aqueous environment under constant atmospheric pressure. In this case, the reactants and products make up the *system* and everything else makes up the *surroundings*, from our frame of reference.

The following conditions hold true:

1. When heat flows from the surroundings into the system, the chemical reaction is endothermic. Therefore, the system absorbs heat energy and the change in enthalpy for the reaction is **positive**.
   The sign of ΔH_{rxn} is positive.

2. When heat flows out of the system into the surroundings, the chemical reaction is exothermic. Therefore, the system releases heat energy and the change in enthalpy for the reaction is **negative**.
   The sign of ΔH_{rxn} is negative.

In both of these cases, the "system" represents the species in the chemical reaction, both reactants and products.

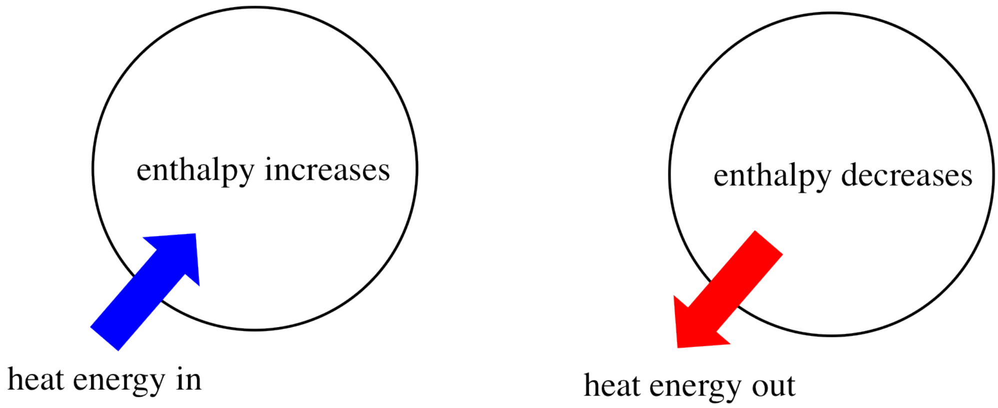


Image Courtesy of Chemistry LibreTexts

It's also worth noting that the enthalpy change of a reaction can also be used to predict how *feasible* it is. Exothermic reactions ($\Delta H_{rxn} < 0$) are generally **thermodynamically favorable**, while endothermic reactions ($\Delta H_{rxn} > 0$) are generally **thermodynamically unfavorable**. However, other factors can influence the feasibility of a reaction, such as the Gibbs free energy change (ΔG) or the equilibrium constant (K). But don't worry about those two metrics at the moment, because they show up in Unit 7 and Unit 9, respectively.

Some Practical Applications of Endothermic vs. Exothermic Reactions

You will see many of these reactions used as examples in both multiple choice and free-response sections of the AP Exam.

1. Exothermic: The combustion of propane to form carbon dioxide and water: $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)$. The enthalpy change for this reaction is negative, indicating that heat is released by the system during combustion. This can be observed as a flame or an increase in temperature in the **surroundings** of the reaction.

2. Endothermic: Melting of ice at 0°C: $H_2O(s) \rightarrow H_2O(l)$. The enthalpy change for this reaction is positive, which means heat was absorbed by the system, and thus the temperature **around** the reaction decreased.

3. Exothermic: Neutralization of hydrochloric acid with sodium hydroxide:
   $HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$.
   ΔH for this reaction is negative, because heat is being released from the reaction and the temperature of the surroundings increases.

There are tons more of possible reactions we can think of, but we have more material to get through, so let's keep going!

Clearing Up Misconceptions Regarding ΔH_{rxn} and Temperature

Let's review what the values of ΔH_{rxn} tell us for a physical or chemical process.

The sign of ΔH is determined by the direction of heat flow in a reaction (according to the system's perspective). If heat energy flows from the surroundings to the system, then the reaction is endothermic, with $\Delta H > 0$. If heat flows out of the system into the surroundings, then ΔH is negative, and the reaction is exothermic.

OK, but haven't we already stated this? Well, the reason I am restating the definition of **endothermic** and **exothermic** reactions is because there are often misconceptions that students make regarding the sign of ΔH and temperature changes.

Earlier, I said that an endothermic reaction may cause the surrounding temperature to decrease and vice versa, but this is not always the case. It's also important to note that heat flow is not necessarily a direct measurement of temperature change, but rather it is a measure of the total energy flow into or out of the system in a reaction.

Also, ΔH does not account for the fact that at different temperatures, different amounts of heat are required to raise the temperature of a substance by some amount. Finally, the enthalpy change does not depend on the initial and final states of a system, but only on the difference between them.

Fortunately, most reactions described on the AP exam take place under standard conditions, unless stated otherwise. Therefore, we can safely inference the type of temperature change (with respect to the surroundings) that occurs depending on whether our reaction is endothermic or exothermic.

Stoichiometry of ΔH in Chemical Reactions

Many times, you are rarely given exact quantities of reactants in a chemical reaction. For most cases, you will have to combine stoichiometry concepts with thermodynamics to determine the energy change associated with the reaction.

Problem 6.6.3 — Stoichiometry and Thermodynamics of Reactions I

Hydrogen peroxide, H_2O_2, in the liquid phase, decomposes into liquid water and oxygen gas when heated. This reaction can be represented by the balanced chemical equation below:

$$2H_2O_2(l) \rightarrow 2H_2O(l) + O_2(g)$$

The ΔH° value for this reaction at standard conditions is $-196\,\text{kJ/mol}_{rxn}$.

If we have a H_2O_2 sample of mass 5.00 g, what is the enthalpy change per ONE mole of H_2O_2?

Solution: First, we need to unpack what the unit of mol_{rxn}, or mole of reaction, actually means. It is simply a UNIT of ONE reaction: in order to define a mole of reaction, we must know the balanced chemical equation representing that said reaction.

Therefore, we can relate the moles of H_2O_2 to moles of reaction using the following stoichiometric ratio:

$$\frac{2\,\text{mol}\,H_2O_2}{1\,\text{mol}_{rxn}}$$

This conversion factor will prove to be very useful when converting units to get to our final answer. We can convert grams of H_2O_2 to moles, use this conversion factor, and determine the change in enthalpy that results.

$$5.00\,\cancel{\text{g}\,H_2O_2} \cdot \frac{1\,\text{mol}\,H_2O_2}{34.0\,\cancel{\text{g}\,H_2O_2}} = 0.147\,\text{mol}\,H_2O_2$$

Now, we will calculate the enthalpy change per mole of H_2O_2 combusted using the mole ratio we created in the previous step.

$$-196\,\frac{\text{kJ}}{\cancel{\text{mol}_{rxn}}} \cdot \frac{1\,\cancel{\text{mol}_{rxn}}}{2\,\text{mol}\,H_2O_2} = -98.0\,\text{kJ/mol}\,H_2O_2$$

Finally, we can multiply this value by the number of moles of H_2O_2 in the sample, so that our units are in kJ!

$$q = 0.147\,\frac{\cancel{\text{mol}\,H_2O_2}}{1} \cdot -98.0\,\frac{\text{kJ}}{\cancel{\text{mol}\,H_2O_2}} = \boxed{-14.4\,\text{kJ}}$$

Additionally, you might be given a problem where you need to calculate the heat released or absorbed by the reaction using more advanced concepts, e.g. limiting reactants.

Problem 6.6.4 — Stoichiometry and Thermodynamics of Reactions II

How much heat is released when 5.00 g of CH_3OH is combusted in excess $O_2(g)$?

Hint: Use the balanced chemical equation

$$CH_3OH(l) + \frac{3}{2}O_2(g) \rightarrow CO_2(g) + 2H_2O(l) \qquad \Delta H^\circ = -677\,\mathrm{kJ/mol}_{rxn}$$

In this problem, we know that CH_3OH is the limiting reactant (since oxygen is in excess). Otherwise, we would have to determine which reactant was limiting (if you need a refresher on this, review the concepts in section 4.5!). The key idea here is that the limiting reactant not only limits the amount of products formed, but it also limits the amount of heat that is absorbed or released during the reaction.

Additionally, remember that we only use the limiting reactant to carry out stoichiometry calculations. Therefore, we can set up the following:

$$5.00\,\cancel{\mathrm{g\ CH_3OH}} \cdot \frac{1\,\cancel{\mathrm{mol\ CH_3OH}}}{32.04\,\cancel{\mathrm{g\ CH_3OH}}} \cdot \frac{1\,\cancel{\mathrm{mol}_{rxn}}}{1\,\cancel{\mathrm{mol\ CH_3OH}}} \cdot \frac{-677\,\mathrm{kJ}}{1\,\cancel{\mathrm{mol}_{rxn}}} = -106\,\mathrm{kJ}$$

$\boxed{106\,\mathrm{kJ}}$ of energy is released by the reaction (which is exothermic, as indicated by the negative sign). Don't forget to take mole ratios into account when solving thermodynamics problems that involve stoichiometry. As a general rule, whenever you are given specific amounts of reactants and asked about ΔH_{rxn}, you will have to use stoichiometry to get the correct answer.

Some More Important Information For This Section

Before we move on to the next section, we will just do a quick overview of the most broad concepts covering this unit on the AP exam. Many students get caught up in the details and forget the big picture, so the following information can help you remember what's really important.

We begin with the definition of **energy**. Energy represents the ability to do work or transfer heat. Its units are typically given in joules (J) or calories (cal). There are many forms of energy that we should be familiar with, including **kinetic energy**, **potential energy**, **chemical energy**, **electrical energy**, etc.

Note 6.6.5

Energy can be converted from one form to another, but it **cannot** be created or destroyed. This statement is referred to as the First Law of Thermodynamics: in an isolated system, the total energy is always conserved.

Internal energy, E, is the sum of all the kinetic and potential energy values within a system. It is known as a **state function** (more details on this in section 6.9), which means that only current states are significant, and **not** the path taken to reach a state. The change in internal energy, ΔE, of the system is the difference between the final and initial energy states and it can be calculated as the heat added to or removed from the system, q, plus the work done on or by the system, w.

$$\boxed{\Delta E = q + w}$$

Heat, q, is the transfer of energy due to a temperature difference between two objects. As with energy, it is also measured in joules (J). The energy transfer pattern of heat is a flow from a higher-temperature object to a lower-temperature object.

Work, w, is the transfer of energy that occurs involves a **force acting over a distance** (for anyone enrolled in physics, don't forget this!) In chemistry, it is associated with the expansion and compression of a gas. For the purposes of this course, just know these two properties of work:

- **Positive work** is done when a gas is compressed, because energy is being transferred from the surroundings (everything but the gas) to the system (the gas).
- **Negative work** is done when a gas expands, releasing energy from the system (gas) to the surroundings (all other objects in the universe).

Positive and negative work also represent instances where work is done on or by the system, respectively.

The work associated with an expanding or compressing gas at constant pressure can be calculated using the following formula:

$$\boxed{w = -P\Delta V}$$

where:

- P is the pressure, usually in atmospheres (atm) and
- ΔV is the change in volume, usually in liters (L).

This type of work is known as "PV work."

Problem 6.6.6 — Internal Energy

Calculate ΔE for a system undergoing an endothermic process in which 12.6 kJ of heat flows and where 1.3 kJ of work is done by the system.

Solution: We use the equation

$$\Delta E = q + w$$

where $q = +12.6$ kJ, since the process is endothermic, and $w = -1.3$ kJ, since work is done by the system. Thus

$$\Delta E = 12.6\,\text{kJ} - 1.3\,\text{kJ} = \boxed{11.3\,\text{kJ}}$$

The system has gained 11.3 kJ of energy.

Problem 6.6.7 — PV Work

Calculate the work associated with the expansion of a gas from 37 L to 61 L at a constant external pressure of 16 atm.

Solution: For a gas at constant pressure,

$$w = -P\Delta V$$

In this case $P = 16$ atm and $\Delta V = 61 - 37 = 24$ L. Thus

$$w = -16\,\text{atm} \cdot 24\,\text{L} = \boxed{-384\,\text{L} \cdot \text{atm}}$$

Note that since the gas expands, it performs work on its surroundings.
Energy flows out of the gas, so w is a negative quantity.

Problem 6.6.8 — Internal Energy, Heat, and Work

A balloon is being inflated to its full extent by heating the air inside it. In the final stages of this process, the volume of the balloon changes from $4.00 \cdot 10^6$ L to $4.50 \cdot 10^6$ L by the addition of $1.3 \cdot 10^8$ J of energy as heat. Assuming the balloon expands against a constant pressure of 1.0 atm, calculate ΔE for this process. Use $1\,\text{L} \cdot \text{atm} = 101.3\,\text{J}$.

Solution: To calculate ΔE, we use the equation

$$\Delta E = q + w$$

Since the problem states that $1.3 \cdot 10^8$ J of energy is *added* as heat,

$$q = +1.3 \cdot 10^8\ \text{J}$$

The work done can be calculated from the equation

$$w = -P\Delta V$$

For this problem $P = 1.0$ atm and

$$\Delta V = V_{\text{final}} - V_{\text{initial}} = 4.50 \cdot 10^6\ \text{L} - 4.00 \cdot 10^6\ \text{L} = 5.0 \cdot 10^5\ \text{L}$$

As a result,

$$w = -1.0\,\text{atm} \cdot 5.0 \cdot 10^5\ \text{L} = -5.0 \cdot 10^5\ \text{L} \cdot \text{atm}$$

Note that w is negative, because the gas expands and thus does work on its surroundings.

To calculate ΔE, we must sum q and w. However, since q is given in units of J and w is given in units of $\text{L} \cdot \text{atm}$, we must change the units of work to joules:

$$w = -5.0 \cdot 10^5\ \cancel{\text{L} \cdot \text{atm}} \cdot \frac{101.3\ \text{J}}{\cancel{\text{L} \cdot \text{atm}}} = -5.1 \cdot 10^7\ \text{J}$$

Finally, we get

$$\Delta E = q + w = (+1.3 \cdot 10^8\ \text{J}) + (-5.1 \cdot 10^7\ \text{J}) = \boxed{8 \cdot 10^7\ \text{J}}$$

Since more energy q is added via heating than the gas expands doing work w, there is a net increase in the internal energy of the gas in the balloon. Thus, ΔE is positive.

The next three sections are more number-crunching heavy. So grab your calculators and get ready for some math!

§6.7 Bond Enthalpies

The **enthalpy of a bond** is the enthalpy change that results from 1 mole of a particular bond being broken in the gas phase. Since energy is ALWAYS required to break bonds, the breaking process is endothermic, so bond enthalpies are only listed as positive values.

It is also important to know that in any chemical reaction,

- Bonds may be broken, which requires an input of energy (endothermic)
- Bonds may also be formed, which releases energy (exothermic)

Definition 6.7.1

Bond energy is the potential energy that is stored in a bond.

- If negative, it is the energy released when a bond forms.
- If positive, it is the energy absorbed when a bond breaks.

Example 6.7.2

The bond energy of a $H-H$ bond in H_2 is 436 kJ/mol. This means two things:

1. 436 kJ of energy would be released when 1 mole of $H-H$ bonds is formed.
2. 436 kJ of energy would be required to break 1 mole of $H-H$ bonds.

Below is a table of some common bonds and their average enthalpies.

Bond	Bond Energy (kJ/mol)
$H-H$	436
$H-C$	414
$H-Cl$	431
$C-C$	347
$C=C$	611
$C\equiv C$	837
$C-O$	360
$C=O$	1072

Note: You don't need to memorize these values. They will be provided on questions where you will need them.

There are multiple rows with 2 carbons in a bond. Why is that?

Well, the reason is the difference in bond order associated with these carbon atoms. One dash means that it's a single bond, two dashes means that it's a double bond, while three dashes means that it's a triple bond.

A greater bond energy means that the bond requires MORE energy to break 1 mole of that bond. Clearly, if the number of bonds is greater between 2 elements, then it should be harder to break which causes it to have a higher **bond energy**.

That is why the carbon with a triple bond has a bond energy of 837 kJ while carbon with a single bond has a bond energy of 347 kJ.

It's also important to note that a shorter bond will be stronger and vice versa.

Note 6.7.3

Breaking a bond requires energy meaning it's an endothermic reaction. On the other hand, forming a bond releases energy which is why it's an exothermic reaction.

Using the bond energy table, this means that 347 kJ of energy is **required** to break 1 mole of $C - C$ bonds. This also means that 347 kJ of energy is **released** when 1 mole of $C - C$ bonds are formed.

Note 6.7.4

Please note that the terms bond energy and bond enthalpy are used interchangeably in AP Chemistry! Many students forget this, especially on the free response section of the exam.

How are Bond Enthalpies Useful to Us?

Bond energies (or bond enthalpies) measure the strength of a bond, and thus, its stability. It can help us understand how chemical systems use energy during reactions.

By knowing the average bond energies of the bonds broken and the bonds formed, we can estimate the overall enthalpy change for a reaction, ΔH_{rxn}.

Definition 6.7.5

In general, ΔH_{rxn} can be estimated from average bond energies using the formula:

$$\Delta H_{rxn} = \sum(\text{BE of bonds broken}) - \sum(\text{BE of bonds formed})$$

To make this easier to understand, bonds between atoms in the reactants are broken and reassembled to form new bonds in the products.

Understanding the above formula can be tough. That is why you must do a few practice problems below to understand how it is applied. Let's work through some problems!

Problem 6.7.6 — Bond Enthalpies I

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

Using the data in the table below, calculate the value, in kJ/mol$_{rxn}$, of the standard enthalpy change, $\Delta H°$, for the reaction at 298 K.

Bond	Bond Energy (kJ/mol)
C – C	348
C – H	413
O – O	146
O = O	498
C – O	358
C = O	799
O – H	467

Solution: Let's figure out what bonds break in the reactants. To do this, it is recommended to be proficient in drawing Lewis diagrams. That is essential to figuring out the number of bonds between each atom.

Clearly, 1 mole of CH_4 has 4 moles of hydrogen and 1 mole of carbon. Drawing a Lewis diagram makes it evident that one CH_4 molecule consists of four C – H bonds. Similarly, one molecule of O_2 consists of one O = O bond. It is important to note that there's a double bond in O_2 between the oxygen atoms, as the O – O and O = O bonds have different enthalpies. You must draw a correct Lewis diagram to avoid making a mistake. On top of this, don't forget that there are 2 moles of O_2 in this reaction!

$$\begin{aligned}\sum(\text{BE of bonds broken}) &= 4\left(\Delta H_{\text{C−H}}\right) + 2\left(\Delta H_{\text{O=O}}\right)\\ &= 4 \cdot 413 + 2 \cdot 498 = 2648 \text{ kJ/mol}_{rxn}\end{aligned}$$

Now, let's observe the bonds formed in the products. CO_2 has 2 C = O bonds.
H_2O has 2 O – H bonds. Don't forget that one mole of the reaction has 2 moles of H_2O. Thus, we must multiply the number of bonds of H_2O by its coefficient (2). One mole of this reaction will have 4 O – H bonds.

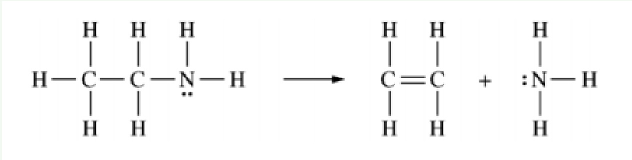
$$\begin{aligned}\sum(\text{BE of bonds formed}) &= 2\left(\Delta H_{\text{C=O}}\right) + 4\left(\Delta H_{\text{O−H}}\right)\\ &= 2 \cdot 799 + 4 \cdot 467 = 3466 \text{ kJ/mol}_{rxn}\end{aligned}$$

Finally, we will subtract these two values to get our final answer.

$$\Delta H° = \sum(\text{BE of bonds broken}) - \sum(\text{BE of bonds formed})$$

$$\Delta H° = 2648\,\text{kJ/mol}_{rxn} - 3466\,\text{kJ/mol}_{rxn} = \boxed{-818\,\text{kJ/mol}_{rxn}}$$

Problem 6.7.7 — Bond Enthalpies II
Source: 2012 AP Chemistry FRQ



A sample of $CH_3CH_2NH_2$ is placed in an insulated container, where it decomposes into ethene and ammonia according to the reaction represented above. Using the data in the table below, calculate the value, in kJ/mol$_{rxn}$, of the standard enthalpy change, $\Delta H°$, for the reaction at 298 K.

Bond	C–C	C=C	C–H	C–N	N–H
Average Bond Enthalpy (kJ/mol)	348	614	413	293	391

Solution: Let's figure out the bonds that must be broken in the reactants. Observing the Lewis diagram reveals that 5 C – H bonds, 1 C – C bond, 2 N – H bonds, and 1 C – N bond must be broken.

$$\begin{aligned}\sum(\text{BE of bonds broken}) &= 5\,(\Delta H_{\text{C}-\text{H}}) + 1\,(\Delta H_{\text{C}-\text{C}}) + 2\,(\Delta H_{\text{N}-\text{H}}) + 1\,(\Delta H_{\text{C}-\text{N}}) \\ &= 5 \cdot 413 + 1 \cdot 348 + 2 \cdot 391 + 1 \cdot 293 = 3488\,\text{kJ/mol}_{rxn}\end{aligned}$$

Now, let's figure out the bonds formed in the products. Ethene and ammonia, the two products, consist of 1 C = C bond, 4 C – H bonds, and 3 N – H bonds.

$$\begin{aligned}\sum(\text{BE of bonds formed}) &= 1\,(\Delta H_{\text{C}=\text{C}}) + 4\,(\Delta H_{\text{C}-\text{H}}) + 3\,(\Delta H_{\text{N}-\text{H}}) \\ &= 1 \cdot 614 + 4 \cdot 413 + 3 \cdot 391 = 3439\,\text{kJ/mol}_{rxn}\end{aligned}$$

Lastly, we use the bond enthalpy formula to find the enthalpy change of the reaction.

$$\begin{aligned}\Delta H° &= \sum(\text{BE of bonds broken}) - \sum(\text{BE of bonds formed}) \\ \Delta H° &= 3488\,\text{kJ/mol}_{rxn} - 3439\,\text{kJ/mol}_{rxn} = \boxed{49\,\text{kJ/mol}_{rxn}}\end{aligned}$$

Problem 6.7.8 — Bond Enthalpies III
Source: 2003 AP Chemistry FRQ

Two nitrogen atoms combine to form a nitrogen molecule, as represented by the following equation.

$$2N(g) \rightarrow N_2(g)$$

Using the table of average bond energies below, determine the enthalpy change, ΔH, for the reaction.

Bond	**Average BE** (kJ mol^{-1})
$N - N$	160
$N = N$	420
$N \equiv N$	950

Solution: This question actually stumped many students when the exam was administered. This problem is NOT asking for a simple usage of

$$\Delta H = \sum(\text{BE of bonds broken}) - \sum(\text{BE of bonds formed})$$

You must understand what's actually happening on a chemical level. We begin with 2 unstable nitrogen atoms, N and N, and when they react,, they form a stable nitrogen molecule, N_2. Note that the coefficient on N_2 is 1, so we have formed exactly ONE mole of N_2. Therefore, ΔH for this reaction is equal to the energy required to form one molecule of N_2. But how do we know which bond energy to use? For that, we will need to draw the correct Lewis structure.

This is the correct Lewis diagram for N_2, consisting of a triple bond between 2 nitrogen atoms as well as a lone pair of electrons on each of them. Therefore, we know that our answer will involve the $N \equiv N$ bond, which has an average bond enthalpy of 950 kJ/mol_{rxn}. However, the answer is NOT $950\,\text{kJ/mol}_{rxn}$. The only thing we are forgetting is the correct sign. Specifically, we need to use the fact that when chemical reactions occur, energy is required to break bonds and energy is *released* to form new bonds. Since we started with two separate N atoms but formed a $N \equiv N$ bond in N_2, energy was released in this process, making it exothermic. Remember that for exothermic processes, the sign of ΔH is *negative*, so our answer is actually $\boxed{-950\,\text{kJ/mol}_{rxn}}$.

§6.8 Enthalpy of Formation

Previously, we established that the enthalpy of reaction (ΔH_{rxn}) is the heat energy that is absorbed or released in a chemical reaction at constant pressure. Mathematically, it represents the difference in enthalpy between the products and the reactants. In this section, we will talk about the heat energy that is transferred when a substance is formed from its constituent elements.

Standard Enthalpy of Formation

The **standard enthalpy of formation** or the standard heat of formation for a compound, ΔH_f°, is change in enthalpy that occurs when 1 mole of the substance is formed by its constituent elements in their most stable states at **standard conditions** (25°C and 1 atm pressure. Essentially, this is the energy required to form a compound.

Example 6.8.1

The ΔH_f° for CO_2 can be understood as ΔH_{rxn}° for the following reaction:

$$C(s) + O_2(g) \rightarrow CO_2(g)$$

First, break down the product into its constituent elements. If the product was CO, then we are just finding the ΔH° for the reaction

$$C(g) + \frac{1}{2}O_2(g) \rightarrow CO(g)$$

since elemental oxygen is most stable as $O_2(g)$.

Note: Any pure element in its standard state will also have a ΔH_f° equal to 0, e.g. the diatomic elements (N_2, O_2, N_2, etc.) as well as metals (Al, Li, K, etc.).

Using ΔH_f° to Calculate ΔH_{rxn}°

There is a simple formula to calculate ΔH_{rxn}° from ΔH_f°, and it is in your formula sheet on the AP exam.

$$\boxed{\Delta H_{rxn}^\circ = \sum n_p \Delta H_f^\circ(\text{products}) - \sum n_r \Delta H_f^\circ(\text{reactants})}$$

where n_r and n_p are the stoichiometric coefficients on each of reactants and products, respectively.

Note 6.8.2

The standard heat of formation is in the form **products - reactants** but the formula for bond dissociation energy is in the form **reactants - products**. Ensure that you don't confuse the two. The reason for the bond dissociation energy being in this form is because the energy of bonds that are broken and formed is associated with the reactants and products, respectively, so the latter is subtracted. Fortunately, the equation for standard heat of formation is already given in your formula sheet.

Problem 6.8.3 — Standard Enthalpy of Formation I
Source: 2011 AP Chemistry FRQ

Hydrogen gas burns in air according to the equation below.

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$$

Calculate the standard enthalpy change, ΔH°_{298}, for the reaction represented by the equation above.
(The molar enthalpy of formation, ΔH°_f, for $H_2O(l)$ is -285.8 kJ mol^{-1} at 298 K.)

Solution: The enthalpy change is equal to the bond energy of bonds broken minus the bond energy of bonds formed, accounting for stoichiometric coefficients.

We need to apply the formula

$$\Delta H^\circ_{rxn} = \sum n_p \Delta H^\circ_f(\text{products}) - \sum n_r \Delta H^\circ_f(\text{reactants})$$

Essentially, the standard enthalpy change for this particular reaction is equal to

$$\Delta H^\circ_{298} = 2(\Delta H^\circ_f(H_2O)) - 2(\Delta H^\circ_f(H_2)) - \Delta H^\circ_f(O_2)$$

Because hydrogen and oxygen exist as $H_2(g)$ and $O_2(g)$ (their standard states), respectively, their ΔH°_f values are both zero. Therefore, ΔH°_{298} is simply equal to twice the molar enthalpy of formation for $H_2O(l)$.

$$\Delta H^\circ_{298} = 2 \cdot \Delta H^\circ_f(H_2O) = 2 \cdot -285.8\text{ kJ mol}^{-1} = \boxed{-571.6\text{ kJ mol}^{-1}}$$

Problem 6.8.4 — Standard Enthalpy of Formation II

Using the standard enthalpies of formation in the table below, calculate ΔH°_{rxn} for the combustion of butane (shown below) in kJ mol^{-1}.

$$2C_4H_{10}(l) + 13O_2(g) \rightarrow 8CO_2(g) + 10H_2O(g)$$

Compound	ΔH°_f (kJ mol^{-1})
$C_4H_{10}(l)$	-147.3
$H_2O(g)$	-241.8
$H_2O(l)$	-285.8
$CO_2(g)$	-393.5

Solution: For all enthalpy of reaction problems, we will apply the formula

$$\Delta H^\circ_{rxn} = \sum n_p \Delta H^\circ_f(\text{products}) - \sum n_r \Delta H^\circ_f(\text{reactants})$$

In order to earn credit on the AP exam, you MUST write the formula that you are using!

Our strategy will be the same, plug in the corresponding ΔH°_f values into the equation as well as multiply by stoichiometric coefficients. However, we need to be careful here. We are given two different ΔH_f° values for H_2O, so we must pick the correct one. Our chemical reaction involves *water vapor*, not *liquid water*, so we must use ΔH_f° for $H_2O(g)$. Always beware of this; College Board likes to play tricks on us!

Additionally, ΔH_f° for $O_2(g)$ is 0 because this this is oxygen in pure elemental form.

Finally, we follow the standard approach when using this formula:

$$\Delta H_{rxn}^\circ = (8 \cdot -393.5) + (10 \cdot -241.8) - (2 \cdot -147.3) - (13 \cdot 0) = \boxed{-5271.4\,\mathrm{kJ\,mol^{-1}}}$$

§6.9 Hess's Law

In this section, we will introduce the concept of heat as a *state function*, and how the enthalpy of reaction can be broken into a series of steps. Moreover, it demonstrates how enthalpy changes are affected when reactions are reversed, combined, and/or multiplied.

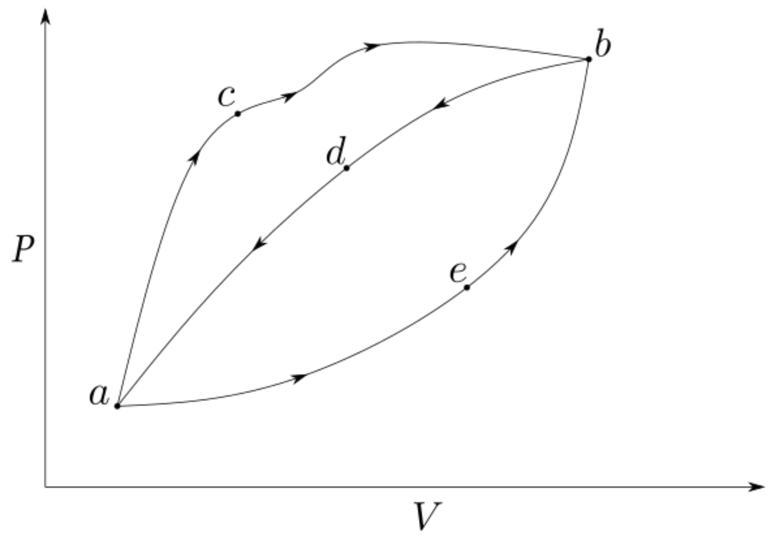
State Functions

Hess's Law is based on the fact that **enthalpy is a state function**. No matter the process you go from reactants to products, the overall enthalpy of reaction, ΔH_{rxn} will be the same. This means that we can use the **enthalpy of formation** for various reactions, manipulate them to get a single reaction, and find the enthalpy change. It's like solving a puzzle, and it can be pretty fun!

Pathway Dependent vs. Pathway Independent

In simple terms, a **pathway** is a route which a process takes. Typically, whether or not these processes are pathway-dependent or pathway-independent is applied to functions. If the result of the process depends on steps by which it was performed, it is pathway-dependent. Otherwise, it is pathway-independent.

The main takeaway from this discussion is to apply it to state functions. Because only the initial and final states of the system are of importance, state functions are **pathway-independent**. More examples include energy, enthalpy, pressure, volume, and temperature.



For this system, the diagram can illustrate that the net changes to the properties moving from states a to b are the same regardless of the shape of the path taken.

Hess's Law - Rules

There are certain rules we must follow in order to have correct enthalpy values when manipulating reactions to generate our requested ΔH_{rxn} value.

1. When a reaction is reversed, ΔH is constant in magnitude, but its sign is reversed.
2. If you multiply the equation by some factor n, ΔH_{rxn} is also multiplied by n.
3. If multiple reactions are combined to obtain an overall reaction, the individual enthalpy changes of each reaction are added to obtain the ΔH_{rxn} value for the overall reaction.

Let us work through two problems. I will also incorporate my thought processes so that you can learn the strategy for answering these questions.

Problem 6.9.1 — Hess's Law I

Thermodynamic data for four different reactions are summarized below:

$$\begin{aligned} C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(l) \qquad & \Delta H^\circ = -1411\,\text{kJ/mol}_{rxn} \\ C_2H_6(g) + \frac{7}{2}O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g) \qquad & \Delta H^\circ = -1561\,\text{kJ/mol}_{rxn} \\ 2H_2(g) + O_2(g) \rightarrow 2H_2O(l) \qquad & \Delta H^\circ = -572\,\text{kJ/mol}_{rxn} \\ C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g) \qquad & \Delta H^\circ = ? \end{aligned}$$

Using the information above, determine the value of ΔH°_{rxn} for reaction 4.

Solution: We need to manipulate the first three chemical equations so that they add up to the overall equation for the last reaction. Remember the rules for Hess's Law that were outlined in the previous page.

The first equation has $C_2H_4(g)$ as a reactant, and so does reaction 4. So we can leave this equation and its $\Delta H°$ value unchanged.

Additionally, the equation for reaction 2 contains $C_2H_6(g)$ as a reactant, but the equation for reaction 4 has $C_2H_6(g)$ as a product. Therefore, we need to reverse the equation for reaction 2 and change the sign of its $\Delta H°$ value:

$$2CO_2(g) + 3H_2O(l) \rightarrow C_2H_6(g) + \frac{7}{2}O_2(g) \qquad \Delta H° = 1561\,\text{kJ/mol}_{rxn}$$

The equation for reaction 3 has $H_2(g)$ as a reactant, which is consistent with the equation for reaction 4. However, the coefficient for $H_2(g)$ in the former reaction is 2, while it is 1 in the latter reaction. Therefore, we need to multiply the equation for reaction 3 and its $\Delta H°$ value by $\frac{1}{2}$:

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) \qquad \Delta H° = \frac{1}{2}(-572\,\text{kJ/mol}_{rxn}) = -286\,\text{kJ/mol}_{rxn}$$

Finally, adding all three equations and their manipulated $\Delta H°$ values, we get

$$\begin{aligned}
C_2H_4(g) + \cancel{3O_2(g)} &\rightarrow \cancel{2CO_2(g)} + \cancel{2H_2O(l)} & \Delta H° &= -1411\,\text{kJ/mol}_{rxn}\\
\cancel{2CO_2(g)} + \cancel{3H_2O(l)} &\rightarrow C_2H_6(g) + \cancel{\tfrac{7}{2}O_2(g)} & \Delta H° &= 1561\,\text{kJ/mol}_{rxn}\\
H_2(g) + \cancel{\tfrac{1}{2}O_2(g)} &\rightarrow \cancel{H_2O(l)} & \Delta H° &= -286\,\text{kJ/mol}_{rxn}\\
\hline
C_2H_4(g) + H_2(g) &\rightarrow C_2H_6(g) & &\boxed{\Delta H°_{rxn} = -136\,\text{kJ/mol}_{rxn}}
\end{aligned}$$

Problem 6.9.2 — Hess's Law II

Consider the reaction represented by the equation

$$I_2(s) + 3Cl_2(g) \rightarrow 2ICl_3(g)$$

Based on the thermodynamic data for two reactions below, what is the value of the enthalpy change per mole of $ICl_3(s)$ that is produced in the reaction?

$$\begin{aligned}
I_2(g) + 3Cl_2(g) &\rightarrow 2ICl_3(s) & \Delta H° &= -214\,\text{kJ/mol}_{rxn}\\
I_2(g) &\rightarrow I_2(s) & \Delta H° &= -38\,\text{kJ/mol}_{rxn}
\end{aligned}$$

Solution: As for all Hess's law problems, we need to manipulate the equations given to us so that they add up to our target equation. Again, keep in mind for manipulating equations and the corresponding $\Delta H°$ values.

The first equation contains 2 mol of $ICl_3(s)$ as a product, which is consistent with our target equation. Therefore, we will leave the equation and its ΔH° value unchanged.

Meanwhile, the second equation contains 1 mol of $I_2(s)$ as a product, while the target equation contains it as a reactant. Therefore, we will flip this equation and reverse the sign of its enthalpy change:

$$I_2(s) \rightarrow I_2(g) \qquad \Delta H^\circ = -(-38\,\text{kJ/mol}_{rxn}) = 38\,\text{kJ/mol}_{rxn}$$

Finally, adding all three equations and their ΔH° values, we get

$$\cancel{I_2(g)} + 3Cl_2(g) \rightarrow 2ICl_3(s) \qquad \Delta H^\circ = -214\,\text{kJ/mol}_{rxn}$$

$$I_2(s) \rightarrow \cancel{I_2(g)} \qquad \Delta H^\circ = 38\,\text{kJ/mol}_{rxn}$$

$$I_2(s) + 3Cl_2(g) \rightarrow 2ICl_3(s) \qquad \Delta H^\circ = -176\,\text{kJ/mol}_{rxn}$$

However, the overall change in enthalpy of this reaction is associated with the formation of TWO moles of $ICl_3(s)$, due to the stoichiometric coefficients in the balanced chemical reaction. To find the enthalpy change for ONE mole of $ICl_3(s)$, we have to divide this value by 2.

Thus, the value of the change in enthalpy per mole of $ICl_3(s)$ formed is $\boxed{-88\,\text{kJ}}$.

§6.10 Practice Problems

Problem 6.10.1 — 1995 AP Chemistry FRQ

Propane, C_3H_8, is a hydrocarbon that is commonly used as fuel for cooking.

(a) Write a balanced equation for the complete combustion of propane gas, which yields $CO_2(g)$ and $H_2O(l)$.

(b) Calculate the volume of air at 30°C and 1.00 atmosphere that is needed to burn completely 10.0 grams of propane. Assume that air is 21.0 percent O_2 by volume.

(c) The heat of combustion of propane is -2220.1 kJ/mol. Calculate the heat of formation, ΔH_f° of propane given that ΔH_f° of $H_2O(l) = -285.3$ kJ/mol and ΔH_f° of $CO_2(g) = -393.5$ kJ/mol.

(d) Assuming that all of the heat evolved in burning 30.0 grams of propane is transferred to 8.00 kilograms of water (specific heat $= 4.18\ \mathrm{J/g \cdot K}$), calculate the increase in temperature of water.

Solution to part a: The unbalanced chemical equation will be written as

$$\mathrm{C_3H_8(g) + O_2(g) \rightarrow CO_2(g) + H_2O(l)}$$

First, we notice that there are 3 carbon atoms on the reactants side and 1 in the products. Therefore, we will multiply $CO_2(g)$ by 3. Next, there are 8 hydrogen atoms on the reactants side and 2 in the products. We multiply $H_2O(l)$ by 4. At this point,

$$\mathrm{C_3H_8(g) + O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)}$$

All elements have been balanced except for oxygen. There are 2 O atoms on the reactants side and 10 on the products. We can multiply O_2 by 5 to account for this. Finally, the balanced equation for the combustion of propane gas is

$$\boxed{\mathrm{C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)}}$$

Solution to part b: First, we calculate the number of moles of O_2 needed to fully react with 10.0 g of C_3H_8. Using stoichiometry, we have

$$10.0\,\cancel{\mathrm{g\,C_3H_8}} \cdot \frac{1\,\cancel{\mathrm{mol\,C_3H_8}}}{44.1\,\cancel{\mathrm{g\,C_3H_8}}} \cdot \frac{5\,\mathrm{mol\,O_2}}{1\,\cancel{\mathrm{mol\,C_3H_8}}} = 1.13\,\mathrm{mol\,O_2}$$

Now, we can calculate the volume of O_2 using the Ideal Gas Law:

$$V = \frac{nRT}{P} = \frac{(1.13\,\cancel{\mathrm{mol}})(0.0821\,\mathrm{L}\,\cancel{\mathrm{atm}}\,\cancel{\mathrm{mol^{-1}}}\,\cancel{\mathrm{K^{-1}}})(303\,\cancel{\mathrm{K}})}{1.00\,\cancel{\mathrm{atm}}} = 28.1\,\mathrm{L\,O_2}$$

Finally, air is 21.0 percent O_2 by volume, so we can convert from L of O_2 to L of air:

$$28.1\,\cancel{\mathrm{L\,O_2}} \cdot \frac{100\,\mathrm{L\,air}}{21.0\,\cancel{\mathrm{L\,O_2}}} = \boxed{134\,\mathrm{L\,air}}$$

Solution to part c: The formula that gives the standard enthalpy change of a reaction in terms of standard heats of formation of the reaction species is

$$\Delta H^\circ_{rxn} = \sum n_p \Delta H^\circ_f \text{ (products)} - \sum n_r \Delta H^\circ_f \text{ (reactants)}$$

The overall standard enthalpy change for the reaction is the heat of combustion of propane, or $\Delta H^\circ_{rxn} = -2220.1$ kJ/mol. We will set up the equation to isolate for ΔH°_f for C_3H_8.

We recognize that O_2(g) is the stable form of elemental oxygen, so it has a standard heat of formation value of 0 kJ/mol. Hence,

$$\Delta H^\circ_{rxn} = 3 \cdot \Delta H^\circ_f \text{ (for } CO_2\text{(g))} + 4 \cdot \Delta H^\circ_f \text{ (for } H_2O\text{(l))} - \Delta H^\circ_f \text{ (for } C_3H_8\text{)}$$

Isolating for ΔH°_f (for C_3H_8(g)), we have

$$\Delta H^\circ_f \text{ (for } C_3H_8\text{(g))} = 3 \cdot \Delta H^\circ_f \text{ (for } CO_2\text{(g))} + 4 \cdot \Delta H^\circ_f \text{ (for } H_2O\text{(l))} - \Delta H^\circ_{rxn}$$

Plugging in values, we find that the standard heat of formation of propane is

$$3 \cdot -393.5 \text{ kJ/mol} + 4 \cdot -285.3 \text{ kJ/mol} - (-2220.1 \text{ kJ/mol}) = \boxed{-101.6 \text{ kJ/mol}}$$

Solution to part d: We need to calculate the amount of heat that is evolved when 30.0 g of C_3H_8 is combusted. This will involve the following stoichiometry:

$$30.0 \cancel{\text{g } C_3H_8} \cdot \frac{1 \cancel{\text{mol } C_3H_8}}{44.1 \cancel{\text{g } C_3H_8}} \cdot \frac{2220.1 \text{ kJ}}{1 \cancel{\text{mol } C_3H_8}} = 1.51 \cdot 10^3 \text{ kJ}$$

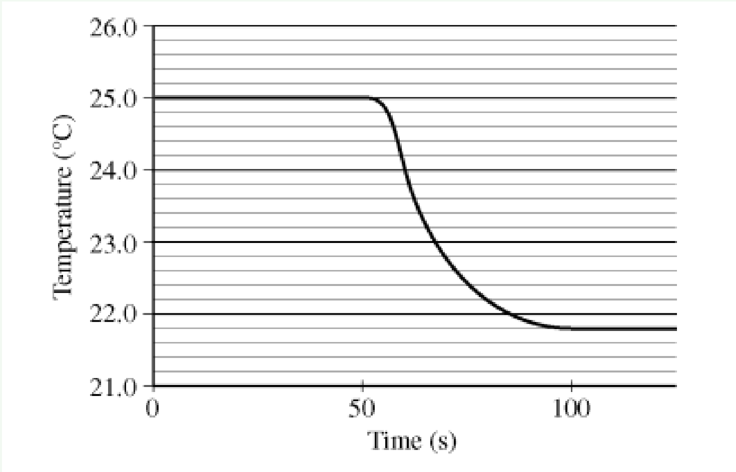
According to the 1st Law of Thermodynamics, the heat evolved in burning 30.0 grams of propane was fully transferred to 8.00 kilograms of water. Therefore, we use this value as q and apply the equation $q = mc\Delta T$ to calculate ΔT, the temperature increase of water.

$$q = mc\Delta T \therefore \Delta T = \frac{q}{mc}$$

$$\Delta T = \frac{1.51 \cdot 10^6 \cancel{\text{J}}}{(8000 \cancel{\text{g}})(4.18 \cancel{\text{J}}/\cancel{\text{g}} \cdot \text{K})} = \boxed{45.1 \text{ K}}$$

Problem 6.10.2 — 2010 AP Chemistry FRQ (Excerpt)

A student performs an experiment to determine the molar enthalpy of solution of urea, H_2NCONH_2. The student places 91.95 g of water at 25°C into a coffee cup calorimeter and immerses a thermometer in the water. After 50 s, the student adds 5.13 g of solid urea, also at 25°C, to the water and measures the temperature of the solution as the urea dissolves. A plot of the temperature data is shown in the graph below.



(a) Determine the change in temperature of the solution that results from the dissolution of the urea.

(b) According to the data, is the dissolution of urea in water an endothermic process or an exothermic process? Justify your answer.

(c) Assume that the specific heat capacity of the calorimeter is negligible and that the specific heat capacity of the solution of urea and water is 4.2 J g^{-1} $°C^{-1}$ throughout the experiment.

(i) Calculate the heat of dissolution of the urea in joules.
(ii) Calculate the molar enthalpy of solution, ΔH°_{soln}, of urea in kJ mol^{-1}.

Solution to part a: Before its dissolution, the urea sample has an initial temperature of 25.0°C. After the urea has fully dissolved, the final temperature of the solution is 21.8°C. The temperature change of the resulting solution is thus

$$\Delta T = \text{final temperature} - \text{initial temperature} = 21.8°\text{C} - 25.0°\text{C} = \boxed{-3.2°\text{C}}$$

Solution to part b: In this scenario, urea represents the *system*, while the resulting solution represents the *surroundings*. Because the temperature of the solution decreases, heat is transferred from the surroundings to the system, so the dissolution of urea in water is $\boxed{\text{endothermic}}$.

Solution to part c(i): Assuming an isolated system and that the specific heat of the calorimeter is negligible, the sum of the heat of dissolution, q_{soln}, and the change in heat energy of the solution must equal 0. This is because heat energy of an isolated system (assuming no external forces/interactions) is always conserved.

$$q_{soln} + m_{soln}c\Delta T = 0 \therefore q_{soln} = -m_{soln}c\Delta T$$
$$m_{soln} = 5.13\text{ g} + 91.95\text{ g} = 97.08\text{ g}$$
$$q_{soln} = -\left(97.08\text{ g}\right)\left(4.2\text{ J g}^{-1}\,{}^\circ\text{C}^{-1}\right)\left(-3.2^\circ\text{C}\right) = \boxed{1.3\cdot 10^3\text{ J}}$$

Solution to part c(ii): By definition, the enthalpy change of the solution per one mole of solute is equal to the heat gained by the solution (endothermic) divided by the number of moles of solute:

$$\Delta H^\circ_{soln} = \frac{+q_{soln}}{\text{mol solute}}$$

We will proceed with the following calculations:

$$\text{molar mass of urea} = 4\,(1.0) + 2\,(14.0) + 12.0 + 16.0 = 60.0\text{ g/mol}$$
$$\text{moles of urea} = \frac{5.13\text{ g}}{60.0\text{ g/mol}} = 0.0855\text{ mol}$$
$$\Delta H^\circ_{soln} = \frac{1.3\cdot 10^3\text{ J}}{0.0855\text{ mol}} = 1.5\cdot 10^4\text{ J mol}^{-1} = \boxed{15\text{ kJ mol}^{-1}}$$

Problem 6.10.3 — 2013 AP Chemistry FRQ

$$MgO(s) + 2H^+(aq) \rightarrow Mg^{2+}(aq) + H_2O(l)$$

A student was assigned the task of determining the enthalpy change for the reaction between solid MgO and aqueous HCl represented by the net ionic equation above. The student uses a polystyrene cup calorimeter and performs four trials. Data for each trial are shown in the table below.

Trial	Volume 1.0 M HCl	Mass MgO Added	Initial Temp	Final Temp
1	100.0 mL	0.25 g	25.5°C	26.5°C
2	100.0 mL	0.50 g	25.0°C	29.1°C
3	100.0 mL	0.25 g	26.0°C	28.1°C
4	100.0 mL	0.50 g	24.1°C	28.1°C

(a) Which is the limiting reactant in all four trials, HCl or MgO? Justify your answer.

(b) The data in one of the trials is inconsistent with the data in the other three trials. Identify the trial with inconsistent data and draw a line through the data from that trial in the table above. Explain how you identified the inconsistent data.

For parts (c) and (d), use the data from one of the three trials (i.e. not from the trial you identified in part (b) above). Assume the calorimeter has a negligible heat capacity and that the specific heat of the contents of the calorimeter is $4.18\ \text{J}/(\text{g} \cdot^\circ \text{C})$. Assume that the density of the HCl(aq) is 1.0 g/mL.

(c) Calculate the magnitude of q, the thermal energy change, when the MgO was added to the 1.0 M HCl(aq). Include units with your answer.

(d) Determine the student's experimental value of ΔH° for the reaction between MgO and HCl in units of kJ/mol_{rxn}.

(e) Enthalpies of formation for substances involved in the reaction are shown in the table below. Using the information in the table, determine the accepted value of ΔH° for the reaction between MgO(s) and HCl(aq).

Substance	ΔH_f° (kJ/mol)
$MgO(s)$	-602
$H_2O(l)$	-286
$H^+(aq)$	0
$Mg^{2+}(aq)$	-467

(f) The accepted value and the experimental value do not agree. If the calorimeter leaked heat energy to the environment, would it help account for the discrepancy between the values? Explain.

Solution to part a: For these problems, it is best to start by determining the number of moles for each reactant. We can use the formula $n = MV$ to calculate the number of moles of HCl, and the molar mass of MgO to calculate the number of moles of MgO.

$$0.100\,\cancel{L} \cdot \frac{1.0\,\text{mol HCl}}{1.0\,\cancel{L}} = 0.10\,\text{mol HCl}$$

$$0.50\,\text{g}\,\cancel{\text{MgO}} \cdot \frac{1\,\text{mol MgO}}{40.30\,\text{g}\,\cancel{\text{MgO}}} = 0.0124\,\text{mol MgO}$$

According to the stoichiometry of the equation, 2 moles of H^+ react for every 1 mole of MgO. Therefore, only $2 \cdot 0.0124\,\text{mol} = 0.025\,\text{mol HCl}$ is needed to fully react with MgO, so HCl is in excess and $\boxed{\text{MgO}}$ is limiting.

Solution to part b: Recall that heat is an *extensive property*, and depends on the amount of substance present. This means that each trial should have an equivalent ratio of $\Delta T/(\text{mass MgO})$ as temperature change should be proportional to the amount of *limiting reactant* present. We can see that this ratio in trial 1 is half of that in trials 2, 3, and 4. Therefore, $\boxed{\text{trial 1}}$ is inconsistent with the other trials.

Solution to part c: Let us use trial 2.

