#### **AP CHEMISTRY**

# The Ultimate Student's Guide to AP Chemistry

**EVERYTHING YOU NEED TO GET STARTED** 



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### Introduction

AP Chemistry is no walk in the park. Some AP courses have a ton of content, some are conceptually difficult, but AP Chem is both. That's why this is our largest, most comprehensive AP subject eBook yet.

Here you'll find an expansive library of guides designed to refine your conceptual knowledge and ability to solve AP problems. We've also packed in our Ultimate List of AP Chemistry Tips as well as a How-to Guide for studying.

It features information from the <u>Albert Blog</u>. If you're looking for additional resources, be sure to regularly check the blog and subscribe to hear about our new posts. Even as we release this eBook, there are several great chemistry guides nearing publication on the blog. We've also got content for all of your other APs, your college entrance exams, and even college coursework.

E-mail us at hello@albert.io if you have any questions, suggestions, or comments!







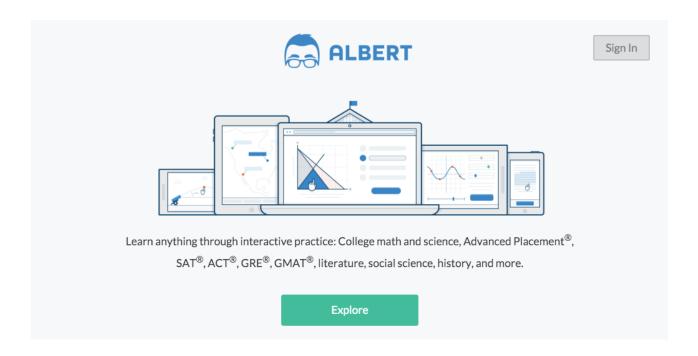
### **About Us**

#### What is Albert?

Albert bridges the gap between learning and mastery with interactive content written by world-class educators.

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### Why Educators Love Us

We asked teachers how their students did after using Albert.

#### Here is what they had to say:



My students had an 81.2% passing rate - the previous year was 76% (the highest rate in our county)! I am thrilled. I had 64 students total, with 6 receiving 5s, 19 scoring 4s, 27 receiving 3s, 10 scored 2s and 2 received 1s.

Susan M., JP Taravella High

70% of my students scored 3 or higher. This is up from last year, and is also well above the national average. Needless to say, I am very happy with my students' success. I used Albert more intentionally this year. In the beginning of the year, I wanted students simply to answer questions and practice. Once they had 150-200 questions answered, we looked for trends, strengths, and weaknesses and worked on addressing them. Students were tasked with increasing their answer accuracy no matter how many questions it took, then they set their own goals (some wanted to focus around tone; others needed practice with meaning as a whole).



Bill S., Lapeer High School



Last year 40% passed with 3s and 4s. This year 87% passed, most had 4s and 5s. We used the stimulus-based multiple choice questions throughout the year and as review for the exam. I think it helped tremendously.

Alice P., First Baptist Christian Academy







### Why Students Love Us

We asked students how they did after using Albert.

#### Here is what they had to say:



I scored very well this year – four 5s and one 4. Albert helped me get used to the types of questions asked on the exam and overall my scores were better this year.

Robyn G., Chambersburg Area Senior High School

Last year was my first year taking an AP test, and unfortunately I did not do as well as I had hoped. The subject had not been my best, and that was definitely displayed on my performance. However this year, I made a much higher score on my AP test. The previous year had been AP World History and I had made a 2. For this year it was AP English Language, and I scored a 4. There was a definite jump in my score, because Albert pushed me to focus on my weaknesses and form them into strengths.



Charlotte R., Rome High