We apply the formula for exchange of heat energy:

$$q = mc\Delta T$$

However, we should be careful regarding our value of m. This represents the total mass: the sum of the mass of HCl (volume multiplied by density) and the mass of MgO.

$$q_{calorimeter} = \left[\left(100.0\,\text{mL} \cdot \frac{1.0\,\text{g}}{\text{mL}}\right) + 0.50\,\text{g}\right]\left(\frac{4.18\,\text{J}}{\text{g} \cdot {}^\circ\text{C}}\right)(4.1^\circ\text{C}) = 1700\,\text{J} = \boxed{1.7\,\text{kJ}}$$

Solution to part d: We will use the 1st Law of Thermodynamics to solve this problem.

Assuming that no heat is lost to the surroundings, the heat gained by the reaction is equal to the heat lost by the calorimeter, so $q_{rxn} = -q_{calorimeter}$.

We know that the limiting reactant, MgO, will limit the enthalpy of reaction, ΔH°. Since the units of q are given in kJ, we need to divide by the number of moles of MgO to calculate ΔH° in kJ/mol_{rxn}.

$$\Delta H^\circ_{rxn} = \frac{-q_{rxn}}{n_{rxn}} = \frac{-1.7\,\text{kJ}}{\left(0.50\,\text{g}\,\cancel{\text{MgO}} \cdot \frac{1\,\cancel{\text{mol MgO}}}{40.30\,\cancel{\text{g MgO}}} \cdot \frac{1\,\text{mol}_{rxn}}{1\,\cancel{\text{mol MgO}}}\right)} = \boxed{-140\,\text{kJ/mol}_{rxn}}$$

Solution to part e: This questions requires a simple use of the equation

$$\Delta H^\circ = \sum n_p \Delta H_f^\circ\,(\text{products}) - \sum n_r \Delta H_f^\circ\,(\text{reactants})$$

Make sure you pay attention to the coefficients for all reactants and products.

Finally, we just plug in to find the accepted value of the enthalpy change as

$$\Delta H^\circ = [-467\,\text{kJ/mol}_{rxn} + (-286\,\text{kJ/mol}_{rxn})] - [-602\,\text{kJ/mol}_{rxn} + 2(0)\,\text{kJ/mol}_{rxn}]$$
$$\Longrightarrow \boxed{-151\,\text{kJ/mol}_{rxn}}$$

Solution to part f: Notice that the experimentally determined value of ΔH° is greater (less negative) than the accepted value, which we calculated in part (e). If heat had leaked outside the calorimeter, it would account for the discrepancy because the calculated value of q would be $\boxed{\text{smaller}}$, causing a *less negative* value of ΔH°.

Problem 6.10.4 — 2016 AP Chemistry FRQ

A student investigates the enthalpy of solution, ΔH_{soln}, for two alkali metal halides, LiCl and NaCl. In addition to the salts, the student has access to a calorimeter, a balance with a precision of ±0.1 g, and a thermometer with a precision of ±0.1°C.

(a) To measure ΔH_{soln} for LiCl, the student adds 100.0 g of water initially at 15.0°C to a calorimeter and adds 10.0 g of LiCl(s), stirring to dissolve. After the LiCl dissolves completely, the maximum temperature reached by the solution is 35.6°C.

(i) Calculate the magnitude of the heat absorbed by the solution during the dissolving process, assuming that the specific heat capacity of the solution is 4.18 J/(g ·° C). Include units with your answer.
(ii) Determine the value of ΔH_{soln} for LiCl in kJ/mol$_{rxn}$.

To explain why ΔH_{soln} for NaCl is different than that for LiCl, the student investigates factors that affect ΔH_{soln} and finds that ionic radius and lattice enthalpy (which can be defined by the ΔH associated with the separation of a solid crystal into gaseous ions) contribute to the process. The student consults references and collects the data shown in the table below.

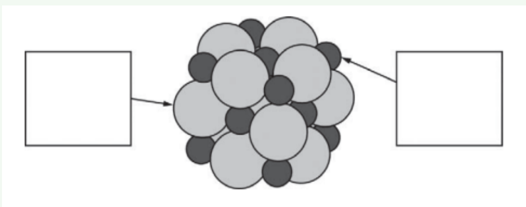
Ion	Ionic Radius (pm)
Li^+	76
Na^+	102

(b) Write the complete electron configuration for the Na^+ ion in the ground state.

(c) Using principles of atomic structure, explain why the Na^+ ion is larger than the Li^+ ion.

(d) Which salt, LiCl, or NaCl, has the greater lattice enthalpy? Justify your answer.

(e) Below is a representation of a portion of a crystal of LiCl. Identify the ions in the representation by writing the appropriate formulas (Li^+ or Cl^-) in the boxes below.



(f) The lattice enthalpy of LiCl is positive, indicating that it takes energy to break the ions apart in LiCl. However, the dissolution of LiCl in water is an exothermic process. Identify all particle-particle interactions that contribute significantly to the dissolution process being exothermic. For each interaction, include the particles that interact as well as the specific type of intermolecular force between those particles.

Solution to part a(i): The initial temperature of the solution is 15.0°C and the final temperature is 35.6°C. Therefore, we can proceed with the following.

$$q = mc\Delta T = (110.0\,\text{g})(4.18\,\text{J}/(\text{g}\cdot^\circ\text{C}))(35.6^\circ\text{C} - 15.0^\circ\text{C}) = 9470\,\text{J} = \boxed{9.47\,\text{kJ}}$$

Note: the TOTAL mass is the combined mass of both the water and LiCl(s), so we used

$$m = 100.0\,\text{g} + 10.0\,\text{g} = 110.0\,\text{g}$$

in the above calculation for q.

Solution to part a(ii): Since the temperature of the solution increases, the reaction with LiCl(s) with water is exothermic, so ΔH° must be negative.

The final answer contains units of moles, so we convert from grams to moles of LiCl:

$$10.0\,\cancel{\text{g LiCl}} \cdot \frac{1\text{ mol LiCl}}{42.39\,\cancel{\text{g LiCl}}} = 0.236\text{ mol LiCl}$$

Finally, we have

$$\Delta H^\circ = -\frac{q_{rxn}}{n_{rxn}} = \frac{-9.47\,\text{kJ}}{0.236\,\cancel{\text{mol LiCl}}} \cdot \frac{1\,\cancel{\text{mol LiCl}}}{1\text{ mol}_{rxn}} = \boxed{-40.1\,\text{kJ/mol}_{rxn}}$$

Solution to part b: Since Na only requires one electron to be removed to achieve a stable octet of 8 valence electrons, the electron configuration of Na^+ should represent a stable octet, i.e. it should parallel the noble gas closest to it on the periodic table, which is neon (Ne). With 10 valence electrons, its ground-state electron configuration is

$$\boxed{1s^2 2s^2 2p^6}$$

Solution to part c: The Na^+ ion is larger than the Li^+ ion because its valence electrons are located in a higher energy level than those in Li^+. On average, electrons at higher energy levels are farther away from the nucleus, so the radius of Na^+ exceeds that of Li^+.

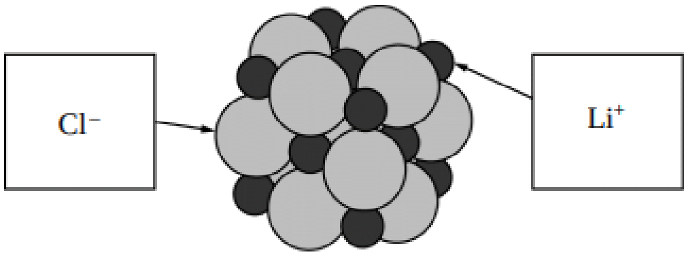
Solution to part d: The salt with more lattice enthalpy is the one with stronger forces of attraction between its cations and anions.

This is the idea of Coulomb's law, which states that the electrostatic force between two charged particles is directly proportional to the magnitudes of their charges, and inversely proportional to their distance from each other. Between LiCl and NaCl, their cations and anions have the same set of charges, $\{-1, 1\}$, but the Li^+ ion is smaller than the Na^+ ion, so the bond length in LiCl will be shorter. The attractions between ions in $\boxed{\text{LiCl}}$ are stronger than in NaCl, which results in an increased lattice enthalpy.

Solution to part e: To pick which slot better represents the Li^+ ion vs. the Cl^-

ion, we will need to compare their radii. Using periodic trends, we find that the Cl^- ion is larger than the Li^+ ion, because the former's valence electrons are located further away from the nucleus.

Thus, the LiCl crystal should be visually represented as

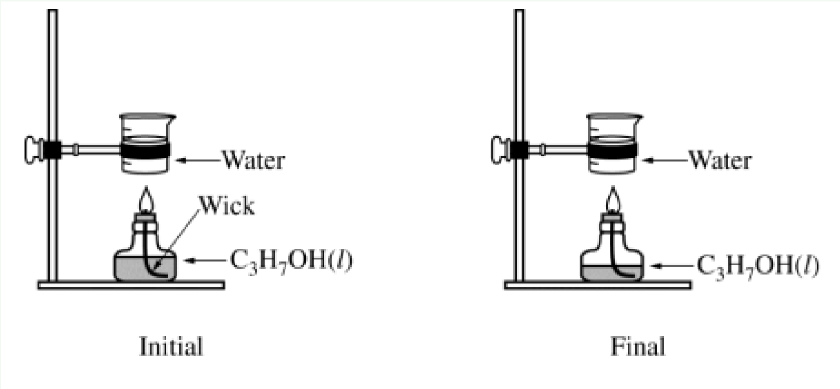


Solution to part f: Recall that ion-dipole forces result from interactions between cations and anions with the corresponding partial negative and partial positive ends of water, when an ionic compound is dissolved. More specifically, for LiCl, the Li^+ ions and Cl^- interact with polar water molecules; the former is attached to the partial negative end of oxygen and the latter is attached to the partial positive end of hydrogen.

Problem 6.10.5 — 2017 AP Chemistry FRQ

$$2C_3H_7OH(l) + 9O_2(g) \rightarrow 6CO_2(g) + 8H_2O(g)$$

A student performs an experiment to determine the enthalpy of combustion of 2-propanol, $C_3H_7OH(l)$, which combusts in oxygen according to the equation above. The student heats a sample of water by burning some of the $C_3H_7OH(l)$ that is in an alcohol burner, as represented below. The alcohol burner uses a wick to draw liquid up into the flame. The mass of $C_3H_7OH(l)$ combusted is determined by weighing the alcohol burner before and after combustion.



Data from the experiment are given in the table below.

Mass of $C_3H_7OH(l)$ combusted	0.55 g
Mass of water heated	125.00 g
Initial temperature of water	22.0°C
Final temperature of water	51.1°C
Specific heat of water	$4.18\ \mathrm{J/(g \cdot ^\circ C)}$

(a) Calculate the magnitude of heat energy, in kJ, absorbed by the water. (Assume that the energy released from the combustion is completely transferred to the water.)

(b) Based on the experimental data, if one mole of $C_3H_7OH(l)$ is combusted, how much heat, in kJ, is released? Report your answer with the correct number of significant figures.

(c) A second student performs the experiment using the same mass of water at the same initial temperature. However, the student uses an alcohol burner containing $C_3H_7OH(l)$ that is contaminated with water, which is miscible with $C_3H_7OH(l)$. The difference in mass of the alcohol burner before and after the combustion in this experiment is also 0.55 g. Would the final temperature of the water in the beaker heated by the alcohol burner in this experiment be greater than, less than, or equal to the final temperature of the water in the beaker in the first student's experiment? Justify your answer.

Solution to part a: We will use the formula $q = mc\Delta T$. The mass of the water is 125.00 g, its specific heat capacity is $4.18\ \mathrm{J/(g \cdot ^\circ C)}$, and it is heated from a temperature of 22.0°C to 51.1°C (an increase in temperature, so q is positive).

Thus, we have the following:

$$q = mc\Delta T = (125.00\text{ g})(4.18\text{ J/(g}\cdot^\circ\text{ C))}(51.1^\circ\text{C} - 22.0^\circ\text{C}) = 15200\text{ J} = \boxed{15.2\text{ kJ}}$$

Solution to part b: Keep in mind that the 15.2 kJ of heat energy absorbed by the water is equivalent to the heat content lost by the $C_3H_7OH(l)$ as it was combusted, according to the 1st Law of Thermodynamics.

Thus, we can set up the following:

$$1\,\cancel{\text{mol } C_3H_7OH} \cdot \frac{60.09\,\cancel{\text{g } C_3H_7OH}}{1\,\cancel{\text{mol } C_3H_7OH}} \cdot \frac{15.2\text{ kJ}}{0.55\,\cancel{\text{g } C_3H_7OH}} = 1661 \therefore \boxed{1.7 \cdot 10^3\text{ kJ}}$$

to account for the correct number of significant figures.

Solution to part c: If the alcohol burner contained $C_7H_3OH(l)$ that was contaminated by water, then the mass of $C_3H_7OH(l)$ combusted will be less than in the previous experiment (0.55 g). This follows from the equation $q = mc\Delta T$. Thus, the final temperature measured by the second student would be $\boxed{\text{less than}}$ that measured by the first student.

Alternatively, you could say that combusting the contaminated sample would require a significant portion of heat energy to vaporize the water present in the sample, rather than to increase the average speed of $CH_3H_7OH(l)$ molecules (measured by temperature).

7 Equilibrium

This unit describes and explains the concept of chemical equilibrium. We will learn many interesting topics such as reversible reactions, equilibrium constant, Le Châtelier's principle, solubility equilibria, ICE tables, and more.

§7.1 Introduction to Equilibrium

So far, we assumed that all reactions proceeded to completion, i.e. reactants were fully consumed and converted into products.

$$\text{reactants} \rightarrow \text{products}$$

However, most chemical processes do *not* actually proceed to completion, but they reach a state of what is known as chemical equilibrium.

> **Definition 7.1.1**
> **Chemical equilibrium** is a state in which the rates of forward and reverse reactions are equal and the concentrations of reactants and products remain constant.

Many chemical processes are **reversible**. They can occur in two directions, the forward direction or the reverse direction. The direction which is favored depends on a number of factors that we will learn about later.

This reaction equation is a better description for most chemical processes.

$$\text{reactants} \rightleftharpoons \text{products}$$

Here's what the equilibrium arrow consists of, and what these components mean:

- The left-to-right arrow describes the FORWARD reaction, where reactants are consumed to form products.
- The right-to-left arrow describes the REVERSE reaction, where products are converted back into reactants.

This implies that the reactants are *in equilibrium* with the products.

§7.2 Direction of Reversible Reactions

Recall from the previous section that when the rates of the forward and reverse reactions are equal, the reaction system is said to be in equilibrium. However, what happens when the rate in one direction is greater than in the other?

Forward Reaction Favored

For a reversible reaction, if the rate of the forward reaction is greater than the rate of the reverse reaction, then the forward reaction is **favored**. Reactants are converted to products *more than* products are converted back to reactants.

Reverse Reaction Favored

For a reversible reaction, if the rate of the reverse reaction is greater than the rate of the reverse reaction, then the reverse reaction is **favored**. Products are converted back to reactants *more than* reactants are converted to products.

Eventually, when equilibrium is reached, neither the forward nor reverse reaction is favored, since the forward and reverse reaction rates equalize over time.

Important Note: In most cases, we may observe more products than reactants at equilibrium, or vice versa.
Equilibrium does NOT mean that the concentrations of products and reactants have to be equal. Only the rates of the forward and reverse reactions have to be equal!

§7.3 Reaction Quotient and Equilibrium Constant

For a reversible process, the **reaction quotient, Q**, represents the relative quantities of reactants and products at *any* given point in time as a ratio of product concentrations to reactant concentrations.

Definition 7.3.1

The **Law of Mass Action** is a principle that states that the rate of a chemical reaction is proportional to the masses of species involved.

When constructing the reaction quotient (Q) and equilibrium constant (K, which we will see later) expressions, we follow the Law of Mass Action.

For a general aqueous-phase reaction

$$a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D},$$

the reaction quotient would be written as

$$Q_c = \frac{[\text{C}]^c[\text{D}]^d}{[\text{A}]^a[\text{B}]^b},$$

where the superscripts $a, b, c,$ and d are the coefficients of species A, B, C, and D, respectively, from the balanced chemical equation. Some information regarding Q_c:

- The subscript c stands for "concentration" because we are working in terms of molarity values.
- Product concentrations ALWAYS appear in the numerator and reactant concentrations ALWAYS appear in the denominator.

Similarly, for gas-phase reactions, the reaction quotient would be written as

$$Q_p = \frac{(P_{\mathrm{C}})^c (P_{\mathrm{D}})^d}{(P_{\mathrm{A}})^a (P_{\mathrm{B}})^b}$$

where p stands for "pressure" because we are in terms of partial pressures.

Important! Concentrations and partial pressures of pure solids (s) and liquids (l) are fixed by their density and molar mass, which do not vary with amount. Therefore, we NEVER include them in our expression for Q.

For example, for the reaction

$$\mathrm{Al(OH)_3(s)} \rightleftharpoons \mathrm{Al^{3+}(aq)} + \mathrm{3OH^-(aq)},$$

the correct expression for Q_c is

$$Q_c = [\mathrm{Al^{3+}}][\mathrm{OH^-}]^3$$

It would be incorrect to write the expression as

$$Q_c = \frac{[\mathrm{Al^{3+}}][\mathrm{OH^-}]^3}{[\mathrm{Al(OH)_3}]}$$

as $\mathrm{Al(OH)_3(s)}$ is a pure solid and will not affect the equilibrium.

Note 7.3.2

Note that Q_c and Q_p are NOT interchangeable. If a question asks for Q_c and you write Q_p, that is incorrect! Always make sure to read the question carefully EVEN IF all species in the reaction are aqueous (aq) or gaseous (g).

Let us walk through some examples.

Example 7.3.3

$$\mathrm{2HF(aq)} \rightleftharpoons \mathrm{H_2(aq)} + \mathrm{F_2(aq)}$$

Write the reaction quotient, Q_c, for the reaction given above.

Solution: First things first, all the species are aqueous, so we will include all of them in the Q_c expression. $\mathrm{H_2(aq)}$ and $\mathrm{F_2(aq)}$ are the products of the reaction, so they will appear in the numerator. Each of them also has a coefficient of 1, which is understood and not explicitly written. HF(aq) is the reactant which will appear in the numerator. Since it has a coefficient of 2, we will raise its concentration to the 2nd power. The reaction quotient is thus

$$\boxed{Q_c = \frac{[\mathrm{H_2}][\mathrm{F_2}]}{[\mathrm{HF}]^2}}$$

Example 7.3.4

$$CaO(s) + CO_2(g) \rightleftharpoons CaCO_3(s)$$

Write the reaction quotient, Q_c, for the reaction given above.

Solution: $CaCO_3$ and CaO are solids, so we will **not** include them in the reaction quotient. Only CO_2 is in the (aq) or (g) phase, so we will include it. Additionally, its coefficient is 1, so it is understood and the first power is not explicitly shown. Finally, CO_2 must be in the denominator. If there are no products present, we place a 1 in the numerator. The reaction quotient is thus

$$\boxed{Q_c = \frac{1}{[CO_2]}}$$

Example 7.3.5

$$2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$$

Write the reaction quotient, Q_p, for the reaction given above.

Solution: All the species are gaseous, so we will include everything in the expression for Q_p. Also, we are asked for Q_p, not Q_c, so we must use partial pressures, not molar concentrations. Thus, the reaction quotient expression is

$$\boxed{Q_p = \frac{(P_{N_2})(P_{H_2})^3}{(P_{NH_3})^2}}$$

That is all there is to the reaction quotient, Q.

The Equilibrium Constant, K

Definition 7.3.6

When a system is at equilibrium, we can describe the relative amounts of reactants and products with the *equilibrium constant*, K, rather than Q.

For a general reaction $a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D}$, the respective equilibrium constant expressions using molar concentrations and partial pressures are

$$K_c = \frac{[\text{C}]^c[\text{D}]^d}{[\text{A}]^a[\text{B}]^b} \text{ and } K_p = \frac{(P_\text{C})^c(P_\text{D})^d}{(P_\text{A})^a(P_\text{B})^b}$$

Important Information:

- Similarly as with Q, pure solids (s) and liquids (l) are not included in the K expression. Only gases (g) and aqueous species (aq) are included.

- K_c and K_p are not interchangeable; $K_c \neq K_p$
- You will **not** need to convert between the two on the AP exam.

Significance of Q and K

- The value of Q tells us the direction the reaction needs to shift in order to reach equilibrium.
- The value of K tells us whether there are more products or more reactants in the reaction mixture once equilibrium has been established.

Here is one last example.

Example 7.3.7

The equilibrium constant of a generic reaction

$$\mathrm{A} + \mathrm{B} \rightarrow \mathrm{C} + \mathrm{D}$$

at some temperature has a value of $K = 1.0 \cdot 10^4$.

At some moment in time, $[\mathrm{A}]_0 = [\mathrm{B}]_0 = 0.30\, M$ and $[\mathrm{C}]_0 = [\mathrm{D}]_0 = 1.40\, M$.

Predict the direction the reaction needs to shift in order to reach equilibrium.

Solution: In order to predict the direction in which the direction will shift to reach equilibrium, we need to compare the values of the reaction quotient Q and the equilibrium constant K.

We will calculate the value of Q_c using the "initial" concentrations, since the system is not at equilibrium.

$$Q_c = \frac{[\mathrm{C}]_0[\mathrm{D}]_0}{[\mathrm{A}]_0[\mathrm{B}_0}$$

Plugging in,

$$Q_c = \frac{(1.40)(1.40)}{(0.30)(0.30)} = 21.8$$

The value of Q_c is far less than K, so the reaction must favor the forward direction, in order to form more products and for Q_c to increase until it is equal to the value of K.

§7.4 Calculating the Equilibrium Constant

Previously, we learned how to write the equilibrium constant expression, K (or K_{eq}, they're both interchangeable), for a balanced chemical reaction. In this section, we will calculate the value of K for a reaction by plugging in the equilibrium concentrations (or partial pressures) of species that participate in the reaction.

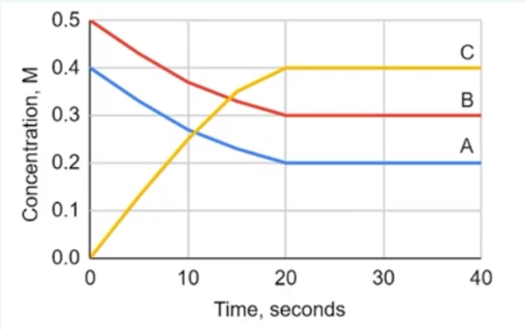
Temperature Dependence of K_{eq}

In problems involving K_{eq}, a specific temperature is usually provided.

- That is because K_{eq} values for a reaction are affected by the temperature and are calculated at specific conditions.
- However, we don't need the temperature to actually *calculate* the value of K_{eq}—we only need the concentrations of all species at equilibrium.

Let us try some problems.

Problem 7.4.1 — Short Answer Practice I



A plot of concentration over time for the reaction $A + B \rightleftharpoons 2C$ at 295 K is shown.

(a) Write the equilibrium constant expression, K_c, for the reaction.
(b) Calculate the value of the equilibrium constant at 295 K.

Example Courtesy of College Board

Solution to part a: K_c is equal to the concentrations of products over the concentrations of reactants, raised to the power of their coefficients. Thus,

$$\boxed{K_c = \frac{[C]^2}{[A][B]}}$$

Solution to part b: To calculate the value of K_c at the given temperature, we need to determine the equilibrium concentrations of species A, B, and C.
Recall that the concentrations of reactants and products remain constant once a state of equilibrium has been established. Observing the graph, we find that all concentrations begin to stabilize after the first 20 seconds of the reaction.
At equilibrium, $[A] = 0.2\ M$, $[B] = 0.3\ M$, and $[C] = 0.4\ M$.

Using part (a), plugging in the equilibrium concentrations of our species yields

$$K_c = \frac{(0.4)^2}{(0.2)(0.3)} = \boxed{2.7}$$

Problem 7.4.2 — Short Answer Practice II

The compound BrCl can decompose into Br_2 and Cl_2, as represented by the balanced chemical equation below.

$$2\text{BrCl(g)} \rightleftharpoons \text{Br}_2\text{(g)} + \text{Cl}_2\text{(g)} \qquad \Delta H^\circ = 1.6\,\text{kJ/mol}_{rxn}$$

A 0.100 mole sample of pure BrCl(g) is placed in a previously evacuated, rigid 2.00 L container at 298 K.

(a) Calculate the pressure in the container before equilibrium is established.

(b) Write the expression for the equilibrium constant, K_{eq}, for the decomposition of reaction of BrCl.

After the system has reached equilibrium, 42% of the original BrCl sample has decomposed.

(c) Determine the value of K_{eq} for the decomposition of BrCl at 298 K.

Solution to part a: Since there is only pure BrCl(g) initially present, and we know the number of moles in the sample, the volume of the container, and the temperature, we can find the pressure in the container by using the Ideal Gas Law.

$$PV = nRT$$

$$P = \frac{nRT}{V} = \frac{(0.100\,\cancel{\text{mol}})(0.0821\,\cancel{\text{L}}\,\text{atm}\,\cancel{\text{mol}^{-1}}\,\cancel{\text{K}^{-1}})(298\,\cancel{\text{K}})}{2.00\,\cancel{\text{L}}} = \boxed{1.22\,\text{atm}}$$

Solution to part b: All of the species are gases, so they can be included in the K_{eq} expression. Since the problem involves molar concentrations, I will write the expression for K_c instead of K_p.

$$\boxed{K_c = \frac{[\text{Br}_2][\text{Cl}_2]}{[\text{BrCl}]^2}}$$

Solution to part c: Using $M = \frac{n}{V}$, the initial concentration of BrCl(g) in the container is $\frac{0.100\,\text{mol}}{2.00\,\text{L}} = 0.0500\,M$. Additionally, since 42% of the original sample has been decomposed, there is 58% of it remaining. Therefore, the equilibrium concentration of BrCl(g) is equal to

$$0.58 \cdot [\text{BrCl}]_i = 0.58 \cdot 0.0500\,M = 0.0290\,M$$

We need to determine how much Br_2(g) and Cl_2(g) are present at equilibrium. Since there are initially 0 moles for each of them, their amount increases proportionally to the amount of BrCl(g) that decomposed. Take a look at the balanced chemical equation.

$$2\text{BrCl(g)} \rightleftharpoons \text{Br}_2\text{(g)} + \text{Cl}_2\text{(g)}$$

For every 2 moles of BrCl(g) that is decomposed, 1 mole of Br_2(g) and Cl_2(g) are formed. Therefore, the amount that is gained by Br_2(g) and Cl_2(g) is equal to one-half the amount of BrCl(g) that was decomposed.

$$\text{At equilibrium,}\ \ [Br_2] = [Cl_2] = \frac{1}{2} \cdot 0.42 \cdot 0.0500\,M = 0.0210\,M$$

Since we have all our equilibrium concentrations, we can calculate the value of K_{eq} for the reaction at 298 K.

$$K_{eq} = \frac{[Br_2][Cl_2]}{[BrCl]^2} = \frac{0.0210 \cdot 0.0210}{0.0290} = \boxed{0.0152}$$

When dealing with values of the equilibrium constant, K_{eq}, we must keep the following in mind:

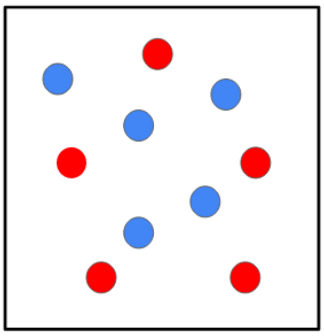
- Remember to watch out for exponents, and make sure to use **equilibrium** concentrations or partial pressures only to calculate the value of K_{eq}.
- Changes in concentration do **not** affect the value of K_{eq}, it is **only** affected by changes in temperature.
- Under constant temperature, the **ratio** of products to reactants will also remain constant.

§7.5 Magnitude of the Equilibrium Constant

The magnitude of the equilibrium constant tells us the relative amounts of products and reactants at equilibrium.

Consider a hypothetical gas phase reaction:

$$X(g) \rightleftharpoons Y(g)$$



Gases X and Y are represented by the blue and red molecules, respectively.

For simplicity purposes, each sphere represents 0.1 mole of gas and the volume of the container is 1.0 L.

The equilibrium constant for this reaction is given by $K_c = \frac{[Y]}{[X]}$, and we can calculate its value if we know the concentrations of both gases.

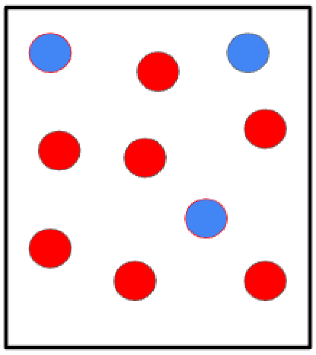
$$[X] = \frac{5 \cdot 0.1\,\text{mol}}{1.0\,\text{L}} = 0.5\,M \qquad [Y] = \frac{5 \cdot 0.1\,\text{mol}}{1.0\,\text{L}} = 0.5\,M$$

Thus, the value of the equilibrium constant is $K_c = \frac{0.5}{0.5} = 1$.

Go back to our particulate diagram. There are 5 molecules of Gas X as well as 5 molecules of Gas Y. This system is a reaction mixture that contains **equal** amounts of products and reactants at equilibrium, since K_c for the reaction is equal to 1.

We will modify our hypothetical reaction and observe how different magnitudes of K_{eq} describe the composition of the reaction mixture at equilibrium.

Now, suppose there were less molecules of Gas X and more molecules of Gas Y in the container.

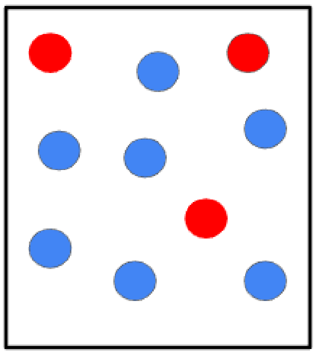


Count the number of blue and red spheres.
There are 3 blue spheres, so $3 \cdot 0.1\,\text{mol} = 0.3\,\text{mol}$ of Gas X.
There are 7 red spheres, so $7 \cdot 0.1\,\text{mol} = 0.7\,\text{mol}$ of Gas Y.
The volume of the container is 1.0 L, so the concentrations of gases X and Y are 0.3 M and 0.7 M, respectively.
The equilibrium constant for this reaction is given by $K_c = \frac{[\text{Y}]}{[\text{X}]}$, and we can calculate its value by substituting the concentrations of both gases.

$$K_c = \frac{0.7}{0.3} = 2.7$$

Because K_c for the reaction is greater than 1, there are more products than reactants in the reaction mixture at equilibrium. You could also say that the reaction is **product-favored**.

Finally, suppose if there were more molecules of Gas X and less molecules of Gas Y in the container.



As with the previous two scenarios, count the number of blue and red spheres.
There are 7 and 3, respectively. The 7 blue spheres indicate that there are $7 \cdot 0.1\,\text{mol} = 0.7\,\text{mol}$ of Gas X and the 3 red spheres indicate that there are $3 \cdot 0.1\,\text{mol} = 0.3\,\text{mol}$ of

Gas Y. Similarly, the volume of the container is 1.0 L, so the concentrations of gases X and Y are 0.7 M and 0.3 M, respectively.

The equilibrium constant for this reaction is given by $K_c = \frac{[Y]}{[X]}$. Substituting known values, we find that

$$K_c = \frac{0.3}{0.7} = 0.43$$

Since K_c for the reaction is less than 1, there are more reactants than products in the reaction mixture at equilibrium. Alternatively, you could state that the reaction is **reactant-favored**.

We can also use relative magnitudes of the equilibrium constant to describe the extent of a chemical reaction.

- If K_c is extremely large (10^6 order of magnitude or greater), then it can be said that the forward reaction essentially proceeds to completion, as the mixture contains a large amount of products and the amount of reactants is nearly negligible.
- If K_c is extremely small (10^{-6} order of magnitude or less), conversely, the forward reaction barely proceeds at all, as the majority of reactants have not proceeded to form any products.

Problem 7.5.1 — Multiple Choice Question

$$2H_2(g) + O_2(g) \rightleftharpoons 2H_2O(g)$$

H_2O can be synthesized from $H_2(g)$ and $O_2(g)$ as represented above.
The value of K_{eq} for the reaction at 2000 K is $1.0 \cdot 10^8$.

From this information, which of the following can be concluded about the reaction at 2000 K?

(A) The reactants are favored over the products at equilibrium.
(B) The product is favored over the reactants at equilibrium.
(C) The concentrations of the reactants and products are equal at equilibrium.
(D) The reaction reaches equilibrium relatively quickly.

Solution: The value of K for the reaction is much greater than one, so there should be more products than reactants present at equilibrium. This is consistent with answer choice (B), but let us check the others to be safe. Eliminate (A), because this is the opposite of our reasoning. Choice (C) is a trap: the concentrations of reactants and products do not change once equilibrium is established, but that does not mean they have to be equal. Eliminate it. Finally, eliminate (D), because the equilibrium position of a reaction is irrelevant to the reaction rate, which exists from a kinetics standpoint. Therefore, the correct answer is $\boxed{\textbf{(B)}}$.

§7.6 Properties of the Equilibrium Constant

Let's think back to our last section of Unit 6. There, we learned about Hess's law and how the enthalpy change, ΔH, for an overall reaction can be affected by adding, multiplying, or reversing a series of elementary step reactions.

In this section, we will look at the K_{eq} values for different reactions and learn how we can manipulate and combine them to find the value of the equilibrium constant for an overall chemical reaction.

Example 7.6.1

Consider two gas-phase reactions.

$$4NH_3(g) + 7O_2(g) \rightleftharpoons 4NO_2(g) + 6H_2O(g) \quad K_1 = 10$$
$$4NO_2(g) + 6H_2O(g) \rightleftharpoons 4NH_3(g) + 7O_2(g) \quad K_2 = ?$$

The first chemical reaction has an equilibrium constant of $K_1 = 10$. Now, let us think, "How is the second equation different from the first?" The first reaction was *reversed* in order to yield the second. Mathematically, how does this change the value of our equilibrium constant?

We know that K is equal to $\frac{[\text{products}]}{[\text{reactants}]}$, raised to the power of the stoichiometric coefficients.

Therefore, if you flip the position of the reactants and products, you are actually taking the **reciprocal** of the original value of the equilibrium constant.

Proof.

$$4NH_3(g) + 7O_2(g) \rightleftharpoons 4NO_2(g) + 6H_2O(g) \quad K_1 = \frac{[NO_2]^4[H_2O]^6}{[NH_3]^4[O_2]^7}$$
$$4NO_2(g) + 6H_2O(g) \rightleftharpoons 4NH_3(g) + 7O_2(g) \quad K_2 = \frac{[NH_3]^4[O_2]^7}{[NO_2]^4[H_2O]^6}$$

By inspection, it is clear that $K_2 = \frac{1}{K_1}$, and since $K_1 = 10$, the value of K_2 must be equal to $\frac{1}{10} = \boxed{0.1}$.

That is the first property we should know when dealing with a series of K values.

Example 7.6.2

Consider these two gas-phase reactions.

$$4NH_3(g) + 7O_2(g) \rightleftharpoons 4NO_2(g) + 6H_2O(g) \quad K_1 = 10$$
$$8NH_3(g) + 14O_2(g) \rightleftharpoons 8NO_2(g) + 12H_2O(g) \quad K_2 = ?$$

Another property involving a direct comparison of K values occurs when you multiply a reaction by a certain factor.

If you multiply the reaction by a factor of n, then its equilibrium constant will be **raised to the nth power**.

Proof.

$$4NH_3(g) + 7O_2(g) \rightleftharpoons 4NO_2(g) + 6H_2O(g) \quad K_1 = \frac{[NO_2]^4[H_2O]^6}{[NH_3]^4[O_2]^7}$$
$$8NH_3(g) + 14O_2(g) \rightleftharpoons 8NO_2(g) + 12H_2O(g) \quad K_2 = \frac{[NO_2]^8[H_2O]^{12}}{[NH_3]^8[O_2]^{14}}$$

All the exponents are doubled, so $K_2 = (K_1)^2$, and since $K_1 = 10$, the value of K_2 is equal to $(10)^2 = \boxed{100}$.

Finally, we can use a series of equilibrium constant values for elementary step reactions to determine the value of K for an overall chemical reaction.

Example 7.6.3

The synthesis of gaseous nitrogen dioxide from nitrogen and oxygen gases is described by the following balanced chemical equation:

$$N_2(g) + 2O_2(g) \rightleftharpoons 2NO_2(g)$$

The reaction can occur in a series of two elementary step reactions:

$$N_2(g) + O_2(g) \rightleftharpoons \cancel{2NO(g)} \quad K_1 = 4.3 \cdot 10^{-25}$$

$$\cancel{2NO(g)} + O_2(g) \rightleftharpoons 2NO_2(g) \quad K_2 = 6.9 \cdot 10^{5}$$

$$N_2(g) + 2O_2(g) \rightleftharpoons 2NO_2(g) \quad K_{\text{eff}} = ?$$

When reactions are added together, the effective equilibrium constant K_{eff} for the overall reaction is the **product** of the K values of the reactions that were summed.

Proof.

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g) \quad K_1 = \frac{[NO]^2}{[N_2][O_2]}$$
$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g) \quad K_2 = \frac{[NO_2]^2}{[NO]^2[O_2]}$$
$$\text{Overall Reaction: } N_2(g) + 2O_2(g) \rightleftharpoons 2NO_2(g) \quad K_{\text{eff}} = \frac{[NO_2]^2}{[N_2][O_2]^2}$$
$$K_1 \cdot K_2 = \frac{\cancel{[NO]^2}}{[N_2][O_2]} \cdot \frac{[NO_2]^2}{\cancel{[NO]^2}[O_2]} = \frac{[NO_2]^2}{[N_2][O_2]^2} = K_{\text{eff}}$$

We have demonstrated that $K_{\text{eff}} = K_1 \cdot K_2$, for two elementary reactions that are added together, and the proof is complete.

In the above example,

$$K_{\text{eff}} = K_1 \cdot K_2 = \left(4.3 \cdot 10^{-25}\right) \cdot \left(6.9 \cdot 10^{5}\right) = \boxed{3.0 \cdot 10^{-19}}$$

This concludes the section on properties of the equilibrium constant. For purposes of the AP exam, this topic will likely be tested in the form of multiple choice questions that require you to perform two to three manipulations to reach the answer.

§7.7 Calculating Equilibrium Concentrations

Knowing the magnitude and properties of the equilibrium constant for a reaction is nice and all, but there is not much we can really do with it. However, if we knew the initial concentrations or pressures, we can use K_{eq} to determine the concentrations or pressures of all species at equilibrium. This concept becomes more important in later sections of the unit.

When reactants and products of a given chemical reaction are mixed, it is useful to determine whether the system is at equilibrium or will need to shift to reach equilibrium. For example, if the initial concentration of one of the reactants or products is zero, the reaction will need to shift to produce the missing species. However, when all of the concentrations (or pressures) are non-zero, the problem becomes more complex. In such a case, we will need to revisit the **reaction quotient, Q**.

Definition 7.7.1

Recall that Q can be used to express the relative amount of reactants and products at **any given time** in the reaction.

We can write the Q expression by using the *law of mass action* but for initial concentrations, rather than equilibrium concentrations. For example, for the synthesis of ammonia from hydrogen and nitrogen gas:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

the expression for the reaction quotient is

$$Q = \frac{[NH_3]_0^2}{[N_2]_0[H_2]_0^3}$$

where the subscript zeros indicate initial concentrations.
We can figure out the direction in which a system will shift to reach equilibrium by comparing the values of Q and K. We have three possible cases:

1. *Q is equal to K.* The system is in equilibrium; no shift will occur.
2. *Q is greater than K.* In this case, the ratio of initial concentrations of products to reactants is too large. To reach equilibrium, there must be a net increase in the number of reactants and a decrease in the number of products. The system will *shift to the left*, which favors the reverse reaction, until equilibrium is achieved.
3. *Q is less than K.* In this case, the ratio of initial concentrations of products to reactants is too small. To reach equilibrium, there must be a net increase in the number of products and a decrease in the number of reactants. The system will *shift to the right*, which favors the forward reaction, to attain equilibrium.

Calculating Equilibrium Concentrations and Pressures

In this course, a classic equilibrium problem involves finding the equilibrium concentrations (or pressures), given the value of the equilibrium constant and the initial concentrations (or pressures). Since the process becomes more complex mathematically, we will develop useful strategies and problem-solving techniques to solve them. We will also work through certain cases in which we know the equilibrium concentrations or pressures for one or more species in a chemical reaction.

Problem 7.7.2 — Calculating Equilibrium Concentrations I

Dinitrogen tetroxide in its liquid state was used as one of the fuels on the lunar lander for the NASA Apollo missions. In the gas phase it decomposes to gaseous nitrogen dioxide:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

Consider an experiment in which gaseous N_2O_4 was placed in a flask and allowed to reach equilibrium at a temperature where $K_p = 0.133$. At equilibrium, the pressure of N_2O_4 was found to be 2.71 atm. Calculate the equilibrium pressure of $NO_2(g)$.

Solution: The equilibrium constant for the reaction is

$$K_p = \frac{(P_{NO_2})^2}{P_{N_2O_4}}$$

Since P_{NO_2} and $P_{N_2O_4}$ must satisfy the above relationship, and we know $P_{N_2O_4}$, then we can solve for P_{NO_2}:

$$(P_{NO_2})^2 = K_p(P_{N_2O_4}) = (0.133)(2.71) = 0.360$$

Finally, $P_{NO_2} = \sqrt{0.360} = \boxed{0.600}$.

Problem 7.7.3 — Calculating Equilibrium Concentrations II

At a certain temperature a 1.00-L flask initially contained 0.298 mol $PCl_3(g)$ and $8.70 \cdot 10^{-3}$ mol $PCl_5(g)$. After the system had reached equilibrium, $2.00 \cdot 10^{-3}$ mol $Cl_2(g)$ was found in the flask. Gaseous $PCl_5(g)$ decomposes according to the reaction

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

Calculate the equilibrium concentrations of all species and the value of K.

Solution: The equilibrium constant for this reaction is

$$K = \frac{[Cl_2][PCl_3]}{[PCl_5]}$$

To find the value of K, we must first find the equilibrium concentrations of all species and then substitute them into the equilibrium constant expression. Our key strategy is to start with the initial concentrations and then appropriately *modify* them to find the equilibrium concentrations.

The initial concentrations are

$$[\mathrm{Cl_2}]_0 = 0$$
$$[\mathrm{PCl_3}]_0 = \frac{0.298\ \mathrm{mol}}{1.00\ \mathrm{L}} = 0.298\ M$$
$$[\mathrm{PCl_5}]_0 = \frac{8.70 \cdot 10^{-3}\ \mathrm{mol}}{1.00\ \mathrm{L}} = 8.70 \cdot 10^{-3}\ M$$

Next, we determine the *changes* in concentration that must have occurred to reach equilibrium. Since no Cl_2 was initially present but $2.00 \cdot 10^{-3}\ M$ was present at equilibrium, $2.00 \cdot 10^{-3}$ mol of PCl_5 must have decomposed to form $2.00 \cdot 10^{-3}$ mol of PCl_3 and Cl_2. Essentially, the reaction shifted to the right to reach equilibrium.

Now we apply this change to the initial concentrations to find the *equilibrium* concentrations of all species.

$$[\mathrm{Cl_2}] = 0 + \frac{2.00 \cdot 10^{-3}\ \mathrm{mol}}{1.00\ \mathrm{L}} = \boxed{2.00 \cdot 10^{-3}\ M}$$
$$[\mathrm{PCl_3}] = 0.298\ M + \frac{2.00 \cdot 10^{-3}\ \mathrm{mol}}{1.00\ \mathrm{L}} = \boxed{0.300\ M}$$
$$[\mathrm{PCl_5}] = 8.70 \cdot 10^{-3}\ M - \frac{2.00 \cdot 10^{-3}\ \mathrm{mol}}{1.00\ \mathrm{L}} = \boxed{6.70 \cdot 10^{-3}\ M}$$

Finally, the value of K can be found by plugging in the equilibrium concentrations:

$$K = \frac{[\mathrm{Cl_2}][\mathrm{PCl_3}]}{[\mathrm{PCl_5}]} = \frac{(2.00 \cdot 10^{-3})(0.300)}{6.70 \cdot 10^{-3}} = \boxed{8.96 \cdot 10^{-2}}$$

Sometimes we are not given any equilibrium concentrations or partial pressures, only initial values. For such problems, we must use the stoichiometry of the reaction to express equilibrium values in terms of the initial values.

Problem 7.7.4 — Calculating Equilibrium Concentrations III

Assume that for the formation of gaseous hydrogen fluoride from hydrogen and fluorine has an equilibrium constant of $1.15 \cdot 10^2$ at a certain temperature. In an experiment, 0.750 mol of each substance was added to a 0.500 L flask. Calculate the equilibrium concentrations of all species.

Solution: The balanced chemical reaction is

$$\mathrm{H_2(g) + F_2(g) \rightleftharpoons 2HF(g)}$$

and the equilibrium constant expression is

$$K = 1.15 \cdot 10^2 = \frac{[\mathrm{HF}]^2}{[\mathrm{H_2}][\mathrm{F_2}]}$$

First, we calculate the initial concentrations:

$$[H_2]_0 = [F_2]_0 = [HF]_0 = \frac{0.750\,\text{mol}}{0.500\,\text{L}} = 1.50\,M$$

and then determine the value of Q:

$$Q = \frac{[HF]_0^2}{[H_2]_0[F_2]_0} = \frac{(1.50)^2}{(1.50)(1.50)} = 1.00$$

Since Q is far less than K, the system must shift to the right to reach equilibrium.

We do not know exactly what change in concentration for each species is necessary. Therefore, we will use an intermediate variable x. Let x be the amount, in mol/L, of H_2 consumed to reach equilibrium. According to the stoichiometry of the reaction, x mol/L F_2 will also be consumed and $2x$ mol/L of HF will be formed.

As you can see, our problem becomes more mathematically complex. To keep track of all these concentrations over time, we can use a tabular method commonly known as an **ICE** (**I**nitial, **C**hange, **E**quilibrium) table. This device allows us to keep track of the concentrations of species in a chemical reaction as it proceeds to reach equilibrium, in an efficient manner.

	H_2(g)	F_2(g)	$\rightleftharpoons$	2HF(g)
Initial (M)	1.50	1.50	-	1.50
Change (M)	$-x$	$-x$	-	$+2x$
Equilibrium (M)	$1.50 - x$	$1.50 - x$	-	$1.50 + 2x$

To solve for x, we substitute the equilibrium concentrations into the K expression:

$$K = 1.15 \cdot 10^2 = \frac{[HF]^2}{[H_2][F_2]} = \frac{(1.50 + 2x)^2}{(1.50 - x)^2}$$

The right hand side of this equation is a perfect square, so we can take the square root of both sides, yielding

$$\sqrt{1.15 \cdot 10^2} = \frac{1.50 + 2x}{1.50 - x} \therefore x = 1.146$$

The equilibrium concentrations can now be calculated:

$$[H_2] = [F_2] = 1.50 - x = 1.50 - 1.146 = \boxed{0.354\,M}$$

$$[HF] = 1.50 + 2x = 1.50 + 2(1.146) = \boxed{3.79\,M}$$

Phew! The math has become increasingly complicated. Unfortunately, the number crunching only gets worse from here on. In most cases, you cannot necessarily take square roots of both sides of an equation and easily solve for the intermediate variable. However, under certain conditions, simplifications are possible that greatly reduce the complexity of calculations.

Problem 7.7.5 — Calculating Equilibrium Concentrations IV

Gaseous NOCl decomposes to form the gases NO and Cl_2 At 35°C, the equilibrium constant is $1.6 \cdot 10^{-5}$. In an experiment in which 1.0 mol NOCl is placed in a 2.0 L flask, what are the equilibrium concentrations?

Solution: We proceed with the balanced chemical reaction.

$$2\text{NOCl(g)} \rightleftharpoons 2\text{NO(g)} + \text{Cl}_2\text{(g)}$$

with equilibrium constant expression

$$K = \frac{[\text{NO}]^2[\text{Cl}_2]}{[\text{NOCl}]^2} = 1.6 \cdot 10^{-5}$$

The initial concentrations are

$$[\text{NOCl}]_0 = \frac{1.0\text{ mol}}{2.0\text{ L}} = 0.50\,M \qquad [\text{NO}]_0 = 0 \qquad [\text{Cl}_2]_0 = 0$$

Because there are zero products initially, the system must shift to the right to achieve equilibrium. The changes in concentration can be obtained from the stoichiometry of the balanced chemical reaction.

Next, we construct the ICE table.

	2NOCl(g)	$\rightleftharpoons$	2NO(g)	Cl_2(g)
Initial (M)	0.50	-	0	0
Change (M)	$-2x$	-	$+2x$	$+x$
Equilibrium (M)	$0.50 - 2x$	-	$2x$	x

Ensure that equilibrium concentrations satisfy the expression

$$K = 1.6 \cdot 10^{-5} = \frac{[\text{NO}]^2[\text{Cl}_2]}{[\text{NOCl}]^2} = \frac{(2x)^2(x)}{(0.50 - 2x)}$$

If we tried to multiply and collect terms to manually solve for x, it would be very complicated. Furthermore, this is college *chemistry*, not college algebra. So, there has to be an easier way to approach the problem, right?

Absolutely!

The key idea here is to recognize that K for the reaction is so small, so the system will not proceed far to the right anyways to reach equilibrium under these conditions. That means, the amount x is *relatively very small.* That being said, the term $0.50 - 2x$ can be approximated by 0.50. When x is small,

$$0.50 - 2x \approx 0.50$$

Using this approximation, we can simplify the equilibrium expression into something much nicer:

$$1.6 \cdot 10^{-5} = \frac{(2x)^2(x)}{(0.50 - 2x)^2} \approx \frac{(2x)^2(x)}{(0.50)^2} = \frac{4x^3}{(0.50)^2}$$

Solving for x^3 gives

$$x^3 = \frac{(1.6 \cdot 10^{-5})(0.50)^2}{4} = 1.0 \cdot 10^{-6} \therefore x = 1.0 \cdot 10^{-2}$$

We can check the validity of this approximation by using the 5% rule.

Definition 7.7.6

The **5% rule** is an error threshold that allows us to determine whether the actual equilibrium concentration can be estimated based on the small K value. If the actual equilibrium concentration differs from the approximated value by no more than 5%, then the approximation is valid.

Since $x = 1.0 \cdot 10^{-2}$, we have

$$0.50 - 2x = 0.50 - 2\left(1.0 \cdot 10^{-2}\right) = 0.48$$

The difference between 0.50 and 0.48 is very small and represents 4% of the initial concentration of NOCl. This discrepancy is relatively small and will have little effect on the outcome. We can use this approximation to calculate the equilibrium concentrations:

$$[\text{NOCl}] = 0.50 - 2x \approx \boxed{0.50\ M}$$

$$[\text{NO}] = 2x = 2(1.0 \cdot 10^{-2}) = \boxed{2.0 \cdot 10^{-2}\ M}$$

$$[\text{Cl}_2] = x = \boxed{1.0 \cdot 10^{-2}\ M}$$

Therefore, when solving problems such as the example above, we can check the validity of our approximation with the 5% rule.

The College Board only uses equilibrium problems where you will NOT need to use complicated methods, like the quadratic formula. Therefore, you can **always** make approximations in such cases when the value of K is so small that the estimate is valid.

§7.8 Representations of Equilibrium

So far in this unit, we have represented equilibrium both via reactions (EX. $A \rightleftharpoons B$) and mathematically (e.g. calculating equilibrium concentrations or partial pressures). In this section, we will think about how we can view equilibrium using visual representations, also called particulate models.

Definition 7.8.1

Particulate models refer to models that represent matter as discrete particles, rather than as a continuous fluid or field.

For the last few sections, we have focused fully on math and more math, calculating everything from equilibrium constants to equilibrium concentrations. While it is important to know the math behind equilibrium, it is *equally* important to have a firm understanding of the abstract concept and how we can represent it visually.

Recap - Magnitude of the Equilibrium Constant

Equilibrium describes how far a reaction goes. Some reactions have a K value much greater than 1 and will essentially proceed to completion, while others with $K << 1$ may not move forward much at all. This means that at equilibrium, the concentrations of reactants and products for various reactions can vary (which we have seen in several instances).

Using Particulate Diagrams

In terms of particulate levels, the above concept can be generalized by observing more amounts of reactants or products in a reaction mixture. This will also help you understand the math behind equilibrium as well!

Example 7.8.2

Consider the following chemical reaction:

$$C_2H_4 + X_2 \rightleftharpoons C_2H_4X_2$$

where X_2 is any diatomic molecule that can be green, brown, or purple.

Examine the three figures below representing equilibrium concentrations in this reaction at the same temperature for the three different halogens. Rank the equilibrium constants for these three reactions from largest to smallest.

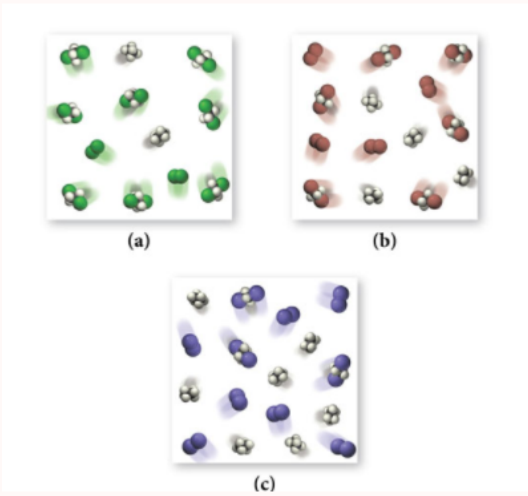


Image Courtesy of BoylanChemistry

Instead of counting each individual product and reactant molecule and plugging them into an equilibrium constant expression, we can figure out the answer logically. Equilibrium describes how far a reaction proceeds in a certain direction. The higher the value of K, the more forward a reaction is moving.

Therefore, we can simply compare the amount of **product molecules** between the three reaction mixtures to find that (a) has the largest K value and (c) has the smallest K value, with (b) lying in the middle.

Equilibrium Particulate Representations on the AP Exam

Many of you must be thinking about how often and in what ways this concept is actually assessed on the AP exam. This is because most of this unit focuses on the *mathematical* aspects of equilibrium, such as ICE tables, equilibrium concentrations, etc.

In later sections, we will make our own theories to investigate both qualitative and quantitative analyses of equilibrium systems. This section is a "mix" between those two scenarios and serves as a reminder that the scope of equilibrium in this course is not limited to only calculations. Additionally, the College Board can test this concept in FRQs where you may be asked to draw a particulate diagram for a new solution based on a reaction system or a shift in equilibrium.

§7.9 Introduction to Le Châtelier's Principle

Le Châtelier's Principle states that when a stress is applied to an equilibrium system, the system will shift in a direction to **counteract** the stress and **re-establish** equilibrium.

Dynamic Equilibrium and Stressors

For this unit, we should always establish that we are in **dynamic equilibrium**. This means that while our reaction is at equilibrium, it has not necessarily stopped or the concentrations of species have become fixed. Now, you may be thinking, "What other type of equilibrium is there?" That is referred to as **static equilibrium**: a state of balance where the system is at rest. However, we will always consider the system to be in *dynamic* equilibrium unless otherwise stated.

Note that equilibrium can be disrupted by changing certain conditions. These are also referred to as **stressors**. Any change to the system from the external environment can be considered a stress. Specific examples include changes in concentration, pressure, volume, and temperature.

Finally, our system will shift in order to **counteract** the stress that has been placed and reach equilibrium again.

Now, we will examine each individual stress and how they affect the equilibrium position for a system or chemical reaction.

Effect of Change in Concentration

This is probably the easiest way for which a reaction can shift. At equilibrium, the concentrations of all species are fixed (K does not change). What happens if an external stress adds or removes some amount of substance? It is very important to note here that the value of K will not be affected, only the reaction quotient Q will increase or decrease. This is great because you can predict the direction where a reaction must shift to reach equilibrium just by comparing the values of Q and K!

If we add **more reactants** to the system, it will counteract that change by forming more products to consume the excess reactants at equilibrium, and the forward reaction rate increases. Meanwhile, if we add **more products** to the system, we will need more reactants to be formed, so the reverse reaction rate will increase.

Essentially, concentration changes are pretty simple: consume the substances that are in excess and create the substances that there are less of.

Example 7.9.1

Consider the following chemical reaction:

$$Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons FeSCN^{2+}(aq)$$

The system is already at equilibrium. Suddenly, a student injects KSCN salt solution into the system. How will the system react to this stress?

KSCN is potassium thiocyanate, a salt that consists of K^+ and SCN^- ions. Therefore, the concentration of thiocyanate ion, SCN^-, also a reactant, will increase. This excess ion will be consumed to form more products and re-establish equilibrium. We can see this in the graph below.

Notice that there is a spike in the concentration of SCN^-, indicating that this is the stress to which the system responds. In response, we see a decrease in $[Fe^{3+}]$ and $[SCN^-]$ as more $FeSCN^{2+}$ is created.

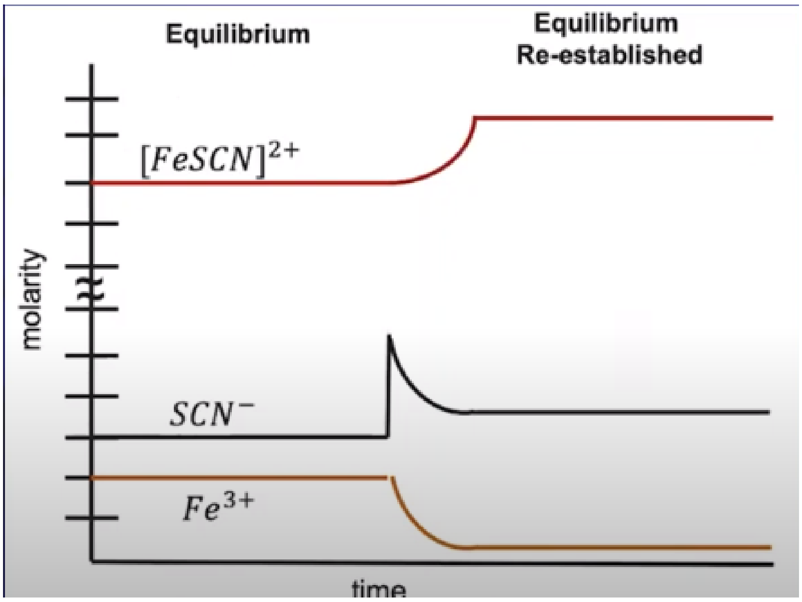


Image Courtesy of Abigail Giordano

Another important aspect of concentration changes on equilibrium is the addition of a compound that will react with a reactant or product that could remove it from the system.

For example, adding a strong base (OH^- ion) will cause the following precipitation reaction to occur:

$$Fe^{3+}(aq) + 3OH^-(aq) \rightarrow Fe(OH)_3(s)$$

The precipitation of iron (III) oxide will remove the Fe^{3+} ion from the system. Based on Le Châtelier's principle, the system will respond by *increasing* the amount of Fe^{3+} and SCN^- present in the system and *decreasing* the concentration of $FeSCN^{2+}$.

Effect of Change in Pressure/Volume

Changes involving pressure and volume of species are most important in gas-phase reactions, where all reactants and products involved are gases.

Recall from the ideal gas law that at constant temperature, the pressure and volume of gas particles are inversely proportional (Boyle's Law). Therefore, changes in pressure/volume will affect the concentrations of species in the system.

The general rule is that if the pressure on a system increases or the volume decreases, the equilibrium will favor the side with **fewer moles of gas** and vice versa.

Note 7.9.2
Moles of gas refer to the stoichiometric coefficients in the balanced chemical reaction.

Example 7.9.3
Consider a generic reaction

$$2\mathrm{A} + \mathrm{B} \rightleftharpoons 3\mathrm{C} + \mathrm{D}$$

On the left, there are 3 total moles of gas (2 molecules of A and 1 molecule of B) and on the right, there are 4 total moles of gas (3 molecules of C and 1 molecule of D). Therefore, the products contain more moles of gas.

If the pressure on the system increases, the equilibrium will shift *to the left* (forming more reactants), and vice versa.

There is an exception to this rule that occurs with **inert gases**. An inert (noble) gas is a gas that does not react when added to a reaction mixture. For example, if you pumped in or removed He(g) from a container where the reaction occurs, there would be *no* impact on equilibrium.

Effect of Change in Temperature

Just as concentrations and pressure/volume, changes in temperature have an impact on equilibrium.

For this form of stress, the direction in which equilibrium shifts depends on whether the reaction is **exothermic** (heat releasing) or **endothermic** (heat absorbing). Recall from Unit 6 that we can identify whether a reaction is exothermic or endothermic by observing the sign of its standard enthalpy change, ΔH°.

- If $\Delta H^\circ < 0$, our reaction is exothermic. Heat energy is released from the system to the surroundings.
- If $\Delta H^\circ > 0$, our reaction is endothermic. Heat energy from the system is absorbed by the system.

Example 7.9.4

Consider the reaction describing the synthesis of ammonia.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \quad \Delta H^\circ = -92\,\text{kJ/mol}$$

Since ΔH° is negative, the reaction is exothermic and heat is released into the surroundings. Therefore, heat can be *thought of as a product*. This means that if the temperature increases, the equilibrium will shift in the direction that will absorb this extra heat, i.e. to the reactants. The reverse reaction will be favored, so more N_2 and H_2 and less NH_3 will be formed as the reaction re-establishes equilibrium.

If we were given an endothermic reaction, the opposite would occur since heat would be considered as a *reactant*.

Important: Note that a temperature change is the ONLY stress that will affect the value of the equilibrium constant for a reaction. Changes in concentration, pressure, or volume will only affect the value of Q, the reaction quotient and the equilibrium will change accordingly to counteract the stress.

Generally, knowing these two properties will assist in solving virtually any equilibrium problem involving changes in temperature.

- If you increase the temperature of the system, the system will shift away from the heat, and the **endothermic** direction is favored. The excess heat needs to be consumed in order to attain equilibrium.
- If you decrease the temperature of the system, the system will shift towards the heat, which favors the **exothermic** direction. This is because more heat needs to be produced to compensate for the loss, as the reaction re-establishes equilibrium.

Let's practice with a couple of exercises.

Problem 7.9.5 — Le Châtelier's Principle I

Arsenic can be extracted from its ores by first reacting the ore with oxygen (in a process called *roasting*) to form solid As_4O_6, which is then reduced using carbon:

$$As_4O_6(s) + 6C(s) \rightleftharpoons As_4(g) + 6CO(g)$$

Predict the direction of the shift of the equilibrium position in response to the following changes in conditions.

(a) Addition of carbon monoxide
(b) Addition or removal of carbon or tetraarsenic hexoxide (As_4O_6)
(c) Removal of gaseous arsenic (As_4)

Solution to part a: Le Châtelier's principle predicts that the shift will be *away* from the substance whose concentration is increased. The equilibrium will *shift to the left*, or favor the reverse reaction, when carbon monoxide is added.

Solution to part b: Remember that pure solids and liquids are not included in the equilibrium constant or reaction quotient expressions. Therefore, they will not affect the equilibrium position of a system. Changing the amount of carbon or tetraarsenic hexoxide will have *no effect*.

Solution to part c: Gaseous arsenic is a product of the reaction. Therefore, if it is removed, the equilibrium position will *shift to the right*, favoring the forward reaction and forming more products.

Problem 7.9.6 — Le Châtelier's Principle II

Predict the shift in equilibrium position that will occur for each of the following processes when the volume is reduced.

(a) The preparation of liquid phosphorus trichloride by the reaction

$$P_4(s) + 6Cl_2(g) \rightleftharpoons 4PCl_3(l)$$

(b) The preparation of gaseous phosphorus pentachloride according to the equation

$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$$

(c) The reaction of phosphorus trichloride with ammonia:

$$PCl_3(g) + 3NH_3(g) \rightleftharpoons P(NH_2)_3(g) + 3HCl(g)$$

Solution to part a: Since we are dealing with pressure/volume changes, our focus should be on the relative number of moles of gas on the reactants and products. Since the volume decreases, equilibrium position will shift towards the side with *fewer* moles of gas. The reactants side contains 6 moles of gas (6 Cl_2) while there are none on the products. Therefore, the equilibrium will *shift to the right*, forming more products, to attain equilibrium.

Solution to part b: Virtually the same idea here: the reactants side has two moles of gas, while the products side has only one. Therefore, a decrease in the volume of the system will cause the equilibrium to *shift to the right*, forming more products, to attain equilibrium.

Solution to part c: On the reactants side, there are four moles of gas (1 molecule of PCl_3 and 3 molecules of NH_3). For the products, there are also four moles of gas (1 molecule of $P(NH_2)_3$ and 3 molecules of HCl). Since the reactants and products contain equal moles of gas, there is *no shift* in the equilibrium position.

Problem 7.9.7 — Le Châtelier's Principle III

For each of the following reactions, predict how the value of K changes as the temperature is increased.

(a) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g) \quad \Delta H^\circ = 181\,\text{kJ}$
(b) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \quad \Delta H^\circ = -198\,\text{kJ}$

Solution to part a: This is an endothermic reaction, as indicated by the positive value of ΔH°. Therefore, heat energy can be viewed as a reactant, and therefore the equilibrium *shifts to the right* to consume the extra heat. The value of K increases.

Solution to part b: This is an exothermic reaction, as indicated by the negative value of ΔH°. Therefore, heat energy can be viewed as a product. If the temperature increases, the equilibrium will *shift to the left*, away from the added heat energy. This causes the value of K to decrease.

§7.10 Reaction Quotient and Le Châtelier's Principle

In the previous section, we learned about Le Châtelier's Principle and described how it can be used to predict changes in concentrations as a result of external stress being placed upon a system. We also learned a few rules and used logic and reasoning skills to solve conceptual problems. In this section, we will look at how Le Châtelier's Principle is actually justified by using Q, the **reaction quotient**.

Review of the Reaction Quotient, Q

There is an important value related to equilibrium that is called the **reaction quotient**, and is denoted by Q.

This value would tell us how an equilibrium would shift based on conditions that are *not* at equilibrium. For example, if $Q < K$ for a reaction, the system would respond by increasing the concentration of products in order for $Q = K$ and vice versa. Remember that when $Q = K$, the system is in equilibrium and there will be no more changes in concentrations for any species. Whenever a system is not at equilibrium, it will proceed to achieve equality at $Q = K$.

Applying Q to Le Châtelier's Principle

Keep in mind that the formulas for Q and K look exactly the same, but we can calculate the value of Q with any set of concentrations while the value of K can only be determined by using *equilibrium* concentrations. This pattern of thinking about Q vs. K will help guide your mathematical justification of Le Châtelier's Principle for concentrations as well as **pressure**, but we will also see how **temperature** stands out as an exception.

Concentration Changes and Q

As we discussed in the last section, increasing the concentration of reactants or products will cause the system to respond by generating more species from the other side. Let's think about how Q vs. K might help us understand why this occurs.

We know that Q is the ratio of product concentrations to reactant concentrations raised to their **stoichiometric** coefficients. Therefore, if we increase the amount of reactants, we are decreasing the value of Q, and if we increase the amount of products, we are increasing the value of Q. Either change will cause the relationship $Q \neq K$, and the reaction will need to respond by shifting *back* to equilibrium, where $Q = K$.

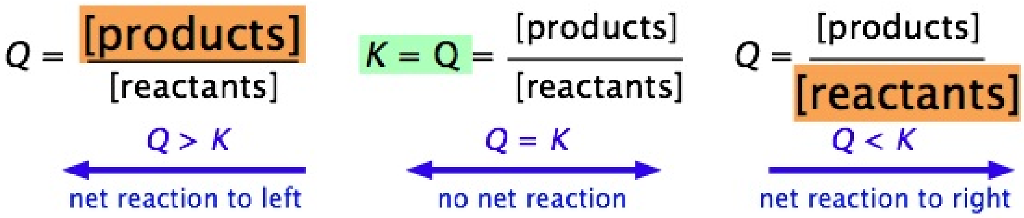


Image Courtesy of LibreTexts

As seen above, when product concentrations are increased, Q increases and $Q > K$. When reactant concentrations are raised, the opposite happens. The most important aspect to understand is that a system always responds in a way that the value Q will *approach back* to the value of K.

Pressure Changes and Q

Similar logic is applied for pressures, however, more emphasis is placed on the **exponents** of the reactants and products when calculating Q. For example, if increasing the pressure on a system causes equilibrium to shift toward the side with fewer moles of gas, then the stoichiometry of the reaction does matter when it comes to changes in pressure.

Example 7.10.1

Suppose we have a gas-phase reaction:

$$4\text{A} + 2\text{B} \rightleftharpoons 3\text{C}$$

The equilibrium constant expression for the reaction (using partial pressures) is

$$K_p = \frac{(P_\text{C})^3}{(P_\text{A})^4(P_\text{B})^2}$$

Note that the same rules between Q and K_c apply to Q_p and K_p. If the overall pressure increases, the partial pressures will also increase proportionally. (Recall that $P_i = \chi_i \cdot P_{total}$, where χ_i is the mole fraction of the ith sample).

Suppose the partial pressures of all substances (A, B, and C) are doubled. Thus, we can rewrite the reaction quotient as

$$Q_p = \frac{(2 \cdot P_\mathrm{C})^3}{(2 \cdot P_\mathrm{A})^4 (2 \cdot P_\mathrm{B})^2} = \frac{(P_\mathrm{C})^3}{8(P_\mathrm{A})^4 (P_\mathrm{B})^2} = \frac{1}{8} K_p \therefore Q_p < K_p$$

Since $Q_p < K_p$, the equilibrium will *shift to the right*, increasing the overall pressure of the products and decreasing the overall pressure of the reactants to attain equilibrium.

Similar logic can be applied if $Q_p > K_p$, where the equilibrium would *shift to the left*, increasing the overall pressure of the reactants and decreasing the overall pressure of the products to reach equilibrium.

Temperature as the Exception for Q

Unlike concentration and pressure, we cannot use Q to justify Le Châtelier's Principle in the case of temperature.

When we addressed temperature in the previous section, the main idea was determining whether the reaction was *endothermic* or *exothermic*. That way, heat energy could be viewed as either a *reactant* or a *product*, respectively. However, that is a simplification; the idea of heat energy being a "part" of the chemical reaction does not conceptualize.

Note 7.10.2

Although this way of thinking is valid and will result in correct answers, what is happening, in reality, is that the **equilibrium constant** is changing. Although we don't really talk about K changing, it's a temperature-dependent value in practical sense. This means that K is only constant when the temperature is constant. Based on your reaction type (endothermic and exothermic), K will either increase or decrease when the temperature is increased. This is when thinking about heat as a reactant or product will help you predict the direction in which the reaction will proceed. Just keep in mind that this case of Le Châtelier's Principle is **not** justified by using Q.

Problem 7.10.3 — Multiple Choice Question

How does Le Châtelier's Principle apply to changes in pressure?

(A) A rise in pressure shifts towards fewer moles of gas and vice versa as per Le Châtelier's Principle.
(B) An increase in pressure always leads to an increase in reactants according to Le Châtelier's Principle.
(C) Decrease in pressure always results in product formation according to Le Châtelier's Principle.
(D) Pressure changes do not affect reactions as per Le Châtelier's Principle.

Solution: We know that increasing the pressure on a system at constant temperature means that the volume decreases. Volume is proportional to moles of gas by Avogadro's law, so increasing pressure/decreasing volume will cause the reaction to favor the side with fewer moles of gas. This is consistent with answer choice $\boxed{\textbf{(A)}}$, which is correct. Eliminate (B) and (C); these are inconclusive statements because we do not know the relative number of moles of gas between the reactants and products. Finally, eliminate (D); pressure changes *do* in fact impact the equilibrium of gas-phase reactions.

§7.11 K_{sp} and Solubility Equilibria

The solubility-product constant, K_{sp}, is an equilibrium constant that demonstrates the extent to which an ionic solid dissolves in water.

Suppose that we have a beaker of distilled water at 25°C. If I were to place a sample of barium sulfate, $BaSO_4$, what reaction will occur?

$BaSO_4$ is a white solid. Some of it will dissociate into Ba^{2+} and SO_4^{2-} ions. However, it will be largely undissociated because of its low solubility in water. The reversible reaction that occurs in the beaker is

$$\mathrm{BaSO_4(s)} \rightleftharpoons \mathrm{Ba^{2+}(aq)} + \mathrm{SO_4^{2-}(aq)}$$

The solubility-product constant expression for the reaction is

$$K_{sp} = [\mathrm{Ba^{2+}}][\mathrm{SO_4^{2-}}]$$

Note that the value of K_{sp} for a given salt is only affected by the temperature by which the reaction occurs.

At 25°C, the value of K_{sp} for $BaSO_4$ is $1.1 \cdot 10^{-10}$.

Note 7.11.1

Keep these in mind when interpreting the value of K_{sp}:

- When K_{sp} is less than 1, this indicates that the salt is not very soluble in water. In the case of barium sulfate, the value of K_{sp} is so small that $BaSO_4$ can be considered insoluble in water.
- When K_{sp} is greater than 1, the ionic compound dissolves easily in water. For example, the value of K_{sp} for sodium chloride, NaCl, is much greater than 1, since it spontaneously dissolves in water.

Here are some important terms we must be familiar with:

1. The **solubility** of a substance is defined as the amount of solid that dissolves to form a saturated solution. The units for solubility are in grams per liter $\left(\frac{\mathrm{g}}{\mathrm{L}}\right)$
2. A **saturated solution** is a solution that has dissolved the maximum amount of solute it could. In a saturated solution, no more solute can be dissolved at a given temperature.

3. **Molar solubility** refers to the number of moles of the solid that dissolve to form ONE liter of saturated solution. The units of molar solubility are in moles per liter ($\mathrm{mol\,L^{-1}}$), or molar (M).

K_{sp} values can also be used to predict the relative solubilities of salts that produce the *same* number of ions in solution.

For example, the K_{sp} values of AgCl, AgBr, and AgI at 25°C are $1.8 \cdot 10^{-10}$, $5.0 \cdot 10^{-13}$, and $8.3 \cdot 10^{-17}$, respectively. These salts produce two ions in solution, so we can predict their relative solubilities simply by comparing their K_{sp} values. Since K_{sp} measures the extent to which an ionic compound dissolves, salts with higher K_{sp} values dissolve more than those with lower K_{sp} values. Thus, the following inequality ranks the solubilities of the three salts in water:

$$\boxed{\mathrm{AgI(s) < AgBr(s) < AgCl(s)}}$$

Key Takeaway: When comparing salts that produce the same number of ions, the substance with the highest K_{sp} has the highest solubility, and vice versa.

We can also use ion concentrations to determine the K_{sp} for an ionic solid at a given temperature.

Suppose we added a sample of solid calcium fluoride to pure water at 25°C. Eventually, the system is allowed to reach equilibrium. If the equilibrium concentration of Ca^{2+} ions is $2.1 \cdot 10^{-4}\,M$, how can we find the value of K_{sp} for CaF_2 at 25°C?
The equation that represents the dissolution of CaF_2 in water is

$$\mathrm{CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq)}$$

The solubility-product constant is given by $K_{sp} = [\mathrm{Ca^{2+}}][\mathrm{F^-}]^2$.

Note that there is an exponent of 2 on the concentration of $[\mathrm{F^-}]$ ions because the coefficient of F^- is 2 in the dissociation reaction.

To calculate the value of K_{sp}, we simply need to determine the equilibrium concentration of F^- ion, and then plug in to the K_{sp} expression.

The mole ratio between Ca^{2+} ions and F^- ions is 1 : 2, so at equilibrium there are twice as many fluoride ions as there are calcium cations, so

$$[\mathrm{F^-}] = 2 \cdot [\mathrm{Ca^{2+}}] = 2 \cdot 2.1 \cdot 10^{-4}\,M = 4.2 \cdot 10^{-4}\,M$$

Plugging in our ion concentrations, the value of K_{sp} for CaF_2 at 25°C is

$$K_{sp} = [\mathrm{Ca^{2+}}][\mathrm{F^-}]^2 \therefore K_{sp} = \left(2.1 \cdot 10^{-4}\right)\left(4.2 \cdot 10^{-4}\right)^2 = \boxed{3.7 \cdot 10^{-11}}$$

Using K_{sp} to Calculate Solubility

Previously, we discussed that molar solubility refers to the number of moles of the solid that dissolves to form one liter of saturated solution. We can calculate the molar solubility of a substance using its K_{sp} value at a certain temperature. I will explain the process in the following problem.

Problem 7.11.2 — Molar Solubility

At 25°C, the value of K_{sp} of lead(II) iodide, PbI_2, is $1.4 \cdot 10^{-8}$. Calculate the solubility of PbI_2 in mol/L.

Assume that before the reaction, only solid lead(II) chloride is present and that the initial concentrations of Pb^{2+} and Cl^- ions are 0 M. As the system approaches equilibrium, these concentrations will change. Therefore, we set up an ICE table.

	PbI_2(s)	$\rightleftharpoons$	Pb^{2+}(aq)	$2I^-$(aq)
Initial (M)	-	-	0	0
Change (M)	-	-	$+x$	$+2x$
Equilibrium (M)	-	-	x	$2x$

We begin with the K_{sp} expression for the dissolution of PbI_2(s):

$$K_{sp} = [Pb^{2+}][I^-]^2$$

In terms of x, the K_{sp} expression is

$$K_{sp} = (x)(2x)^2 = 4x^3$$

Here, x represents the molar solubility of PbI_2, the maximum amount of solid in moles that can be dissolved in one liter of saturated solution.

We know the value of K_{sp}, so we can plug in and solve for x:

$$1.4 \cdot 10^{-8} = 4x^3$$

Dividing by 4 and taking the cube root, we find that the solubility of PbI_2(s) is

$$x = \sqrt[3]{\frac{1.8 \cdot 10^{-4}}{4}} = \boxed{0.036 \text{ mol/L}}$$

Comparing The Values Of Q And K_{sp}

We can use the reaction quotient, Q, to predict whether precipitation occurs when two solutions containing dissolved ionic compounds are mixed.
The value of Q_{sp}, the **ion-product constant** is calculated by using the concentrations of the species in the *net* ionic reaction immediately after the solutions are mixed.
Finally, we can predict whether a precipitate forms or not by comparing the values of Q_{sp} and K_{sp}.

1. If $Q_{sp} < K_{sp}$, the solution is *undersaturated*, and no precipitate will form.
2. If $Q_{sp} = K_{sp}$, the rate of dissolution is equal to the rate of precipitate (the system is at equilibrium), and the solution is *saturated*. No net change in the amount of dissolved solid will occur.

3. If $Q_{sp} > K_{sp}$, the solution is *supersaturated*, and a precipitate will continue to form until $Q_{sp} = K_{sp}$ and the system reaches equilibrium.

Let's walk through an example.

Problem 7.11.3 — Will Precipitation Occur?

0.20 L of a $4.0 \cdot 10^{-3}\, M$ solution of $Pb\,(NO_3)_2$ is mixed with 0.80 L of a $8.0 \cdot 10^{-3}\, M$ solution of Na_2SO_4. Also, the value of K_{sp} for $PbSO_4$ is $6.3 \cdot 10^{-7}$ at 25°C. Determine whether $PbSO_4$ will precipitate after the solutions are mixed.

Solution: The net ionic reaction that occurs when the two solutions are mixed is

$$\mathrm{Pb^{2+}(aq) + SO_4^{2-}(aq) \rightarrow PbSO_4(s)}$$

The dissolution of $PbSO_4$ in water is represented by the reaction below:

$$\mathrm{PbSO_4(s) \rightleftharpoons Pb^{2+}(aq) + SO_4^{2-}(aq)}$$

The expression for Q_{sp} is $[Pb^{2+}]_0[SO_4^{2-}]_0$, where the $_0$ symbol indicates that these are the concentrations of Pb^{2+} and SO_4^{2-} ions immediately after the solutions are mixed. We used Q instead of K_{sp} here because $[Pb^{2+}]_0$ and $[SO_4^{2-}]_0$ are not equilibrium concentrations.

For the following calculations, note that $n = MV$: the number of moles of any substance is equal to the concentration multiplied by the volume of the solution.

$$[\mathrm{Pb^{2+}}]_0 = \frac{\text{mol Pb}^{2+}}{\text{mixture volume}} = \frac{0.20\,\mathrm{L} \cdot 4.0 \cdot 10^{-3}\, M}{0.20\,\mathrm{L} + 0.80\,\mathrm{L}} = 8.0 \cdot 10^{-4}\, M$$

$$[\mathrm{SO_4^{2-}}]_0 = \frac{\text{mol SO}_4^{2-}}{\text{mixture volume}} = \frac{0.80\,\mathrm{L} \cdot 8.0 \cdot 10^{-3}\, M}{0.20\,\mathrm{L} + 0.80\,\mathrm{L}} = 6.4 \cdot 10^{-3}\, M$$

We use these values to determine the value of the reaction quotient.

$$Q_{sp} = [\mathrm{Pb^{2+}}]_0[\mathrm{SO_4^{2-}}]_0 = \left(8.0 \cdot 10^{-4}\right)\left(6.4 \cdot 10^{-3}\right) = 5.1 \cdot 10^{-6}$$

Q_{sp} is greater than K_{sp} and the limit on how much $PbSO_4(s)$ can be dissolved has been exceeded. Therefore, the solution is supersaturated and a precipitate will form. Precipitation of $PbSO_4(s)$ will continue until the system reaches equilibrium and $Q_{sp} = K_{sp}$.

§7.12 Common-Ion Effect

In the previous section, we learned about K_{sp}, the equilibrium constant for dissolution of a salt. However, we only discussed the solubility of salts in water. What if dissolution occurred in a different solution? Specifically, what would happen if a solute was added to a solution that contained an ion that the solute dissolves into? This concept is known as the common-ion effect.

Definition 7.12.1

The **common-ion effect** describes how a common ion can *suppress*, or reduce, the solubility of an ionic compound with a common ion (an ion that is present in two or more different compounds) is added to a solution containing a salt of that ion.

The common-ion effect can significantly affect the **equilibrium** of the solution and cause concentrations of ionic species to change.

Example 7.12.2

Let's try dissolving solid AgBr into an aqueous solution of NaBr. Note that there will already be some concentration of Br^- ion present due to the dissolved NaBr. Therefore, our solubility equilibrium will adjust by producing more reactants.

As we can see, the common-ion effect is HIGHLY related to the concept of Le Châtelier's principle. The common ion's concentration can be considered as a *stress* that is introduced into the chemical system. This is just another example of Le Châtelier's principle that can be explained by the reaction quotient, Q.

Consider the dissociation of a generic slightly soluble salt XY:

$$\mathrm{XY(s)} \rightleftharpoons \mathrm{X^+(aq)} + \mathrm{Y^-(aq)}$$

The equilibrium constant expression for this reaction can be written as

$$K_{sp} = [\mathrm{X^+}][\mathrm{Y^-}]$$

If we placed XY in an aqueous solution that contains some initial concentration c_0 of Y^-, we can write the *reaction quotient* expression as the following:

$$Q_{sp} = [\mathrm{X^+}]\left([\mathrm{Y^-}] + c_0\right)$$

Since $c_0 > 0$, we know that $Q_{sp} > K_{sp}$ and thus the dissolution of XY(s) is inhibited by the presence of the common Y^- ion. The excess ions will precipitate out of the solution until the solution is saturated. This concept will make more sense in the practice problem that follows.

Problem 7.12.3 — Molar Solubility in Presence of Common Ion

Calculate the molar solubility of AgBr $\left(K_{sp} = 7.7 \cdot 10^{-13}\right)$ in a solution of both pure water and 0.0010 M NaBr.

Solution: First, let's find the molar solubility in pure water as we did in the previous section, 7.11.

We know that the dissolution of AgBr is given by

$$\mathrm{AgBr(s)} \rightleftharpoons \mathrm{Ag^+(aq)} + \mathrm{Br^-(aq)}$$

Now, we can set up an ICE table and determine the molar solubility of AgBr.

	AgBr(s)	$\rightleftharpoons$	Ag^+(aq)	Br^-(aq)
Initial (M)	-	-	0	0
Change (M)	-	-	$+x$	$+x$
Equilibrium (M)	-	-	x	x

We can plug in the relevant equation into our K_{sp} expression:

$$K_{sp} = [Ag^+][Br^-] = (x)\,(x) \therefore 7.7 \cdot 10^{-13} = x^2$$

x denotes the molar solubility of AgBr, and solving yields

$$x = \sqrt{7.7 \cdot 10^{-13}} = \boxed{8.8 \cdot 10^{-7}\,M}$$

Let's compare this molar solubility value to that in a 0.0010 M solution of NaBr. We can simplify this by assigning an initial Br^- concentration of 0.0010 M. Adjusting our ICE table gives

	AgBr(s)	$\rightleftharpoons$	Ag^+(aq)	Br^-(aq)
Initial (M)	-	-	0	0.0010
Change (M)	-	-	$+x$	$+x$
Equilibrium (M)	-	-	x	$0.0010 + x$

It follows that $K_{sp} = [Ag^+][Br^-]$, and in terms of x, we have

$$K_{sp} = (x)\,(0.0010 + x)$$

Watch Out! Solving for an exact value of x would require using the quadratic formula, which is excluded from the AP Chemistry syllabus. We will use our approximation that is valid for very small equilibrium constant values. Since the value of K_{sp} has an order of magnitude of 10^{-13}, the concentration of its constituent ions, denoted by x, will be very small.

We will use the following approximation:

$$0.0010 + x \approx 0.0010$$

Plugging in,

$$7.7 \cdot 10^{-13} = (x)(0.0010) \therefore x = \boxed{7.7 \cdot 10^{-10}\,M}$$

Note that this is a much smaller value than the calculated molar solubility of AgBr in a solution of pure water, so the presence of Br^- significantly reduces the solubility of AgBr(s) in water.

Justifying the Common Ion Effect

We dug a little bit into why the common ion effect is the way it is and how to calculate molar solubilities when common ions come into play, but why exactly does it work? The simple answer is Le Châtelier's principle! Like most other rules regarding non-standard conditions and equilibrium, Le Châtelier's principle can help us understand why the common-ion effect affects molar solubility.

For example, the common-ion effect would occur in the following scenario. If we wanted to dissolve $CaSO_4$ ($K_{sp} = 2.4 \cdot 10^{-5}$) in a solution of Na_2SO_4, then the common ion would be sulfate, SO_4^{2-}. We can write the equilibrium for the dissolution of $CaSO_4$:

$$CaSO_4(s) \rightleftharpoons Ca^{2+}(aq) + SO_4^{2-}(aq)$$

According to Le Châtelier's Principle, the common ion can be thought of as an **external stress** on our system, the stress being an already existing concentration of sulfate ion. Therefore, as $[SO_4^{2-}]$ increases, $Q_{sp} > K_{sp}$ and the reaction will proceed towards the reactants, decreasing the solubility of $CaSO_4$(s).

Essentially, we saw how Le Châtelier's principle can justify the common-ion effect. This can be qualitatively seen either by calculating Q or simply calculating the new molar solubility and observing it as lower than in a solution of pure water. By understanding Le Châtelier's principle, we can understand and articulate the common ion effect more clearly, which will be useful in answering free-response questions.

Speaking of which, we will end this section with a free-response practice problem.

Problem 7.12.4 — Free-Response Practice

Answer the following questions about the solubility of AgCl(s). The value of K_{sp} for AgCl(s) is $1.8 \cdot 10^{-10}$.

(a) Calculate the value of $[Ag^+]$ in a saturated solution of AgCl in water.

(b) The concentration of Cl^-(aq) in seawater is 0.54 M.

(i) Calculate the molar solubility of AgCl(s) in seawater.
(ii) Explain why AgCl(s) is less soluble in seawater than in distilled water.

Solution to part a: First, we construct the equilibrium constant expression for the dissolution of AgCl:

$$K_{sp} = [Ag^+][Cl^-]$$

Let $x = [Ag^+] = [Cl^-]$ which represent the molar solubility of AgCl(s).

$$1.8 \cdot 10^{-10} = (x)(x) = x^2$$
$$x = [Ag^+] = \sqrt{1.8 \cdot 10^{-10}} = \boxed{1.3 \cdot 10^{-5}\ M}$$

Solution to part b(i): The most important thing to note here is that even the ions are in a 1 : 1 ratio, $[Ag^+]$ does NOT equal $[Cl^-]$. In part (a), the only reason their concentrations were stoichiometrically equivalent was because the AgCl solution was SATURATED. Don't forget that the dissolution of AgCl is an *equilibrium*, so we cannot simply use the coefficients in the balanced chemical equation to describe relative amounts.

Instead, we need to use the K_{sp} expression and solve for $[\mathrm{Ag}^+]$. We have

$$K_{sp} = [\mathrm{Ag}^+][\mathrm{Cl}^-] \therefore [\mathrm{Ag}^+] = \frac{K_{sp}}{[\mathrm{Cl}^-]}$$
$$[\mathrm{Ag}^+] = \frac{K_{sp}}{[\mathrm{Cl}^-]} = \frac{1.8 \cdot 10^{-10}}{0.54} = \boxed{3.3 \cdot 10^{-10}\ M}$$

Solution to part b(ii): We know that seawater is essentially a solution of NaCl. Additionally, NaCl is a highly soluble salt, so seawater consists of freely floating Na^+ and Cl^- ions.

The dissolution equilibrium for AgCl is given by the reaction

$$\mathrm{AgCl(s)} \rightleftharpoons \mathrm{Ag^+(aq)} + \mathrm{Cl^-(aq)}$$

Therefore, Cl^- from seawater introduces the *common-ion effect* and the molar solubility of AgCl(s) is less than in distilled water.

§7.13 pH and Solubility

The solubility of some slightly soluble ionic substances can be affected by changes in the pH of their solutions.

We will examine the solubility of two ionic compounds, strontium fluoride, SrF_2, and lead (II) chloride, $PbCl_2$, and observe how they are affected by changes in pH.

Case Study 1: If we placed a sample of SrF_2 in a beaker with distilled water, the following reaction will occur:

$$\mathrm{SrF_2(s)} \rightleftharpoons \mathrm{Sr^{2+}(aq)} + 2\mathrm{F^-(aq)}$$

At equilibrium, the solution is saturated, so the concentrations of ions remains constant. Now, we will introduce a stress to the equilibrium system. Specifically, we will add H^+ ions, thus decreasing the pH of the solution. The H^+ ions will react with some F^- ions, forming HF, according to the reaction

$$\mathrm{H^+(aq)} + \mathrm{F^-(aq)} \rightleftharpoons \mathrm{HF(aq)}$$

Since some of the F^- was consumed by the formation of HF, the free ion concentration of F^- decreased. Let's revisit the dissolution of SrF_2 in water.

$$\mathrm{SrF_2(s)} \rightleftharpoons \mathrm{Sr^{2+}(aq)} + 2\mathrm{F^-(aq)}$$

According to Le Châtelier's principle, decreasing $[F^-]$ will cause the system to shift to the right, increasing the solubility of SrF_2(s).

Case Study 2: If we placed a sample of $PbCl_2$ in a beaker with distilled water, the following reaction will occur:

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$$

Similarly, the solution becomes saturated when the reaction reaches equilibrium. We will introduce the same stress to the system: the addition of H^+ ions, which will decrease the pH of the solution. However, Cl^- ions do NOT react with H^+ ions introduced to the system. Thus, decreasing the pH did NOT affect the solubility of $PbCl_2(s)$, because neither $[Pb^{2+}]$ nor $[Cl^-]$ had changed.

Important: Now, you might be asking, "Why was the F^- ion concentration decreased by adding H^+ to the system, but the Cl^- ion concentration remained the same?"

Excellent question! In the first case study, we observed that the F^- ions reacted with the introduced H^+ ions and formed HF. However, in the second case study, the Cl^- ions did NOT react with the introduced H^+ ions and form HCl. The reason lies in the relative strengths of HF and HCl as acids.

HF is a weak acid; when placed in water, the following reaction occurs:

$$HF(aq) \rightleftharpoons H^+(aq) + F^-(aq)$$

Because HF is a weak acid, its conjugate base, $F^-(aq)$, must have a strong affinity for protons (we will see the reason why in section 8.6), so there is a tendency for the reverse reaction to occur: the formation of HF(aq) by $H^+(aq)$ and $F^-(aq)$ ions.

However, HCl is a very strong acid; when placed in water, the following reaction occurs:

$$HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$$

There is no equilibrium arrow for this reaction, since dissociation of strong acids proceeds to completion. As HCl is strong, its conjugate base, $Cl^-(aq)$, has a very weak affinity for protons, so there is no tendency for the reverse reaction−the formation of HCl(aq) by $H^+(aq)$ and $Cl^-(aq)$ ions−to occur.

Key Takeaway: In general, ionic compounds containing basic anions (such as conjugate bases of weak acids), solubility increases as the pH of the solution decreases. For ionic compounds containing anions of negligible base strength (such as conjugate bases of strong acids), solubility is unaffected by changes in pH.

§7.14 Free Energy of Dissolution

Free energy of dissolution refers to the total energy change when a solute is dissolved in a solvent. This topic is closely related to thermodynamics and its applications (units 6 and 9, respectively). If you face some trouble understanding this, don't worry. Just skim through the first few sections of Unit 9 and you should make more sense of it.

Key Question: Why Are Some Salts Soluble In Water While Others Are

Insoluble Or Only Partially Soluble?

There are a number of factors that come into play here.

- Enthalpy, or the heat energy that is exchanged at a constant pressure.
- Entropy, the *dispersion* of energy throughout a set system.
- When both of these functions are combined, we obtain a third function called **free energy**. This measures the energy available to do work.

Free energy helps in understanding **thermodynamic favorability** of certain processes.

> **Note 7.14.1**
> If chemical reactions are considered thermodynamically favorable, then they are highly likely to proceed and form significant amounts of products under the specified conditions.

Enthalpy of Dissolution, $\Delta H^\circ_{dissolution}$

When a salt (ionic compound) is placed in water, energy is required to *break* hydrogen bonding between water molecules as well as the cation-anion attractions within the ionic structure, both **endothermic** processes ($\Delta H^\circ > 0$). Next, the water molecules SURROUND the ions, referred to as **ion-dipole** attractions. When these attractive forces are formed, energy is released, indicating an **exothermic** process ($\Delta H^\circ < 0$).

> **Definition 7.14.2**
> The overall enthalpy of dissolution, $\Delta H^\circ_{dissolution}$, is given by the formula
>
> $$\Delta H^\circ_{dissolution} = \Delta H^\circ_1 + \Delta H^\circ_2 + \Delta H^\circ_3$$
>
> where ΔH°_1 is the energy required to break hydrogen bonds, ΔH°_2 is the energy required to break cation-ion attractions, and ΔH°_3 is the energy released by forming ion-dipole attractions.

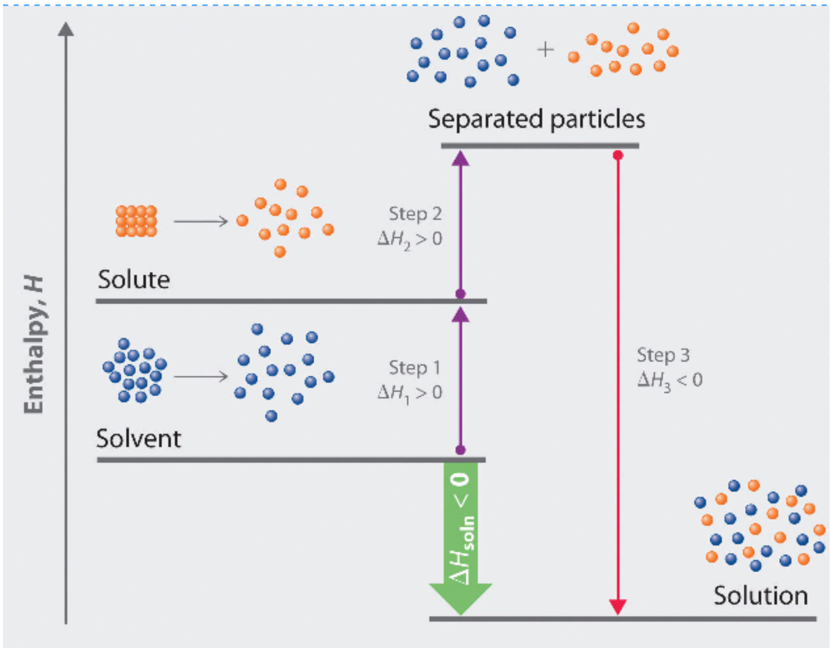


Image Courtesy of Chemistry LibreTexts

- If $\Delta H^\circ_{dissolution} < 0$, the dissolution of the solute is considered **favorable**. However, this does not mean that all such solutes will dissolve; it only indicates that there are no barriers to the process of dissolution itself.
- If $\Delta H^\circ_{dissolution} > 0$, the dissolution of the solute is considered **unfavorable**. Again, this does not mean that all such solutes will not dissolve; it only says that, in terms of energetics, there is a barrier that must be overcome.

Entropy of Dissolution, $\Delta S^\circ_{dissolution}$

Entropy is a measure of the dispersal of energy and matter.
As the number of attractive forces *decreases*, the molecules tend to separate, so the entropy *increases*. An increase in entropy means that a system is more dispersed; there are more available **microstates**, or ways to rearrange the system.

Note 7.14.3
Entropy will be studied more thoroughly in Unit 9.

For dissolving of salts, the process is favorable if $\Delta S^\circ_{dissolution} > 0$ and unfavorable if $\Delta S^\circ_{dissolution} < 0$. This is because entropy increases as attractive forces are broken, and it decreases as they are formed.

Free Energy Dissolution, $\Delta G^\circ_{dissolution}$

Recall that when enthalpy and entropy functions are combined, a function called free energy forms. The value of ΔG° determines whether a salt is likely to dissolve.

Definition 7.14.4

The standard free energy change, ΔG°, is given by the equation

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

where ΔH° is the enthalpy change, ΔS° is the entropy change, and T is the temperature in Kelvins.

Pay attention to these notes−they will be useful in Unit 9.

- Free energy represents the energy available to do work.
- ΔG° combines contributions from ΔH° and ΔS°.
- If $\Delta G^\circ > 0$, dissolving a salt is thermodynamically unfavorable, and thermodynamically favorable if $\Delta G^\circ < 0$.
- For soluble salts, $\Delta G^\circ_{dissolution} < 0$, and $\Delta G^\circ_{dissolution} > 0$ for insoluble/slightly soluble salts.

§7.15 Practice Problems

Problem 7.15.1 — 1988 AP Chemistry FRQ

$$NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g) \qquad \Delta H = +93\,\text{kJ/mol}$$

The equilibrium above is established by placing solid NH_4HS in an evacuated container at 25°C.
At equilibrium, some solid NH_4HS remains in the container. Predict and explain each of the following.

(a) The effect on the equilibrium partial pressure of NH_3 gas when additional solid NH_4HS is introduced into the container.

(b) The effect on the equilibrium partial pressure of NH_3 gas when additional H_2S gas is introduced into the container.

(c) The effect on the mass of solid NH_4HS present when the volume of the container is decreased.

(d) The effect on the mass of solid NH_4HS present when the temperature is increased.

Solution to part a:

$$K_p = (P_{NH_3})(P_{H_2S})$$

Since NH_4HS is a solid and is not included in the K_p expression, it does not affect the equilibrium and the equilibrium partial pressure of NH_3 gas would be $\boxed{\text{unaffected}}$.

Solution to part b: Introducing more of existing gas into a container increases its partial pressure. Since K_p must be constant at the same temperature, the equilibrium partial pressure of NH_3 $\boxed{\text{decreases}}$ as the partial pressure of H_2S increases.

Solution to part c: The mass of NH_4HS increases. According to Le Châtelier's principle, a decrease in the volume of the system will cause the reaction to shift to the side with fewer moles of gaseous species. Looking at the equilibrium reaction, the reactants side (containing NH_4HS) will be favored when the system reestablishes equilibrium. Thus, the mass of solid NH_4HS $\boxed{\text{increases}}$.

Solution to part d: According to the problem statement, the value of ΔH is positive, indicating an endothermic reaction. As an endothermic process absorbs heat, the forward reaction will proceed closer to completion as the temperature is raised. Therefore, the mass of solid NH_4HS $\boxed{\text{decreases}}$.

Problem 7.15.2 — 2001 AP Chemistry FRQ

Answer the following questions related to the solubility of the chlorides of silver and lead.

(a) At 10°C, $8.9 \cdot 10^{-5}$ g of AgCl(s) will dissolve in 100. mL of water.

(i) Write the equation for the dissociation of AgCl(s) in water.
(ii) Calculate the solubility, in mol L^{-1}, of AgCl(s) in water at 10°C.
(iii) Calculate the value of the solubility-product constant, K_{sp}, for AgCl(s) at 10°C.

(b) At 25°C, the value of K_{sp} for $PbCl_2(s)$ is $1.6 \cdot 10^{-5}$ and the value of K_{sp} for AgCl(s) is $1.8 \cdot 10^{-10}$.

(i) If 60.0 mL of 0.0400 M NaCl(aq) is added to 60.0 mL of 0.0300 M $Pb(NO_3)_2(aq)$, will a precipitate form? Assume that volumes are additive. Show calculations to support your answer.
(ii) Calculate the equilibrium value of $[Pb^{2+}(aq)]$ in 1.00 L of saturated $PbCl_2$ solution to which 0.250 mole of NaCl(s) has been added. Assume that no volume change occurs.
(iii) If 0.100 M NaCl(aq) is added slowly to a beaker containing both 0.120 M $AgNO_3(aq)$ and 0.150 M $Pb(NO_3)_2(aq)$ at 25°C, which will precipitate first, AgCl(s) or $PbCl_2(s)$? Show calculations to support your answer.

Solution to part a(i): AgCl is an insoluble salt and does not fully dissociate in water, that is, the reaction does not reach completion, so our chemical equation is

$$\boxed{\text{AgCl(s)} \rightleftharpoons \text{Ag}^+\text{(aq)} + \text{Cl}^-\text{(aq)}}$$

Solution to part a(ii): Since we are asked to calculate the solubility, x, in mol L^{-1}, we need to convert the mass of AgCl(s) from grams to moles and then divide by the volume of water in liters.

$$\text{molar solubility} = \frac{\text{mol solute}}{\text{liters solution}}$$

$$\therefore x = 8.9 \cdot 10^{-5} \cancel{\text{g AgCl}} \cdot \frac{1 \text{ mol AgCl}}{\cancel{143.32 \text{ g AgCl}}} \cdot \frac{1}{0.100 \text{ L}} = \boxed{6.2 \cdot 10^{-6} \text{ mol L}^{-1}}$$

Solution to part a(iii): Since the chemical equation that describes the dissolution of AgCl(s) is given by

$$\text{AgCl(s)} \rightleftharpoons \text{Ag}^+\text{(aq)} + \text{Cl}^-\text{(aq)}$$

the solubility-product constant has an equilibrium expression given by

$$K_{sp} = [\text{Ag}^+][\text{Cl}^-]$$

Because molar solubility refers to the maximum amount of an ionic salt that can dissolve in water, the solution is saturated and thus $[Ag^+] = [Cl^-]$ and thus

$$K_{sp} = x^2 = \left(6.2 \cdot 10^{-6}\right)^2 = \boxed{3.8 \cdot 10^{-11}}$$

Solution to part b(i): For these types of problems, we calculate the concentrations of each constituent ion (in the ionic salt) immediately after the solutions are mixed.

The general strategy is to use $n = MV$ to calculate the number of moles of that ion initially present, and then divide by the total volume (the sum of the volumes of both solutions).

Thus, we have

$$[Cl^-]_0 = \frac{0.060\text{ L} \cdot 0.040\ M}{0.060\text{ L} + 0.060\text{ L}} = 0.020\ M$$

$$[Pb^{2+}]_0 = \frac{0.060\text{ L} \cdot 0.030\ M}{0.060\text{ L} + 0.060\text{ L}} = 0.015\ M$$

Additionally, once the solutions are mixed, the system is no longer at equilibrium, so

$$Q_{sp} = [Pb^{2+}]_0[Cl^-]_0^2 = (0.015)\,(0.020)^2 = 6.0 \cdot 10^{-6}$$

Because Q_{sp} is less than the K_{sp} for $PbCl_2$ (at this temperature), the solution is undersaturated so no precipitate forms.

Solution to part b(ii): If 0.250 mol of NaCl(s) has been added to 1.00 L of saturated $PbCl_2$ solution, then the equilibrium concentration of Cl^- ion is 0.25 M. We can rearrange the K_{sp} expression of $PbCl_2$ to solve for $[Pb^{2+}]$ at equilibrium:

$$K_{sp} = [Pb^{2+}][Cl^-]^2 \therefore [Pb^{2+}] = \frac{K_{sp}}{[Cl^-]^2} = \frac{1.6 \cdot 10^{-5}}{(0.25)^2} = \boxed{2.6 \cdot 10^{-4}\ M}$$

Solution to part b(iii): The answer here lies in the equilibrium concentration of Cl^- for both ionic compounds.

We will proceed with the following:

$$\text{For AgCl solution : } K_{sp} = [Ag^+][Cl^-] \therefore [Cl^-] = \frac{K_{sp}^{\text{AgCl}}}{[Ag^+]}$$

$$[Cl^-] = \frac{1.8 \cdot 10^{-10}}{0.120} = 1.5 \cdot 10^{-9}\ M$$

$$\text{For PbCl}_2\text{ solution : } K_{sp} = [Pb^{2+}][Cl^-]^2 \therefore [Cl^-] = \sqrt{\frac{K_{sp}^{\text{PbCl}_2}}{[Pb^{2+}]}}$$

$$[Cl^-] = \sqrt{\frac{1.6 \cdot 10^{-5}}{0.150}} = 1.0 \cdot 10^{-2}\ M$$

Now, let's consider the scale of the difference between these two values. For AgCl(s), the equilibrium concentration of Cl^- is far less than that of in $PbCl_2$. Essentially, $[Cl^-]$ will reach a concentration of $1.5 \cdot 10^{-9}\ M$ much before it reaches a concentration of $1.0 \cdot 10^{-2}\ M$, so $\boxed{\text{AgCl(s)}}$ will precipitate first.

Problem 7.15.3 — 2008 AP Chemistry FRQ

Answer the following questions regarding the decomposition of or arsenic pentafluoride, $AsF_5(g)$.

(a) A 55.8 g sample of $AsF_5(g)$ is introduced into an evacuated 10.5 L container at 105°C.

(i) What is the initial molar concentration of $AsF_5(g)$ in the container?
(ii) What is the initial pressure, in atmospheres, of the $AsF_5(g)$ in the container?

At 105°C, $AsF_5(g)$ decomposes into $AsF_3(g)$ and $F_2(g)$ by the following chemical equation

$$AsF_5(g) \rightleftharpoons AsF_3(g) + F_2(g)$$

(b) In terms of molar concentrations, write the equilibrium constant expression for the decomposition of $AsF_5(g)$.

(c) When the equilibrium is established, 27.7 percent of the original number of moles of $AsF_5(g)$ has decomposed.

(i) Calculate the molar concentration of $AsF_5(g)$ at equilibrium.
(ii) Using molar concentrations, calculate the value of the equilibrium constant, K_{eq}, at 105°C.

(d) Calculate the mole fraction of $F_2(g)$ in the container at equilibrium.

Solution to part a: We find the number of moles of $AsF_5(g)$.

$$55.8\,\cancel{\text{g AsF}_5} \cdot \frac{1\text{ mol AsF}_5}{169.9\,\cancel{\text{g AsF}_5}} = 0.328\text{ mol AsF}_5$$

Since molarity is defined as moles of solute per liter of solution, we have

$$[\text{AsF}_5]_0 = \frac{0.328\text{ mol}}{10.5\text{ L}} = \boxed{0.0313\ M}$$

Solution to part a(ii): We rearrange the Ideal Gas Law equation to solve for pressure:

$$PV = nRT \therefore P = \frac{nRT}{V}$$

$$P = \frac{(0.328\,\cancel{\text{mol}})(0.0821\,\cancel{\text{L}}\text{ atm }\cancel{\text{mol}^{-1}}\,\cancel{\text{K}^{-1}})(378\,\cancel{\text{K}})}{10.5\,\cancel{\text{L}}} = \boxed{0.969\text{ atm}}$$

Solution to part b: Since $K_c = \frac{[\text{products}]}{[\text{reactants}]}$ raised to the power of their coefficients, the expression for the equilibrium constant of this reaction is

$$\boxed{K_c = \frac{[\text{AsF}_3][\text{F}_2]}{[\text{AsF}_5]}}$$

Solution to part c(i): Since 27.7% of the original sample of AsF_5(g) has decomposed, there is $100\% - 27.7\% = 72.3\%$ of the number of moles of AsF_5(g) remaining at equilibrium.
The molar concentration of AsF_5(g) at equilibrium is thus

$$[\text{AsF}_5] = 0.723 \cdot [\text{AsF}_5]_0 = 0.723 \cdot 0.0313\,M = \boxed{0.0226\,M}$$

Solution to part c(ii): Initially, the molar concentrations of AsF_3(g) and F_2(g) are both $0\,M$. As the reaction progresses, the amount of AsF_5(g) decreased by $0.277 \cdot [\text{AsF}_5]_i = 0.277 \cdot 0.0313\,M = 0.00867\,M$. Because all three species react in a $1:1:1$ ratio, the molar concentrations of AsF_3(g) and F_2(g) also increased by $0.00867\,M$.
However, the equilibrium concentrations of the three species are NOT equal. Don't fall for this! The equilibrium concentration of AsF_5(g) is what we found in part (c)(i): $0.0226\,M$.

$$K_{eq} = \frac{[\text{AsF}_3][\text{F}_2]}{[\text{AsF}_5]} = \frac{(0.00867)(0.00867)}{(0.0226)} = \boxed{0.00333}$$

Alternatively, you could've also used an ICE (Initial, Change, Equilibrium) table. If you need a refresher on this method, refer back to section 7.7.

Solution to part d: Since we know the molar concentrations of all species at equilibrium, we can multiply these values by the container volume to find the number of moles for each substance at equilibrium.

$$\text{moles AsF}_5 = 0.0226\,M \cdot 10.5\,\text{L} = 0.237\,\text{mol}$$

$$\text{moles F}_2 = \text{moles AsF}_3 = 0.00867\,M \cdot 10.5\,\text{L} = 0.0910\,\text{mol}$$

Since the mole fraction of a substance is equal to moles of substance divided by total number of moles, the mole fraction of F_2(g) in the container is

$$\chi_{\text{F}_2} = \frac{0.0910\,\text{mol}}{0.0910\,\text{mol} + 0.0910\,\text{mol} + 0.2376\,\text{mol}} = \boxed{0.217}$$

Problem 7.15.4 — 2010 AP Chemistry FRQ

Several reactions are carried out using AgBr, a cream-colored silver salt for which the value of the solubility-product constant, K_{sp}, is $5.0 \cdot 10^{-13}$ at 298 K.

(a) Write the expression for the solubility-product constant, K_{sp}, of AgBr.

(b) Calculate the value of $[Ag^+]$ in 50.0 mL of a saturated solution of AgBr at 298 K.

(c) A 50.0 mL sample of distilled water is added to the solution described in part (b), which is in a beaker with some solid AgBr at the bottom. The solution is stirred and equilibrium is reestablished. Some solid AgBr remains in the beaker. Is the value of $[Ag^+]$ greater than, less than, or equal to the value you calculated in part (b)? Justify your answer.

(d) Calculate the minimum volume of distilled water, in liters, necessary to completely dissolve a 5.0 g sample of AgBr(s) at 298 K. (The molar mass of AgBr is 188 g mol^{-1}.)

(e) A student mixes 10.0 mL of $1.5 \cdot 10^{-4}$ M $AgNO_3$ with 2.0 mL of $5.0 \cdot 10^{-4}$ M NaBr and stirs the resulting mixture. What will the student observe? Justify your answer with calculations.

(f) The color of another salt of silver, AgI(s), is yellow. A student adds a solution of NaI to a test tube containing a small amount of solid, cream-colored AgBr. After stirring the contents of the test tube, the student observes that the solid in the test tube changes color from cream to yellow.

(i) Write the chemical equation for the reaction that occurred in the test tube.
(ii) Which salt has the greater value of K_{sp}: AgBr or AgI? Justify your answer.

Solution to part a: The dissociation reaction of solid AgBr in water is

$$\mathrm{AgBr(s)} \rightleftharpoons \mathrm{Ag^+(aq)} + \mathrm{Br^-(aq)}$$

Excluding AgBr as it is a pure solid, the expression for the solubility-product constant is

$$\boxed{K_{sp} = [\mathrm{Ag^+}][\mathrm{Br^-}]}$$

Solution to part b: Once the solution of AgBr is saturated, it is in *equilibrium* with its constituent ions, Ag^+ and Br^-, both having equal concentration.

Let x represent the equilibrium concentrations of both Ag^+(aq) and Br^-(aq).

$$K_{sp} = (x)\,(x) = x^2$$
$$x = [\mathrm{Ag^+}] = \sqrt{5.0 \cdot 10^{-13}} = \boxed{7.1 \cdot 10^{-7}\ M}$$

Solution to part c: The solution is already saturated. Therefore, the concentrations of ions do not depend on the volume of the solution. Thus, the value of $[Ag^+]$ after the addition of distilled water is $\boxed{\text{equal}}$ to the value in part (b).

Solution to part d: We can determine the number of moles in the sample of AgBr(s) by using the molar mass.

$$5.0\,\cancel{\text{g AgBr}} \cdot \frac{1\text{ mol AgBr}}{188\,\cancel{\text{g AgBr}}} = 0.0266\text{ mol AgBr}$$

Note that since we are minimizing volume, we are maximizing the concentration of ions in solution. The maximum concentration of Ag^+ (and also Br^-) ion is achieved when the solution is saturated; $[Ag^+] = [Br^-] = 7.1 \cdot 10^7\text{ mol L}^{-1}$.

Molarity is defined as moles per liter, or $M = \frac{n}{V}$.
Rearranging for volume, we have

$$V = \frac{n}{M} = \frac{0.0266\,\cancel{\text{mol}}}{7.1 \cdot 10^{-7}\,\cancel{\text{mol}}\,\text{L}^{-1}} = \boxed{3.7 \cdot 10^4\text{ L}}$$

Solution to part e: We will calculate the concentration of each of Ag^+ and Br^- immediately after the solutions are mixed. Since $n = MV$, our setup will be

$$[Ag^+]_0 = \frac{(10.0\,\cancel{\text{mL}})\left(1.5 \cdot 10^{-4}\,M\right)}{12.0\,\cancel{\text{mL}}} = 1.3 \cdot 10^{-4}\,M$$

$$[Br^-]_0 = \frac{(2.0\,\cancel{\text{mL}})\left(5.0 \cdot 10^{-4}\,M\right)}{12.0\,\cancel{\text{mL}}} = 8.3 \cdot 10^{-5}\,M$$

Since we are no longer in equilibrium, these concentrations are not equilibrium concentrations. However, they will allow us to find the ion-product constant, which represents the reaction quotient expression.

$$Q_{sp} = [Ag^+]_0[Br^-]_0 = \left(1.3 \cdot 10^{-4}\right)\left(8.3 \cdot 10^{-5}\right) = 1.1 \cdot 10^{-8}$$

Now that we know the value of Q_{sp}, we can compare it to K_{sp}, and this comparison will tell us whether precipitation occurs or not.

$$K_{sp} = 5.0 \cdot 10^{-13} \therefore Q_{sp} > K_{sp}$$

The solution is supersaturated, so the equilibrium will shift to the left, favoring the reactants, and resulting in $\boxed{\text{precipitation of AgBr(s)}}$.

Solution to part f(i): Since the contents of the test tube changed color from cream to yellow, the yellow precipitate AgI(s) formed as a result of adding NaI(aq) to the AgBr(s) sample.
Moreover, when two ionic substances react with each other, their cations and anions exchange. The reaction that occurs is

$$\boxed{\text{AgBr(s)} + \text{NaI(s)} \rightarrow \text{AgI(s)} + \text{NaBr(aq)}}$$

Alternatively, we could recognize $Na^+(aq)$ as a spectator ion, cancel it off, and find the net ionic equation as

$$\boxed{AgBr(s) + I^-(aq) \rightarrow AgI(s) + Br^-(aq)}$$

Solution to part f(ii): Based on the information given and our answers to previous parts of the problem, we should conclude that $\boxed{AgBr}$ must have the greater value of K_{sp}. The precipitate consists of the *less soluble* salt when both I^- and Br^- ions are present. Because the color of the test tube turns yellow, it is AgI(s) that precipitates, not AgBr(s), which means the former has a lower equilibrium concentration of its constituent ions than the latter, and thus a lower K_{sp} value.

Alternatively, you could have used properties of K_{eq} to realize that the overall reaction has an equilibrium constant that can be represented as

$$K_{eq} = \frac{K_{sp} \text{ of AgBr}}{K_{sp} \text{ of AgI}}$$

Since yellow AgI precipitates, the equilibrium positions favors the products and $K_{eq} > 1$. This implies that

$$\boxed{K_{sp} \text{ of AgBr} > K_{sp} \text{ of AgI}}$$

Problem 7.15.5 — 2016 AP Chemistry FRQ

$$Ba^{2+}(aq) + EDTA^{4-}(aq) \rightleftharpoons Ba(EDTA)^{2-}(aq) \qquad K = 7.7 \cdot 10^7$$

The polyatomic ion $C_{10}H_{12}N_2O_8^{4-}$ is commonly abbreviated as $EDTA^{4-}$. The ion can form complexes with metal ions in aqueous solutions. A complex of $EDTA^{4-}$ with Ba^{2+} ion forms according to the equation above. A 50.0 mL volume of a solution that has an $EDTA^{4-}(aq)$ concentration of 0.30 M is mixed with 50.0 mL of a 0.20 M $Ba(NO_3)_2$ to produce 100.0 mL of solution.

(a) Considering the value of K for the reaction, determine the concentration of $Ba(EDTA)^{2-}(aq)$ in the 100.0 mL of solution. Justify your answer.

(b) The solution is diluted with distilled water to a total volume of 1.00 L. After equilibrium has been reestablished, is the number of moles of $Ba^{2+}(aq)$ present in the solution greater than, less than, or equal to the number of moles of $Ba^{2+}(aq)$ present in the original solution before it was diluted? Justify your answer.

Solution to part a: The value of K for this reaction is very large (10^7 order of magnitude), so it essentially proceeds to completion. Also, we can calculate the number of moles for each reactant to determine which one is limiting.

We proceed using $n = MV$.

$$n_{Ba^{2+}} = 0.20\, M \cdot 0.050\, \text{L} = 0.010\, \text{mol}$$

$$n_{\text{EDTA}^{4-}} = 0.30\,M \cdot 0.050\,\text{L} = 0.015\,\text{mol}$$

Because the Ba^{2+} and $EDTA^{4-}$ react in a $1:1$ ratio, Ba^{2+}(aq) depletes first, and is the limiting reactant.

The concentration of Ba^{2+}—when the solutions are immediately mixed but prior to any reaction—is equal to half the concentration of $0.20\,M$, or $0.20\,M/2 = 0.10\,M$.

Finally, using $M = \frac{n}{V}$, we find that the equilibrium concentration of Ba^{2+} is equal to $\boxed{0.10\,M}$.

Solution to part b: According to Le Châtelier's principle, dilution causes the reaction to shift in the direction with more aqueous species. That direction is towards the reactants side. Therefore, the number of moles of Ba^{2+}(aq) in the solution will be greater than the number of moles of Ba^{2+}(aq) present in the original solution before it was diluted.

You could also justify your answer mathematically.
Immediately after the solution is diluted, the concentrations of all species are reduced to one-tenth of their equilibrium values (their volume increased by a factor of 10).

$$Q = \frac{\frac{1}{10}[\text{Ba(EDTA)}^{2-}]}{\frac{1}{10}[\text{Ba}^{2+}] \cdot \frac{1}{10}[\text{EDTA}^{-4}]} = 10K \therefore Q > K$$

Because $Q > K$, the reaction will produce more reactants as it re-establishes equilibrium. Therefore, the number of moles of Ba^{2+}(aq) will be $\boxed{\text{greater than}}$ the number of moles of Ba^{2+}(aq) in the original solution.

Problem 7.15.6 — 2017 AP Chemistry FRQ

Answer the following questions about $Mg(OH)_2$. At 25°C, the value of the solubility-product constant, K_{sp}, for $Mg(OH)_2$(s) is $1.8 \cdot 10^{-11}$.

(a) Calculate the number of grams of $Mg(OH)_2$ (molar mass 58.32 g/mol) that is dissolved in 100. mL of a saturated solution of $Mg(OH)_2$ at 25°C.

(b) The energy required to separate the ions in the $Mg(OH)_2$ crystal lattice into individual Mg^{2+}(g) and OH^-(g) ions, as represented in the table below, is known as the lattice energy of $Mg(OH)_2$(s). As shown in the table, the lattice energy of $Sr(OH)_2$(s) is less than the lattice energy of $Mg(OH)_2$(s). Explain why in terms of periodic properties and Coulomb's law.

Reaction	Lattice Energy (kJ/mol)
$Mg(OH)_2(s) \rightarrow Mg^{2+}(g) + 2\,OH^-(g)$	2900
$Sr(OH)_2(s) \rightarrow Sr^{2+}(g) + 2\,OH^-(g)$	2300

Solution to part a: The dissolution of $Mg(OH)_2(s)$ in water is given by the following chemical equation:

$$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq)$$

Thus, the solubility-product constant expression can be written as

$$K_{sp} = [Mg^{2+}][OH^-]^2$$

If we call x the molar solubility of $Mg(OH)_2$ in water, then x and $2x$, respectively, are the concentrations of Mg^{2+} and OH^- ions. (The equilibrium concentration of OH^- is $2x$ due to the stoichiometric coefficients in the dissolution equation for $Mg(OH)_2$.)

Thus, the K_{sp} expression can be written as

$$1.8 \cdot 10^{-11} = (x)(2x)^2 = 4x^3$$

and the molar solubility of $Mg(OH)_2$ is

$$x = [Mg^{2+}] = \sqrt[3]{\frac{1.8 \cdot 10^{-11}}{4}} = 1.65 \cdot 10^{-4}\ M$$

This is also the amount concentration of $Mg(OH)_2$ that dissolved!

Based on the molar solubility and molar mass of $Mg(OH)_2$, we can convert number of moles to number of grams:

$$0.100\,\cancel{L} \cdot \frac{1.65 \cdot 10^{-4}\,\cancel{mol}}{1\,\cancel{L}} \cdot \frac{58.32\text{ g } Mg(OH)_2}{1\,\cancel{mol}} = \boxed{9.6 \cdot 10^{-4}\text{ g } Mg(OH)_2}$$

Solution to part b: Lattice energy is related to the strength of electrostatic forces between ions in a crystal lattice of a compound. Thus, the ionic compound with stronger forces of electrostatic attraction will have greater lattice energy.

Coulomb's law states that the electrostatic force of attraction is proportional to the magnitudes of charge and inversely proportional to the distance between ions:

$$F \propto \frac{q_1 q_2}{r^2}$$

Since both $Mg(OH)_2$ and $Sr(OH)_2$ share the OH^- ion, the difference in lattice energy must be attributed to the chemical properties of the Mg^{2+} and Sr^{2+} cations.

Mg^{2+} and Sr^{2+} both have a charge of +2, so this cannot cause the difference. However, the Sr^{2+} ion is larger than the Mg^{2+} ion because it occupies more energy levels (or electron shells). Coulomb's law states that the force of attraction between cation and anion is inversely proportional to the square of the distance between them. Since the distance between Mg^{2+} and OH^- is shorter than the distance between Sr^{2+} and OH^-, the attractive forces in $Sr(OH)_2$ are weaker; therefore, its lattice energy is smaller.

8 Acids and Bases

This unit is conceptually similar to equilibrium, but with a greater emphasis on acid-base chemistry. We will learn about pH and pOH, weak and strong acids and bases, buffers, titration, etc.

§8.1 Introduction to Acids and Bases

Definition 8.1.1

A Brønsted-Lowry **acid** is any chemical species that can *donate* a proton or H^+ ion in a chemical reaction.

Definition 8.1.2

A Brønsted-Lowry **base** is any chemical species that can *accept* a proton or H^+ ion in a chemical reaction.

Autoionization of Water

A very critical equilibrium involving water is given by the chemical equation:

$$2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

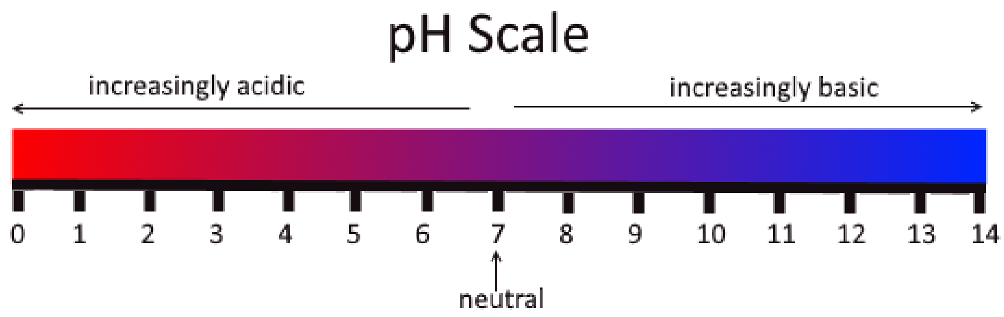
In this reaction, one molecule of water acts as a Brønsted-Lowry acid and donates a H^+ ion to another water molecule, which acts as a Brønsted-Lowry base and accepts it.
The hydronium ion, H_3O^+, results from accepting a proton from one molecule of water, while the hydroxide ion, OH^-, is the result of donating a proton by the other molecule.

The equilibrium constant expression is given by K_w, where w indicates the equilibrium of water, and $K_w = [H_3O^+][OH^-]$. Remember, pure water is a liquid, so it is excluded from the K_w expression.

At 25°C, the value of K_w is $1.0 \cdot 10^{-14}$.

The pH Scale

The pH scale is a simplified device that can communicate whether a solution is acidic, basic, or neutral at some temperature.



In the pH scale lies the foundation of comparisons between hydronium and hydroxide ion concentrations.

That being said, the following properties are valid at 25°C:

1. If $[H_3O^+] > [OH^-]$, then pH < 7 and the solution is acidic.
2. If $[H_3O^+] = [OH^-]$, then pH $= 7$ and the solution is neutral.
3. If $[H_3O^+] < [OH^-]$, then pH > 7 and the solution is basic, or alkaline.

Note 8.1.3

The neutral pH of 7 only holds at temperatures of 25°C. It is important to note that for neutral solutions at different temperatures, the pH will NOT be equal to 7. In those cases, you will need to directly compare the ion concentrations to determine whether a solution is acidic, basic, or neutral.

The pH scale is a simple way to interpret a wide range of hydronium and hydroxide ion concentrations: from $1.0\ M$ to $1.0 \cdot 10^{-14}\ M$. It is based on a decreasing base-10 logarithmic function. Additionally, the "p" in front instructs us to take the negative base-10 logarithm of whatever follows.

$$\text{pH} = -\log[H_3O^+]$$

If you know the H_3O^+ concentration of a solution, you can calculate its pH by taking the negative log. Your teacher may use H^+, the hydrogen ion, as an abbreviation, and that is perfectly fine. In AP Chemistry, H^+ and H_3O^+ are interchangeable.

Here are some generalizations that follow from the pH formula:

1. As the $[H_3O^+]$ of a solution *increases*, the pH *decreases*, and the solution becomes more acidic.
2. As the $[H_3O^+]$ of a solution *decreases*, the pH *increases*, and the solution becomes more basic.

Be sure to keep these two in mind, because many students confuse them and assume that the hydronium ion concentration and the pH of a solution are directly related. Remember that the pH scale is based on a *decreasing* logarithmic function of the H_3O^+ ion concentration.

Definition 8.1.4

The following properties are valid for 25°C:

$$\begin{aligned}
&[H_3O^+][OH^-] = K_w \\
&pH = -\log[H_3O^+] \therefore [H_3O^+] = 10^{-pH} \\
&pOH = -\log[OH^-] \therefore [OH^-] = 10^{-pOH} \\
&pK_w = -\log K_w = -\log\left(1.0 \cdot 10^{-14}\right) = 14 \\
&pH + pOH = 14
\end{aligned}$$

Let's try a couple of practice problems using these equations.

Problem 8.1.5 — pH and pOH I

Calculate the pH of a solution at 25°C given that $[OH^-] = 4.3 \cdot 10^{-8}\ M$. Also, classify whether the solution is acidic, basic, or neutral.

Solution: At 25°C, the value of K_w is $1.0 \cdot 10^{-14}$. We setup the following:

$$1.0 \cdot 10^{-14} = [H_3O^+][OH^-]$$

To solve for $[H_3O^+]$, divide K_w by $[OH^-]$:

$$[H_3O^+] = \frac{1.0 \cdot 10^{-14}}{4.3 \cdot 10^{-8}\ M} = 2.3 \cdot 10^{-7}\ M$$

Finally, we know that pH is the negative log of the $[H_3O^+]$ in solution, so

$$pH = -\log[H_3O^+] = -\log\left(2.3 \cdot 10^{-7}\right) = \boxed{6.64}$$

To classify the solution as acidic, basic, or neutral, we can look at the pH of the solution which we just determined. Since the solution has a pH of $6.64 < 7$ at a temperature of 25°C, it is $\boxed{\text{acidic}}$.

Problem 8.1.6 — pH and pOH II

At 35°C, the value of K_w is $2.09 \cdot 10^{-14}$. If the pH of the solution is 3.97, determine the value of $[OH^-]$. Also, classify whether the solution is acidic, basic, or neutral.

Solution: We are not given the value of $[H_3O^+]$ but our task is to determine the value of $[OH^-]$. Aha! We proceed with the following:

$$pH = -\log[H_3O^+] \therefore [H_3O^+] = 10^{-pH} = 10^{-3.97} = 1.1 \cdot 10^{-4}\ M$$

Knowing this and the value of K_w at 35°C, we can solve for $[OH^-]$:

$$K_w = 2.09 \cdot 10^{-14} = [H_3O^+][OH^-]$$

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{2.09 \cdot 10^{-14}}{1.1 \cdot 10^{-4}\ M} = \boxed{1.9 \cdot 10^{-10}\ M}$$

To classify the solution as acidic, basic, or neutral, we need to compare the values of $[H_3O^+]$ and $[OH^-]$. Since the H_3O^+ concentration is greater than the OH^- concentration, the solution is $\boxed{\text{acidic}}$.

Temperature Dependence of K_w

K_w is an equilibrium constant for the autoionization of water. This implies that the value of K_w is affected by the temperature of the environment.

$$2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

For the reaction above, the following data were obtained:

Temperature (°C)	**Value of** K_w
0	$1.14 \cdot 10^{-15}$
25	$1.00 \cdot 10^{-14}$
50	$5.50 \cdot 10^{-14}$

The general trend is: as the temperature increases, the value of the equilibrium constant K_w increases. The equilibrium position shifts to the right, forming more products and consuming the extra heat. The temperature favors the endothermic direction, according to Le Châtelier's principle, so the autoionization of water is **endothermic**.

Again, let's do a couple of practice problems.

Problem 8.1.7 — pH, pOH, and Kw I

Calculate the pH of pure water at 40°C. At 40°C, the value of K_w is $2.92 \cdot 10^{-14}$.

Solution: Pure water is a neutral solution, so $[H_3O^+] = [OH^-]$ and we can substitute one of these values for the other and solve the problem.

We proceed with the following:

$$K_w = [H_3O^+][OH^-] = [H_3O^+]^2$$

Solving, we have

$$2.92 \cdot 10^{-14} = [H_3O^+]^2 \therefore [H_3O^+] = \sqrt{2.92 \cdot 10^{-14}} = 1.71 \cdot 10^{-7}\ M$$
$$\text{pH} = -\log[H_3O^+] = -\log\left(1.71 \cdot 10^{-7}\right) = \boxed{6.767}$$

Important! Even though water is neutral, its pH was NOT equal to 7 for this problem. This does not mean our answer was wrong, rather, it is because neutral substances have a pH of 7 only at 25°C, since the value of K_w varies with temperature.

Problem 8.1.8 — pH, pOH, and Kw II

A solution has hydronium ion concentration of $7.5 \cdot 10^{-8}\ M$ at 50°C.

(a) Calculate the hydroxide ion concentration of the solution at this temperature. At 50°C, the value of pK_w is 13.262.

(b) Is this solution acidic or basic? Justify your answer.

Solution to part a: First, we can determine the value of K_w by using the equation

$$\begin{aligned} &pK_w = -\log K_w \\ &\therefore K_w = 10^{-pK_w} = 10^{-13.262} = 5.47 \cdot 10^{-14} \end{aligned}$$

Then, by the autoionization of water, we have

$$\begin{aligned} 5.47 \cdot 10^{-14} &= [H_3O^+][OH^-] \\ [OH^-] &= \frac{5.47 \cdot 10^{-14}}{[H_3O^+]} = \frac{5.47 \cdot 10^{-14}}{7.5 \cdot 10^{-8}\ M} = \boxed{7.3 \cdot 10^{-7}\ M} \end{aligned}$$

Solution to part b: Let's compare the concentrations of hydronium ion and hydroxide ion in solution. Since $[H_3O^+] = 7.5 \cdot 10^{-8}\ M$ and $[OH^-] = 7.3 \cdot 10^{-7}\ M$, we have $[OH^-] > [H_3O^+]$ and the solution is $\boxed{\text{basic}}$.

§8.2 pH and pOH of Strong Acids and Bases

Definition 8.2.1

Strong acids dissociate completely in water, so the reaction essentially reaches completion.

Additionally, they never reach equilibrium with their conjugate bases. Thus, there is no equilibrium constant, and no dissociation constant for strong acids.

Important Strong Acids

1. Hydrochloric acid, HCl
2. Hydrobromic acid, HBr
3. Hydroiodic acid, HI
4. Nitric acid, HNO_3
5. Perchloric acid, $HClO_4$
6. The first H^+ in sulfuric acid, H_2SO_4

Example 8.2.2

The dissociation of nitric acid in water is given by the reaction:

$$HNO_3(aq) + H_2O(l) \rightarrow NO_3^-(aq) + H_3O^+(aq)$$

Suppose we had a $4.9 \cdot 10^{-3}$ M solution of HNO_3 at 25°C. What is the pH of that solution?

HNO_3 is a strong acid, so it dissociates 100%, and the concentration of H_3O^+ is equal to the initial concentration of HNO_3.

$$[HNO_3] = [H_3O^+] = 4.9 \cdot 10^{-3}\ M$$
$$\text{pH} = -\log[H_3O^+] = -\log\left(4.9 \cdot 10^{-3}\right) = \boxed{2.31}$$

Note 8.2.3

Since exactly one H^+ is released when a strong acid dissociates, we make the following generalization: The value of $[H^+]$ after dissociation is equal to the initial concentration of the acid.

Definition 8.2.4

Strong bases also dissociate completely in water, so the dissociation reaction essentially reaches completion.

Strong bases never reach equilibrium with their conjugate acids, because their dissociation in water all proceed to completion. Thus, there is no equilibrium constant, which implies there is no dissociation constant for strong bases.

Important Strong Bases

1. Lithium hydroxide, LiOH
2. Sodium hydroxide, NaOH
3. Potassium hydroxide, KOH
4. Barium hydroxide, $Ba(OH)_2$
5. Strontium hydroxide, $Sr(OH)_2$
6. Generally, any Group 1 and Group 2 hydroxides, unless stated otherwise.

Example 8.2.5

The dissociation of barium hydroxide, a strong base, in water is given by the following reaction:

$$Ba(OH)_2 \rightarrow Ba^{2+}(aq) + 2OH^-(aq)$$

What is the pH of a $5.9 \cdot 10^{-5}$ M solution of $Ba(OH)_2$ at 25°C?

Here, we have to be a little careful. Although barium hydroxide is a strong base that fully dissociates, the concentration of hydroxide ions is NOT equal to the initial base concentration. We need to pay close attention to stoichiometry: for every 1 mole of $Ba(OH)_2$ that dissociates, 2 moles of OH^- ions are produced. Therefore, $[OH^-]$ will be twice the initial concentration of $Ba(OH)_2$.

$$[\mathrm{OH^-}] = 2 \cdot [\mathrm{Ba(OH)_2}] = 2 \cdot 5.9 \cdot 10^{-5}\ M = 1.18 \cdot 10^{-4}\ M$$

We know the concentration of OH^- ions and are asked to determine the pH of the solution. This means our problem-solving strategy will involve pH, pOH, as well as K_w.

First, we calculate the pOH of the solution:

$$\mathrm{pOH} = -\log[\mathrm{OH^-}] = -\log\left(1.18 \cdot 10^{-4}\right) = 3.928$$

Finally, we use pH + pOH = 14 (the value of pK_w at 25°C) to solve for pH:

$$\mathrm{pH} = 14 - \mathrm{pOH} \therefore \mathrm{pH} = 14 - 3.928 = \boxed{10.07}$$

Note 8.2.6

Using the stoichiometry of strong base dissociations, we can make two generalizations:

1. For Group 1 hydroxides, the $[OH^-]$ after dissociation is equal to the original base concentration.
2. For Group 2 hydroxides, the $[OH^-]$ after dissociation is equal to twice the original base concentration.

§8.3 Weak Acid and Base Equilibria

In this section, we will discuss the difference between strong acids and bases versus weak acids and bases, using mathematical representations of equilibrium to find the pH of solutions involving weak acids and bases.

But first, what do these terms mean?

Definition 8.3.1

A **weak acid** does not completely dissociate into its constituent ions in aqueous solution.

Thus, the reaction of weak acids with water is reversible, so a homogeneous equilibrium forms between the acid, its conjugate base, and H_3O^+ ions.

Weak Acid Equilibria

When a weak acid HA is placed in water, the following reaction occurs:

$$\mathrm{HA(aq)} + \mathrm{H_2O(l)} \rightleftharpoons \mathrm{H_3O^+(aq)} + \mathrm{A^-(aq)}$$

The equilibrium constant expression for the reaction between HA(aq) and H_2O(l) is denoted by K_a, the **acid dissociation constant**.

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

Because a weak acid does not fully ionize, the concentration of HA will significantly exceed those of H_3O^+ and A^- at equilibrium. Thus, the K_a value of a weak acid will be much less than 1.

You should also be able to compare the relative strengths of acids based on their K_a values. Specifically, an acid with a large K_a value will be stronger than an acid with a relatively small K_a value.

Example 8.3.2

Hydrofluoric acid, HF, and acetic acid, CH_3COOH, are weak acids that only partially ionize in an aqueous environment. At 25°C, the K_a values for HF and CH_3COOH are $6.3 \cdot 10^{-4}$ and $1.8 \cdot 10^{-5}$, respectively. However, hydrofluoric acid has a *higher K_a value* at the given temperature, so it is the *stronger acid* between the two.

We can also determine the K_a values of weak acids at certain temperatures if we are given its concentration and the pH of their solution.

Problem 8.3.3 — Weak Acid Equilibria I

A 0.10 M solution of benzoic acid, C_6H_5COOH, has a pH of 2.60 at 25°C. How can we determine the K_a value for benzoic acid at 25°C?

Solution: Since C_6H_5COOH is a weak acid, we cannot directly use the stoichiometric coefficients to calculate the value of K_a. That is why we will use an ICE (Initial, Change, Equilibrium) table, just as in Unit 7, where we would track the concentrations of species over time in an equilibrium.

	C_6H_5COOH(aq)	H_2O(l)	$\rightleftharpoons$	$C_6H_5COO^-$(aq)	H_3O^+(aq)
Initial (M)	0.10	-	-	0	0
Change (M)	$-x$	-	-	$+x$	$+x$
Equilibrium (M)	$0.10 - x$	-	-	x	x

The problem with a weak acid is that we do not know how much of it will dissociate. That is why we bring an intermediate variable x in to model the change in concentration. Since C_6H_5COOH dissociates, the concentration of it will decrease, which is why we accounted for the change as $-x$.

Benzoic acid will dissociate into $C_6H_5COO^-$ and H_3O^+ ions. The concentrations of these species will increase as C_6H_5COOH dissociates, and we assume that benzoic acid is the only species present prior to the reaction. Thus, we account for the changes as $+x$.

We know that the K_a expression for this reaction is given by

$$\frac{[C_6H_5COO^-][H_3O^+]}{[C_6H_5COOH]}$$

Now, we can use our equilibrium concentrations and plug them in:

$$K_a = \frac{(x)\,(x)}{0.10 - x} = \frac{x^2}{0.10 - x}$$

Now to find x, we must first realize that the pH of this acid is already given. It is 2.60. This means that we can find the concentration of H_3O^+ ions.

We can use the formula $\text{pH} = -\log[H_3O^+]$ to solve for the equilibrium concentration of H_3O^+ ions in the solution mixture:

$$2.60 = -\log[H_3O^+] \therefore [H_3O^+] = 10^{-\text{pH}} = 10^{-2.60} = 0.00251\ M$$

This also means that $x = 0.00251$. We can substitute into our K_a expression:

$$K_a = \frac{x^2}{0.10 - x} = \frac{(0.00251)^2}{(0.10 - 0.00251)} = \boxed{6.46 \cdot 10^{-5}}$$

An important thing to note here is that mole ratios make a big difference! The reason why all changes in the ICE Table are written as $-x$ or $+x$ is that all species in the dissociation equation reacts in a $1 : 1$ mole ratio. However, if there were twice the amount of H^+, then we would need to account for it by making the change $+2x$ rather than $+x$. The best way to get familiar with this is through practice.

Alternatively, if we know the K_a for a weak acid, we can calculate the pH of a solution whose concentration is known.

Problem 8.3.4 — Weak Acid Equilibria II

Hydrofluoric acid, HF, is a highly corrosive acid used in many industrial applications such as the manufacturing of computer chips. What is the pH of a 0.155 M solution of HF? $\text{p}K_a = 3.14$ for HF.

Solution: Again, as this is a weak acid, the equilibrium concentration of H_3O^+ will not be the same as the original concentration of HF(aq). Therefore, we will construct an ICE table, similar to the previous problem.

	HF(aq)	H_2O(l)	$\rightleftharpoons$	F^-(aq)	H_3O^+(aq)
Initial (M)	0.155	-	-	0	0
Change (M)	$-x$	-	-	$+x$	$+x$
Equilibrium (M)	$0.155 - x$	-	-	x	x

For this reaction, the equilibrium constant expression is given by

$$K_a = \frac{[F^-][H_3O^+]}{[HF]}$$

We do not know the value of K_a, but we know the value of $\text{p}K_a$. Recall that the "p" indicates to take the negative log of whatever follows. We have

$$\text{p}K_a = -\log K_a \therefore K_a = 10^{-\text{p}K_a} = 10^{-3.14} = 7.2 \cdot 10^{-4}$$

Next, we need to determine the equilibrium concentration of $H_3O^+(aq)$. We can use our equilibrium concentrations and plug them into the expression for K_a:

$$7.2 \cdot 10^{-4} = \frac{(x)\,(x)}{0.155 - x} = \frac{x^2}{0.155 - x}$$

Here, x represents the concentration of $H_3O^+(aq)$ at equilibrium. However, we have a complicated equation that will require using the quadratic formula to solve for x.

In such problems, we will make an approximation, as College Board does not require the use of the quadratic formula, so we are permitted to use this.
The term that is causing us trouble is the equilibrium concentration of hydrofluoric acid, or $0.155 - x$. Because HF(aq) is a weak acid, it partially dissociates. The amount dissociated is denoted by x. In fact, for weak acids (and also weak bases, for that matter), we can consider the change in concentration to be negligible in cases where we would otherwise need the quadratic formula.

Here is the concept in action:

$$\begin{aligned}
&K_a = \frac{[F^-][H_3O^+]}{[HF]} \\
&7.2 \cdot 10^{-4} = \frac{x^2}{0.155 - x} \\
&0.155 - x \approx 0.155 \therefore 7.2 \cdot 10^{-4} = \frac{x^2}{0.155} \\
&x^2 = 0.155 \cdot 7.2 \cdot 10^{-4} \therefore x = [H_3O^+] = 0.0106\,M \\
&\text{pH} = -\log[H_3O^+] = -\log(0.0106) = \boxed{1.97}
\end{aligned}$$

Now, we will move our discussion towards weak bases and equilibrium.

Definition 8.3.5

A **weak base** does not completely ionize in an aqueous solution.

Similarly, the reaction of weak bases with water is reversible, so a homogeneous equilibrium forms between the base, its conjugate acid, and OH^- ions.

Weak Base Equilibria

When a weak base B is placed in water, the following reaction occurs:

$$B(aq) + H_2O(l) \rightleftharpoons HB^+(aq) + OH^-(aq)$$

The equilibrium constant expression for the reaction between B(aq) and $H_2O(l)$ is denoted by K_b, the **base dissociation constant**.

$$K_b = \frac{[HB^+][OH^-]}{[B]}$$

Because a weak base does not fully ionize, the concentration of B will significantly exceed those of OH^- and HB^+ at equilibrium. Thus, the K_b value describing a weak base will much less than 1.

You should be able to rank relative base strengths based on their K_b values.
That is, a base with a large K_b value will be stronger than a base with a relatively small K_b value.

Example 8.3.6

Ammonia, NH_3, and aniline, $C_6H_5NH_2$, are weak bases that only partially ionize in an aqueous environment. At 25°C, the K_b values of NH_3 and $C_5H_5NH_2$ are $1.8 \cdot 10^{-5}$ and $4.3 \cdot 10^{-3}$, respectively. However, aniline has a *higher K_b value* at the given temperature, so it is the *stronger base* between the two.

Similarly, as with weak acids, we can also determine the pH of weakly basic solutions at certain temperatures if we are given its concentration and K_b value. There is just one extra step in the calculations, compared to if we were handling a weak acid.

Problem 8.3.7 — Weak Base Equilibria

Determine the pH of a 0.63 M solution of methylamine, CH_3NH_2. At 25°C, the K_b for methylamine is $4.2 \cdot 10^{-4}$.

Solution: The ionization of methylamine in water is represented by

$$CH_3NH_2(aq) + H_2O(l) \rightleftharpoons CH_3NH_3^+(aq) + OH^-(aq)$$

Because methylamine is a weak base, we can't directly use the stoichiometric coefficients to solve for $[OH^-]$ at equilibrium. Thus, we will construct an ICE table.

	$CH_3NH_2(aq)$	$H_2O(l)$	$\rightleftharpoons$	$CH_3NH_3^+(aq)$	$OH^-(aq)$
Initial (M)	0.63	-	-	0	0
Change (M)	$-x$	-	-	$+x$	$+x$
Equilibrium (M)	$0.63 - x$	-	-	x	x

The equilibrium constant expression for the reaction is given by

$$K_b = \frac{[CH_3NH_3^+][OH^-]}{[CH_3NH_2]}$$

We can plug in the values of K_b and the equilibrium concentrations of all species into our expression:

$$4.2 \cdot 10^{-4} = \frac{(x)\,(x)}{0.63 - x}$$

To avoid using the quadratic formula, we assume that the amount dissociated x was significantly less than the initial base concentration.

$$0.63 - x \approx 0.63 \therefore 4.2 \cdot 10^{-4} = \frac{x^2}{0.63}$$

Here, x represents the equilibrium concentration of OH^-. Using some algebra,

$$[OH^-] = \sqrt{0.63 \cdot 4.2 \cdot 10^{-4}} = 0.01627\,M$$

We can take the negative log of $[OH^-]$ to determine the pOH of the solution, and then apply the formula $\text{pH} + \text{pOH} = 14$, valid for 25°C, to determine the pH.

$$\text{pOH} = -\log[OH^-] = -\log(0.01627) = 1.789$$

Using $\text{pH} + \text{pOH} = 14$, we obtain the following:

$$\text{pH} = 14 - \text{pOH} = 14 - 1.789 = \boxed{12.21}$$

Important: Some crucial connections we need to know regarding weak acids and weak bases are the generalizations between K_a and K_b against pH and pOH.

Definition 8.3.8

For **all** conjugate acid-base pairs, and at **all** temperatures, we have

$$K_a \cdot K_b = K_w$$

$$\text{p}K_a + \text{p}K_b = \text{p}K_w$$

This will be important in later sections as we discuss buffers and titrations.

Percent Ionization and Relative Strengths of Weak Acids

We can also rank the strengths of acids by the extent to which they ionize or dissociate in aqueous solution. The reaction of an acid with water is given by the general chemical equation

$$\text{HA(aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{H}_3\text{O}^+\text{(aq)} + \text{A}^-\text{(aq)}$$

Water acts as a base, A^- is the conjugate base of the acid HA, and H_3O^+ is the conjugate acid of water. A strong acid yields 100% of H_3O^+ and A^- when the acid ionizes in water. Meanwhile, a weak acid gives very small amounts of H_3O^+ and A^-.

Definition 8.3.9

The **percent ionization** of a weak acid is the ratio of the concentration of the ionized acid to the initial acid concentration, multiplied by 100:

$$\%\text{ ionization} = \frac{[\text{H}_3\text{O}^+]_{eq}}{[\text{HA}]_0} \cdot 100\%$$

Watch Out! Because the ratio includes the initial acid concentration, the percent ionization depends on the original concentration of the acid, and actually decreases with increasing acid concentration. A common pitfall is for students to assume that more acid would result in higher percent ionization. (**PRO TIP**: You can avoid this mistake by understanding Le Châtelier's Principle)

Let's practice!

Problem 8.3.10 — Percent Ionization I

Calculate the percent ionization of a 0.10 M solution of HF. ($K_a = 7.2 \cdot 10^{-4}$)

Solution: In order to determine the percent ionization of this acid, we need to first calculate the equilibrium concentration of H_3O^+ ions. As always, we will use an ICE table to track concentrations of species in an equilibrium.

	HF(aq)	H_2O(l)	$\rightleftharpoons$	F^-(aq)	H_3O^+(aq)
Initial (M)	0.10	-	-	0	0
Change (M)	$-x$	-	-	$+x$	$+x$
Equilibrium (M)	$0.10 - x$	-	-	x	x

The equilibrium constant expression for this reaction is

$$K_a = \frac{[H_3O^+][F^-]}{[HF]}$$

Plugging in values and approximating (so as we do not use the quadratic formula),

$$7.2 \cdot 10^{-4} = \frac{(x)\,(x)}{0.10 - x} \approx \frac{x^2}{0.10}$$

Rearranging the equation, we find that the equilibrium concentration of H_3O^+, represented by x, is equal to

$$x = [H_3O^+]_{eq} = \sqrt{0.10 \cdot 7.2 \cdot 10^{-4}} = 8.5 \cdot 10^{-3}\,M$$

and thus the percent ionization of the solution is calculated as

$$\%\text{ ionization} = \frac{[H_3O^+]_{eq}}{[HF]_0} \cdot 100\% = \frac{8.5 \cdot 10^{-3}}{0.10} \cdot 100\% = \boxed{8.49\%}$$

Problem 8.3.11 — Percent Ionization II

Calculate the % ionization of a 0.125 M HNO_2 solution with a pH of 2.09.

Solution: Because we know the pH of the solution, we can calculate the equilibrium concentration of H_3O^+ ion:

$$\text{pH} = -\log[H_3O^+] \therefore [H_3O^+] = 10^{-\text{pH}} = 10^{-2.09} = 8.13 \cdot 10^{-3}\,M$$

Additionally, we are given the initial concentration of the HNO_2 solution, so our percent ionization is equal to

$$\%\text{ ionization} = \frac{8.13 \cdot 10^{-3}}{0.125} \cdot 100\% = \boxed{6.50\%}$$

Note: This concept works for bases as well−simply calculate the amount of base that was ionized, divide by the initial base concentration, and then multiply by 100.

More generally,

$$\% \text{ ionization} = \frac{[\text{OH}^-]_{eq}}{[\text{B}]_0} \cdot 100\%$$

where B is a weak base and $[\text{OH}^-]_{eq}$ is the equilibrium concentration of hydroxide ions.

Let's solve one more problem before we move on to the next section.

Problem 8.3.12 — Percent Ionization III

Calculate the percent ionization of a 0.0784 M solution of $C_6H_5NH_2$(aq), a weak base. K_b for $C_6H_5NH_2$ is $4.6 \cdot 10^{-10}$.

Solution: The reaction that describes the ionization of $C_6H_5NH_2$ in water is

$$\text{C}_6\text{H}_5\text{NH}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{C}_6\text{H}_5\text{NH}_3^+(\text{aq}) + \text{OH}^-(\text{aq})$$

We know that the weak base $C_6H_5NH_2$ will dissociate to some extent, but we do not know the exact value, so we will use x. Additionally, we assume that there is no $C_6H_5NH_3^+$ or OH^- initially present in the system. As the concentration of $C_6H_5NH_2$ decreases by x, the concentration of $C_6H_5NH_3^+$ and OH^- ions increases by x.

With this information, we can set up the following:

$$K_b = \frac{[\text{C}_6\text{H}_5\text{NH}_3^+][\text{OH}^-]}{[\text{C}_6\text{H}_5\text{NH}_2]}$$

In terms of x and using the approximation $0.0784 - x \approx 0.0784$, we have

$$4.6 \cdot 10^{-10} = \frac{(x)\,(x)}{0.0784 - x} \approx \frac{x^2}{0.0784}$$

Now, we can calculate x, the amount of base that was ionized:

$$x = \sqrt{0.0784 \cdot 4.6 \cdot 10^{-10}} = 6.01 \cdot 10^{-6}\ M$$

Thus, the percent ionization for this solution of $C_6H_5NH_2$ is

$$\frac{6.01 \cdot 10^{-6}}{0.0784} \cdot 100\% = \boxed{7.7 \cdot 10^{-3}\,\%}$$

§8.4 Acid-Base Reactions and Buffers

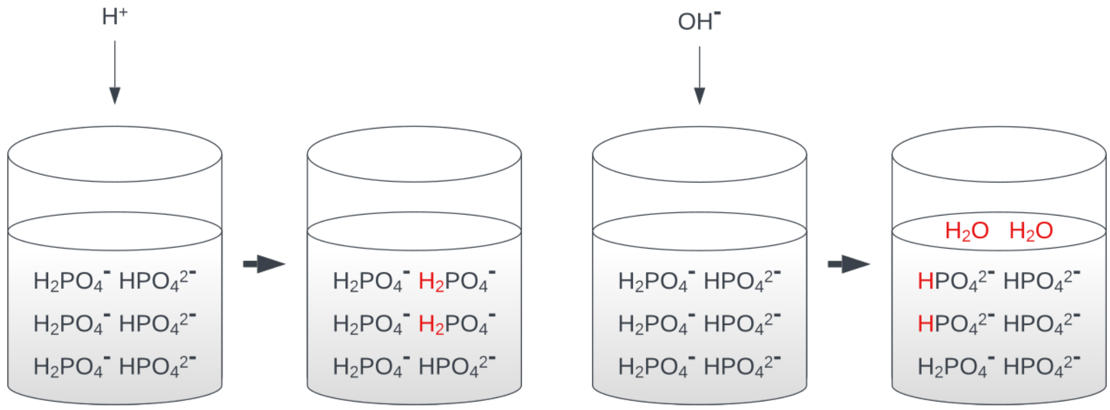
In a laboratory setting, you are often tasked with not only calculating the concentrations of certain species (acids or bases) in an experiment. You also need to explain the quantitative *relationship* among these values and describe the *major species*, those that are significant in the mixture of weak and/or strong acids and bases. Finally, we will assume that the temperature of our setting is 25°C and thus make calculations simple.

Now that we understand equilibrium between acids and bases, we are going to talk about acid base reactions. But before that, we need to introduce a new topic it relates to: buffers.

Definition 8.4.1

Buffers are a mixture of a weak acid (HA) and its conjugate base (A^-) in a solution.

Buffered solutions are very resistant to changes in pH, i.e. if you add some acid or base to a buffered solution, its pH will not change that much. Why? If you add an acid, e.g. H^+(aq) ions, the conjugate base A^-(aq) will work to neutralize it and vice versa.



Strong Acid + Strong Base Reactions

The most elementary acid-base reaction we will see in both theoretical and applied chemistry is the one between a strong acid and a strong base. Recall from earlier sections that strong acids and bases fully ionize in aqueous solution. Thus, the net ionic equation that describes their reaction is:

$$H^+(aq) + OH^-(aq) \to H_2O(l)$$

Also, the pH of the resulting solution is determined by the concentration of the excess reactant. Note the stoichiometry of the above reaction. H^+(aq) and OH^-(aq) both react in a 1 : 1 ratio. For example, if there are equimolar (same number of moles) amounts of both acid and base, then the solution is neutral with pH = 7, assuming a temperature of 25°C. However, if either H^+ or OH^- is in excess, then the solution is not neutral with a pH $\neq$ 7.

Let's take a look at a problem involving a strong acid strong base reaction.

Problem 8.4.2 — Strong Acid-Strong Base Reaction

What is the pH of the resulting solution when 10.0 mL of 0.100 M NaOH is mixed with 25.0 mL of 0.100 M HCl?

Solution: Start by writing out the net ionic equation:

$$H^+(aq) + OH^-(aq) \to H_2O(l)$$

as Na^+(aq) and Cl^-(aq) are spectator ions.

We can determine the number of moles of both $H^+(aq)$ and $OH^-(aq)$ by multiplying the volume by the molarity of both acid and base solutions, respectively.

$$n_{H^+} = 25.0\,\cancel{mL} \cdot \frac{1\,\cancel{L}}{1000\,\cancel{mL}} \cdot \frac{0.100\,\text{mol H}^+}{\cancel{L}} = 2.5 \cdot 10^{-3}\,\text{mol H}^+$$
$$n_{OH^-} = 10.0\,\cancel{mL} \cdot \frac{1\,\cancel{L}}{1000\,\cancel{mL}} \cdot \frac{0.100\,\text{mol OH}^+}{\cancel{L}} = 1.0 \cdot 10^{-3}\,\text{mol OH}^-$$

Clearly, the H^+ is in excess, so we use stoichiometry to find how much is left over. There is $2.5 \cdot 10^{-3} - 1.0 \cdot 10^{-3} = 1.5 \cdot 10^{-3}\,\text{mol H}^+$ in excess, and we can divide by the total volume to find its concentration:

$$[\text{H}^+] = \frac{1.5 \cdot 10^{-3}\,\text{mol H}^+}{0.025\,\text{L} + 0.010\,\text{L}} = 4.8 \cdot 10^{-2}\,M$$

Finally, take the negative log of this value to calculate your pH:

$$\text{pH} = -\log[\text{H}^+] = -\log\left(4.8 \cdot 10^{-2}\right) = \boxed{1.37}$$

Weak Acid + Strong Base Reactions

Weak acid and strong base reactions are very similar to strong acid strong base reactions, but the weak acid does not fully dissociate, so our net ionic equation will be slightly different:

$$\text{HA(aq)} + \text{OH}^-\text{(aq)} \rightleftharpoons \text{A}^-\text{(aq)} + \text{H}_2\text{O(l)}$$

In general, your first step in solving acid-base reaction problems should be writing the net ionic equation. In these problems, we will start noticing buffers−mixtures of a weak acid and its conjugate base−more frequently. This occurs when the *weak acid is in excess.* We can calculate the pH of a buffered solution using the following equation:

$$\boxed{\text{pH} = \text{p}K_a + \log\frac{[\text{A}^-]}{[\text{HA}]}}$$

where K_a is the acid dissociation constant for a weak acid and [HA] and $[\text{A}^-]$ are the molar concentrations of the weak acid and its conjugate base, respectively.

This equation is referred to as the **Henderson-Hasselbalch equation**. More details will be covered in section 8.9.

However, when the *strong base is in excess*, we can determine the pH by calculating the amount of excess OH^-.

Finally, if they are equimolar, then there is no H^+ and OH^- left after equilibrium is established. The only species present then is the conjugate base A^-. Recall that bases are proton acceptors. In this case, there is only one source of protons: water. Thus, the conjugate base A^- will react with water in the following reaction:

$$\text{A}^- + \text{H}_2\text{O(l)} \rightleftharpoons \text{HA(aq)} + \text{OH}^-\text{(aq)}$$

This process by where the conjugate base of a weak acid reacts with water is known as **hydrolysis**. Moreover, the pH of the solution can be determined from the equilibrium concentration of hydroxide ions produced in the hydrolysis reaction.

Problem 8.4.3 — Weak Acid-Strong Base Reaction

Calculate the pH of the resulting solution when 25.0 mL of 0.100 M acetic acid is mixed with 10.0 mL of 0.100 M KOH. At 25°C, K_a for CH_3COOH is $1.8 \cdot 10^{-5}$.

Solution: We begin with our net ionic equation.

$$\mathrm{CH_3COOH(aq) + OH^-(aq) \rightleftharpoons CH_3COO^-(aq) + H_2O(l)}$$

As with the previous example, we will use stoichiometry to determine the amount of excess reactant that remains. For these types of problems, it may be helpful to use a table. The key difference is that we are going to track changes in the number of moles, rather than molar concentrations. Note: the equation $n = MV$ will be used to determine the initial number of moles for each reactant.

	$C_6H_5COOH(aq)$	$OH^-(aq)$	$\rightarrow$	$C_6H_5COO^-(aq)$	$H_3O^+(aq)$
Initial (mol)	0.0025	0.001	-	0	0
Change (mol)	$-\left(\frac{1}{1}\right) 0.001$	-0.001	-	$+\left(\frac{1}{1}\right) 0.001$	$+\left(\frac{1}{1}\right) 0.001$
Final (mol)	0.0015	0	-	0.001	0.001

The reason I added the $\pm\left(\frac{1}{1}\right)$ terms was to emphasize the fact that the coefficients on all species were equal to 1, and AP usually follows this convention, but there can be exceptions in which mole ratios make a big difference to our solution.

Here, we have a mixture of $CH_3COOH(aq)$ and its conjugate base, $CH_3COO^-(aq)$. Therefore, we use the equation for calculating the pH of buffered solutions:

$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{[\mathrm{A^-}]}{[\mathrm{HA}]}$$

$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{[\mathrm{CH_3COO^-}]}{[\mathrm{CH_3COOH}]}$$

$$\mathrm{pH} = -\log\left(1.8 \cdot 10^{-5}\right) + \log\left(\frac{\frac{1.0\cdot 10^{-3}\ \mathrm{mol}}{0.035\ \mathrm{L}}}{\frac{1.5\cdot 10^{-3}\ \mathrm{mol}}{0.035\ \mathrm{L}}}\right) = \boxed{4.57}$$

For the next couple of acid-base reactions, they are very unlikely to show up on the AP Exam compared to the strong acid-strong base and weak acid-strong base reactions. However, you should still have a general idea of them.

- **Strong Acid-Weak Base:**

  $$\mathrm{H_3O^+(aq) + B(aq) \rightleftharpoons HB^+(aq) + H_2O(l)} \leftarrow \text{net ionic equation}$$

  - If the weak base in excess, the pH is determined using the formula for buffered solutions.
  - If the strong acid is in excess, pH is determined by calculating the amount of excess H^+ (or H_3O^+).
  - If they are equimolar, the conjugate acid undergoes hydrolysis in order to donate a proton:

  $$\mathrm{HB^+(aq) + H_2O(l) \rightleftharpoons B(aq) + H_3O^+(aq)}$$

and the pH of the solution can be determined from the equilibrium concentration of hydronium ions.

- **Weak Acid-Weak Base:**

$$\mathrm{HA(aq) + B(aq) \rightleftharpoons A^-(aq) + HB^+(aq)} \leftarrow \text{net ionic equation}$$

Important: The strategies shown in this example can be applied to strong acid weak base reactions. Just remember to be careful when differentiating between conjugate acids versus conjugate bases and pH versus pOH. For the AP Exam, the examples shown in this section are much more likely, but be prepared for either.

Let's try some more exercises before we move on.

Problem 8.4.4 — Acid-Base Reactions I

Calculate the pH of the resulting solution when 15.0 mL of 0.100 M HNO_3 is mixed with 10.0 mL of 0.0250 M NH_3.

Solution: This problem requires the use of stoichiometry. To keep track of our measurements efficiently, we will use a table.

We will start with our net ionic equation to make things simple:

$$\mathrm{H^+(aq) + NH_3(aq) \rightarrow NH_4^+(aq)}$$

For review on writing net ionic equations, refer to section 4.2 of this book.

	$H^+(aq)$	$NH_3(aq)$	$\rightarrow$	$NH_4^+(aq)$
Initial (mol)	0.0015	0.00025	-	0
Change (mol)	$-\left(\frac{1}{1}\right)$ 0.00025	-0.00025	-	$+\left(\frac{1}{1}\right)$ 0.00025
Final (mol)	0.00125	0	-	0.00025

This shows that, when the reaction is complete, all of the NH_3 has been consumed by H^+ with only H^+ and the conjugate acid NH_4^+ remaining. However, only the former remains in significant amounts, so it will control the pH of the solution. Therefore, we can use the formula

$$\mathrm{pH} = -\log[\mathrm{H^+}]$$

where $[H^+]$ is the concentration of hydrogen ions after the reaction is complete.

$$[\mathrm{H^+}] = \frac{0.00125\ \mathrm{mol}}{0.015\ \mathrm{L} + 0.010\ \mathrm{L}} = 0.05\ M \therefore \mathrm{pH} = -\log(0.05) = \boxed{1.30}$$

Problem 8.4.5 — Acid-Base Reactions II

Which of the following pairs of substances, when mixed in equimolar amounts, results in a basic solution?

(A) HBr(aq) and NH_3(aq)
(B) HBr(aq) and NaOH(aq)
(C) NaOH(aq) and NH_3(aq)
(D) NaOH(aq) and HOBr(aq)

Solution: Let's go through each answer choice. For choice (A), we have HBr, a strong acid, and NH_3, a weak base. Mixing equimolar amounts of these substances will produce a salt containing the conjugate acid of the weak base (NH_4^+). This conjugate acid will react with H_2O to form H_3O^+ ions, resulting in an acidic solution. Eliminate this.
For choice (B), we have HBr and NaOH, where the latter is a strong base. If you mix equimolar amounts of these substances, the resulting solution is neutral, since the H^+ and OH^- completely neutralized each other. Eliminate this.
For choice (C), NaOH is a strong base and NH_3 is a weak base. Since both are bases, mixing them together will still result in a basic solution. Eliminate this.
Using process of elimination, we get (D) as the correct answer. However, we should also understand the reason why. NaOH is a strong base and HOBr is a weak acid, so when these solutions are mixed, the conjugate base, OBr^- is produced will then react with H_2O to produce OH^- ions, resulting in a basic solution. Therefore, we can be sure that $\boxed{\textbf{(D)}}$ is the correct answer.

Problem 8.4.6 — Acid-Base Reactions III

Write the balanced, net ionic equation for the reaction between formic acid (also known as methanoic acid), HCOOH(aq), and potassium hydroxide, KOH(aq).

Solution: First, let's identify the species. Formic acid is a weak acid that only partially dissociates, while potassium hydroxide is a very strong base that fully ionizes in an aqueous environment.

Next, write the balanced chemical equation:

$$\mathrm{HCOOH(aq) + KOH(aq) \rightleftharpoons HCOOK(aq) + H_2O(l)}$$

Now, we write the complete ionic equation. Note: weak acids and weak bases should be left as single units in the complete ionic equation.

$$\mathrm{HCOOH(aq) + K^+(aq) + OH^-(aq) \rightleftharpoons HCOO^-(aq) + K^+(aq) + H_2O(l)}$$

We can cancel the spectator ion, K^+(aq).

$$\mathrm{HCOOH(aq) + \cancel{K^+(aq)} + OH^-(aq) \rightleftharpoons HCOO^-(aq) + \cancel{K^+(aq)} + H_2O(l)}$$

Finally, the net ionic equation for the reaction between HCOOH(aq) and KOH(aq) is

$$\boxed{\mathrm{HCOOH(aq) + OH^-(aq) \rightleftharpoons HCOO^-(aq) + H_2O(l)}}$$

§8.5 Acid-Base Titrations

It's time for the most notorious part of AP Chemistry: acid-base titrations. Many students dread this topic, but if you can combine all the skills you learned regarding equilibrium, pH, pKa, and some stoichiometry, you will find titration a lot more approachable.

Titration: Defined

In Unit 4, we loosely defined what a titration is. It is a lab procedure conducted to determine the concentration of an unknown solution, called the **analyte**. Using a burette (or buret), small amounts of a **titrant** solution are added to the analyte until a point called the **equivalence point** is reached.

Definition 8.5.1

The **equivalence point** is the point where the moles of analyte present are equal to the moles of titrant added.

This can be mathematically represented by the formula

$$nM_aV_a = mM_bV_b$$

where M and V represent the molarity and volume of both solutions and n and m are the **stoichiometric coefficients** of the analyte and titrant, respectively.

Note 8.5.2

Since AP is usually straightforward with titration problems, the analyte and titrant will react in a $1:1$ ratio, so $n = 1$ and $m = 1$ and the formula can be understood simply as

$$\boxed{M_aV_a = M_bV_b}$$

Usually, titration is used to calculate the concentration of an acidic solution by adding gradual amounts of a base, since acids and bases effectively neutralize each other. This task is made easier using an **acid-base indicator**. The image below shows the setup for an acid-base titration that you will likely use in your classrooms.

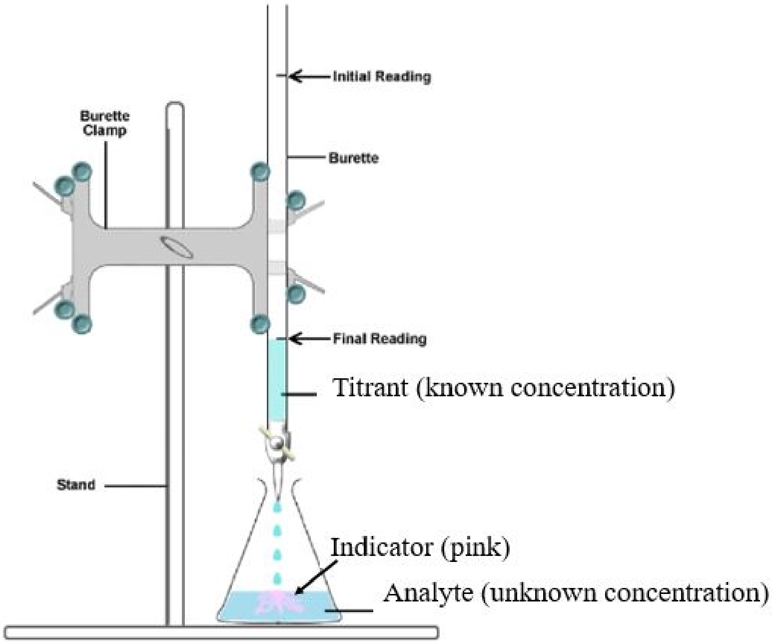


Image Courtesy of Chemistry LibreTexts

When a titrant of known concentration is dripped into an analyte of unknown concentration, we can monitor the pH for each addition of the titrant. Experiments involving titration generally use a **titration curve**, or **pH curve** which shows the pH of the resulting solution as a function of volume of titrant added.

Titration Curves

> **Example 8.5.3**
> Consider what happens when different volumes of 1.0 M NaOH are gradually added to 25 mL of a 1.0 M HCl solution.

Step 1 - Before Reaction

Before any titration takes place, we first calculate the initial pH of the solution. Initially, there is HCl, a strong acid, with concentration of 1.0 M, so $[\text{HCl}] = [\text{H}^+] = 1.0\ M$ and $\text{pH} = -\log(1.0) = 0$.

Step 2 - Before Equivalence Point

As NaOH is added, the following net ionic reaction takes place:

$$\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{H}_2\text{O(l)}$$

If we add OH^- up to the equivalence point, then the resulting solution will be predominantly acidic. H^+ will be in excess, but to a lesser extent because some of the initial H^+ will produce water. Therefore, the pH *slowly* increases before the equivalence point.

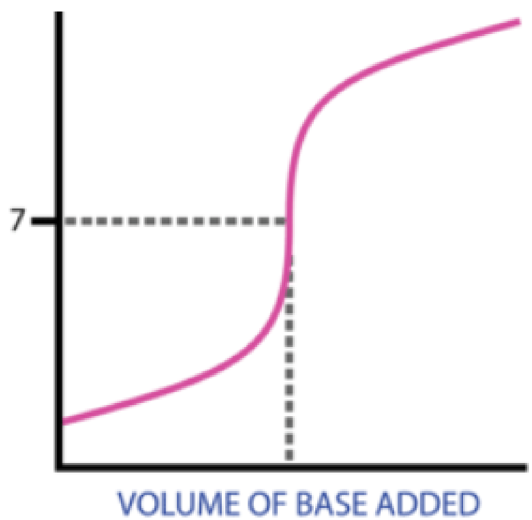
Step 3 - Equivalence Point

Then, we reach a point where the moles of HCl in the solution (25 mmol) originally in the sample equals the number of moles of NaOH that was added. Using the equation $M_a V_a = M_b V_b$, we realize that this equivalence point is reached when 25 mL of NaOH is added. Thus, H^+ and OH^- are in equimolar quantities, and only water remains.
At the equivalence point the pH of the solution is 7 (assuming the temperature is 25°C). This is true for **all** titrations involving a strong acid and strong base. We will cover weak acids and weak bases later.

Step 4 - Past Equivalence Point

Any OH^- added to the solution beyond the equivalence point will be in excess, so the pH *slowly* increases, similar to Step 2.

Overall, the pH curve for the titration of HCl with NaOH should look like this:



Titration curve of a strong acid (HCl) with a strong base (NaOH)

Image Courtesy of CK-12 Foundation

Titrations with Weak Acids and Bases

The main problem is that most acids and bases are not strong! However, the process by which a weak acid is titrated by a strong base (or vice versa, but the former is much more common on the AP exam) is similar.

Consider the case of weak acid-strong base titrations.

The subtle difference between these and strong acid-strong base titrations is that prior to the equivalence point, both the weak acid and its **conjugate base** will be present. You should immediately be thinking of buffers! In the net ionic equation, the weak acid and conjugate base are separate units because the acid does not fully ionize in solution.

Consider the titration of acetic acid with NaOH:

$$CH_3COOH(aq) + OH^-(aq) \rightleftharpoons CH_3COO^-(aq) + H_2O(l)$$

When acetic acid is in excess, acetate ion is also present, creating a buffer solution. (The same goes for the opposite case, if NH_3 were titrated by a strong acid, and the conjugate acid NH_4^+ is present in significant amounts.) Thus, the solution can counteract changes in pH and will have a **half-equivalence point** at exactly 1/2 the **volume** where the equivalence point occurs. Additionally, optimal buffering occurs at the half-equivalence point, where $\text{pH} = \text{p}K_a$ (or $\text{pOH} = \text{p}K_b$, depending on the analyte and titrant being used).

Furthermore, the pH at the equivalence point of a weak acid-strong base titration (and vice versa) will **never** be equal to 7. If a weak base is titrated with a strong acid, the solution at the equivalence point will be acidic. This happens because the conjugate base is present at the equivalence point.

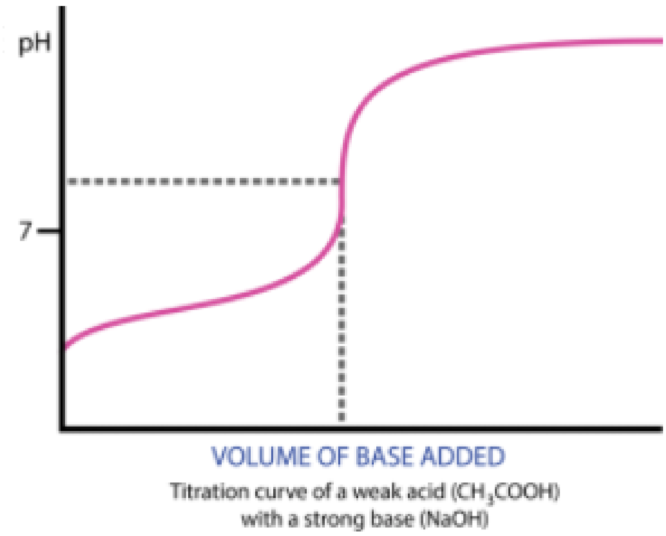


Image Courtesy of CK-12 Foundation

Finally, we will solve some problems to enforce the concepts of titrations.

Problem 8.5.4 — Determining Unknown Concentration

If 10.0 mL of HF is titrated with 0.100 M NaOH, determine the concentration of the HF solution if the equivalence point occurs when 20 mL of NaOH is added.

Solution: At the equivalence point of the titration, the acid and base are in equimolar quantities, therefore, $M_aV_a = M_bV_b$. Since we wish to determine the concentration of HF (analyte), we will rearrange this equation for M_a:

$$M_a = \frac{M_bV_b}{V_a} = \frac{(0.100\,M)(20.0\,\cancel{\text{mL}})}{(10.0\,\cancel{\text{mL}})} = \boxed{0.200\,M}$$

Problem 8.5.5 — Weak Acid-Strong Base Titration

Find the pH of the resulting solution associated with the titration of 25 mL of 0.100 M CH_3COOH with 10.0 mL of 0.100 M KOH.

The value of K_a for CH_3COOH is $1.8 \cdot 10^{-5}$.

Solution: When CH_3COOH, a weak acid, reacts with KOH, a strong base, the net ionic reaction that occurs is

$$\mathrm{CH_3COOH(aq) + OH^-(aq) \rightleftharpoons CH_3COO^-(aq) + H_2O(l)}$$

We can use $n = MV$ to determine the initial number of moles for each reactant:

$$25\,\text{mL} \cdot 0.100\,M = 2.5\,\text{mmol}\,\mathrm{CH_3COOH}$$
$$10\,\text{mL} \cdot 0.100\,M = 1.0\,\text{mmol}\,\mathrm{OH^-}$$

Note: Because volume in titrations is usually measured at a small scale (because the measuring instrument is a buret in most cases), it is more convenient to use units of **milliliters** (mL) instead of liters (L). We can still use $n = MV$, but our units will be in **millimoles** (mmol), rather than moles. Moreover, we can still calculate molarity, but the only difference is that

$$M = \frac{\text{mmol}}{\text{mL}}$$

Now that things are cleared up, we proceed with the stoichiometry.

	$CH_3COOH(aq)$	$OH^-(aq)$	$\rightleftharpoons$	$CH_3COO^-(aq)$	$H_2O(l)$
Before (mmol)	2.5	1.0	-	0	-
Change (mmol)	−1.0	−1.0	-	+1.0	-
After (mmol)	1.5	0	-	1.0	-

Because we have a weak acid (CH_3COOH) and its conjugate base (CH_3COO^-), the solution is buffered and resists changes in pH.

We can calculate the pH using the Henderson-Hasselbalch equation:

$$\text{pH} = \text{p}K_a + \log\frac{[\mathrm{CH_3COO^-}]}{[\mathrm{CH_3COOH}]} = -\log\left(1.8 \cdot 10^{-5}\right) + \log\left(\frac{\frac{1.0\,\text{mmol}}{35\,\text{mL}}}{\frac{1.5\,\text{mmol}}{35\,\text{mL}}}\right) = \boxed{4.57}$$

§8.6 Molecular Structure of Acids and Bases

In this section, we will explore how the relative strengths of acids and bases are affected by the structure of their molecules and constituent ions.

Describing Acid and Base Strength

The simplest way to gauge the strength of an acid or a base is to consider their molecular structure (think **Lewis diagrams**). In previous sections, we established that there are strong and weak acids and bases. However, our two key questions for this section are

1. How can we describe their **relative** strengths, asking questions such as "which acid is weaker" or "which base is stronger?"

2. How can we visually differentiate acids by strength?

Our understanding of acid/base strength stems from conjugate base/acid strength, i.e. the strength of a conjugate base/acid is inversely related to the strength of the acid/base in question.

Consider a conjugate acid-base pair HA (weak acid) and A^- (conjugate base). Their ionization reactions in water are given by the following:

$$\mathrm{HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)} \quad K_a = \frac{[\mathrm{H_3O^+}][\mathrm{A^-}]}{[\mathrm{HA}]}$$

$$\mathrm{A^-(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + HA(aq)} \quad K_b = \frac{[\mathrm{HA}][\mathrm{OH^-}]}{[\mathrm{A^-}]}$$

If we add these two chemical reactions together, we will yield the equation for the autoionization of water:

$$\cancel{\mathrm{HA(aq)}} + \mathrm{H_2O(l)} + \cancel{\mathrm{A^-(aq)}} + \mathrm{H_2O(l)} \rightleftharpoons \mathrm{H_3O^+(aq)} + \cancel{\mathrm{A^-(aq)}} + \mathrm{OH^-(aq)} + \cancel{\mathrm{HA(aq)}}$$

$$\boxed{\mathrm{2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)}}$$

Using properties of K (a more comprehensive discussion in section 7.6), the equilibrium constant expression for a chemical reaction obtained by adding two or more other equations is the **product** of the other equations' K values. Therefore, we can see that

$$K_a \cdot K_b = \frac{[\mathrm{H_3O^+}]\cancel{[\mathrm{A^-}]}}{\cancel{[\mathrm{HA}]}} \cdot \frac{\cancel{[\mathrm{HA}]}[\mathrm{OH^-}]}{\cancel{[\mathrm{A^-}]}} = [\mathrm{H_3O^+}][\mathrm{OH^-}] = K_w$$

Thus, for any conjugate acid-base pair, we derive the following equation:

$$\boxed{K_a \cdot K_b = K_w}$$

Note that this equation is valid for ALL temperatures.

Additionally, we can take the negative log of both sides of the equation to get

$$\boxed{\mathrm{p}K_a + \mathrm{p}K_b = \mathrm{p}K_w}$$

The following is implied from the above equations: the extent to which an acid donates protons to water molecules depends on the strength of the conjugate base of the acid and vice versa. If A^- is a strong base, it will react with any protons that are donated to water molecules. Thus, there is very little A^- and H_3O^+ in solution, which means HA, by definition, is weak. In contrast, if A^- is a weak base, then water binds the protons more strongly, and the solution mostly contains A^- and H_3O^+, which indicates a stronger acid.

Strong acids form very weak conjugate bases, while weak acids form strong conjugate bases, as seen below.

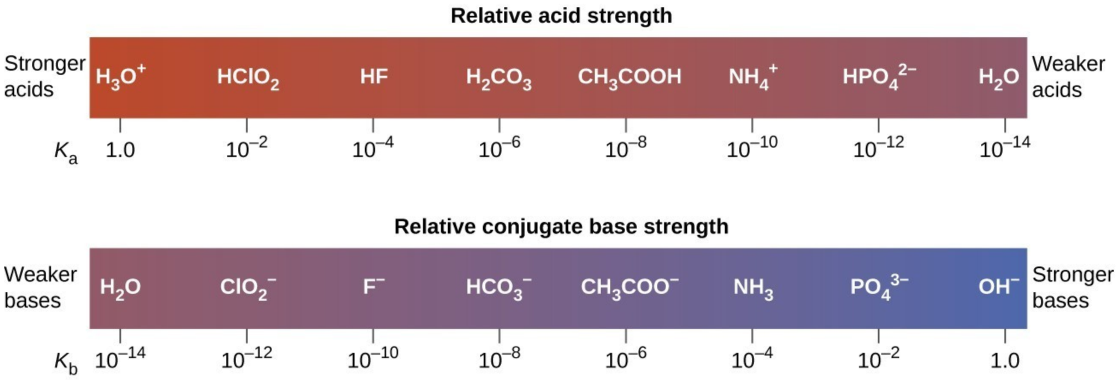


Image Courtesy of Lumen Learning

The same concept applies with weak bases and conjugate acids.

Problem 8.6.1 — Relating Ka and Kb

The value of K_b for the nitrite ion, NO_2^-, is $2.22 \cdot 10^{-11}$ at 25°C. What is the value of K_a for nitric acid, HNO_2?

Solution: Because NO_2^- is the conjugate base of HNO_2, and HNO_2 is the conjugate acid of NO_2^-, we can determine the value of K_a using the relationship

$$K_a \cdot K_b = K_w$$

Rearranging the equation for K_a, we have

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \cdot 10^{-14}}{2.22 \cdot 10^{-11}} = \boxed{4.5 \cdot 10^{-4}}$$

Effect of Molecular Structure on Acid-Base Strength

The first thing to consider when connecting strength to structure is bond polarity, i.e. hydrogen atom bonded to atom of another element.

In the absence of any leveling effect, the strength of **binary acids** (those of type $H-X$, where X is a nonmetal) increases as the strength of the $H-X$ bond decreases going down a group in the periodic table.

A simple generalization that follows is that weaker bonds will hold the hydrogen atom less tightly, so it is more likely for H^+ to "fall off," indicating a stronger acid.

Thus, the order of increasing acid strength for the Group 7A binary compounds is HF $<$ HCl $<$ HBr $<$ HI. Likewise, for Group 6A, the order of increasing acidity is $H_2O < H_2S < H_2Se < H_2Te$.

Note 8.6.2

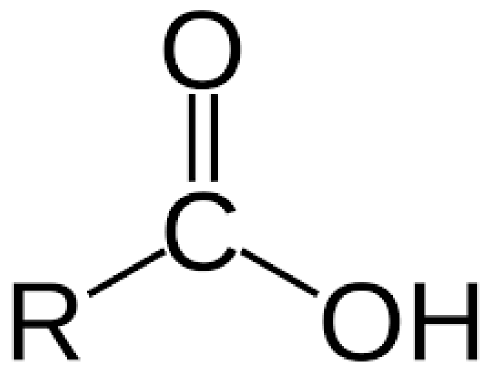
For the **halogenic hydrides**, e.g. HI, HBr, HCl, etc., the weakest $H-X$ interactions occur within larger halogens. This is because as we move down the halogen group, the acid strengths increase as larger atoms give weaker interactions.

In general, acid strength increases from left to right across a period and increases down a group. This actually helps us understand why strong acids have weak conjugate bases. Consider hydrochloric acid, HCl, a strong acid. When it dissociates, the conjugate base, Cl^-, is very stable and is not very reactive.

The other class of acids we will be studying is called the **oxyacids** (sometimes called oxoacids). These molecules contain hydrogen, oxygen, and at least one other element.

When dealing with these, the structure can be described by observing the polarity of the bond between the acidic oxygen (the oxygen atom attached to the acidic hydrogen). The easier it is for the $O-H$ bond to break, the stronger the acid.

Let R represent the remainder of the acid molecule. If R is very electronegative or has a high oxidation state, the $O-H$ bond breaks very easily. One subclass of oxyacids is called the **carboxylic** acids. These organic compounds contain a **-COOH group** on one end of their structure, e.g. CH_3COOH and HCOOH. Because carbon has a low electronegativity, the bonds are less polar, so these acids are relatively weak.



Finally, for oxyacids of the type $H-O-X$, the X represents a neighboring nonmetal atom, usually a halogen. As the number of neighboring atoms increases, the polarity of the bond increases, and the H is held more and more loosely. As the probability of a H^+ ion "falling off" the molecule increases, the strength of the acid also increases.

Problem 8.6.3 — Relative Acid/Base Strength I

Consider four acids containing hydrogen, oxygen, and chlorine:

$$HClO, HClO_2, HClO_3, \text{and } HClO_4$$

How would we rank the strengths of these acids in increasing order?

Solution: Using periodic trends, we know that oxygen is more electronegative than chlorine. As the number of oxygen atoms attached to chlorine increases, we should infer that more electrons are pulled away from the $O-H$ bond, and thus the $O-H$ bond becomes weaker. Since H^+ is more likely to separate, the acid becomes stronger.

Thus, the increasing order of acid strength is

$$\boxed{HClO < HClO_2 < HClO_3 < HClO_4}$$

Problem 8.6.4 — Relative Acid/Base Strength II

Rank the strength of the conjugate bases (in increasing order) for the acids described in problem 8.6.2.

Solution: Conjugate base strength is inversely related to the strength of weak acids. This is because the conjugate base of a weaker acid will have a greater affinity for protons. This means that the weakest conjugate base should be associated with the strongest acid, and vice versa. Thus, the increasing order of conjugate base strength is

$$\boxed{ClO_4^- < ClO_3^- < ClO_2^- < ClO^-}$$

§8.7 pH and pKa

Using pK_a values is another convenient approach for describing the strengths of acids relative to each other. For example, if one acid has a pK_a value of 4 and the other acid has a pK_a of 3, we know that the latter acid is 10 times as acidic (**Note:** this does not mean that the pH is 10 times lower). Recall that 'p' notation refers to a decreasing logarithmic scale.

Thus, like pH, where a lower pH corresponds to a high $[H^+]$, a lower pK_a implies a higher K_a, i.e. a stronger acid and vice versa. However, be careful when relating acids to bases. The pK_a value does NOT describe the alkalinity of anything.

Finally, as with $\text{pH} + \text{pOH} = \text{p}K_w$, at 25°C, we have

$$\boxed{\text{p}K_a + \text{p}K_b = 14}$$

pH, pKa, and Buffer Solutions

pH and pK_a are directly related to buffered solutions. Recall that a buffer is a mixture of a weak acid and its conjugate base and is significant due to its resistance to changes in pH. Since buffers are so important for many chemical processes and the survival of all creatures, one question arises: *When is a certain buffer solution the most effective?*

To effectively answer this question, we can apply the Henderson-Hasselbalch Equation, to calculate the pH of a buffer solution.

$$\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

The *strongest* buffer occurs when the weak acid and conjugate base are in equimolar amounts, or $[\text{HA}] = [\text{A}^-]$. In such a case, the ratio $\frac{[\text{A}^-]}{[\text{HA}]}$ has a value of 1.

$$\text{pH} = \text{p}K_a + \cancelto{0}{\log(1)} \therefore \boxed{\text{pH} = \text{p}K_a}$$

This relationship is crucial because it has strong applications in titrations. It also occurs at the **half-equivalence point** of the titration of a weak acid with a strong base, indicating that you have achieved optimal buffering at this point.

Acid-Base Indicators

Finally, we will discuss acid-base indicators.

Definition 8.7.1

An acid-base **indicator** can refer to a class of compounds that change color depending on the pH of the solution they are used in.

Image Courtesy of Chemistry, Seventh Edition (Zumdahl)

The indicator phenolphthalein is colorless in acidic solution and pink in basic solution. A change in color of the solution "indicates" the instant when the pH changes drastically. For a titration, this is called the **equivalence point**.

In your classroom laboratory experiments, you may have used indicators when performing titrations. For example, phenolphthalein is a common indicator used in acid-base titrations, changing color once the equivalence point is reached. Other examples of indicators include thymol blue, bromthymol blue, and methyl red.

Indicators are important in terms of how you choose them for different experiments. Usually, you want to choose one in which your overall pH will end up in an **effective range**, which is better understood as $pK_a \pm 1$. Note that many indicators are weak acids themselves, so they can be associated with pK_a!

In this way, a buffer that arises should operate relatively well, with both the weak acid and its conjugate base present in significant amounts.

Note 8.7.2

You will not need to memorize specific indicators or their effective ranges on the exam. However, you may be asked to choose the most effective indicator for a certain experiment given a list of different options.

To see how molecules can function as indicators, consider the following equilibrium for some generic indicator HIn, a weak acid with $K_a = 1.0 \cdot 10^{-8}$. Also, suppose that HIn is present as red in solution, while its deprotonated form, In^-, is blue.

$$\mathrm{HIn(aq)} \rightleftharpoons \mathrm{H^+(aq)} + \mathrm{In^-(aq)}$$

$$K_a = \frac{[H^+][In^-]}{[HIn]}$$

By rearranging, we get

$$\frac{K_a}{[H^+]} = \frac{[In^-]}{[HIn]}$$

Suppose we add a few drops of this indicator to an acidic solution with pH of 1.0 ($[H^+] = 1.0 \cdot 10^{-1}\ M$).

$$\frac{K_a}{[H^+]} = \frac{1.0 \cdot 10^{-8}}{1.0 \cdot 10^{-1}} = 1.0 \cdot 10^{-7} \therefore \frac{1}{10,000,000} = \frac{[In^-]}{[HIn]}$$

This ratio demonstrates that the indicator predominantly exists as HIn, resulting in a red solution. Imagine adding some strong base (OH^- ions) to the system. This will reduce the concentration of free H^+ ions, since hydroxide and hydronium ions spontaneously react and neutralize each other, producing water. According to Le Châtelier's principle, a decrease in $[H^+]$ causes the equilibrium to shift to the right, reducing the amount of HIn and increasing the amount of In^-. Eventually, enough In^- will be present so that a color change from red to reddish-purple will be noticeable.

In the next section, we will discuss buffers with more emphasis on their chemical behavior, unpacking some of their important properties that form the backbone of acid-base chemistry. This will allow us to see what actually happens in a buffered solution.

§8.8 Properties of Buffers

Buffer systems are vital to the survival of all living beings. They help maintain a balance in chemical processes that occur in nature. In this section, we will learn why buffers are a crucial part of acid-base chemistry.

What are Buffered Solutions?

A **buffer** is a solution that resists changes in pH in response to addition of a strong acid (H^+ ion) or strong base (OH^- ion).

To accomplish this, two important substances are needed:

1. An acid capable of reacting with any added OH^- ions.
2. A base that can consume any added H_3O^+ ions.

Additionally, the acid and the base should not react with each other because it is critical for both to be present in significant amounts to counteract changes in the pH of the solution.

This is important because there are many processes critical to our survival that are governed by buffered solutions. For example, the pH of our blood needs to maintain a certain threshold range. If it extends beyond that range (in both directions), we could face life-threatening consequences.

In practice, buffer solutions contain high concentrations of both a weak acid and its conjugate base (or a weak base and its conjugate acid). Therefore, they effectively stabilize the pH of a solution for a good duration of time.

The following picture shows what happens when a strong acid or strong base is added to a buffered solution:

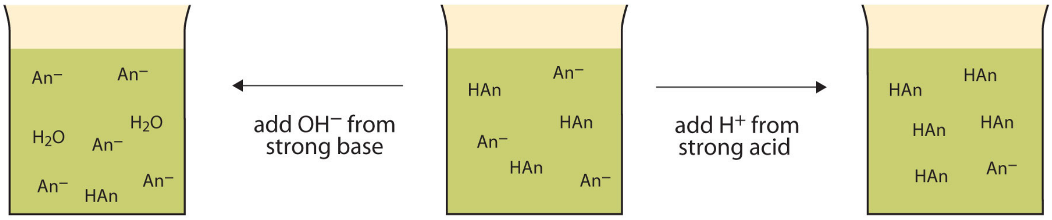


Image Courtesy of LibreTexts

Before we move on to the next section, let's try an AP-style problem.

Problem 8.8.1 — Buffers Practice

Concentration (*M*)	pH of Acid 1	pH of Acid 2	pH of Acid 3	pH of Acid 4
0.010	3.44	2.00	2.92	2.20
0.050	3.09	1.30	2.58	1.73
0.10	2.94	1.00	2.42	1.55
0.50	2.69	0.30	2.08	1.16
1.00	2.44	0.00	1.92	0.98

The pH of solutions of four acids prepared at various concentrations were measured and recorded in the table above.

The four acids are, in no particular order: chlorous, hydrochloric, lactic, and propanoic.

A 25 mL sample of a 1.0 M solution of acid 1 is mixed with 25 mL of 0.50 M NaOH. Which of the following best explains what happens to the pH of the mixture after a few drops of HNO_3 are added?

(A) The pH of the mixture increases sharply because H_3O^+ is a strong acid.
(B) The pH of the mixture decreases sharply because H_3o^+ ions were added.
(C) The pH of the mixture stays about the same because the conjugate base of acid 1 reacts with the added H_3O^+ ions.
(D) The pH of the mixture stays about the same, because the OH^- ions in the solution react with the added H_3O^+ ions.

Solution: Acid 1 has the highest pH, which means that it has the lowest concentration of hydronium ions (remember that pH is based on a decreasing base-10 logarithm function!).

Having the lowest $[H_3O^+]$ indicates that acid 1 dissociates the least, so it is the weakest of the four acids given.

When acid 1 is mixed with NaOH, the following net ionic reaction occurs:

$$\text{Acid 1} + OH^-(aq) \rightleftharpoons \text{Conjugate Base of Acid 1} + H_2O(l)$$

This leads to acid 1 being in equilibrium with its conjugate base.

HNO_3 is a strong acid, so it has the potential to disrupt the equilibrium system of acid 1 and its conjugate base. However, the system can act as a buffer; as long as the conjugate base of acid 1 is available, it will continue to neutralize H_3O^+ ions from the addition of HNO_3. Assuming that sufficient conjugate base is present, the pH of the mixture will stay about the same, which is consistent with choice $\boxed{\textbf{(C)}}$.

Note that we did not need to know which of the four acids corresponded to acid 1!

§8.9 Henderson-Hasselbalch Equation

In previous sections, we have seen this equation a few times:

$$\text{pH} = \text{p}K_a + \log\frac{[A^-]}{[HA]}$$

where K_a is the value of the acid dissociation constant, [HA] is the weak acid concentration, and $[A^-]$ is the conjugate base concentration.

This equation, the **Henderson-Hasselbalch equation**, is useful for buffer solutions when you know the amounts of weak acid and conjugate base present in a solution.

Note 8.9.1

Recall that p(anything) means the negative log of that thing! Thus, $\text{p}K_a = -\log K_a$, for the equation we are studying in this section.

Problem 8.9.2 — pH of Buffered Solutions I

Calculate the pH of a buffer solution containing 0.50 M of H_3CCOOH and 0.50 M of $H_3CCOONa$. The K_a for H_3CCOOH at 25°C is $1.8 \cdot 10^{-5}$.

Solution: $H_3HCCOONa$ fully ionizes into H_3CCOO^- and Na^+, so we have $[H_3CCOO^-] = 0.50\,M$. We also know the initial concentration of H_3CCOOH, so we can calculate pH through a simple use of the Henderson-Hasselbalch equation:

$$\text{pH} = \text{p}K_a + \log\frac{[H_3CCOO^-]}{[H_3CCOOH]}$$

$$\text{pH} = -\log\left(1.8 \cdot 10^{-5}\right) + \log\left(\frac{0.50}{0.50}\right) = \boxed{4.74}$$

Problem 8.9.3 — pH of Buffered Solutions II

Calculate the pH of a solution containing 0.75 M lactic acid ($K_a = 1.4 \cdot 10^{-4}$) and 0.25 M sodium lactate. Lactic acid ($HC_3H_5O_3$) is a common component of biological systems. For example, it is found in milk and is present in human muscle tissue during exertion.

Solution: Sodium lactate fully ionizes into Na^+ and $C_3H_5O_3^-$, so $[C_3H_5O_3^-] = 0.25\ M$.

Because our solution consists of lactic acid, a weak acid, as well as its conjugate base, lactate ion, we can simply use the Henderson-Hasselbalch equation to determine the pH.

$$\text{pH} = \text{p}K_a + \log\frac{[C_3H_5O_3^-]}{[HC_3H_5O_3]}$$

$$\text{pH} = -\log\left(1.4 \cdot 10^{-4}\right) + \log\left(\frac{0.25}{0.75}\right) = \boxed{3.38}$$

Buffered solutions can also be formed from a weak base and the corresponding conjugate acid. In these solutions, the weak base can neutralize any strong acid H^+ added:

$$B + H^+ \to BH^+$$

and the conjugate acid BH^+ reacts with any strong base OH^- added:

$$BH^+ + OH^- \to B + H_2O$$

The approach to solve pH calculations for these buffer systems is virtually identical to those involving weak acid-conjugate base systems described previously.

Problem 8.9.4 — pH of Buffered Solutions III

A buffered solution contains 0.15 M NH_3 ($K_b = 1.8 \cdot 10^{-5}$) and 0.75 M NH_4Cl. Calculate the pH of this solution.

Solution: NH_4Cl dissociates into NH_4^+ and Cl^-. However, Cl^- is the conjugate base of HCl, a strong acid, so it will not be significant to this problem. Also, the solution contains relatively large quantities of both NH_4^+ and NH_3, we can use the equilibrium

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

to determine $[OH^-]$ at equilibrium and calculate $[H^+]$ using the equilibrium expression K_w. Alternatively, we can use the dissociation equilibrium of NH_4^+:

$$NH_4^+(aq) \rightleftharpoons NH_3(aq) + H^+(aq)$$

to calculate $[H^+]$ directly. Either choice will give the same answer, because the equilibrium concentrations of NH_3 and NH_4^+ must satisfy both equilibria.

Using $K_a \cdot K_b = K_w$, we can obtain the value of K_a for NH_4^+, which is the conjugate acid of NH_3:

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \cdot 10^{-14}}{1.8 \cdot 10^{-5}} = 5.6 \cdot 10^{-10}$$

Then, using the Henderson-Hasselbalch equation, we have

$$\text{pH} = \text{p}K_a + \log \frac{[NH_3]}{[NH_4^+]} = -\log\left(5.6 \cdot 10^{-10}\right) + \log\left(\frac{0.15}{0.75}\right) = \boxed{8.55}$$

§8.10 Buffer Capacity

Recall that a buffer is a solution that effectively resists changes in its pH. There are many different types of buffers, with some working more or less effectively than others. This represents the concept of relative buffer capacity.

Definition 8.10.1

Buffer capacity represents the maximum amount of H^+ or OH^- a buffer system can absorb without experiencing a significant change in its pH.

Recall from the Henderson-Hasselbalch equation that the pH of a buffered solution depends on the **ratio** of the conjugate base concentration to the weak acid concentration, or $\frac{[A^-]}{[HA]}$. Meanwhile, the capacity of a buffered solution is determined by the *magnitudes* of $[A^-]$ and $[HA]$.

At this point, we explore the difference between buffer pH and capacity.

Example 8.10.2

Acetic acid, CH_3COOH, is sometimes abbreviated as HAc. At 25°C, the value of K_a is $1.8 \cdot 10^-5$. Calculate the pH of each buffer system below. Also, describe the relative capacities of both buffer systems.

- 5.00 M HAc and 5.00 M NaAc
- 0.050 M HAc and 0.050 M NaAc

Solution: NaAc is an alkali metal salt (ionic compound), so it completely dissociates into its ions, Na^+ and Ac^-. Therefore, 5.00 M NaAc forms 5.00 M Ac^- and so on.

For buffer systems, the Henderson-Hasselbalch equation gives

$$\text{pH} = \text{p}K_a + \log \frac{[A^-]}{[HA]}$$

In both cases, $\frac{[Ac^-]}{[HAc]} = 1$, so the pH of both buffer systems is

$$\text{pH} = \text{p}K_a = -\log K_a = -\log\left(1.8 \cdot 10^{-5}\right) = \boxed{4.74}$$

Question: Now, how can we compare the relative capacities of the two systems?
Answer: We need to consider the magnitudes of the weak acid and conjugate base concentrations in each system.

In the first system, there are significantly more HAc and Ac^- ($5.00\,M$) than in the second system ($0.050\,M$). More HAc and Ac^- are available to react with and neutralize any additional H^+ or OH^- ions for a longer duration. Thus, the $\boxed{\text{first}}$ buffer system has the greater capacity.

Here is a hypothetical situation.

In the previous example, gaseous hydrochloric acid, HCl(g), is added to both buffer systems. The first has a resulting pH of 4.74 and the second has a resulting pH of 4.56. This is because the first buffer system contained more weak acid and more conjugate base, and could neutralize more additions of H^+ and OH^- for more time. Thus, its pH remained 4.74 while the second system experienced a pH decrease from 4.74 to 4.56, since the H^+ ions caused it to increase in acidity.

How to Choose a Buffer

- The that is, most effective buffer systems (most resistant to pH changes) exist when the ratio of the conjugate base concentration to the weak acid concentration (and vice versa) are equal, or
$$[A^-] = [HA]$$
- In terms of the Henderson-Hasselbalch equation,
$$\text{pH} = \text{p}K_a + \log\frac{[A^-]}{HA} = \text{p}K_a + \cancelto{0}{\log(1)} \therefore \text{pH} = \text{p}K_a$$

Therefore, when choosing a buffer, you should choose a buffer system such that the desired pH is as close to the pK_a of the weak acid as possible.

§8.11 Practice Problems

Problem 8.11.1 — 2002 AP Chemistry FRQ

$$HOBr(aq) \rightleftharpoons H^+(aq) + OBr^-(aq) \qquad K_a = 2.3 \cdot 10^{-9}$$

Hypobromous acid, HOBr, is a weak acid that dissociates in water, as represented by the equation above.

(a) Calculate the value of $[H^+]$ in an HOBr solution that has a pH of 4.95.

(b) Write the equilibrium constant expression for the ionization of HOBr in water, then calculate the concentration of HOBr(aq) in an HOBr solution that has $[H^+]$ equal to $1.8 \cdot 10^{-5}\ M$.

(c) A solution of $Ba(OH)_2$ is titrated into a solution of HOBr.

(i) Calculate the volume of 0.155 M $Ba(OH)_2(aq)$ needed to reach the equivalence point when titrated into a 65.0 mL sample of 0.146 M HOBr(aq).
(ii) Indicate whether the pH at the equivalence point is less than 7, equal to 7, or greater than 7. Explain.

(d) Calculate the number of moles of NaOBr(s) that would have to be added to 125 mL of 0.160 M HOBr to produce a buffer solution with $[H^+] = 5.00 \cdot 10^{-9}\ M$. Assume that volume change is negligible.

(e) HOBr is a weaker acid than $HBrO_3$. Account for this fact in terms of molecular structure.

Solution to part a: We know that the pH of any solution is equal to the negative log of its hydrogen ion concentration, or $[H^+]$.

$$\text{pH} = -\log[H^+]$$

Since the problem tells us the pH of the solution, we can rearrange the equation for $[H^+]$:

$$[H^+] = 10^{-\text{pH}} = 10^{-4.95} = \boxed{1.1 \cdot 10^{-5}\ M}$$

Solution to part b: The equilibrium constant expression describing the ionization of HOBr in water is given by

$$\boxed{K_a = \frac{[H^+][OBr^-]}{[HOBr]}}$$

Since both H^+ and OBr^- have the same stoichiometric coefficients (both 1), their concentrations when equilibrium is established will be the same, so $[H^+] = [OBr^-] = 1.8 \cdot 10^{-5}\ M$.

Plugging in, we have

$$2.3 \cdot 10^{-9} = \frac{\left(1.8 \cdot 10^{-5}\right)^2}{[HOBr]}$$

and the concentration of HOBr(aq) in solution with this H^+ concentration is

$$[\text{HOBr}] = \frac{\left(1.8 \cdot 10^{-5}\right)^2}{2.3 \cdot 10^{-9}} = \boxed{0.14\,M}$$

Solution to part c(i): When a $Ba(OH)_2$ solution is titrated into a solution of HOBr, the following balanced, chemical reaction occurs:

$$2\text{HOBr(aq)} + \text{Ba(OH)}_2\text{(aq)} \rightarrow \text{Ba(OBr)}_2\text{(aq)} + 2\text{H}_2\text{O(l)}$$

Additionally, we know that the analyte and titrant are in equimolar amounts at the equivalence point of the titration. In this case, our analyte is HOBr and the titrant is $Ba(OH)_2$. The formula we will use to determine the volume of $0.115\,M$ $Ba(OH)_2$(aq) needed to reach the equivalence point is

$$M_a V_a = 2 M_b V_b$$

Notice that stoichiometric coefficients make a big difference here! If we did not include the 2 factor on the moles of base, we would get an incorrect answer.

Solving for V_b, we have

$$V_b = \frac{M_a V_a}{2M_b} = \frac{\left(0.146\,\cancel{M}\right)(65.0\,\text{mL})}{2\left(0.115\,\cancel{M}\right)} = \boxed{41.3\,\text{mL}}$$

Solution to part c(ii): At the equivalence point of the titration, HOBr and $Ba(OH)_2$ are completely consumed.

However, the conjugate base of HOBr, OBr^- ion, is still present and affects the pH of the resulting solution. We know that conjugate bases of weak acids have a strong affinity for protons. The only source of protons is water, so OBr^- will undergo the following hydrolysis reaction:

$$\text{OBr}^- + \text{H}_2\text{O} \rightleftharpoons \text{HOBr} + \text{OH}^-$$

Because this reaction produces OH^- ions, the resulting solution is basic and the pH at the equivalence point is $\boxed{\text{greater than 7}}$.

Solution to part d: This problem is a bit more conceptually challenging. Our first step should be to write the expression for K_a:

$$K_a = \frac{[\text{H}^+][\text{OBr}^-]}{[\text{HOBr}]}$$

Since we already know the value of K_a for HOBr and this problem tells us the concentration of H^+, let's try and see if we can make use of solving for the concentration of OBr^-:

$$[\text{OBr}^-] = \frac{[\text{HOBr}] \cdot K_a}{[\text{H}^+]} = \frac{\left(0.160\,\cancel{M}\right)\left(2.3 \cdot 10^{-9}\right)}{5.00 \cdot 10^{-9}\,\cancel{M}} = 0.074\,M$$

Because we want to determine the number of moles of NaOBr(s) that should be added to produce this buffer, we can apply the formula $n = MV$, taking M as the molarity of

OBr^- because NaOBr is a very soluble salt that produces stoichiometric amounts of Na^+ and OBr^- when dissociated:

$$n_{\mathrm{NaOBr}} = 0.125\,\cancel{\mathrm{L}} \cdot \frac{0.074\,\mathrm{mol\,OBr^-}}{1\,\cancel{\mathrm{L}}} = \boxed{9.2 \cdot 10^{-3}\,\mathrm{mol}}$$

Solution to part e: This question requires knowledge about molecular structure of acids and bases and how this affects their relative strengths. $HBrO_3$ has two more oxygen atoms than HOBr. Additionally, both acids have a central bromine atom. $HBrO_3$ has more electronegative O atoms surrounding the central atom than HOBr, so the $O-H$ bond becomes more polarized. When this happens, the acidic hydrogen, as H^+, is more likely to break apart, indicating a stronger acid. Thus, HOBr is weaker and $HBrO_3$ is stronger.

Problem 8.11.2 — 2009 AP Chemistry FRQ

Answer the following questions that relate to the chemistry of halogen oxoacids.

(a) Use the information in the table below to answer part (a)(i).

Acid	K_a at 298 K
HOCl	2.9×10^{-8}
HOBr	2.4×10^{-9}

(i) Which of the two acids is stronger, HOCl or HOBr? Justify your answer in terms of K_a.
(ii) Draw a complete Lewis electron-dot diagram for the acid that you identified in part (a)(i).
(iii) Hypoiodous acid has the formula HOI. Predict whether HOI is a stronger acid or a weaker acid than the acid you identified in part (a)(i). Justify your prediction in terms of chemical bonding.

(b) Write the equation for the reaction that occurs between hypochlorous acid and water.

(c) A 1.2 M NaOCl solution is prepared by dissolving solid NaOCl in distilled water at 298 K. The hydrolysis reaction $OCl^-(aq) + H_2O(l) \rightleftharpoons HOCl(aq) + OH^-(aq)$ occurs.

(i) Write the equilibrium-constant expression for the hydrolysis reaction that occurs between $OCl^-(aq)$ and $H_2O(l)$.
(ii) Calculate the value of the equilibrium constant at 298 K for the hydrolysis reaction.
(iii) Calculate the value of $[OH^-]$ in the 1.2 M NaOCl solution at 298 K.

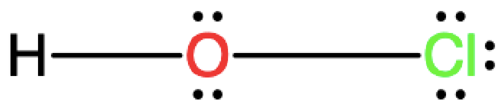
(d) A buffer solution is prepared by dissolving some solid NaOCl in a solution of HOCl at 298 K. The pH of the buffer solution is determined to be 6.48.

(i) Calculate the value of $[H_3O^+]$ in the buffer solution.
(ii) Indicate which of HOCl(aq) or $OCl^-(aq)$ is present at the higher concentration in the buffer solution. Support your answer with a calculation.

Solution to part a(i): The value of K_a describes the strength of an acid, because it is proportional to the equilibrium concentration of H_3O^+ that is dissociated. At 298 K, the K_a of HOCl is greater than the K_a of HOBr, so HOCl dissociates more into H_3O^+ ions compared to HOBr. Thus, $\boxed{\text{HOCl}}$ is the stronger acid.

Solution to part a(ii): The first step in drawing Lewis diagrams is to count the total number of valence electrons in the molecule. Hydrogen has 1, oxygen has 6, and chlorine has 7, so HOCl contains a total of $1 + 6 + 7 = 14$ valence electrons.

Now, O is the least electronegative element of all three, so it will be placed in the center, with H bonded from the left and Cl bonded from the right. H only requires two valence electrons to be stable, while O and Cl require eight. Therefore, we will add lone pairs of electrons on both atoms until all atoms are in their most stable form. However, do not forget that ensuring stability for the *central* atom is prioritized. Your Lewis diagram should look something like this:



Solution to part a(iii): Both HOI and HOCl are weak oxoacids. We need to use differences in their molecular structures to predict whether HOI is a stronger acid or weaker acid. Notice that iodine is less electronegative than chlorine, which results in a higher electron density between the H and O atoms in HOI than in HOCl. Overall, the O – H bond is stronger in HOI than in HOCl, and the acidic hydrogen is less likely to break apart. We conclude that HOI is a $\boxed{\text{weaker}}$ acid than HOCl.

Solution to part b: When hypochlorous acid reacts with water, water acts as a Brønsted–Lowry base, accepting a H^+ from HOCl, and resulting in the formation of H_3O^+ and OCl^- ions:

$$\boxed{HOCl(aq) + H_2O(l) \rightleftharpoons OCl^-(aq) + H_3O^+(aq)}$$

Solution to part c(i): Since the equilibrium constant expression is proportional to concentrations of products over reactants, raised to the power of coefficients, we have

$$\boxed{K_b = \frac{[HOCl][OH^-]}{[OCl^-]}}$$

Note: the little b subscript is used to emphasize that OCl^- is a base.

Solution to part c(ii): The value of the equilibrium constant for the hydrolysis reaction at 298 K simply represents the value of K_b for OCl^-. Note that OCl^- is the conjugate acid of HOCl, whose K_a value is given. Therefore, we can use the formula

$$K_a \cdot K_b = K_w$$

to solve for K_b as shown:

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \cdot 10^{-14}}{2.9 \cdot 10^{-8}} = \boxed{3.4 \cdot 10^{-7}}$$

Solution to part c(iii): Since we are given the initial concentration of OCl^-, the value of K_b for OCl^-, and do not know the equilibrium concentrations of each species, we will need to use an ICE table.

	$OCl^-(aq)$	$H_2O(l)$	$\rightleftharpoons$	$HOCl(aq)$	$OH^-(aq)$
Initial (M)	1.2	-	-	0	0
Change (M)	$-x$	-	-	$+x$	$+x$
Equilibrium (M)	$1.2 - x$	-	-	x	x

The K_b expression is given by

$$K_b = \frac{[HOCl][OH^-]}{[OCl^-]}$$

We can substitute the values that we know to solve for x, the equilibrium concentration of OH^- ions:

$$3.4 \cdot 10^{-7} = \frac{(x)\,(x)}{(1.2 - x)} \approx \frac{x^2}{1.2}$$
$$x^2 = (1.2)\left(3.4 \cdot 10^{-7}\right) \therefore x = [OH^-] = \boxed{6.4 \cdot 10^{-4}\,M}$$

Solution to part d(i): We know that the pH of a solution is equal to the negative log of the H_3O^+ concentration. Since the problem gives the pH but the value of $[H_3O^+]$ is unknown, we can rearrange the equation as shown:

$$\text{pH} = -\log[H_3O^+] \therefore [H_3O^+] = 10^{-\text{pH}} = 10^{-6.48} = \boxed{3.3 \cdot 10^{-7}\,M}$$

Solution to part d(ii): We can use the fact that $[H^+] = 3.3 \cdot 10^{-7}\,M$ at equilibrium and the value of K_a for HOCl is $2.9 \cdot 10^{-8}$.

The K_a expression for HOCl is given by

$$K_a = \frac{[H^+][OCl^-]}{[HOCl]}$$

and plugging in our two known values, we have

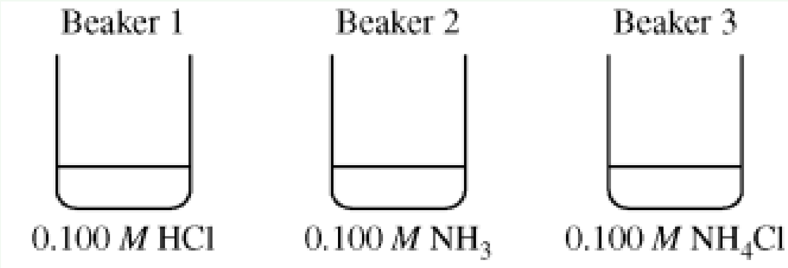
$$2.9 \cdot 10^{-8} = \frac{\left(3.3 \cdot 10^{-7}\right)[OCl^-]}{[HOCl]}$$

From here, we can calculate the ratio of hypochlorite ion concentration to hypochlorous acid concentration:

$$\frac{[OCl^-]}{[HOCl]} = \frac{2.9 \cdot 10^{-8}}{3.3 \cdot 10^{-7}} = 0.088 \therefore \frac{[OCl^-]}{[HOCl]} < 1$$

This ratio indicates that $[HOCl] > [OCl^-]$, so $\boxed{HOCl(aq)}$ is present at the higher concentration in the buffer solution at equilibrium.

Problem 8.11.3 — 2011 AP Chemistry FRQ



Each of three beakers contain 25.0 mL of a 0.100 M solution of HCl, NH_3, or NH_4Cl, as shown above.
Each solution is at 25°C.

(a) Determine the pH of the solution in beaker 1. Justify your answer.

(b) In beaker 2, the reaction $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$ occurs. The value of K_b for $NH_3(aq)$ is $1.8 \cdot 10^{-5}$ at 25°C.

(i) Write the K_b expression for the reaction of $NH_3(aq)$ with $H_2O(l)$.
(ii) Calculate the $[OH^-]$ in the solution in beaker 2.

(c) In beaker 3, the reaction $NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + OH^-(aq)$ occurs.

(i) Calculate the value of K_a for $NH_4^+(aq)$ at 25°C.
(ii) The contents of beaker 2 are poured into beaker 3 and the resulting solution is stirred. Assume that volumes are additive. Calculate the pH of the resulting solution.

(d) The contents of beaker 2 are poured into the solution made in part (c)(ii). The resulting solution is stirred. Assume that volumes are additive.

(i) Is the resulting solution an effective buffer? Justify your answer.
(ii) Calculate the final $[NH_4^+]$ in the resulting solution at 25°C.

Solution to part a: Beaker 1 contains a 0.100 M of hydrochloric acid, a strong acid. Therefore, we have $[H^+] = [HCl] = 0.100\,M$.

As pH is defined as the negative base-10 logarithm of the H^+ concentration in solution,

$$pH = -\log[H^+] = -\log(0.100) = \boxed{1.000}$$

Solution to part b(i): Use the definition of the equilibrium constant.

$$\boxed{K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}}$$

Solution to part b(ii): We are asked to calculate the equilibrium concentration of OH^-. Because we know the initial concentration of NH_3 as well as the temperature, we can use an ICE table to solve this problem.

	NH_3(aq)	H_2O(l)	$\rightleftharpoons$	NH_4^+(aq)	OH^-(aq)
Initial (M)	0.100	-	-	0	0
Change (M)	$-x$	-	-	$+x$	$+x$
Equilibrium (M)	$0.100 - x$	-	-	x	x

The K_b expression for the reaction between NH_3 and water is

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

as we found in part (b)(i).

Plugging in our variables and using the approximation method,

$$1.8 \cdot 10^{-5} = \frac{(x)\,(x)}{(0.100 - x)} \approx \frac{x^2}{0.100}$$

Here, x represents the equilibrium concentration of hydroxide ions. We can rearrange this equation for x:

$$x = [OH^-] = \sqrt{0.100 \cdot 1.8 \cdot 10^{-5}} = \boxed{1.3 \cdot 10^{-3}\ M}$$

Solution to part c(i): For conjugate acid-base pairs, $K_a \cdot K_b = K_w$, so

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \cdot 10^{-14}}{1.8 \cdot 10^{-5}} = \boxed{5.6 \cdot 10^{-10}}$$

Solution to part c(ii): The resulting solution is a buffered solution with $[NH_3] = [NH_4^+]$. Additionally, we know that

$$K_a = 5.6 \cdot 10^{-10} = \frac{[NH_3][H_3O^+]}{[NH_4^+]}$$

Since $[NH_3] = [NH_4^+]$, the equation nicely reduces to $5.6 \cdot 10^{-10} = [H_3O^+]$, and thus

$$\text{pH} = -\log\left(5.6 \cdot 10^{-10}\right) = \boxed{9.25}$$

Solution to part d(i): If the contents of beaker 1 are poured into the solution made in part (c)(i), the following reaction occurs:

$$NH_3(aq) + H_3O^+(aq) \rightarrow NH_4^+(aq) + H_2O(l)$$

The reason why this cannot be an effective buffer is that virtually all of the NH_3 in the solution formed in part (c)(i) will be consumed by the H_3O^+ in solution 1. This leads to only NH_4^+ being present in significant quantities.

Recall that a buffer must contain significant amounts of a weak acid and its conjugate base **OR** significant amounts of a weak base and its conjugate acid. Because the NH_3 is not present in significant amounts, this solution cannot effectively counteract both strong base and strong acid.

Solution to part d(ii): This question warrants a rigorous use of $n = MV$.

We will calculate the number of moles of H_3O^+, NH_3, and NH_4^+ in solutions 1, 2, and 3, respectively, since we are given their initial concentrations and volumes.

moles H_3O^+: $(0.100\,M)(0.0250\,\text{L}) = 0.00250\,\text{mol}$
moles NH_3: $(0.100\,M)(0.0250\,\text{L}) = 0.00250\,\text{mol}$
moles NH_4^+: $(0.100\,M)(0.0250\,\text{L}) = 0.00250\,\text{mol}$

When the solutions are mixed, H_3O^+ and NH_3 react completely, resulting in a total of $0.00500\,\text{mol}\,NH_4^+$. The final volume is the sum of the individual volumes:

$$0.0250\,\text{L} + 0.0250\,\text{L} + 0.0250\,\text{L} = 0.0750\,\text{L}$$

Since $M = \frac{n}{V}$, we calculate the final concentration of NH_4^+ as

$$[NH_4^+] = \frac{0.00500\,\text{mol}}{0.0750\,\text{L}} = \boxed{0.0667\,M}$$

Problem 8.11.4 — 2014 AP Chemistry FRQ

$$CH_3CH_2COOH(aq) + H_2O(l) \rightleftharpoons CH_3CH_2COO^-(aq) + H_3O^+(aq)$$

Propanoic acid, $CH_3CH_2COOH(aq)$, is a carboxylic acid that reacts with water according to the equation above. At 25°C the pH of a 50.0 mL sample of 0.20 M $CH_3CH_2COOH(aq)$ is 2.79.

(a) Identify a Brønsted-Lowry conjugate acid-base pair in the reaction. Clearly label which is the acid and which is the base.

(b) Determine the value of K_a for the reaction at 25°C.

(c) For each of the following statements, determine whether the statement is true or false. In each case, explain the reasoning that supports your answer.

(i) The pH of a solution prepared by mixing the 50.0 mL sample of 0.20 M CH_3CH_2COOH with a 50.0 mL sample of 0.20 M NaOH is 7.00.
(ii) If the pH of a hydrochloric acid solution is the same as the pH of a propanoic acid solution, then the molar concentration of the hydrochloric acid solution must be less than the molar concentration of the propanoic acid solution.

A student is given the task of determining the concentration of a propanoic acid solution of unknown concentration. A 0.173 M NaOH is available to use as the titrant. The student uses a 25.00 mL volumetric pipet to deliver the propanoic acid solution to a clean, dry flask. After adding an appropriate indicator to the flask, the student titrates the solution with the 0.173 M NaOH, reaching the end point after 20.52 mL of the base solution has been added.

(d) Calculate the molarity of the propanoic acid solution.

(e) The student is asked to redesign the experiment to determine the concentration of a butanoic acid solution instead of a propanoic acid solution. For butanoic acid, the value of pK_a is 4.83. The student claims that a different indicator will be required to determine the equivalence point of the titration accurately. Based on your response to part (b), do you agree with the student's claim? Justify your answer.

Solution to part a: Recall that an acid is a proton donor and a base is a proton acceptor according to the Brønsted-Lowry definition. Therefore, we have two possible pairs.

- Pair 1: CH_3CH_2COOH (acid) and $CH_3CH_2COO^-$ (base)
  CH_3CH_2COOH is the acid, which donates a proton to H_2O, becoming $CH_3CH_2COO^-$ (conjugate base).
- Pair 2: H_3O^+(acid) and H_2O (base)
  H_3O^+ donates a proton in the reaction, and becomes H_2O, the conjugate base.

Solution to part b: The pH of the propanoic acid solution is given, so we can determine the concentration of H_3O^+ ions when equilibrium is established.

$$\text{pH} = -\log[H_3O^+] \therefore [H_3O^+] = 10^{-\text{pH}} = 10^{-2.79} = 1.62 \cdot 10^{-3}\ M$$

Moreover, both H_3O^+ and $CH_3CH_2COO^-$ have a coefficient of 1 in the balanced chemical equation and the same initial concentration, so their equilibrium concentrations will be equal: $[CH_3CH_2COO^-] = [H_3O^+] = 1.62 \cdot 10^{-3}\ M$. Finally, we are given that the initial concentration of propanoic acid is $0.20\ M$ and because it is weak, we can use its small value of K_a and assume that its equilibrium concentration is $\approx 0.20\ M$, avoiding the use of the quadratic formula.

Thus, we can calculate the K_a value for the reaction using these three values:

$$K_a = \frac{[CH_3CH_2COO^-][H_3O^+]}{[CH_3CH_2COOH]} = \frac{\left(1.62 \cdot 10^{-3}\right)^2}{0.20} = \boxed{1.3 \cdot 10^{-5}}$$

Solution to part c(i): The net ionic reaction that occurs is:

$$CH_3CH_2COOH(aq) + OH^-(aq) \rightleftharpoons CH_3CH_2COO^-(aq) + H_2O(l)$$

We can use a variation of the ICE (Initial, Change, Equilibrium) table to track the molar amounts of each species as the reaction progresses. Recall that $n = MV$, so we can determine the number of moles for both propanoic acid and NaOH.

	$CH_3CH_2COOH(aq)$	OH^-	$\rightarrow$	$CH_3CH_2COO^-(aq)$	$H_2O(l)$
Before (mol)	0.01	0.01	-	0	-
Change (mol)	-0.01	-0.01	-	$+0.01$	-
After (mol)	0	0	-	0.01	-

We see that once the reaction is complete, CH_3CH_2COOH and NaOH have been fully consumed, but there is 0.01 mol of $CH_3CH_2COO^-$, the conjugate base of propanoic acid. We know that conjugate bases of weak acids have a high affinity for protons, but there is only one source of protons: H_2O. The following reaction will occur:

$$CH_3CH_2COO^-(aq) + H_2O(l) \rightleftharpoons CH_3CH_2COO^-(aq) + OH^-(aq)$$

Thus, the conjugate base undergoes hydrolysis at equivalence to form a basic solution with pH > 7, and the statement is $\boxed{\text{false}}$.

Solution to part c(ii): This question appears difficult but only requires us to notice one small detail: the relative strengths of HCl and propanoic acid.

HCl(aq) is a strong acid, which will fully ionize into H_3O^+ ions when in solution. Meanwhile, propanoic acid is a weak acid and only partially ionizes in solution. Therefore, fewer moles of HCl are needed to produce the same concentration of H_3O^+ ions as the propanoic acid solution, and because molar concentration is proportional to the number of moles, the statement is $\boxed{\text{true}}$.

Solution to part d: At the equivalence point of the titration, the acid and base are in equal amounts (equal number of moles), and thus

$$M_a V_a = M_b V_b$$

Since we wish to find the molarity of the propanoic acid solution, we will rearrange this equation and solve for M_a:

$$M_a = \frac{M_b V_b}{V_a} = \frac{(0.173\ M\ \text{NaOH})(20.52\ \text{mL NaOH})}{25.00\ \text{mL acid}} = \boxed{0.142\ M}$$

Solution to part e: Let's make things easier for ourselves by comparing the pK_a values of butanoic acid and propanoic acid to decide whether the student's claim is correct or incorrect.

The pK_a value of a weak acid can be calculated by taking the negative log of the value of K_a, so for propanoic acid,

$$\text{p}K_a = -\log\left(1.3 \cdot 10^{-5}\right) = 4.89$$

Also, we know that the pK_a value of butanoic acid is 4.83. If propanoic acid was to be replaced by butanoic acid, the pH of the resulting solution at the equivalence point in the titration should be close enough to the pH in the titration of propanoic acid. This is because 4.83 is in close proximity to 4.89, so the original indicator would be appropriate for the titration of butanoic acid. Thus, we will not need to use a different indicator, and we $\boxed{\text{disagree}}$ with the student's claim.

Problem 8.11.5 — 2016 AP Chemistry FRQ

$$C_6H_5OH(aq) + H_2O(l) \rightleftharpoons C_6H_5O^-(aq) + H_3O^+(aq) \qquad K_a = 1.12 \cdot 10^{-10}$$

Phenol is a weak acid that partially dissociates in water according to the equation above.

(a) What is the pH of a 0.75 M $C_6H_5OH(aq)$ solution?

(b) For a certain reaction involving $C_6H_5OH(aq)$ to proceed at a significant rate, the phenol must be primarily in its deprotonated form, $C_6H_5O^-(aq)$. In order to ensure that the $C_6H_5OH(aq)$ is deprotonated, the reaction must be conducted in a buffered solution. On the number scale below, circle each pH for which more than 50 percent of the phenol molecules are in the deprotonated form ($C_6H_5O^-(aq)$). Justify your answer.

1 2 3 4 5 6 7 8 9 10 11 12 13 14

Solution to part a: To find the pH, we need to determine the equilibrium concentration of H_3O^+ in the solution. To do that, we construct the following ICE table:

	$C_6H_5OH(aq)$	$H_2O(l)$	$\rightleftharpoons$	$C_6H_5O^-(aq)$	$H_3O^+(aq)$
Initial (M)	0.75	-	-	0	0
Change (M)	$-x$	-	-	$+x$	$+x$
Equilibrium (M)	$0.75 - x$	-	-	x	x

We know that the equilibrium expression is given by

$$K_a = 1.12 \cdot 10^{-10} = \frac{[C_6H_5O^-][H_3O^+]}{[C_6H_5OH]}$$

Plugging in our equilibrium concentrations, we have

$$1.12 \cdot 10^{-10} = \frac{(x)\,(x)}{(0.75 - x)} \approx \frac{x^2}{0.75}$$

Here, x represents the equilibrium concentration of H_3O^+. Solving for x, and taking the negative log to calculate the pH, we have

$$x = [H_3O^+] = \sqrt{0.75 \cdot 1.12 \cdot 10^{-10}} = 9.2 \cdot 10^{-6}\ M$$
$$\text{pH} = -\log[H_3O^+] = -\log\left(9.2 \cdot 10^{-6}\right) = \boxed{5.04}$$

Solution to part b: We are told that the solution is buffered, which goes back to a special formula, the Henderson-Hasselbalch equations.

$$\text{pH} = \text{p}K_a + \log\frac{[A^-]}{[HA]}$$

where HA and A^- represent the weak acid and its conjugate base, respectively.

For this solution, the pH can be determined via the following:

$$\text{pH} = \text{p}K_a + \log\frac{[C_6H_5O^-]}{[C_6H_5OH]}$$

The deprotonated form of phenol, $C_6H_5O^-$(aq), is its conjugate base. For this to comprise more than 50 percent of phenol molecules, the term $\frac{[C_6H_5O^-]}{[C_6H_5OH]}$ term must be greater than 1. Since the logarithmic function is positive for domain values strictly greater than 1, the Henderson-Hasselbalch equation in this problem can be written as

$$\text{pH} = \text{p}K_a + \text{positive quantity}$$

For this to be true, we must have pH > pK_a. We can calculate the pK_a by taking the negative log of K_a for phenol.

$$\text{p}K_a = -\log K_a = -\log\left(1.12 \cdot 10^{-10}\right) = 9.95$$

Since pH must exceed this value, the numbers $\boxed{\text{10 to 14, inclusive}}$ should be circled.

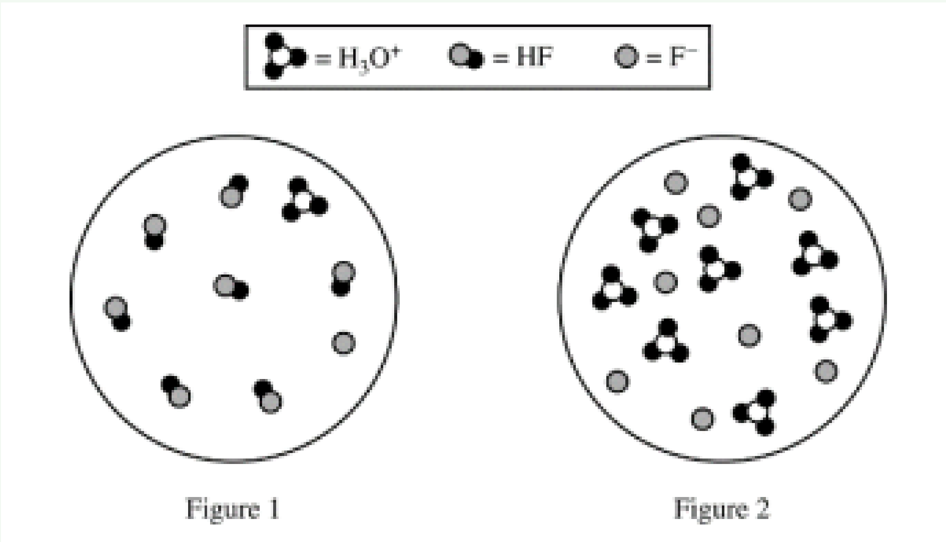
Problem 8.11.6 — 2018 AP Chemistry FRQ

$$HF(aq) + H_2O(l) \rightleftharpoons F^-(aq) + H_3O^+(aq)$$

The ionization of HF(aq) in water is represented by the equation above. In a 0.0350 M HF(aq) solution, the percent ionization of HF is 13.0 percent.

(a) Two particulate representations of the ionization of HF molecules in the 0.0350 M HF(aq) solution are shown below in Figure 1 and Figure 2. Water molecules are not shown. Explain why the representation of the ionization of HF molecules in water in Figure 1 is more accurate than the representation of Figure 2.

(The key below identifies the particles in the representations.)



(b) Use the percent ionization data above to calculate the value of K_a for HF.

(c) If 50.0 mL of distilled water is added to 50.0 mL of 0.035 M HF(aq), will the percent ionization of HF(aq) in the solution increase, decrease, or remain the same? Justify your answer with an explanation or calculation.

Solution to part a: We are told that HF(aq) has a percent ionization value of 13.0, much less than 100, so it is a weak acid. The reason why Figure 1 is a more accurate representation than Figure 2 for the ionization of HF is the fact that the former shows only one H_3O^+ ion for every 8 undissociated HF(aq) molecules - approximately 13.0% - which is consistent with the information given above.

Alternatively, you could have explained why Figure 2 could not represent the ionization of HF(aq) molecules. If you look closely, you will notice that 100% of the acid has been ionized - only H_3O^+ and F^- ions are present. However, this representation is incorrect, since HF(aq) actually has a percent dissociation of only 13%.

Solution to part b: The percent ionization for a weak acid is given by

$$\%\,\text{ionization} = \frac{[H_3O^+]}{[HA]_0} \cdot 100\%$$

where $[H_3O^+]$ is the equilibrium concentration of H_3O^+ ions and $[HA]_0$ is the initial concentration of the weak acid.

Thus, we have

$$\frac{[H_3O^+]}{0.0350\,M} = 0.130 \therefore [H_3O^+] = 0.00455\,M$$

Now, we can set up an ICE table to determine the equilibrium concentrations of F^-(aq) and HF(aq), and thus calculate the value of K_a for HF.

	HF(aq)	H_2O(l)	$\rightleftharpoons$	F^-(aq)	H_3O^+(aq)
Initial (M)	0.0350	-	-	0	~ 0
Change (M)	-0.00455	-	-	$+0.00455$	$+0.00455$
Equilibrium (M)	0.0304	-	-	0.00455	0.00455

Question: Why did I put a ~ 0 for the initial concentration of H_3O^+?
Clarification: This is due to the autoionization of water into H_3O^+ and OH^- ions. However, the contribution of H_3O^+ by water is negligible here because the constant K_w is very small, but I indicated that water always ionizes, although the equilibrium of HF dominates. This was simply to remind students that it is not because the autoionization of water does not exist in this case, but because it is not significant.

The expression for K_a for HF is given by

$$K_a = \frac{[H_3O^+][F^-]}{[HF]}$$

and we can calculate its value by substituting our equilibrium concentrations:

$$K_a = \frac{(0.00455)^2}{0.0304} = \boxed{6.81 \cdot 10^{-4}}$$

Solution to part c: Recall that molarity is given by moles per liter, or $M = \frac{n}{V}$, so doubling the volume of each species will cause their equilibrium concentrations to decrease by half. The system is no longer at equilibrium and we have

$$Q = \frac{\left(\frac{1}{2}[H_3O^+]\right)\left(\frac{1}{2}[F^-]\right)}{\left(\frac{1}{2}[HF]\right)} = \frac{1}{2}K_a \therefore Q < K_a$$

This will cause the equilibrium to shift towards the products, favoring the formation of H_3O^+ ions. Thus, the percent ionization of HF(aq) in the solution will $\boxed{\text{increase}}$.

Problem 8.11.7 — 2021 AP Chemistry FRQ (Excerpt)

$$HCOOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCOO^-(aq) \qquad K_a = 1.8 \cdot 10^{-4}$$

Methanoic acid, HCOOH, ionizes according to the equation above.

(a) Write the expression for the equilibrium constant, K_a, for the reaction.

(b) Calculate the pH of a 0.25 M solution of HCOOH.

$$H_2NNH_2(aq) + H_2O(l) \rightleftharpoons H_2NNH_3^+(aq) + OH^-(aq) \qquad K_b = 1.3 \cdot 10^{-6}$$

(c) In aqueous solution, the compound H_2NNH_2 reacts according to the equation above. A 50.0 mL sample of 0.25 M H_2NNH_2(aq) is combined with a 50.0 mL sample of 0.25 M HCOOH(aq).

(i) Write the balanced net ionic equation for the reaction that occurs when H_2NNH_2 is combined with HCOOH.
(ii) Is the resulting solution acidic, basic, or neutral? Justify your answer.

Solution to part a: Since the equilibrium constant expression is equal to the concentration of products over the concentration of reactants (at equilibrium) raised to the power of their coefficients, we have

$$\boxed{K_a = \frac{[H_3O^+][HCOO^-]}{[HCOOH]}}$$

Solution to part b: Because we are given the initial concentration of HCOOH and the value of K_a, we can solve for the equilibrium concentration of H_3O^+ and therefore determine the pH of the solution.

To simplify this process, we will set up an ICE table.

	HCOOH(aq)	H_2O(l)	$\rightleftharpoons$	H_3O^+(aq)	$HCOO^-$(aq)
Initial (M)	0.25	-	-	0	0
Change (M)	$-x$	-	-	$+x$	$+x$
Equilibrium (M)	$0.25 - x$	-	-	x	x

It follows that x represents the equilibrium concentration of H_3O^+.

Using the expression for K_a in part (a), we can plug in equilibrium concentrations in terms of x:

$$1.8 \cdot 10^{-4} = \frac{(x)(x)}{(0.25 - x)}$$

and to avoid using the quadratic formula, use $0.25 - x \approx 0.25$ to get

$$1.8 \cdot 10^{-4} = \frac{x^2}{0.25} \therefore x = [H_3O^+] = 6.71 \cdot 10^{-3}\, M$$

Finally, we know that the pH is equal to the negative log of H_3O^+ concentration, so

$$\text{pH} = -\log\left(6.71 \cdot 10^{-3}\right) = \boxed{2.17}$$

Solution to part c(i): Don't be intimidated by the complex chemical formulas of HCOOH and H_2NNH_2. They are just another Brønsted–Lowry acid and base, respectively. When they react, HCOOH will donate a proton which H_2NNH_2 accepts, and thus the conjugate base and conjugate acid formed are $HCOO^-$ and $H_2NNH_3^+$, respectively.

Additionally, these are both weak acids and bases, so they will not be dissociated and thus will remain as single units in the chemical equation.

The balanced net ionic equation for the reaction is therefore

$$\boxed{\text{HCOOH(aq)} + \text{H}_2\text{NNH}_2\text{(aq)} \rightarrow \text{HCOO}^-\text{(aq)} + \text{H}_2\text{NNH}_3^+\text{(aq)}}$$

Solution to part c(ii): Notice that the net ionic equation found in part (c)(ii) is actually the result of adding two other chemical equations. Can you spot them? Indeed, the net ionic equation is the combination of the ionization reactions for HCOOH(aq) and H_2NNH_2(aq):

$$\text{HCOOH(aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{HCOO}^-\text{(aq)} + \text{H}_3\text{O}^+\text{(aq)} \qquad K_a = 1.8 \cdot 10^{-4}$$

$$\text{H}_2\text{NNH}_2\text{(aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{H}_2\text{NNH}_3^+\text{(aq)} + \text{OH}^-\text{(aq)} \qquad K_b = 1.3 \cdot 10^{-6}$$

$$\text{Overall Reaction: } \text{HCOOH(aq)} + \text{H}_2\text{NNH}_2\text{(aq)} \rightleftharpoons \text{HCOO}^-\text{(aq)} + \text{H}_2\text{NNH}_3^+\text{(aq)}$$

Here, we can compare the K_a value of HCOOH with the K_b value of H_2NNH_2.

We see that $K_a > K_b$, which means the HCOOH dissociates more into H_3O^+ than the H_2NNH_2 dissociates into OH^-, because they have the same initial concentration of $0.25\,M$. Therefore, the resulting solution will contain more free H^+ ions than OH^- ions, and it will be $\boxed{\text{acidic}}$.

9 Applications of Thermodynamics

This unit explores the intersection of kinetics, thermodynamics, equilibrium, and electrochemistry. We will discuss Gibbs free energy, randomness, electrolysis, cell potential, and more.

§9.1 Introduction to Entropy

Do you ever notice that whenever you clean your room (even if your parents force you to), your environment becomes less *spread out* in a sense? This process requires energy from you. However, when you make your room more disorganized, it actually releases your energy. This illustrates the concepts of microstates and entropy, an important thermodynamic function for this unit.

Microstates refer to the number of arrangements for a system at a given instant.

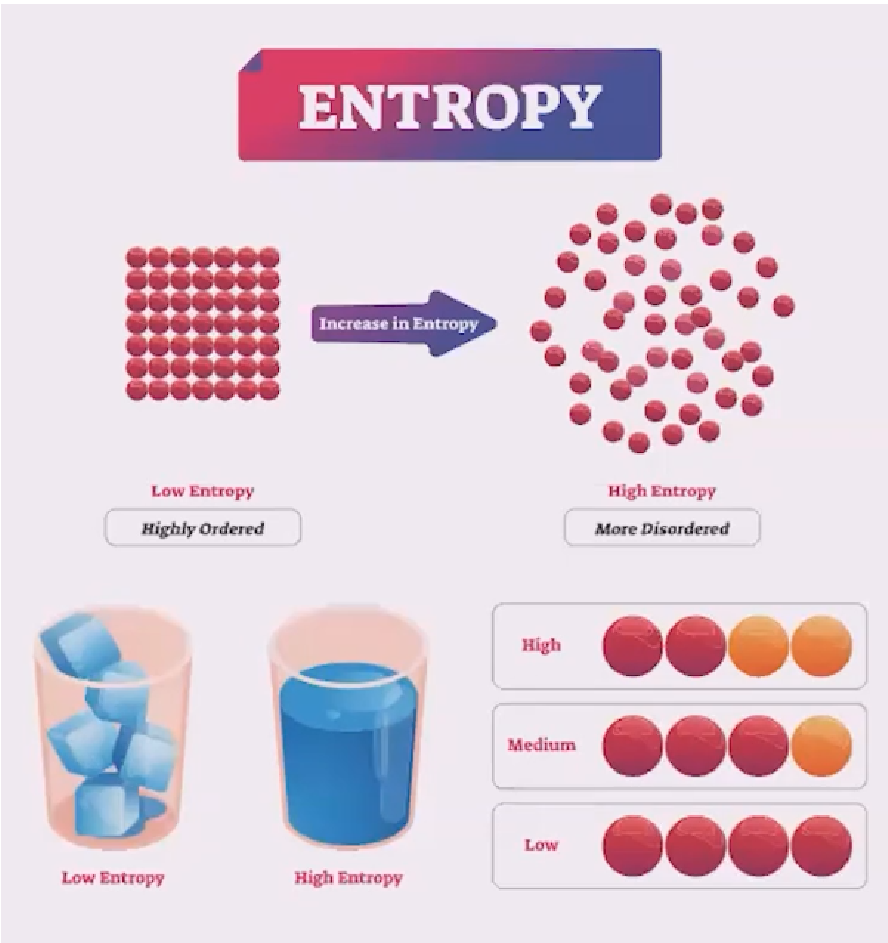


Image Courtesy of VectorMine/Shutterstock.com

Definition 9.1.1

Entropy, denoted by $S°$, is defined by the dispersal of matter or energy in a system. More generally, it is related to the number of microstates in a system.

Virtually any process involves a change in entropy, which can be negative or positive, depending on whether the change was a loss or gain, respectively.

Note 9.1.2

The units of entropy are typically given in $\text{J}/(\text{mol}\cdot\text{K})$.

Entropy change, $\Delta S°$, can be described as a measure of how much more or less dispersed the matter or energy becomes over an elapsed period of time.

Let's analyze the diagram shown in the previous page.

As matter becomes more dispersed, the entropy increases. Classic examples include phase changes. As solid ice melts into liquid water, the matter becomes more dispersed as the individual particles move more freely and occupy more volume. Additionally, molecules in the gas phase have maximum entropy when the volume increases because they can move in a large space with their constant speeds (at a given temperature).

A simple way to predict the sign of $\Delta S°$ for a chemical process is by comparing the total number of moles for gaseous species from the reactants and the products. For example, if there are more moles of gaseous species as products than as reactants, then the entropy of the reaction (or system, for our understanding) *increases*. This logic also works in the opposite manner.

More Information About Entropy for Gases

Recall from Kinetic Molecular Theory that the average kinetic energy of a gas increases as temperature increases, so there is a wider distribution of molecular velocities. Therefore, we can generalize that the entropy of a system *increases* as temperature increases, and vice versa.

The best way to improve your understanding of the concepts is through practice!

Problem 9.1.3 — Sign of Entropy Change

$$3\text{Ag(s)} + 4\text{HNO}_3\text{(aq)} \rightarrow 3\text{AgNO}_3\text{(aq)} + \text{NO(g)} + 2\text{H}_2\text{O(l)}$$

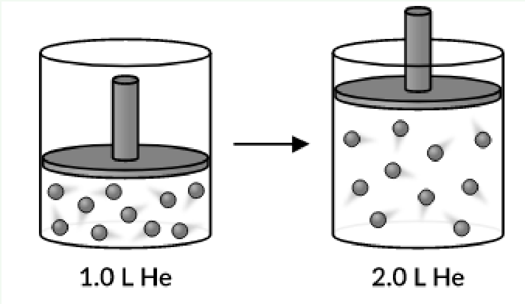
A student investigates the reaction between Ag(s) and HNO_3(aq) represented by the equation above.

Predict the sign of the entropy change, $\Delta S°$, for the reaction. Justify your claim using particle-level reasoning.

Solution: Gases have the maximum entropy, compared to all other phases (solid, liquid, or aqueous). Since the reaction has one mole of gas in the products and none in the reactants, the entropy of the reaction must be increasing, and $\Delta S°$ will be $\boxed{\text{positive}}$.

Problem 9.1.4 — Changes in Volume

The volume of a sample of He(g) is increased from 1.0 L to 2.0 L at constant temperature, as shown in the diagram below.



How does the entropy of the He(g) sample at 2.0 L compare with its value at 1.0 L?

(A) The entropy is lower since the He(g) atoms collide with each other less frequently.
(B) The entropy is higher since the He(g) atoms are distributed within a larger space.
(C) The entropy is the same since the number of moles of He(g) is constant.
(D) The entropy is the same since the average kinetic energy of the He(g) atoms is constant.

Example Courtesy of Khan Academy

Solution: Eliminate (A). With a larger volume, there are more ways for the He(g) to be arranged, so the entropy increases, NOT decreases.
Choice (C) is a classic trap. Although the number of moles of He(g) in the two containers is the same, this is not the only factor that affects the entropy of a gas—it is also affected by changes in volume and temperature.
For choice (D), it is true that the average kinetic energy of the He(g) atoms is the same, since no change in temperature occurred. However, the entropy of a gas is not affected by the average kinetic energy.
Finally, we know that increasing the volume of a gas sample at a constant temperature increases the entropy of the gas. The reason is that there are more ways to arrange He(g) atoms in a larger volume. This is consistent with choice $\boxed{\textbf{(B)}}$, and it is the correct answer.

§9.2 Absolute Entropy and Entropy Change

In this section, we will expand on our knowledge of entropy. We will also learn the calculations we can perform with regard to entropy as well as entropy changes for various chemical processes.

Definition 9.2.1

The **Third Law Of Thermodynamics** states that the entropy of a *perfect crystal* is zero at a temperature of 0 K.

Recall from section 9.1 that entropy is a measure of disorder, or chaos, in a system. However, a set of particles can be described as a ”perfect crystal” when their temperature is 0 K. Therefore, there is absolutely no motion occurring and the net entropy content of the system is zero.

Note: A temperature of 0 K has *never* been recorded for any experimental procedure. This is a mere generalization. Also, the entropy of a system at any other temperature MUST be greater than zero.

Standard Entropy

In many cases, you will be provided with information about the standard entropies S° of substances (at 298 K temperature and 1 atm pressure).

Definition 9.2.2

The **standard molar entropy** is the entropy content of 1 mole of pure substance at standard pressure and a specified temperature (most likely 25°C).

- Typically, the more complex a molecule is (think Lewis diagrams), it will have a higher standard *positional* entropy.
- ΔS° is a *state function*. More information on this term is in Unit 6.

For a chemical reaction, the standard entropy change can be calculated by finding the difference between the standard entropies of the products and those of the reactants, with respect to their coefficients in the balanced chemical equation.

$$\boxed{\Delta S^\circ_{rxn} = \sum n_p S^\circ(\text{products}) - \sum n_r S^\circ(\text{reactants})}$$

This equation is in your formula sheet, and it will be very useful. You will need to use it for both multiple-choice and free-response questions related to thermodynamics.

Positional Entropy

Sometimes, we might be given a balanced chemical equation for a certain process and asked to predict the sign of ΔS°. Note that we can only manually calculate ΔS°_{rxn} when we are given the standard entropies for all species in the reaction.

The way we can do this is by understanding the concept of positional entropy.

Definition 9.2.3

Positional entropy is a metric that is based on the number of molecular positions or arrangements available to the system. This concept is closely related to microstates.

For the purposes of this course, you only need to know the relative positional entropies for the three states of matter.

- Solids have the lowest positional entropy because the particles barely have space to move around.
- Liquids have a greater positional entropy than solids because the particles have more space to move around, but their shape is limited by the solid container that holds.
- Gases have the greatest positional entropy among all phases. The particles have virtually infinite space to travel in random motion. Additionally, their geometric arrangements are not restricted by the shape of the container that occupies them.

Let's test our understanding (and finish section 9.2) with the following exercise.

Example 9.2.4

$$2\text{Na(s)} + \text{Cl}_2\text{(g)} \rightarrow 2\text{NaCl(s)} \quad \Delta H = -410\,\text{kJ/mol}_{rxn}$$

Answer the following questions about the reaction above at 298 K.

(a) Predict the sign of ΔS° for this reaction. Justify your prediction.

The absolute entropies of Na(s), Cl_2(g), and NaCl(s) at 298 K are 51.1 J/(mol · K), 223.1 J/(mol · K), and 72.1 J/(mol · K), respectively.

(b) Using the above information, calculate the value of ΔS° for the reaction.

Solution to part a: We know that gases have the highest positional entropy among all phases of matter. Therefore, whichever side has *more moles of gas* should have the greater entropy. Since there is one mole of gas (Cl_2(g)) in the reactants and none in the products, the overall entropy decreases as the forward reaction progresses. Thus, the sign of ΔS° will be $\boxed{\text{negative}}$.

Solution to part b: Here, we know the standard entropies for each of the species in the reaction. Therefore, we can use this formula to calculate ΔS° for the reaction.

$$\Delta S^\circ_{rxn} = \sum n_p S^\circ(\text{products}) - \sum n_r S^\circ(\text{reactants})$$

The total entropy of the products is $2 \cdot 72.1 = 144.2$ J/(mol · K). This is because the standard entropy for a substance is the entropy content for ONE mole of that substance. Since we had 2 molecules of NaCl(s) on the products, the total entropy of the products was 2 times the standard entropy for NaCl(s).

We will now do the same for the reactants.

$$\sum n_r S^\circ(\text{reactants}) = 2 \cdot 51.1\ \text{J}/(\text{mol} \cdot \text{K}) + 223.1\ \text{J}/(\text{mol} \cdot \text{K})$$

Note that there was only one molecule of $Cl_2(g)$, so we did not multiply the standard entropy by any factor. Finally, we plug everything in:

$$\Delta S^\circ = 2 \cdot 72.1\,\text{J}/(\text{mol} \cdot \text{K}) - [2 \cdot 51.1\,\text{J}/(\text{mol} \cdot \text{K}) + 223.1\,\text{J}/(\text{mol} \cdot \text{K})] = \boxed{-181.1\ \text{J}/(\text{mol} \cdot \text{K})}$$

§9.3 Gibbs Free Energy and Thermodynamic Favorability

So far, in thermodynamics, we have learned about enthalpy and entropy and how they relate to energy and matter. In this section, we will talk about *Gibbs free energy*, denoted by ΔG°, and how it is a combination of enthalpy and entropy.

Definition 9.3.1

Gibbs free energy, ΔG°, describes a process occurring at constant temperature and pressure and is favored in the direction where free energy decreases.

From the definition, we take note of one important concept:
If the change in free energy, ΔG°, is negative, then the process we are considering is *thermodynamically favored*. This means that it will occur *spontaneously*.

Note 9.3.2

Prior to the 2014 exam administration, the term **spontaneous**, instead of **thermodynamically favorable**, was used to describe chemical and physical processes that occurred without external intervention.

The standard Gibbs free energy change, ΔG°, for a chemical reaction can be calculated using the following equation:

$$\boxed{\Delta G^\circ = \sum n_p \Delta G_f^\circ\,(\text{products}) - \sum n_r \Delta G_f^\circ\,(\text{reactants})}$$

We have seen equations that are very similar to this. For example, the respective standard enthalpy and entropy change of a reaction are given by these two equations:

$$\Delta H^\circ = \sum n_p \Delta H_f^\circ\,(\text{products}) - \sum n_r \Delta H_f^\circ\,(\text{reactants})$$
$$\Delta S^\circ = \sum n_p S^\circ\,(\text{products}) - \sum n_r S^\circ\,(\text{reactants})$$

Let's walk through the following problems.

Problem 9.3.3 — Gibbs Free Energy I

$$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g) \quad \Delta H^\circ = -196\,\text{kJ/mol}_{rxn}$$

The decomposition of $H_2O_2(aq)$ is represented by the equation above. A student monitored the decomposition of a 1.0 L sample of $H_2O_2(aq)$ at a constant temperature of 300 K and recorded the concentration of H_2O_2 as a function of time.

The reaction is thermodynamically favorable. The signs of ΔG° and ΔS° for the reaction are which of the following?

(A) ΔG° is positive, ΔS° is negative.
(B) ΔG° is negative, ΔS° is positive.
(C) ΔG° is positive, ΔS° is negative.
(D) ΔG° is negative, ΔS° is negative.

Solution: We are told that the reaction is thermodynamically favorable, so the change in Gibbs free energy must be **negative**. Therefore, eliminate (A) and (C). Between (B) and (D), we need to determine the sign of the standard change in entropy, ΔS°. We can do this by comparing the entropy of the reactants vs. the entropy of the products. On the products side of the reaction, there is 1 molecule of gas. Meanwhile, there are none in the reactants. Therefore, we should expect ΔS° for the reaction to be positive. This is consistent with answer choice $\boxed{\textbf{(B)}}$, which is correct.

Free Energy Change and Chemical Reactions

The standard Gibbs free energy change (ΔG°) for a chemical reaction can also be expressed as a function of its Kelvin temperature (T) in the following equation:

$$\boxed{\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ}$$

where both ΔH° and ΔS° are assumed to be *independent* of temperature.

Using the above formula, we can make several generalizations that will help us predict the *spontaneity*, or thermodynamic favorability, for a chemical reaction. This means that the sign of ΔG° can be predicted from the signs of ΔH° and ΔS°.

- **Case 1.** $\Delta H^\circ < 0$ and $\Delta S^\circ > 0$. Using the equation $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$, we know that if ΔS° is positive, then the $-T\Delta S^\circ$ term will also be **negative**. Thus, ΔG° will always be negative and the reaction is thermodynamically favored at *all* temperatures.

- **Case 2.** $\Delta H^\circ > 0$ and $\Delta S^\circ > 0$. Since ΔH° is positive, we need the $-T\Delta S^\circ$ term to be **large and negative** for the overall $\Delta H^\circ - T\Delta S^\circ$ to become negative. For this, T should be relatively large. Thus, the reaction is thermodynamically favored at *high* temperatures only.

- **Case 3.** $\Delta H^\circ < 0$ and $\Delta S^\circ < 0$. We already know that ΔH° drives the reaction, because it is negative and helps ΔG° be negative. Meanwhile, when ΔS° is negative, then the term $-T\Delta S^\circ$ will be **positive**. However, we want its magnitude to be small compared to ΔH° so the overall value of ΔG° does not become positive. Thus, ΔG° will stay negative when T is relatively small and the reaction is thermodynamically favored at *low* temperatures only.

- **Case 4.** $\Delta H^\circ > 0$ and $\Delta S^\circ < 0$. Since the reaction is endothermic, enthalpy change does not help generate a negative ΔG° value. Furthermore, since $\Delta S^\circ < 0$, the $-T\Delta S^\circ$ term becomes **positive**, so the overall value of ΔG° will be positive, regardless of temperature. Thus, the reaction is *not* thermodynamically favored at any temperature.

When solving problems, we can also predict at what temperature does the reaction change from thermodynamically favorable to unfavorable, and vice versa. We can also determine the exact range of temperatures for a certain reaction to be thermodynamically favorable.

There is nor much theory in this section, so I will just walk through some problems and explain the remaining concepts as we go.

Problem 9.3.4 — Gibbs Free Energy Practice III

For ammonia, NH_3, the enthalpy of fusion is 5.65 kJ/mol and the entropy of fusion is 28.9 J/(mol · K). Note: *fusion* is a physical change that causes the phase transition from solid to liquid. This process is also known as melting.

(a) Will solid ammonia spontaneously melt at 200. K?
(b) What is the approximate melting point of ammonia?

Solution to part a: Since we are given the change in both entropy and enthalpy for the process, we can apply the equation that expresses ΔG° in terms of these two quantities.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

We can plug in the temperature that is given to us and see if this causes ΔG° to be negative or not.

But first, we should be careful with our units. Enthalpy has units of kilojoules (kJ), while entropy is associated with units of joules (J). I will convert the units of enthalpy into J/mol, so we can express ΔG° in J/mol.

$$5.65\,\frac{\cancel{\text{kJ}}}{\text{mol}} \cdot \frac{1000\text{ J}}{\cancel{\text{kJ}}} = 5650.\text{ J/mol}$$

Now, we are ready to substitute our values.

$$\Delta G^\circ = 5650.\text{ J/mol} - (200\,\cancel{\text{K}})(28.9\text{ J/(mol}\cdot\cancel{\text{K}})) = -130.\text{ J/mol}$$

We see that the value of ΔG° is negative at 200. K. Therefore, solid ammonia $\boxed{\text{will}}$ spontaneously melt at this temperature.

Solution to part b: For this question, I will introduce one important concept:
A phase change represents a state of *equilibrium*, so ΔG° for any process representing a

phase change should be set to 0.

When ΔG° is equal to 0, the forward and reverse reactions are *equally* favorable. In terms of phase changes, the melting of solid ammonia indicates that the species is equally favorable as a solid and a liquid during the phase change.

$$\mathrm{NH_3(s)} \rightarrow \mathrm{NH_3(l)}$$

Thus, we will set ΔG° equal to 0 and solve for our melting point, denoted by T.

$$0 = (5650\,\mathrm{J/mol}) - T(28.9\,\mathrm{J/(mol \cdot K)}) \therefore \boxed{T = 196\,\mathrm{K}}$$

Therefore, 196 K is the approximate melting point of NH_3.

Problem 9.3.5 — Gibbs Free Energy Practice IV

Using the following data (at 25°C):

$$\mathrm{C}_{diamond}\mathrm{(s)} + \mathrm{O_2(g)} \rightarrow \mathrm{CO_2(g)} \quad \Delta G^\circ = -397\,\mathrm{kJ}$$

$$\mathrm{C}_{graphite}\mathrm{(s)} + \mathrm{O_2(g)} \rightarrow \mathrm{CO_2(g)} \quad \Delta G^\circ = -394\,\mathrm{kJ}$$

Calculate ΔG° for the reaction:

$$\mathrm{C}_{diamond}\mathrm{(s)} \rightarrow \mathrm{C}_{graphite}\mathrm{(s)}$$

Solution: For this problem, I will bring back an important topic we learned in Unit 6: Hess's law. You can use it when you are given some elementary steps and you have to rearrange them so when combined, they result in an *overall* reaction. In Unit 6, we used Hess's law for enthalpy change, but we can also apply it to problems asking us to calculate ΔG° for a reaction.

Let's look at the overall reaction. $\mathrm{C}_{diamond}$(s) is on the left side and $\mathrm{C}_{graphite}$(s) is on the right side. Now, let's look at each of our elementary steps. For the first step, $\mathrm{C}_{diamond}$(s) is already on the reactants side of the equation, so we do not need to flip the reaction. Meanwhile, for the second step, $\mathrm{C}_{graphite}$(s) is on the reactants side of the equation, so we must flip it so that it appears as a product in the overall reaction. Also, none of the coefficients have changed, so O_2(g) and CO_2(g) will just cancel out.

Our setup should look like this:

$$\mathrm{C}_{diamond}\mathrm{(s)} + \cancel{\mathrm{O_2(g)}} \rightarrow \cancel{\mathrm{CO_2(g)}} \quad \Delta G^\circ = -397\,\mathrm{kJ}$$

$$\cancel{\mathrm{CO_2(g)}} \rightarrow \mathrm{C}_{graphite}\mathrm{(s)} + \cancel{\mathrm{O_2(g)}} \quad \Delta G^\circ = -(-394\,\mathrm{kJ})$$

$$\text{Overall Reaction: } \mathrm{C}_{diamond}\mathrm{(s)} \rightarrow \mathrm{C}_{graphite}\mathrm{(s)} \quad \boxed{\Delta G^\circ = -3\,\mathrm{kJ}}$$

§9.4 Thermodynamic and Kinetic Control

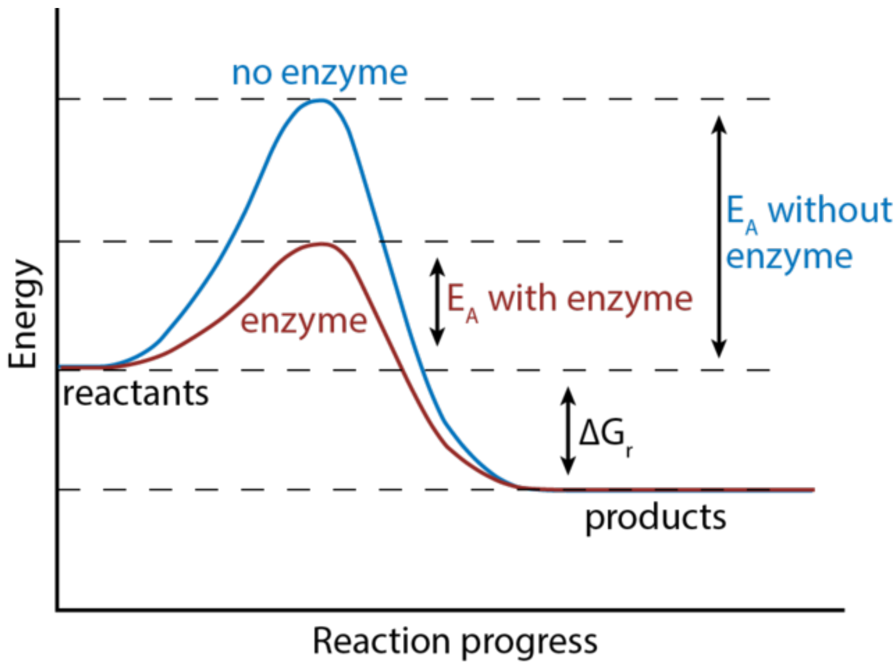
In thermodynamics, if the change in standard Gibbs free energy (ΔG°) is negative, then the corresponding chemical process is thermodynamically favorable. However, not all thermodynamically favorable reactions proceed to form products at a significant rate. Why is this?

Such processes are under what is known as **"kinetic control"**, which means that they have a high activation energy responsible for the slow rate of the reaction.

Important! Even if a process occurs at a very slow rate or perhaps not at all, DO NOT assume that it is at equilibrium. Equilibrium only means that the *rates* of the forward and reverse reactions are equal.

Recall from Unit 5 that **catalysts** are effective measures to increase the rate of a chemical reaction by lowering its activation energy.

Important! However, addition of a catalyst does NOT affect or change the thermodynamic favorability of a reaction, since ΔG° is not affected. We can see this in the energy diagram below.



Let's practice the concepts we just learned in the following problem.

Problem 9.4.1 — Short Answer Question

$$A(g) + B(g) \rightleftharpoons 2C(g) \quad \Delta G^\circ < 0$$

Consider the reaction represented above at a certain temperature. When equal volumes of A(g) and B(g), each at 1 atm, are mixed in a closed container at the same temperature, no formation of C(g) is observed. Develop a claim with reasoning to explain this observation.

Solution: We are given that the standard free energy change, ΔG°, is negative. Therefore, our forward reaction is thermodynamically favorable. However, since no significant amounts of C(g) are produced, there are kinetic factors at play here. The most reasonable explanation follows as: "Although the reaction is thermodynamically favored, it is under kinetic control and has a high activation energy. Thus, the forward reaction proceeds very slowly, which explains why virtually no C(g) formation was observed."

This concludes our discussion on thermodynamic and kinetic control, a relatively short section in Unit 9. In the next section, we will explore how the concepts of chemical equilibrium can be applied to free energy even at conditions that are not standard.

§9.5 Free Energy and Equilibrium

In Unit 7, we spent a lot of time defining equilibrium and understanding how reversible reactions can behave at certain circumstances. However, this aligns with the *kinetic* definition of equilibrium. In this section, we will focus more on the *thermodynamic* definition of equilibrium, where we can relate it with spontaneity and the value of ΔG°. The thermodynamic definition defines equilibrium as the point of *minimum free energy*. When reactions occur spontaneously, the value of ΔG will be negative, so free energy is being released. Once equilibrium has been reached, ΔG will be positive and thus, the system will require external sources of energy to operate.

Free Energy at Nonstandard Conditions

So far, we have discussed free energy of processes when all the species involved are in their *standard states*. But what does this mean?

Definition 9.5.1

Standard states are reference points used to determine the properties of a substance under various conditions.

So far, we only talked about the *standard* free energy change, ΔG° for a reaction. Therefore, all our reactants and products were in their standard states, i.e. 1.0 atm gas pressures, 1.0 M concentrations for aqueous species, 25°C (298 K), and pure solids/liquids in their most stable form.

Here is a formula that is no longer on your formula sheet, which used to be tested on the AP Exam. Now, you do not need to perform any calculations associated with it, but you can still use the mathematical *relationships* between the variables to justify your answer or explain something for free-response questions.

$$\Delta G = \Delta G^\circ + RT \ln Q$$

The important things to note here are the two different Gibbs free energy changes (ΔG and ΔG°). Notice that one has a $^\circ$ superscript, while the other one does not. This is because ΔG° indicates the change in free energy measured **at standard conditions**, and ΔG does not.

Thus, the above equation allows us to determine the change in free energy for a reaction at **nonstandard conditions**.

Note: the signs of ΔG° and ΔG both indicate the same thing:

1. If ΔG is negative, then the forward reaction is thermodynamically favorable.
2. If ΔG is positive, then the forward reaction is thermodynamically unfavorable.

Finally, Q is the reaction quotient for the chemical reaction (If you forgot this, feel free to refer back to Unit 7: Equilibrium.)

Before we talk more about thermodynamics, we'll walk through a practice problem to refresh your understanding of equilibrium.

Problem 9.5.2 — Gas-Phase Equilibrium and Free Energy

$$\mathrm{CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(l)} \quad \Delta H = -85\,\mathrm{kJ/mol}$$

Indicate whether ΔG increases, decreases, or does not change when the following stresses are applied to the equilibrium system. (Hint: Think about this problem in terms of Le Châtelier's principle, rather than free energy.)

(a) $CO(g)$ is added.
(b) $H_2(g)$ is removed.
(c) The pressure of the system is increased.
(d) The temperature of the system is increased.
(e) $CH_3OH(l)$ is added.

Solution to part a: Since we should think about this in terms of Le Châtelier's principle rather than free energy, we can start by writing out the equilibrium constant expression.

$$Q = \frac{1}{[\mathrm{CO}][\mathrm{H_2}]^2}$$

Therefore, if $CO(g)$ is added to the system, then we are no longer in equilibrium and $Q < K$. This will cause the equilibrium to shift in the forward direction. This means that more products will be formed to counteract this stress. Now, think back to free energy: ΔG is negative when the forward reaction is thermodynamically favored, and since we are forming more products, the forward reaction is *more favored*. Thus, ΔG should be *more negative*, as it $\boxed{\text{decreases}}$.

Solution to part b: Let's use the same logic for this part and parts (c)-(e).

$$Q = \frac{1}{[\text{CO}][\text{H}_2]^2}$$

If H_2(g) is removed from the system, then we are no longer in equilibrium and $Q > K$. This will cause the equilibrium to shift in the reverse direction because there are too many products. Therefore, the forward reaction will not be thermodynamically favored, so ΔG will become *more positive*, so it $\boxed{\text{increases}}$.

Solution to part c:

$$Q = \frac{1}{[\text{CO}][\text{H}_2]^2}$$

If the pressure of the system is increased, the denominator in the Q expression will increase, causing Q to decrease, and $Q < K$. Therefore, the equilibrium will shift to favor the forward reaction. Using the same reasoning in part (a), when the forward reaction is favored, ΔG is likely to become more negative, and it $\boxed{\text{decreases}}$.

Solution to part d: ΔH for the reaction is negative, indicating that it is an exothermic reaction. Therefore, heat can be thought of as a product, so increasing the temperature will increase the value of K, so the reverse reaction must occur in order to re-establish equilibrium. This means that the forward reaction is **not** thermodynamically favored, so ΔG will become *more positive* and it $\boxed{\text{increases}}$.

Solution to part e: CH_3OH(l) is a pure liquid, and it will not change the equilibrium. Therefore, $Q = K$ and ΔG $\boxed{\text{does not change}}$.

Relationship Between Free Energy Change and Equilibrium Constant

Let's revisit the equation we saw at the beginning of this section.

$$\Delta G = \Delta G^\circ + RT \ln Q$$

Although this equation is not in your formula sheet, its special case is.

The important concept is that the *nonstandard* free energy change, ΔG is equal to 0 whenever a system is at equilibrium. Also, we know $Q = K$ at equilibrium. Therefore, we can alter the equation like this:

$$\Delta G = \Delta G^\circ + RT \ln Q$$

$$0 = \Delta G^\circ + RT \ln K$$

$$\boxed{\Delta G^\circ = -RT \ln K}$$

where R is the ideal gas constant, with a value of 8.314 J mol^{-1} K^{-1}, and T is the temperature in Kelvins (K).

The sign of the change in free energy for a process can be related to the magnitude of its equilibrium constant.

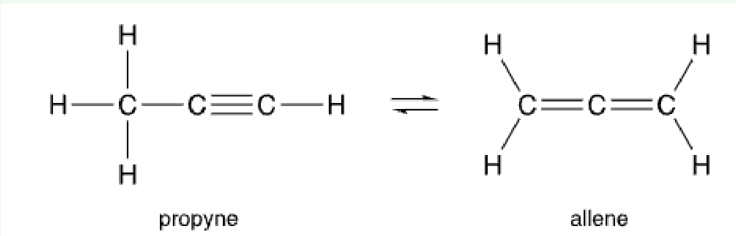
The phrase "thermodynamically favorable" is associated with a negative free energy change ($\Delta G^\circ < 0$) simply means that the reactants proceed to form a significant amount of products. In other words, the products are favored at equilibrium, where $K > 1$. Alternatively, if reactants are favored at equilibrium, $K < 1$ and the forward reaction is not thermodynamically favorable, i.e. $\Delta G^\circ > 0$.

The above generalization indicates that the change in Gibbs free energy and the magnitude of the equilibrium constant **always** have opposite signs.

- When ΔG° is negative, $K > 1$ and the formation of products is favored.
- When ΔG° is positive, $K < 1$ and the formation of reactants is favored.
- When $\Delta G^\circ = 0$, the reaction is at equilibrium.

As always, we will wrap up with some problems.

Problem 9.5.3 — Calculate K given ΔG°



The gas-phase isomerization of propyne to produce allene is represented by the equation above. The value of the standard free energy change, ΔG°_{rxn}, for the reaction is $8.6\,\mathrm{kJ/mol}_{rxn}$ at 298 K.

Calculate the value of the equilibrium constant, K_{eq}, for the reaction at 298 K.

Example Courtesy of Khan Academy

Solution: Since the standard free energy change for the reaction is negative, most of the propyne will remain unreacted, with little allene produced when the reaction reaches equilibrium.

We use the equation

$$\Delta G^\circ_{rxn} = -RT \ln K_{eq}$$

We need to rearrange for K_{eq}:

$$K_{eq} = e^{-\frac{\Delta G^\circ_{rxn}}{RT}}$$

At this point, we need to ensure that we are working in the correct units. Or else, our result could be ridiculous.

The easiest way to do this is by converting the units of ΔG°_{rxn} to J/mol_{rxn}:

$$8.6\ \frac{\cancel{\text{kJ}}}{\text{mol}_{rxn}} \cdot \frac{1000\ \text{J}}{\cancel{\text{kJ}}} = 8600\ \text{J/mol}_{rxn}$$

Now, we can plug in our values to solve for K_{eq}:

$$K_{eq} = e^{-\frac{8600\ \text{J/mol}_{rxn}}{\left(8.314\ \frac{\text{J}}{\text{mol}\cdot\text{K}}\right)(298\ \text{K})}} = \boxed{3.1 \cdot 10^{-2}}$$

Reality Check: Our value of $K_{eq} < 1$ should make sense, because it is known that ΔG° for the reaction is positive.

Problem 9.5.4 — Calculate K Given Standard ΔG° Formation

$$\text{AgCl(s)} \rightleftharpoons \text{Ag}^+\text{(aq)} + \text{Cl}^-\text{(aq)}$$

Given that the standard free energies of formation (ΔG°_f) for AgCl(s), Ag^+(aq), and Cl^-(aq) are −109.8 kJ/mol, 77.1 kJ/mol, and −131.2 kJ/mol, respectively, calculate the value of K_{sp} for AgCl at 298.15 K.

Solution: The first step is to calculate ΔG° for the overall reaction.
We will use the formula for ΔG° based on the standard free energies of formation for all species in a reaction:

$$\Delta G^\circ = \sum n_p \Delta G^\circ_f(\text{products}) - \sum n_r \Delta G^\circ_f(\text{reactants})$$

Substituting the values, we have

$$\Delta G^\circ = (77.1\ \text{kJ/mol} + (-131.2\ \text{kJ/mol})) - (-109.8\ \text{kJ/mol}) = 55.7\ \text{kJ/mol}$$

Before we set up the formula relating ΔG° with K, let's convert our units from kJ/mol to J/mol, since R is in units of J mol^{-1} K^{-1}.

$$\Delta G^\circ = \frac{55.7\ \cancel{\text{kJ}}}{\text{mol}} \cdot \frac{1000\ \text{J}}{\cancel{\text{kJ}}} = 5.57 \cdot 10^4\ \text{J/mol}$$

Now, we can use the equation

$$\Delta G^\circ = -RT \ln K$$

Rearranging to solve for K_{sp} gives

$$K_{sp} = e^{-\frac{\Delta G^\circ}{RT}} = e^{-\frac{5.57\cdot 10^4\ \text{J/mol}}{(8.314\ \text{J mol}^{-1}\ \text{K}^{-1})(298.15\ \text{K})}} = \boxed{1.74 \cdot 10^{-10}}$$

Reality Check: Our very low value of K_{sp} should make sense: ΔG° is very positive, so the forward reaction is *not* thermodynamically favorable. The forward reaction will not proceed at a significant rate to form products.

§9.6 Coupled Reactions

In the real world, there are many important chemical processes that are not thermodynamically favorable—they are not spontaneous—but would otherwise be very necessary to take place.

Review of Thermodynamic Favorability

In terms of Gibbs free energy, a process with a positive $\Delta G°$ value is considered thermodynamically unfavorable.

The two different methods to make such a process occur are

- Using an **external source of energy**, such as sunlight or electrical power.
- "Coupling" the thermodynamically unfavorable reaction with a thermodynamically favorable one that has a more negative $\Delta G°$ value.

Definition 9.6.1

Coupled reactions are two reactions that share a common intermediate (recall from Unit 5 that an intermediate is a product of one reaction and a reactant in the other) that can be combined.

Hess's law (as we saw with enthalpy change, $\Delta H°$) can be applied to determine the free energy change, $\Delta G°$, for the coupled reaction. You can brush up on this topic in Unit 6!

Moreover, coupled reactions are performed to ensure that the **sum of the ΔG values** is negative, making the overall process thermodynamically favorable.

EX. Decomposition of Iron (III) Oxide Via Coupling

$$\text{Equation 1: } Fe_2O_3(s) \rightarrow 2Fe(s) + \frac{3}{2}O_2(g) \quad \Delta G° = +742.2\,\text{kJ}$$

$$\text{Equation 2: } CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g) \quad \Delta G° = -283.5\,\text{kJ}$$

$$\text{Equation 3: } Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(s) + 3CO_2(g)$$

The decomposition of iron (III) oxide is a thermodynamically unfavorable process (represented by Equation 1) but it can be accomplished by coupling the reaction to the combustion of carbon monoxide (represented by Equation 2), which results in the overall reaction represented by Equation 3.

Question: How can we determine the standard free energy change of the overall reaction?

Answer: We need to use Hess's Law.

Notice that O_2(g) is not present in the overall reaction, i.e. it is an intermediate. We must cancel it by generating the same amount in both reactions on opposite sides. The simplest way to do this is to multiply the second equation by 3:

$$\text{Equation 2'}: \ 3\text{CO(g)} + \frac{3}{2}\text{O}_2\text{(g)} \to 3\text{CO}_2\text{(g)}$$

Additionally, since ΔG is an extensive property, which depends on the amount of substance present, we must also multiply its value by 3 for Equation 2';

$$\Delta G^\circ = 3 \cdot -283.5\,\text{kJ} = -850.5\,\text{kJ}$$

Adding everything up, we find that

$$\text{Equation 1}: \ \text{Fe}_2\text{O}_3\text{(s)} \to 2\text{Fe(s)} + \cancel{\frac{3}{2}\text{O}_2\text{(g)}} \qquad \Delta G^\circ = +742.2\,\text{kJ/mol}_{rxn}$$

$$\text{Equation 2'}: \ 3\text{CO(g)} + \cancel{\frac{3}{2}\text{O}_2\text{(g)}} \to 3\text{CO}_2\text{(g)} \qquad \Delta G^\circ = -850.5\,\text{kJ/mol}_{rxn}$$

$$\text{Equation 3}: \ \text{Fe}_2\text{O}_3\text{(s)} + 3\text{CO(g)} \to 2\text{Fe(s)} + 3\text{CO}_2\text{(g)} \qquad \Delta G^\circ = \boxed{-108.3\,\text{kJ/mol}_{rxn}}$$

Question: Why were the reactions represented in Equations 1 and 2 suitable for coupling to produce a thermodynamically favorable process?

Answer: There were two criteria that needed to be fulfilled.

1. The two reactions share a common intermediate (in this case, O_2(g)) and when coupled,
2. The reactions yield an overall reaction with a negative free energy change (ΔG°).

That is all there is to coupled reactions!

§9.7 Galvanic (Voltaic) and Electrolytic Cells

In this section, we will talk about the intersection between electricity and thermodynamics, as well as their connections in the practical world.

Definition 9.7.1

Electrochemistry is the study of the processes that lead to the conversion of chemical energy (from chemical reactions) to electrical energy.

We can produce electrical energy using **redox reactions**. Additionally, to understand electrochemistry and its applications, we need to examine **cell potentials**, or measures of voltage released during redox reactions. Finally, we can connect voltage to spontaneity to equilibrium, as well as how power can be used to drive nonspontaneous reactions, but all this will be for the last three sections of this unit.

Review of Redox Reactions

In order to gain anything out of the electrochemistry concepts, you must be proficient with redox reactions, which we learned in Unit 4. Also known as an **oxidation-reduction reaction**, a redox reaction involves the transfer of electrons from a **reducing agent** to an **oxidizing agent**.

The reducing agent and oxidizing agent are the species that are oxidized (loses electrons) and reduced (gains electrons), respectively. A good acronym to remember this easily mixed up distinction is **OIL RIG** (oxidation is loss, reduction is gain). Note: the terms *reducing agent* and *oxidizing agent* are no longer used on the AP exam, but knowing them can help develop a conceptual understanding of the chemistry that actually occurs.

Example 9.7.2

The reaction between silver nitrate solution and copper metal is a redox reaction, and the balanced chemical equation is

$$2AgNO_3 + Cu \to Cu(NO_3)_2 + 2Ag$$

We see that copper begins with an oxidation number of 0 and ends with an oxidation number of +2. Silver begins with an oxidation number of +1 and ends with an oxidation number of 0. Therefore, copper was oxidized and silver was reduced. Electrons were transferred *from* copper *to* silver.

We can write the reaction in terms of oxidation and reduction half-reactions that add up to the equation representing the overall reaction.

- Copper is oxidized to form Cu^{2+}: $Cu \to Cu^{2+} + 2e^-$
- Silver is reduced from Ag^+ to Ag: $2Ag^+ + 2e^- \to 2Ag$

Note: we had to multiply the reduction half-reaction by 2, so that the electrons cancel when both half-reactions are added. This is because **the total number of electrons lost during oxidization must be equal to the total number of electrons gained during reduction**.

Reduction Potentials

When redox reactions occur, the electrons that are transferred experience an **electromotive force** (E), or *emf*, for short. This force allows electrons to be "launched" from the reducing agent to the oxidizing agent. The stronger the emf, the more spontaneous the reaction. Emf is also referred to as voltage, and its units are in **volts** (V).

To make things easier, we use **standard reduction potentials** (SRP) to calculate the voltage of a redox reaction. SRPs represent the voltage of reduction reactions. Also, it is important to note that voltage can be a negative value, which means energy is required to drive a redox reaction, i.e. the reaction is *not* thermodynamically favorable. The table of standard reduction potentials that we will reference in this book can be accessed here.

Consider the reaction given in Example 9.7.2.

The half-reactions are:

1. $Cu \rightarrow Cu^{2+} + 2e^-$ (oxidation)
2. $2Ag^+ + 2e^- \rightarrow 2Ag$ (reduction)

Looking at the table, the standard reduction potential for Ag^+ is +0.80 V, and for Cu^{2+}, the SRP is +0.34 V. However, our half-reaction involving Cu^{2+} is an oxidation reaction. Therefore, we will flip the sign of the voltage, which means that the potential of $Cu \rightarrow Cu^{2+} + 2e^-$ is −0.34 V. Finally, we can add these two numbers together to determine the overall voltage of the reaction as $0.80\,\text{V} + (-0.34\,\text{V}) = \boxed{0.56\text{ V}}$.

Note 9.7.3

The oxidation reaction was $2Ag^+ + 2e^- \rightarrow 2Ag$. However, even though the stoichiometric coefficients were doubled, we did not double the value of E for the reaction. This is because emf/cell potential/voltage is an *intensive property*, which does not depend on the amount of substance present.

For any given reaction, E can be calculated using the equation

$$\boxed{E = E_{red} + E_{ox}}$$

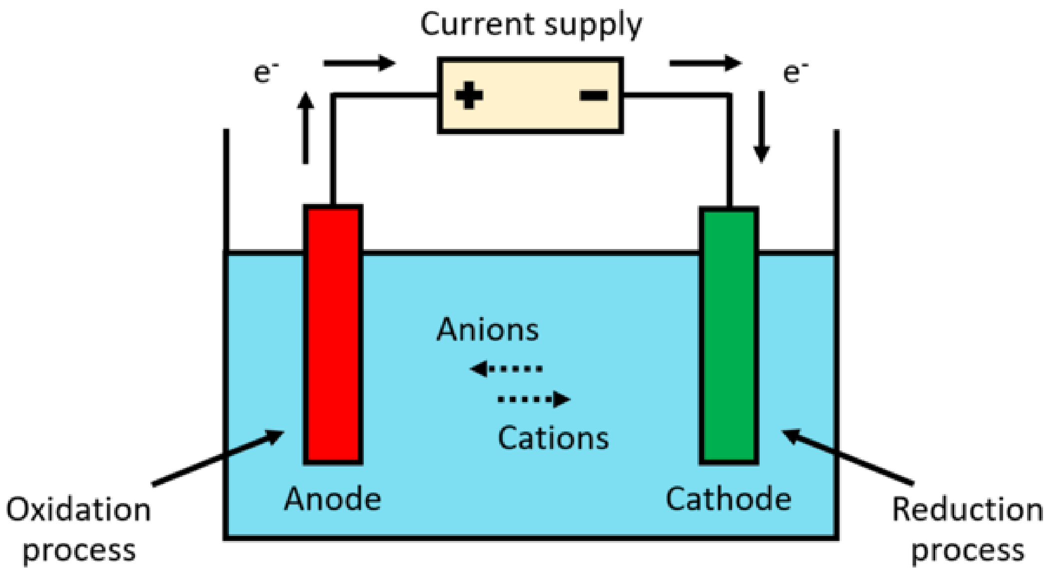
Later in this unit, we will calculate electrical energy of cells, or E_{cell}, using our knowledge of **galvanic and electrolytic cells**.

Electrochemical Cells

Definition 9.7.4

An **electrochemical cell** is a device that can transfer energy in two ways:

- Energy that is released from a thermodynamically favorable redox reaction.
- Use electrical energy to drive a thermodynamically unfavorable redox reaction.



The illustration above is an example of an electrochemical cell, where the movement of positively and negatively charged ions in a solution maintains steady flow of electrons across the wire.

Generally, electrochemical cells are classified into two categories:

1. **Galvanic, or voltaic cells** are electrochemical cells that operate through thermodynamically favorable reactions, taking place spontaneously.

2. **Electrolytic cells** are electrochemical cells where the reactions are thermodynamically unfavorable and not spontaneous. They require an external power source to operate.

In both electrochemical cells, there are two important compartments, namely the **anode** and **cathode**. These compartments are referred to as **half cells**: they both work together simultaneously and are equally critical to operating an electrochemical cell.

Definition 9.7.5
In the **anode** of an electrochemical cell, **oxidation** occurs and electrons are lost.

Definition 9.7.6
In contrast, at the **cathode**, **reduction** occurs and and electrons are gained.

Galvanic/Voltaic Cells

The more common type of electrochemical cell for this course will be the galvanic or voltaic cell. Again, consider the reaction

$$Cu(s) + 2Ag^{+}(aq) \rightarrow 2Ag(s) + Cu^{2+}(aq)$$

Visually, the galvanic cell looks like this:

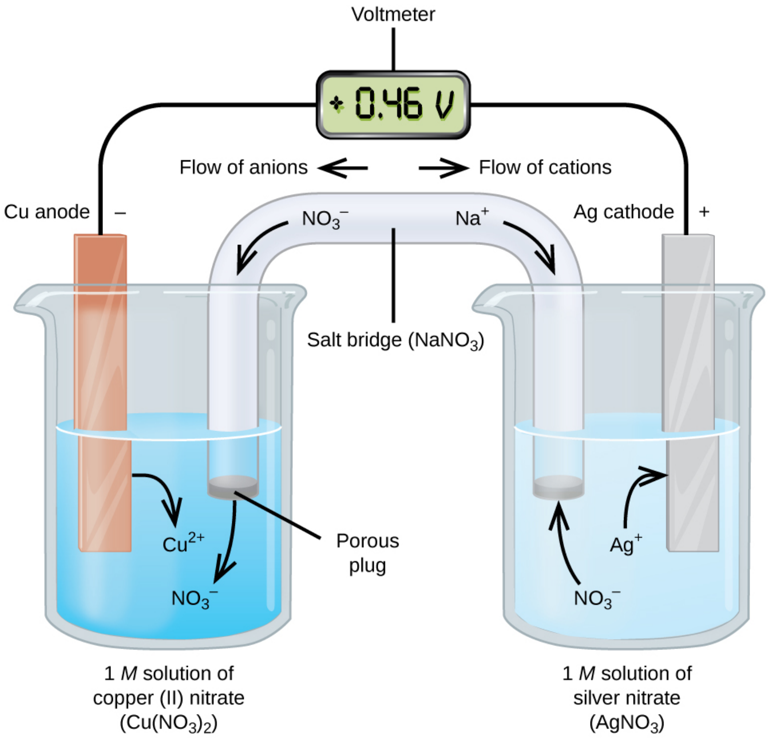


Image Courtesy of BCCampus

On both sides, we can see the two half-reactions occurring. We know that reduction takes place at the cathode and oxidation occurs at the anode, so we have a copper anode and a silver cathode.

When a wire connects these two *electrodes*, electrons can flow from the copper to the Ag^+ solution and generate Ag. As a result, the copper anode shrinks and the silver cathode grows because Cu is used to form Cu^{2+} ions in solution, and Ag^+ is consumed to deposit Ag metal. A **voltmeter** can be added to the wire to measure the voltage of this reaction, and we find $E = +0.46$ V.

Alternatively, you can use the formula $E_{cell} = E_{red} + E_{ox}$ to calculate cell voltage, or **cell potential**.

Note 9.7.7

The formula for calculating cell voltage is also written as $E_{cell} = E_{cathode} - E_{anode}$, because reduction occurs at the cathode and oxidation occurs at the anode of an electrochemical cell.

Electrolytic Cells

For a galvanic cell, E_{cell} is greater than 0, so the corresponding redox reaction is spontaneous. However, for reactions that are not spontaneous, an external power source is needed to drive them. Thus, E_{cell} is less than 0, and the cell is **electrolytic**.

Example 9.7.8

Suppose we wished to separate Na^+ and Cl^- from the original Na and Cl_2 which created the solution:

$$2NaCl \rightarrow 2Na + Cl_2$$

This is a nonspontaneous redox reaction, so a battery will be needed to generate an emf to move the electrons from Cl^- to Na^+.

First, we can prove that this reaction is indeed not spontaneous. Breaking it into half-reactions and manipulating standard reduction potential values, we obtain the following:

- $2Na^+ + 2e^- \rightarrow 2Na \quad E = -2.71\text{ V}$
- $2Cl^- \rightarrow Cl_2 + 2e^- \quad E = -1.36\text{ V}$

At the anode, oxidation of Cl^- into Cl_2 occurs, so $E_{anode} = -1.36$ V. Meanwhile, the reduction of Na^+ into Na occurs at the cathode, so $E_{cathode} = -2.71$ V. The overall cell potential is calculated as $E_{cell} = E_{cathode} - E_{anode}$, so $-2.37\text{ V} - (-1.36\text{ V}) = -1.35$ V. Because E_{cell} is negative, the redox reaction not spontaneous and we will need a battery to relocate the electrons from the anode to the cathode.

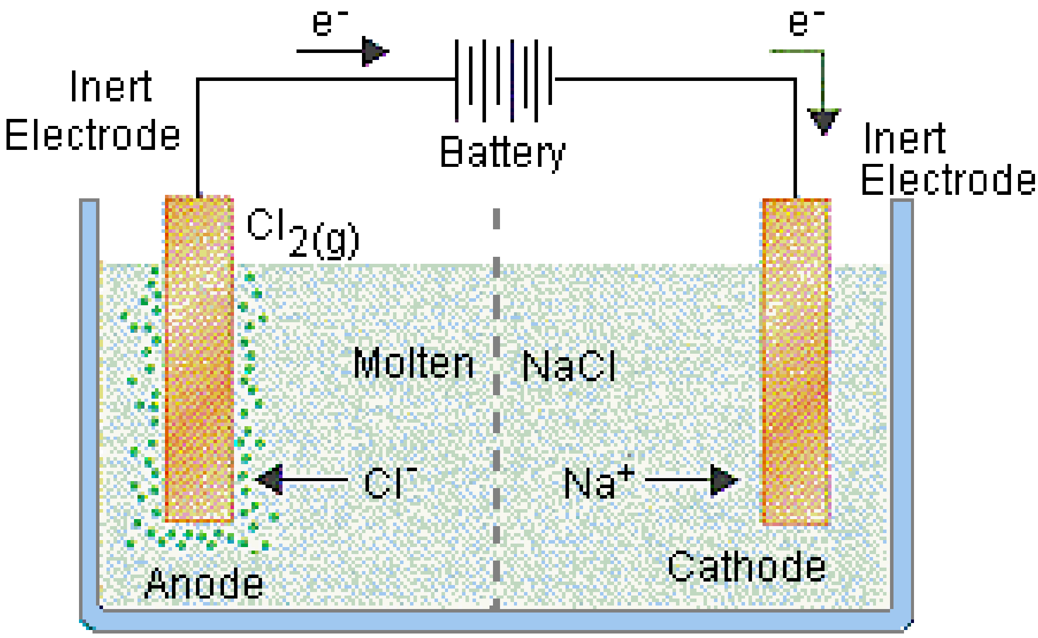


Image Courtesy of Purdue University

Since the ions themselves represent the molten NaCl, we use **inert electrodes** to collect our products, which in this case are Cl_2 (you can see the gas bubbles) and Na (the metal is being deposited at the cathode). As the electrons are propelled by the battery's voltage, Cl^- ions are oxidized into Cl_2 gas and Na^+ ions are being reduced into Na metal. Additionally, it's very important to note that the battery voltage MUST be greater than or equal to the magnitude of the voltage of the overall redox reaction. In this case, the battery must have a minimum voltage of 1.35 V.

§9.8 Cell Potential and Free Energy

In the previous section, we talked about **electromotive force** (emf) from redox reactions. This is the "pull" on electrons from a reducing agent to an oxidizing agent. The greater the emf, the more spontaneous, or thermodynamically favorable, the reaction will be.

Understanding Standard States

To simplify it further, emf can be conceptualized by asking how eager certain chemical species are to gain or lose electrons. Electromotive force, in units of volts, is a way to measure **cell potential**.

More importantly, for this section, if a cell is under **standard conditions**, that means that aqueous species are 1 M and is at a temperature of 298 K and a pressure of 1 atm. We can calculate standard cell potential using the following formula:

$$\boxed{E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}}$$

Note that the $^\circ$ subscript means *standard*, just as we saw with spontaneity and Gibbs free energy in earlier sections of this unit.

Problem 9.8.1 — Standard Cell Potential

Calculate the cell potential for the following cell reaction below

$$2\mathrm{AgBr} + 2\mathrm{Hg} \rightarrow 2\mathrm{Ag} + \mathrm{Hg_2Br_2}$$

The half-reactions and their standard cell potentials are given below:

$$\mathrm{Hg_2Br_2} + 2e^- \rightarrow 2\mathrm{Hg} + 2\mathrm{Br}^- \quad E^\circ = +0.140\ \mathrm{V}$$

$$2\mathrm{AgBr} + 2e^- \rightarrow 2\mathrm{Ag} + 2\mathrm{Br}^- \quad E^\circ = +0.071\ \mathrm{V}$$

Solution: In order to identify which species represent the cathode and anode, we need to identify which half-reaction involves reduction and oxidation, respectively.

AgBr, which contains Ag^+ ion, reduces into Ag (oxidation number decreases from +1 to 0) so the cathode will be AgBr. Meanwhile at the anode, Hg oxidizes into Hg_2^{2+} ion (oxidation number increases from 0 to +2).

Now, we can plug into the equation to find our answer:

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$
$$E^\circ_{cell} = +0.071\ \mathrm{V} - (+0.140\ \mathrm{V}) = \boxed{-0.069\ \mathrm{V}}$$

Calculating Cell Potential Using Standard Reduction Potentials

We will have a short discussion on standard reduction potentials before we move on to spontaneity and free energy.

Let's revisit this table of standard reduction potentials. The most important aspect of this chart is the reduction of H^+ to H_2 having a voltage of 0 V. It follows that each standard reduction potential is modeled by comparing their voltage to the voltage of this reduction.

Essentially, based on these values, you can determine which reactions are more spontaneous or less spontaneous than the reaction $2H^+ + 2e^- \rightarrow H_2$.

Standard Cell Potential and Spontaneity

The main concern regarding cell potential is how it relates to spontaneity, or thermodynamic favorability. For example, if E°_{cell} is positive, then the reaction is spontaneous, and vice versa. Why? Well, the emf is strong enough to pull the electrons from the reducing agent to the oxidizing agent in the reaction. The converse statement also holds true for the opposite case. Like this, we can predict the sign of ΔG° for a reaction with a given E°_{cell} value.

- If $E^\circ_{cell} > 0$, the reaction is thermodynamically favored, so ΔG° is negative.
- If $E^\circ_{cell} < 0$, the reaction is not thermodynamically favored, so ΔG° is positive.

The equation that allows you to calculate ΔG° given E°_{cell} is given in your reference sheet, and it reads as

$$\boxed{\Delta G^\circ = -nFE^\circ_{cell}}$$

where:

- ΔG° is the standard Gibbs free energy change,
- E°_{cell} is the voltage of the cell under standard conditions,
- n is the number of moles of electrons transferred in the redox reaction,
- and F is **Faraday's constant**, with a value of $\frac{96485\text{ C}}{\text{mol } e^-}$.

Note 9.8.2
A **coulomb** is a unit of electric charge.

Additionally, units for volts can be given by joules per coulomb, or $\text{V} = \frac{\text{J}}{\text{C}}$. This will be important in ensuring that we have the correct units when solving problems!

Before we end this section, we will solve a couple of problems.

Problem 9.8.3 — Cell Potential and Spontaneity I

Consider a galvanic cell that runs on a voltage of $E^\circ_{cell} = 0.94$ V. The chemical reaction that occurs involves 1 mole of electrons transferred. At 283 K, what is ΔG° for this cell?

Solution: We will proceed using the formula

$$\Delta G^\circ = -nFE^\circ_{cell}$$

We are given the number of moles of electrons transferred (1 mol e^-), the voltage of the cell ($E^\circ_{cell} = 0.94$ V), and we know Faraday's constant. Now all we need is a one-step calculation and to ensure our units match up. Finally, remember that 1 volt is equivalent to 1 joule per coulomb of charge.

$$\Delta G^\circ = -\left(1\,\cancel{\text{mol}\,e^-}\right)\left(96485\,\frac{\cancel{\text{C}}}{\cancel{\text{mol}\,e^-}}\right)\left(0.94\,\frac{\text{J}}{\cancel{\text{C}}}\right) = -90695.9\text{ J} = \boxed{-90.696\text{ kJ}}$$

Problem 9.8.4 — Cell Potential and Spontaneity II

Assuming the same conditions as the previous problem, what is the value of the equilibrium constant K?

Solution: For this problem, we will need to use a formula that was introduced to us back in section 9.5:

$$\Delta G^\circ = -RT \ln K$$

where:

- R is the universal gas constant, $R = 8.314\text{ J mol}^{-1}\text{ K}^{-1}$,
- T is the temperature in Kelvins (K), and
- K is the equilibrium constant for the reaction.

Since we are looking for the equilibrium constant, K_{eq}, we rearrange the equation:

$$K = e^{-\frac{\Delta G^\circ}{RT}}$$

Keep in mind we need to be extra careful with units! In the previous problem, we set our units for ΔG° to kJ, to have a more reasonable size. However, for this problem, we will need our ΔG° value to be in joules (J), because the universal gas constant, R, is in terms of J, not kJ.

Adjusting our units and plugging in, we find

$$K = e^{\left[-\frac{-90695.9\,\cancel{\text{J}}}{\left(8.314\,\cancel{\text{J}}\,\text{mol}^{-1}\,\cancel{\text{K}^{-1}}\right)\left(283\,\cancel{\text{K}}\right)}\right]} = \boxed{1.82 \cdot 10^{-17}}$$

In the next section, we will extend our discussion of cell potential towards situations involving species that are at nonstandard conditions and how we would adjust the cell potential to reflect real-life situations.

§9.9 Cell Potential Under Nonstandard Conditions

We have performed calculations for the voltage of an electrochemical cell, but only at standard conditions, i.e. 1.0 M concentrations (or 1.0 atm pressures), 298 K temperature, which imply a reaction quotient of $Q = 1$.

Actually, the concept of "standard conditions" is an arbitrary **point of reference**. In most cases, standard conditions are very difficult to achieve in the environment and especially involving electricity, there are many external disruptions (which we consider negligible, for simplicity) to power supply, current, etc. that can alter the concentrations (or pressures) of species involved in a cell reaction.

For surroundings-dependent processes, the cell potential (denoted by E_{cell} instead of E°_{cell}) is constantly changing at random rates. This is also known as the **instantaneous** cell potential, or instantaneous voltage.

As the reaction progresses, the general statement that follows always holds true:
reactants are consumed and products are formed.

Note 9.9.1

As reactants are being consumed and products are being formed, their relative concentrations change, which affects the value of E_{cell}. Keep reading to learn why!

At standard conditions, we can calculate E°_{cell} using standard reduction potentials. If the cell is under **nonstandard conditions**, we have to make a prediction as to whether the nonstandard cell voltage, E_{cell}, will be larger or smaller than the standard voltage, E°_{cell}. This section will focus entirely on interpreting the value of E_{cell} and drawing connections to concentration, cell potential, and equilibrium.

The Connection Between E_{cell} with E°_{cell}

Recall that in section 9.5 we discussed the difference between ΔG and ΔG° for a chemical reaction as well as their connection to equilibrium. The same concept applies when dealing with E_{cell} and E°_{cell} for an electrochemical cell.

However, it is important to note that for *galvanic cells* that operate, they are NOT at equilibrium. Therefore, we cannot use Le Châtelier's principle to justify any observations we can make. Instead, the cell is actually MOVING TOWARDS equilibrium as it operates, which means the farther the reaction is from equilibrium, the higher the magnitude of E_{cell}. Once equilibrium is established, there is zero voltage in the cell−think about a dead battery! (Note: a battery represents a series of galvanic cells.)

We can demonstrate the relationship between the nonstandard voltage E_{cell} and the reaction quotient Q using the following equation:

$$\boxed{E_{cell} = E^\circ_{cell} - \frac{RT}{nF}\ln Q}$$

where:

- $R = 8.314\ \text{J mol}^{-1}\ \text{K}^{-1}$,
- T is the temperature in Kelvins,
- Q is the reaction quotient, which is proportional to $\frac{[\text{anode}]}{[\text{cathode}]}$ (try to see why!),
- n is the number of moles of electrons transferred in the reaction, and
- F is Faraday's constant, equal to $96485\ \frac{\text{C}}{\text{mol}\ e^-}$.

This equation is called the **Nernst equation** and it demonstrates the relationship between E°_{cell} (instantaneous cell potential), E_{cell} (standard cell potential), and Q (reaction quotient).

Cell Potential and Concentration

The most important factor in predicting cell potential at nonstandard conditions is the concentration of all species. At standard conditions, all concentrations are 1.0 M, but otherwise we can make quantitative relationships between E_{cell} and E°_{cell}.

The key concept is that standard conditions, $Q = 1$ and if otherwise, we have $Q \neq 1$. Depending on the concentrations of various species, we can have two cases:

1. If $Q > 1$, the products are in excess, and the reverse reaction will be favored. Thus, the cell potential will decrease and $E_{cell} < E^\circ_{cell}$.
2. If $Q < 1$, the reactants are in excess, and the forward reaction will be favored. Thus, the cell potential will increase and $E_{cell} > E^\circ_{cell}$.

To solidify this concept, we'll work through the following exercise.

Problem 9.9.2 — Standard vs. Nonstandard Voltage

Consider the reaction $2\text{Al(s)} + 3\text{Mn}^{2+}\text{(aq)} \rightarrow 2\text{Al}^{3+}\text{(aq)} + 3\text{Mn(s)}$ and compare E_{cell} to E°_{cell} for the following sets of Mn^{2+} and Al^{3+} concentrations:

(a) $[\text{Al}^{3+}] = 1.5\ M$ and $[\text{Mn}^{2+}] = 1.0\ M$
(b) $[\text{Al}^{3+}] = 1.0\ M$ and $[\text{Mn}^{2+}] = 1.5\ M$
(c) $[\text{Al}^{3+}] = 1.5\ M$ and $[\text{Mn}^{2+}] = 1.5\ M$

Solution to part a: We will determine the value of Q, compare it to $Q = 1$, and then draw conclusions. This approach will also apply for parts (b) and (c).

$$Q = \frac{[\text{anode}]}{[\text{cathode}]} = \frac{[\text{Al}^{3+}]^2}{[\text{Mn}^{2+}]^3}$$

Substituting given concentrations, we have

$$Q = \frac{(1.5)^2}{(1.0)^3} = 2.25 > 1$$

Since $Q > 1$, the products are in excess and the reverse reaction will be favored. This will result in $\boxed{E_{cell} < E^\circ_{cell}}$ as the cell potential decreases in order to reach equilibrium.

Solution to part b:

$$Q = \frac{[\mathrm{Al}^{3+}]^2}{[\mathrm{Mn}^{2+}]^3}$$

Plugging in, we have

$$Q = \frac{(1.0)^2}{(1.5)^3} = 0.\overline{296} < 1$$

Since $Q < 1$, the reactants are in excess and the forward reaction will be favored. This will result in $\boxed{E_{cell} > E^\circ_{cell}}$ because the cell potential increases to reach equilibrium.

Solution to part c:

$$Q = \frac{[\mathrm{Al}^{3+}]^2}{[\mathrm{Mn}^{2+}]^3}$$

Plugging in concentrations, we have

$$Q = \frac{(1.5)^2}{(1.5)^3} = 0.\overline{6} < 1$$

Again, since $Q < 1$, the reactants are in excess and the forward reaction will be favored in order to reach equilibrium. This results in $\boxed{E_{cell} > E^\circ_{cell}}$ as the cell potential increases to reach equilibrium.

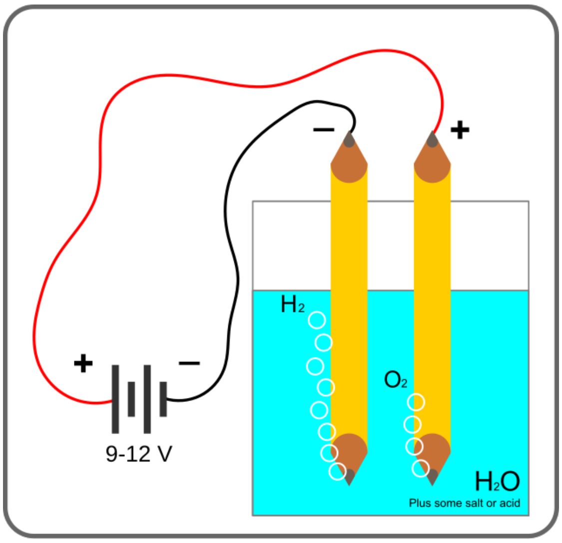
§9.10 Electrolysis and Faraday's Law

This is the last section of AP Chemistry. Before we move on, I want to congratulate each and every one of you for making it this far! Over the year, you have learned everything from acids and bases to equilibrium and thermodynamics. Your hard work and efforts will pay off on exam day.

For our final topic of Unit 9 and AP Chemistry, we will talk about *nonspontaneous* redox reactions and how we can use electrolytic cells cells to drive them. This builds on the foundation of how galvanic (voltaic) cells and electrolytic cells are different from each other, and we will also use **Faraday's Law** for calculations involving electrolysis.

The Process of Electrolysis

In simple terms, **electrolysis** is the process of running a galvanic cell backwards.



Recall that galvanic cells are electrochemical cells where chemical energy is converted into electrical energy by a spontaneous redox reaction. Additionally, the value of E°_{cell} for a galvanic cell is always positive.

Meanwhile, electrolytic cells require a current to be forced throughout the cell to generate a chemical change because the associated redox reaction is nonspontaneous, with a negative E°_{cell} value.

Electrolysis is generally used for *decomposition* and *electroplating* purposes, examples of which we will see later in this section.

Electrolytic Cells - Review

In previous sections, we learned that electrolytic cells consist of non-spontaneous redox reactions, i.e. reactions that require external sources of energy. Usually, this source is a **battery** that drives the reaction by generating an emf.

Note: In order to benefit the most from both the theory and practice problems that follow, you must be able to distinguish between galvanic and electrolytic cells. If you need a refresher, please feel free to reference section 9.7.

Defining Faraday's Law of Electrolysis

All electrochemical processes, spontaneous or not, involve some quantity of electric charge being transferred when species are both oxidized and reduced. It is possible to measure the **current**, or the rate at which the charge is transferred over time. Usually, an **ammeter** measures the current that flows through a device (also called a circuit) that runs an electrochemical cell reaction.

The units for current are in **amperes** (A), or amps for short. Unlike voltmeters, ammeters allow the passage of electrons and track them one by one. The quantity of charge that passes through a circuit can then be calculated by a simple relationship:

$$q = I \cdot t$$

where:

- q is the electric charge in Coulombs (C),
- I is the current in amperes (A), and
- t is the elapsed time in seconds (s).

College Board rearranges the equation for current passing through the cell:

$$\boxed{I = \frac{q}{t}}$$

This relationship enables us to use stoichiometry to better understand experimental measurements. The vast majority of these scenarios were originally worked out by the English scientist, Michael Faraday, in the first half of the 19th century.

Faraday's Law of Electrolysis can be stated this way:
At each electrode, the amount of substance produced is proportional to the quantity of charge that flows through the cell. More explicitly, substances undergoing different oxidation/reduction changes will not necessarily be produced in the same molar amounts. However, when additional ratios are taken into consideration, the law is correct for all cases.

Faraday's Law and Electrolysis Practice Problems

You are likely to see similar problems appear at least once on either the multiple-choice or free-response sections on the AP exam. Therefore, if you practice these problems enough, you can pretty much learn the "pattern" that is involved, effectively making them trivial.

Problem 9.10.1 — Electrolysis Practice I

In an electroplating process, 97.5 g of platinum metal is deposited from a solution of Pt^{4+}(aq) ions.

How many coulombs of charge are transferred during this process? Your answer should be accurate to three significant figures.

Solution: First, we will use the molar mass of platinum to convert grams of Pt to moles of Pt. We can apply a mental math trick by taking the molar mass of Pt to only three significant figures (using 195 instead of 195.08).

$$97.5\,\cancel{\text{g Pt}} \cdot \frac{1\text{ mol Pt}}{195\,\cancel{\text{g Pt}}} = 0.500\text{ mol Pt}$$

Next, we can use the stoichiometry of the half reaction associated with platinum to convert from moles of Pt to moles of electrons. In this case, the platinum has a charge of +4 in aqueous solution, so the half reaction is the reduction of Pt^{4+}(aq) into Pt(s):

$$\mathrm{Pt^{4+}(aq)} + 4e^- \rightarrow \mathrm{Pt(s)}$$

Thus, 4 moles of electrons to form 1 mole of Pt, and we get

$$0.500\,\cancel{\text{mol Pt}} \cdot \frac{4\,\text{mol}\,e^-}{1\,\cancel{\text{mol Pt}}} = 2.00\,\text{mol}\,e^-$$

Finally, we will use Faraday's constant to convert moles of electrons to coulombs of charge. Again, we can take Faraday's constant to three significant figures (using 96500 instead of 96485) and simplify our overall calculations.

$$2.00\,\cancel{\text{mol}\,e^-} \cdot \frac{96500\text{ C}}{1\,\cancel{\text{mol}\,e^-}} = \boxed{193000\text{ C}}$$

Problem 9.10.2 — Electrolysis Practice II

Determine the time, in seconds, needed to produce exactly 1.00 mol of Mg metal from molten $MgCl_2$ that is electrolyzed with a current of 50.0 A. Your answer should be accurate to three significant figures.

Solution: Since charge, current, and time, are all related to each other by Faraday's Law, our first step should be to convert our moles of Mg to moles of electrons. We can do this by using the stoichiometry of the magnesium half reaction, where Mg is +2 charged:

$$\mathrm{Mg^{2+}(l)} + 2e^- \rightarrow \mathrm{Mg(s)}$$

Note: the $MgCl_2$ is molten, so Mg^{2+} will be in the liquid phase.

Thus, 2 moles of electrons are required to form 1 mole of Mg, and we have

$$1.00\,\cancel{\text{mol Mg}} \cdot \frac{2\,\text{mol}\,e^-}{1\,\cancel{\text{mol Mg}}} = 2.00\,\text{mol}\,e^-$$

Next, we will use Faraday's constant to convert from moles of electrons to coulombs of charge.

$$2.00\,\cancel{\text{mol}\,e^-} \cdot \frac{96485\text{ C}}{1\,\cancel{\text{mol}\,e^-}} = 193000\text{ C}$$

Finally, to determine how much time is required to produce this charge using a current of 50.0 A, we will use the fact that 1 ampere is equivalent to 1 coulomb per second.

$$193000\,\cancel{\text{C}} \cdot \frac{1\text{ s}}{50.0\,\cancel{\text{C}}} = \boxed{3860\text{ s}}$$

§9.11 Practice Problems

Problem 9.11.1 — 2007 AP Chemistry FRQ

$$N_2(g) + 3F_2(g) \rightarrow 2NF_3(g) \quad \Delta H^\circ_{298} = -264\,\text{kJ mol}^{-1};\ \Delta S^\circ_{298} = -278\,\text{J K}^{-1}\,\text{mol}^{-1}$$

The following questions relate to the synthesis reaction represented by the chemical equation above.

(a) Calculate the value of the standard free energy change, ΔG°_{298}, for the reaction.

(b) Determine the temperature at which the equilibrium constant, K_{eq}, for the reaction is equal to 1.00. (Assume that ΔH° and ΔS° are independent of temperature.)

(c) Calculate the standard enthalpy change, ΔH°, that occurs when a 0.256 mol sample of $NF_3(g)$ is formed from $N_2(g)$ and $F_2(g)$ at 1.00 atm and 298 K.

The enthalpy change in a chemical reaction is the difference between energy absorbed in breaking bonds in the reactants and the energy released by bond formation in the products.

(d) How many bonds are formed when two molecules of NF_3 are produced according to the equation shown above?

(e) Use both the information in the above chemical equation and the table of average bond enthalpies to calculate the average enthalpy of the F − F bond.

Bond	Average Bond Enthalpy (kJ mol^{-1})
N≡N	946
N–F	272
F–F	?

Solution to part a: When we know the standard enthalpy and entropy changes for a chemical reaction, we can calculate the standard free energy change using the formula

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

Plugging in our values, we have

$$\Delta G^\circ_{298} = -264\,\text{kJ mol}^{-1} - (298\,\cancel{K})\left(-0.278\,\text{kJ mol}^{-1}\,\cancel{K^{-1}}\right) = \boxed{-181\,\text{kJ mol}^{-1}}$$

Don't forget to pay attention to units!

Solution to part b: The equation that relates thermodynamics to equilibrium is well known as

$$\Delta G^\circ = -RT \ln K$$

We note that if $K_{eq} = 1$, then $\Delta G^\circ = -RT \ln(1) = 0 \therefore \Delta H^\circ - T\Delta S^\circ = 0$.

We rearrange the equation to solve for temperature:

$$T = \frac{\Delta H^\circ_{298}}{\Delta S^\circ_{298}} = \frac{-264\,\cancel{\text{kJ mol}^{-1}}}{-0.278\,\cancel{\text{kJ mol}^{-1}}\,\text{K}^{-1}} = \boxed{950.\,\text{K}}$$

Solution to part c: This is a classic question involving concepts of both stoichiometry and thermodynamics. The first step is to realize that the standard enthalpy change of $-264\,\text{kJ mol}^{-1}$ is the change in heat energy associated with 1 mole of reaction.

We know that according to the balanced chemical equation, there are 2 moles of $NF_3(g)$ for every 1 mole of reaction.

Finally, we can use dimensional analysis to find our answer:

$$\frac{-264\,\text{kJ}}{1\,\cancel{\text{mol}_{rxn}}} \cdot \frac{1\,\cancel{\text{mol}_{rxn}}}{2\,\cancel{\text{mol NF}_3}} \cdot \frac{0.256\,\cancel{\text{mol NF}_3}}{1} = \boxed{-33.8\,\text{kJ}}$$

Solution to part d: By inspection, we realize that 1 molecule of NF_3 is composed of 3 N − F bonds, so 2 molecules should contain a total of $2 \cdot 3 = \boxed{6}$ N − F bonds. You can draw a Lewis diagram of NF_3 to verify this result.

Solution to part e: We can approximate the overall enthalpy change for a reaction using bond enthalpies by the following equation:

$$\Delta H^\circ_{rxn} = \sum(\text{BE of bonds broken}) - \sum(\text{BE of bonds formed})$$

Additionally, we know the value of ΔH°_{298}, so we can substitute the values we know in this equation and ultimately solve for the average enthalpy of the F − F bond.

We proceed with the following:

$$\Delta H^\circ_{298} = \sum(\text{BE of bonds broken}) - \sum(\text{BE of bonds formed}) = -264\,\text{kJ mol}^{-1}$$
$$\therefore \Delta H^\circ_{298} = [\text{BE}_{\text{N}\equiv\text{N}} + (3 \cdot \text{BE}_{\text{F}-\text{F}})] - (6 \cdot \text{BE}_{\text{N}-\text{F}})$$
$$[946\,\text{kJ mol}^{-1} + (3 \cdot \text{BE}_{\text{F}-\text{F}})] - 6\left(272\,\text{kJ mol}^{-1}\right) = -264\,\text{kJ mol}^{-1}$$
$$3 \cdot \text{BE}_{\text{F}-\text{F}} = (-264 - 946 + 1632)\ \text{kJ mol}^{-1} \therefore \boxed{\text{BE}_{\text{F}-\text{F}} = 141\,\text{kJ mol}^{-1}}$$

Problem 9.11.2 — 2010 AP Chemistry FRQ

$$2Al(s) + 3Zn^{2+}(aq) \rightarrow 2Al^{3+}(aq) + 3Zn(s)$$

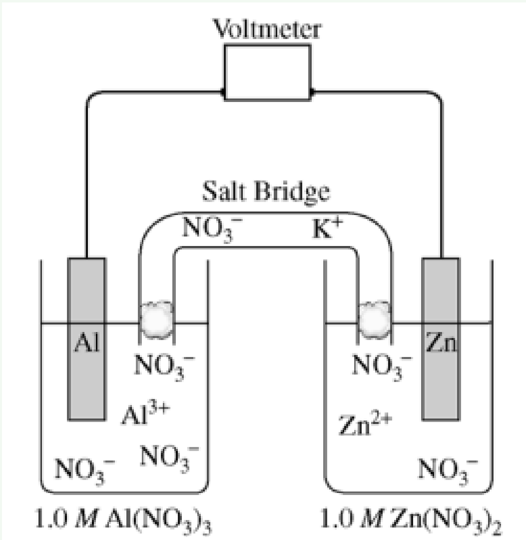
Respond to the following statements and questions that relate to the species and the reaction represented above.

(a) Write the complete electron configuration (e.g., $1s^2 2s^2 \ldots$) for Zn^{2+}.

(b) Which species, Zn or Zn^{2+}, has the greater ionization energy? Justify your answer.

(c) Identify the species that is oxidized in the reaction.

The diagram below shows a galvanic cell based on the reaction. Assume that the temperature is 25°C.



(d) The diagram includes a salt bridge that is filled with a saturated solution of KNO_3. Describe what happens in the salt bridge as the cell operates.

(e) Determine the value of the standard voltage, $E°$, for the cell. The standard reduction potentials for Al^{3+} and Zn^{2+} are −1.66 V and −0.76 V, respectively (at 25°C).

(f) Indicate whether the value of the standard free-energy change, $\Delta G°$, for the cell reaction is positive, negative, or zero. Justify your answer.

(g) If the concentration of $Al(NO_3)_3$ in the $Al(s)/Al^{3+}(aq)$ half-cell is lowered from 1.0 M to 0.01 M at 25 °C, does the cell voltage increase, decrease, or remain the same? Justify your answer.

Solution to part a: Zn^{2+} has 2 fewer electrons than a neutral Zn atom. A neutral atom of Zn contains 30 electrons, so an ionized atom Zn^{2+} will contain 28 electrons. According to the Aufbau principle, as well as electron configuration rules discussed in

Unit 1, we determine that the complete electron configuration for Zn^{2+} is

$$\boxed{1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}}$$

Solution to part b: To actually see what is happening, we can compare the electron configurations for Zn and Zn^{2+}.

In part (a), we already determined the electron configuration of Zn^{2+}. Additionally, we know that Zn will contain two more electrons. More specifically, the $3d$ subshell in Zn^{2+} has been completely filled. Therefore, these 2 electrons will fill the $4s$ subshell, according to the Aufbau principle.

$$\text{electron configuration for Zn} = 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$$

Electrons removed from Zn^{2+} experience a larger effective nuclear charge than electrons removed from Zn, so $\boxed{Zn^{2+}}$ has the greater ionization energy. This is because Zn^{2+} has two fewer core electrons shielding the valence electrons from the nucleus.

Alternatively, you could have stated that more energy is required to remove a negatively charged electron from a cation than from a neutral atom, for similar reasons discussed above.

Solution to part c: The species that is oxidized is the one that experiences an increase in oxidation number. We will look at both aluminum and zinc's initial and final oxidation states, and determine which species was oxidized.

On the reactants side, aluminum is in pure elemental form, so its oxidation number is 0 and zinc is ionized as Zn^{2+}, with oxidation number simply equal to the charge on its monoatomic ion: -2. On the products side, aluminum is a monoatomic ion Al^{3+} with a charge of $+3$ and zinc is in pure elemental form, so its final oxidation state is equal to 0.

Clearly, $\boxed{\text{Al(s)}}$ was oxidized, because it experienced an increase in oxidation number from 0 to $+3$ as the reaction progressed.

Solution to part d: For all galvanic cells, salt bridges are generally placed to keep the cell electrically neutral. This bridge contains a saturated solution of a very soluble salt, which connects the anode and cathode of the cell. To facilitate the cell reaction, the salt solution consists of freely-floating cations and anions. We know that the cations travel to the cathode and the anions travel to the anode. According to the diagram, as well as the oxidation states for each of the species in the cell reaction, we can conclude that the Al and Zn electrodes represent the anode and cathode, respectively. Thus, as the cell operates, NO_3^- ions flow toward the Al half-cell and K^+ ions flow toward the Zn half-cell.

Solution to part e: We will use the standard reduction potentials for the reactions $Al^{3+} + 3e^- \rightarrow Al$ and $Zn^{2+} + 2e^- \rightarrow Zn$ to solve this problem.

The formula for standard voltage, E°, for an electrochemical cell is equal to

$$E^\circ = E^\circ_{cathode} - E^\circ_{anode}$$

Since Zn is being reduced, $E^\circ_{cathode}$ is simply equal to the standard reduction potential for the half-reaction $Zn^{2+} + 2e^- \rightarrow Zn$. However, we need to be careful when determining the value for E°_{anode}. We are given that the standard reduction potential for $Al^{3+} + 3e^- \rightarrow Al$ at 25°C is -1.66 V, however, we must account for the fact that Al is OXIDIZED in this reaction, not reduced, so we will have to flip the sign of this value.

Putting all this together, we have

$$E^\circ = E^\circ_{cathode} - E^\circ_{anode} = (-0.76 \text{ V}) - (-1.66 \text{ V}) = \boxed{0.90 \text{ V}}$$

Solution to part f: We can relate the standard free energy change, ΔG°, to the standard voltage, E°, using the following equation:

$$\Delta G^\circ = -nFE^\circ$$

Because our E° value is positive (as calculated in part (e)), ΔG° is negative. Additionally, ΔG° must be negative because the reaction is thermodynamically favorable/spontaneous under standard conditions!

Solution to part g: This problem requires us to invoke the Nernst equation for cell potential under nonstandard conditions. Note that for the current exam, you won't need to make actual calculations but even this problem only asks us to draw basic relationships between variables in the formula.

Below shows the Nernst equation:

$$E_{cell} = E^\circ_{cell} - \frac{RT}{nF} \ln Q$$

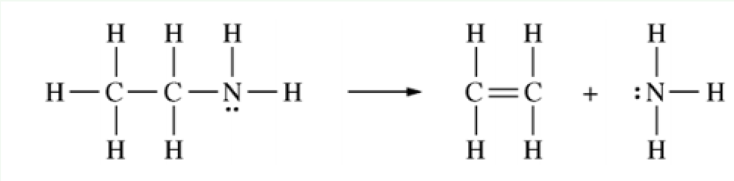
where Q refers to the reaction quotient. Using the law of mass action (this basically just means that Q and K to describe equilibrium are dependent upon relative amounts of reactants and products in a reaction mixture), we write the expression for Q as

$$Q = \frac{[Al^{3+}]^2}{[Zn^{2+}]^3}$$

The main idea is that when the cell is under standard conditions, all concentrations and pressures are at 1 M and 1 atm, respectively. This means that $Q = 1$, and thus $E_{cell} = E^\circ_{cell}$ (the cell potential remains stable).

In this case, we have a stress that lowers the concentration of Al^{3+}, causing the value of Q to decrease. Therefore, the value of Q will fall below 1, and thus the log term in the Nernst equation will become more negative, causing the value of E_{cell} to become more positive, i.e. the cell voltage $\boxed{\text{increases}}$.

Problem 9.11.3 — 2012 AP Chemistry FRQ



A sample of $CH_3CH_2NH_2$ is placed in an insulated container, where it decomposes into ethene and ammonia according to the reaction represented above.

Substance	Absolute Entropy, $S°$, in J/(mol·K) at 298 K
$CH_3CH_2NH_2(g)$	284.9
$CH_2CH_2(g)$	219.3
$NH_3(g)$	192.8

(a) Using the data in the table above, calculate the value, in $\text{J}/(\text{mol}_{rxn} \cdot \text{K})$, of the standard entropy change, $\Delta S°$, for the reaction at 298 K.

(b) Using the data in the table below, calculate the value, in $\text{kJ}/\text{mol}_{rxn}$, of the standard enthalpy change, $\Delta H°$, for the reaction at 298 K.

Bond	C–C	C=C	C–H	C–N	N–H
Average Bond Enthalpy (kJ/mol)	348	614	413	293	391

(c) Based on your answer to part (b), predict whether the temperature of the contents of the insulated container will increase, decrease, or remain the same as the reaction proceeds. Justify your prediction.

An experiment is carried out to measure the rate of the reaction, which is first order. A $4.70 \cdot 10^{-3}$ mol sample of $CH_3CH_2NH_2$ is placed in a previously evacuated 2.00 L container at 773 K. After 20.0 minutes, the concentration of the $CH_3CH_2NH_2$ is found to be $3.60 \cdot 10^{-4}$ mol/L.

(d) Calculate the rate constant for the reaction at 773 K. Include units with your answer.

(e) Calculate the initial rate, in $M\ \text{min}^{-1}$, of the reaction at 773 K.

(f) If $\frac{1}{[CH_3CH_2NH_2]}$ is plotted versus time for this reaction, would the plot result in a straight line or would it result in a curve? Explain your reasoning.

Solution to part a: The standard entropy change, $\Delta S°$, for a chemical reaction can be determined by calculating the difference between the total entropy of the products and the total entropy of the reactants.

$$\Delta S^\circ = \sum n_p S^\circ(\text{products}) - \sum n_r S^\circ(\text{reactants})$$

This is similar to finding the standard enthalpy change - plug in the absolute entropy for each species in the equation, accounting for their stoichiometric coefficients in the chemical reaction.

Therefore, we have

$$\Delta S^\circ = [(219.3 + 192.8) - 284.9]\ \text{J}/(\text{mol}_{rxn} \cdot \text{K}) = \boxed{127.2\ \text{J}/(\text{mol}_{rxn} \cdot \text{K})}$$

Solution to part b: Let's figure out the bonds that must be broken in the reactants. Observing the Lewis diagram reveals that 5 C − H bonds, 1 C − C bond, 2 N − H bonds, and 1 C − N bond must be broken.

$$\begin{aligned}\sum (\text{BE of bonds broken}) &= 5\,(\Delta H_{\text{C−H}}) + 1\,(\Delta H_{\text{C−C}}) + 2\,(\Delta H_{\text{N−H}}) + 1\,(\Delta H_{\text{C−N}}) \\ &= 5 \cdot 413 + 1 \cdot 348 + 2 \cdot 391 + 1 \cdot 293 = 3488\ \text{kJ}/\text{mol}_{rxn}\end{aligned}$$

Now let's figure out the bonds formed in the products. Ethene and ammonia, the two products, consist of 1 C = C bond, 4 C − H bonds, and 3 N − H bonds.

$$\begin{aligned}\sum (\text{BE of bonds formed}) &= 1\,(\Delta H_{\text{C=C}}) + 4\,(\Delta H_{\text{C−H}}) + 3\,(\Delta H_{\text{N−H}}) \\ &= 1 \cdot 614 + 4 \cdot 413 + 3 \cdot 391 = 3439\ \text{kJ}/\text{mol}_{rxn}\end{aligned}$$

We know that the enthalpy change of a reaction can be estimated with bond enthalpies using the equation

$$\Delta H_{rxn} = \sum (\text{BE of bonds broken}) - \sum (\text{BE of bonds formed})$$

Thus, we determine that ΔH for our reaction is equal to

$$\Delta H_{rxn} = 3488\ \text{kJ}/\text{mol}_{rxn} - 3439\ \text{kJ}/\text{mol}_{rxn} = \boxed{49\ \text{kJ}/\text{mol}_{rxn}}$$

Solution to part c: Our answer to part (b) was the standard enthalpy change, ΔH°, for the reaction at 298 K. Since $\Delta H^\circ > 0$, the reaction is endothermic. Now, we need to be careful here. The *system* is what gains heat energy, and the *surroundings* loses heat energy. The contents of the insulated flask actually represent the surroundings here, so we predict that their temperature will $\boxed{\text{decrease}}$.

Solution to part d: Since we are given that the decomposition of $CH_3CH_2NH_2$ is a first-order process, we should think about the integrated rate law:

$$\ln[CH_3CH_2NH_2]_t - \ln[CH_3CH_2NH_2]_0 = -kt$$

where $[CH_3CH_2NH_2]_0$ and $[CH_3CH_2NH_2]_t$ represent the initial and final concentrations of $CH_3CH_2NH_2$, respectively.

We can plug in values and solve for the rate constant, k, for the reaction at 773 K.

$$\ln\left(3.60 \cdot 10^{-4}\,\text{mol/L}\right) - \ln\left(\frac{4.70 \cdot 10^{-3}\,\text{mol}}{2.00\,\text{L}}\right) = -k\,(20.0\,\text{min})$$
$$-7.929 - (-6.053) = -k\,(20.0\,\text{min}) \therefore k = \boxed{9.38 \cdot 10^{-2}\,\text{min}^{-1}}$$

Solution to part e: The rate law for this reaction is given by

$$rate = k[CH_3CH_2NH_2]$$

so the initial rate of reaction will depend on the initial concentration of $CH_3CH_2NH_2$:

$$\text{initial rate} = k[CH_3CH_2NH_2]_0$$

Substituting the relevant information, we get

$$\text{initial rate} = \left(9.38 \cdot 10^{-2}\,\text{min}^{-1}\right)\left(\frac{4.70 \cdot 10^{-3}\,\text{mol}}{2.00\,\text{L}}\right) = \boxed{2.20 \cdot 10^{-4}\,M\,\text{min}^{-1}}$$

Solution to part f: This question tests our knowledge of integrated rate laws. Specifically, which plots yield a linear graph that can tell us the value of the rate constant?

We know that the decomposition of $CH_3CH_2NH_2$ is a first-order process, and can be described by the integrated rate law

$$\ln[CH_3CH_2NH_2]_t - \ln[CH_3CH_2NH_2]_0 = -kt$$

This means that the graph of $\ln[CH_3CH_2NH_2]$ over time t will yield a linear graph with a slope of $-k$. However, the question asks us whether $1/[CH_3CH_2NH_2]$, the reciprocal of the concentration of $CH_3CH_2NH_2$, will generate a straight line or a curve.

This plot would generate a $\boxed{\text{curve}}$, as our reaction is first-order and only a plot of $\ln[CH_3CH_2NH_2]$ over t will give us a straight line. In reality, we would only get a straight line by plotting $1/[CH_3CH_2NH_2]$ over t if the decomposition of $CH_3CH_2NH_2$ were a second-order process.

Problem 9.11.4 — 2013 AP Chemistry FRQ

Answer the following questions involving the stoichiometry and thermodynamics of reactions containing aluminum species.

$$2Al_2O_3(l) + 3C(s) \rightarrow 4Al(l) + 3CO_2(g)$$

An electrolytic cell produces 235 g of Al(l) according to the equation above.

(a) Calculate the number of moles of electrons that must be transferred in the cell to produce the 235 g of Al(l).

(b) A steady current of 152 amp was used during the process. Determine the amount of time, in seconds, that was needed to produce Al(l).

(c) Calculate the volume of CO_2(g), measured at 301 K and 0.952 atm, that is produced in the process.

(d) For the electrolytic cell to operate, the Al_2O_3 must be in the liquid state rather than in the solid state. Explain.

When Al(s) is placed in a concentrated solution of KOH at 25°C, the reaction represented below occurs.

$$2Al(s) + 2OH^-(aq) + 6H_2O(l) \rightarrow 2[Al(OH)_4]^-(aq) + 3H_2(g)$$

Half-reaction	$E°$ (V)
$[Al(OH)_4]^-(aq) + 3\,e^- \rightarrow Al(s) + 4\,OH^-(aq)$	–2.35
$2\,H_2O(l) + 2\,e^- \rightarrow H_2(g) + 2\,OH^-(aq)$	–0.83

(e) Using the table of standard reduction potentials shown above, calculate the following.

(i) $E°$, in volts, for the formation of $[Al(OH)_4]^-$(aq) and H_2(g) at 25°C
(ii) $\Delta G°$, in kJ/mol$_{rxn}$, for the formation of $[Al(OH)_4]^-$(aq) and H_2(g) at 25°C

Solution to part a: First, we need to convert grams of Al(l) to moles of Al(l), and then use mole ratios to solve for the number of moles of electrons that must be transferred in the cell.

$$235\,\cancel{\text{g Al}} \cdot \frac{1\text{ mol Al}}{26.98\,\cancel{\text{g Al}}} = 8.71\text{ mol Al}$$

Moreover, aluminum is reduced in this electrolytic cell reaction, and the reaction that describes the reduction is

$$Al^{3+} + 3e^- \rightarrow Al$$

According to the stoichiometry of this reaction, 3 mol e^- is transferred for every mol of Al. Now, we can convert from moles of Al to moles of electrons:

$$8.71\,\cancel{\text{mol Al}} \cdot \frac{3\text{ mol }e^-}{1\,\cancel{\text{mol Al}}} = \boxed{26.1\text{ mol }e^-}$$

Solution to part b: This is a standard Faraday's Law and electrolysis problem, where dimensional analysis will be very useful as we can convert from one unit to another.

Specifically, we are given the number of moles of electrons as well as Faraday's constant, we can multiply them together, and we will be left with the units of charge q:

$$\cancel{\text{mol}\, e^-} \cdot \frac{\text{C}}{\cancel{\text{mol}\, e^-}} = \text{C}$$

Thus, we will set up the following:

$$\begin{aligned} &\text{charge} = \text{moles}\, e^- \cdot \text{Faraday's constant} \\ &q = nF = 26.1\, \cancel{\text{mol}\, e^-} \cdot \frac{96485\ \text{C}}{\cancel{\text{mol}\, e^-}} = 2.52 \cdot 10^6\ \text{C} \end{aligned}$$

We use our equation which expresses current as the rate of change of charge with respect to time:

$$I = \frac{q}{t}$$

Rearrange the equation for time to obtain

$$t = \frac{q}{I} = \frac{2.52 \cdot 10^6\ \text{C}}{152\ \text{amp}} = \frac{2.52 \cdot 10^6\, \cancel{C}}{152\, \cancel{C}/s} = \boxed{1.66 \cdot 10^4\ \text{s}}$$

Solution to part c: Since we know both pressure and temperature, we can use the ideal gas law to determine the dry volume of $CO_2(g)$.

But first, we need to know how many moles of $CO_2(g)$ are produced in this reaction. In previous steps, we determined the number of moles of Al that were initially present. We can use the mole ratio between CO_2 and Al to convert to number of moles of CO_2 (You must show this step to get full credit):

$$8.71\, \cancel{\text{mol Al}} \cdot \frac{3\ \text{mol}\ CO_2}{4\, \cancel{\text{mol Al}}} = 6.53\ \text{mol}\ CO_2$$

Now, we can use this molar measurement to solve for V in the Ideal Gas Law:

$$V = \frac{nRT}{P} = \frac{(6.53\, \cancel{\text{mol}})(0.0821\ \text{L}\, \cancel{\text{atm}}\, \cancel{\text{mol}^{-1}}\, \cancel{\text{K}^{-1}})(301\, \cancel{\text{K}})}{0.952\, \cancel{\text{atm}}} = \boxed{1.70 \cdot 10^2\ \text{L}}$$

Solution to part d: Al_2O_3 is an ionic compound, with bonds formed by a metal and nonmetal. We know that ionic compounds are excellent conductors of electricity in the liquid and aqueous phases. However, they are very poor conductors of electricity as solids. If the compound cannot conduct electricity, the electrolytic cell cannot operate because the movement of ions is necessary to keep the cell operating properly. Therefore, Al_2O_3 must be in the liquid state and not the solid state, so that it conducts electricity.

Solution to part e(i): To form $[Al(OH)_4]^-(aq)$ and $H_2(g)$, they both must appear on the products of the overall reaction. We need to reverse the first half-reaction, so that aluminum is oxidized from Al(s) to $[Al(OH)_4]^-(aq)$.

Note that we do not multiply the E° values when balancing the number of electrons in the overall reaction. Finally,

$$E^\circ = E^\circ_{cathode} - E^\circ_{anode} = -0.83\text{ V} - (-2.35\text{ V}) = \boxed{1.52\text{ V}}$$

Solution to part e(ii): We will use the formula

$$\Delta G^\circ = -nFE^\circ$$

Note that when we calculated E° for the overall reaction, we did not multiply any of the half-reactions by a factor (E° is an intensive property), but the total number of moles of electrons that were transferred is actually the least common multiple of those given in both half-reactions. Since the first reaction transferred 2 mol e^- and the second transferred $3\,\text{mol}\,e^-$, the overall reaction transferred a total of lcm(2, 3) = $6\,\text{mol}\,e^-$.

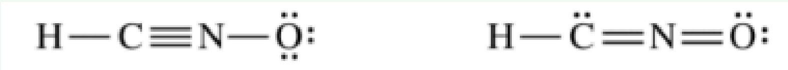
Here, lcm(a, b) denotes "the least common multiple of a and b."

Moreover, the question asks us to find ΔG° for the reaction in units of kJ/mol_{rxn}. Since 6 moles of electrons are transferred for every mole of reaction, we can set up the following:

$$\Delta G^\circ = -\left(\frac{6\,\cancel{\text{mol}\,e^-}}{1\,\text{mol}_{rxn}}\right)\left(96485\,\frac{\cancel{\text{C}}}{\cancel{\text{mol}\,e^-}}\right)\left(1.52\,\frac{\cancel{\text{J}}}{\cancel{\text{C}}}\right)\left(\frac{\text{kJ}}{1000\,\cancel{\text{J}}}\right) = \boxed{-880.\text{ kJ/mol}_{rxn}}$$

Problem 9.11.5 — 2017 AP Chemistry FRQ (Excerpt)

Answer the following questions about the isomers fulminic acid and isocyanic acid. Two possible Lewis electron-dot diagrams for fulminic acid, HCNO, are shown below.



(a) Explain why the diagram on the left is the better representation for the bonding in fulminic acid. Justify your answer based on formal charges.

Fulminic acid can convert to isocyanic acid according to the equation below.

$$HCNO(g) \rightleftharpoons HNCO(g)$$

$$\text{fulminic acid} \rightleftharpoons \text{isocyanic acid}$$

Fulminic Acid	Isocyanic Acid
$H-C\equiv N-\ddot{O}:$	$H-\ddot{N}=C=\ddot{O}:$

(b) Using the Lewis electron-dot diagrams of fulminic acid and isocyanic acid shown in the boxes above and the table of average bond enthalpies below, determine the value of $\Delta H°$ for the reaction of HCNO(g) to form HNCO(g).

Bond	Enthalpy (kJ/mol)	Bond	Enthalpy (kJ/mol)	Bond	Enthalpy (kJ/mol)
N–O	201	C=N	615	H–C	413
C=O	745	C≡N	891	H–N	391

(c) A student claims that $\Delta S°$ for the reaction is close to zero. Explain why the student's claim is accurate.

(d) Which species, fulminic acid (HCNO) or isocyanic acid (HNCO), is present in higher concentration at equilibrium at 298 K? Justify your answer in terms of thermodynamic favorability and the equilibrium constant.

Solution to part a: Recall that formal charge can be calculated using the simple trick:

$$\text{formal charge} = \#\text{ valence electrons} - \#\text{ of dots} - \#\text{ of dashes}$$

For each structure, we can calculate the formal charge on each atom and explain why the diagram on the left is the better representation for the chemical bonding in fulminic acid.

For the left diagram:

- H: $1 - 0 - 1 = 0$

- C: $4 - 0 - 4 = 0$
- O: $6 - 6 - 1 = -1$

For the right diagram:

- H: $1 - 0 - 1 = 0$
- C: $4 - 2 - 3 = -1$
- O: $6 - 4 - 2 = 0$

In the diagram on the left, the C atom has a formal charge of zero and the O atom has a formal charge of -1. In the diagram on the right, the C atom has a formal charge of -1 and the O atom has a formal charge of zero.

Using this information, we conclude that the diagram on the left is the better representation of fulminic acid because it places the negative formal charge on oxygen, which is more electronegative than carbon. Additionally, the formal charges on both H and C are zero.

Solution to part b: We know the average bond enthalpies for different bonds that occur within both HCNO(g) and HNCO(g). Therefore, we will use the formula

$$\Delta H^\circ = \sum(\text{BE of bonds broken}) - \sum(\text{BE of bonds formed})$$

I will keep track of the different bonds within both molecules in the chart below, so that you can avoid careless errors and solve the problem in a more organized way.

Compound	HCNO	HNCO
Bond Enthalpies (kJ/mol)	$413 + 891 + 201$	$391 + 615 + 745$
Total Bond Enthalpy (kJ/mol)	1505	1751

$$\Delta H^\circ = \sum(\text{BE of bonds broken}) - \sum(\text{BE of bonds formed})$$

After plugging in all the values, we have

$$\Delta H^\circ = 1505\,\text{kJ/mol} - 1751\,\text{kJ/mol} = \boxed{-246\,\text{kJ/mol}_{rxn}}$$

Solution to part c: Whenever we have a reaction, we can gauge the value of ΔS°, or the standard change in entropy. Entropy is a measure of disorder, so if the arrangement of atoms becomes highly disordered as the reaction progresses, the sign of ΔS° is expected to be very positive. However, not much rearrangement actually happens, just by looking at the Lewis dot structures for HCNO(g) and HNCO(g). Additionally, we can compare the number of moles of gaseous particles on each side of the chemical equation and predict the magnitude of ΔS°. Because we have one mole of HCNO(g) on the reactants and one mole of HNCO(g) on the products, the number of moles of gas remains the same. Therefore, the student's claim that ΔS° for the reaction is approximately zero is accurate.

Solution to part d: We will need to use ΔG° as well as the equilibrium constant K to describe the thermodynamic favorability of the conversion of fulminic acid (HCNO) to isocyanic acid (HNCO).

Recall that the equation

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

can be used to relate thermodynamic favorability to both enthalpy and entropy changes in a chemical reaction.

In this case, ΔS° is essentially zero, so

$$\Delta G^\circ \approx \Delta H^\circ \therefore \Delta G^\circ \approx -246\,\text{kJ/mol}_{rxn} \therefore \Delta G^\circ < 0$$

This indicates that the forward reaction is thermodynamically favorable. As a result, fulminic acid will be consumed and isocyanic acid will be produced in significant amounts.

Lastly, we will use the formula

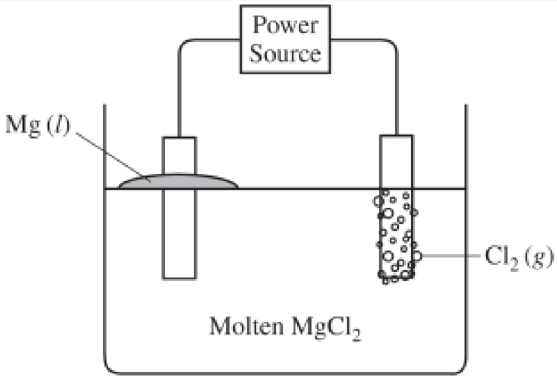
$$\Delta G^\circ = -RT\ln K$$

to describe the value of the equilibrium constant.

Since ΔG° is negative, $K > 1$ and more products than reactants are present in the reaction mixture at equilibrium. Thus, isocyanic acid (HNCO) will be present at a higher concentration.

$$K = \frac{[\text{HNCO}]}{[\text{HCNO}]} > 1 \therefore \boxed{[\text{HNCO}] > [\text{HCNO}]} \quad \checkmark$$

Problem 9.11.6 — 2021 AP Chemistry FRQ



Half-Reaction	E° (V)
$Mg^{2+} + 2e^- \rightarrow Mg$	−2.37
$Cl_2 + 2e^- \rightarrow 2Cl^-$	+1.36

Molten $MgCl_2$ can be decomposed into its elements if a sufficient voltage is applied using inert electrodes. The products of the reaction are liquid Mg (at the cathode) and Cl_2 gas (at the anode). A simplified representation of the cell is shown above. The reduction half-reactions related to the overall reaction in the cell are given in the table.

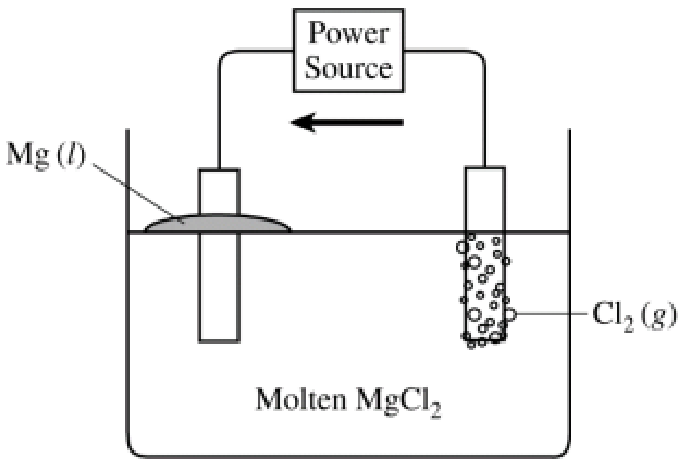
(a) Draw an arrow on the diagram to show the direction of of electron flow through the external circuit as the cell operates.

(b) Would an applied voltage of 2.0 V be sufficient for the reaction to occur? Support your claim with a calculation as part of your answer.

(c) If the current in the cell is kept at a constant 5.00 amps, how many seconds does it take to produce 2.00 g of Mg(l) at the cathode?

Solution to part a: Recall that the cathode increases in size and the anode decreases in size as an electrochemical cell operates. Therefore, the electron flow should be indicated by a single, *counterclockwise* direction arrow via the external circuit, traveling from the Cl_2 anode to the Mg cathode.

Essentially, your diagram should be consistent with the following:



Solution to part b: For this problem, we must first calculate the voltage of the cell. Since we are supplying power through an external circuit, this process is not thermodynamically favorable, so the value of E°_{cell} would be negative.

$$E^\circ_{cell} = E^\circ_{red} + E^\circ_{ox} = -2.37\,\text{V} + (-1.36\,\text{V}) = -3.73\,\text{V}$$

Note that this is another way to write the equation

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$

Because the overall voltage of the cell is -3.73 V, the only way this reaction can be thermodynamically favorable and occur spontaneously is if the applied voltage in the circuit is greater than 3.73 V. Thus, a voltage of 2.0 V is <u>not</u> sufficient for the reaction to occur.

Solution to part c: First, we write the half-reaction that represents the reduction of $MgCl_2$ into Mg:

$$Mg^{2+} + 2e^- \rightarrow Mg$$

Additionally, we are given that 2.00 g of Mg(l) is produced at the cathode and the current through the cell is fixed at 5.00 A.

Because this problem involves electrolysis, we should convert grams of Mg to moles of Mg and eventually to moles of electrons transferred.

$$2.00\,\cancel{\text{g Mg}} \cdot \frac{1\,\cancel{\text{mol Mg}}}{24.30\,\cancel{\text{g Mg}}} \cdot \frac{2\,\text{mol}\,e^-}{1\,\cancel{\text{mol Mg}}} = 0.165\,\text{mol}\,e^-$$

We can multiply this value by Faraday's constant to solve for charge:

$$0.165\,\cancel{\text{mol}\,e^-} \cdot \frac{96485\,\text{C}}{1\,\cancel{\text{mol}\,e^-}} = 1.59 \cdot 10^4\,\text{C}$$

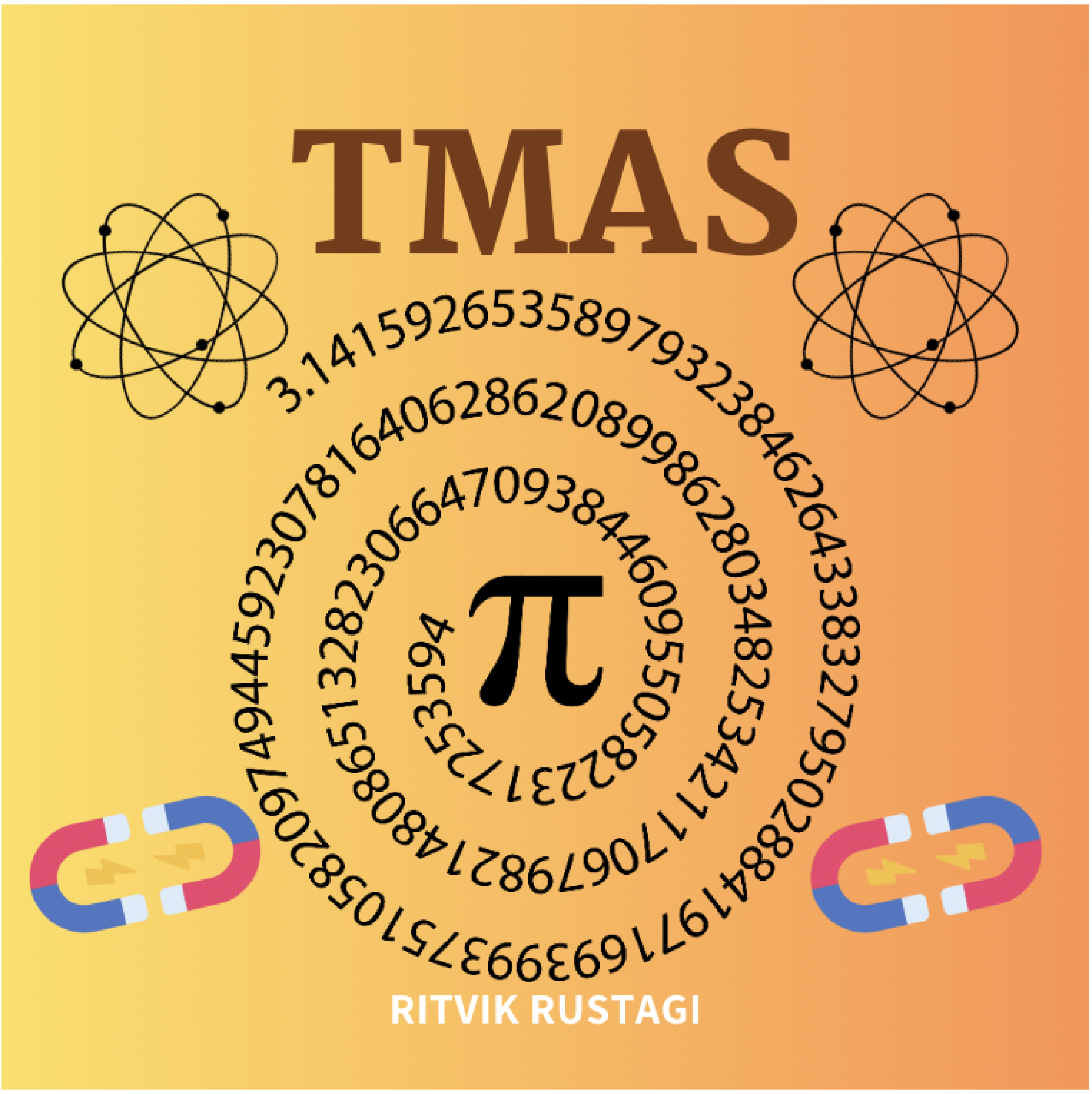
Finally, we will apply the formula that relates current with charge over time:

$$I = \frac{q}{t}$$

and rearranging for time, we have

$$t = \frac{q}{I} = \frac{1.59 \cdot 10^4\,\text{C}}{5.00\,\text{A}} = \frac{1.59 \cdot 10^4\,\cancel{\text{C}}}{5.00\,\cancel{\text{C}}/\text{s}} = \boxed{3180\,\text{s}}$$

Thank you so much for reading this book! I am honored to have contributed to your academic journey in some way!



Thanks,

Aditya Baisakh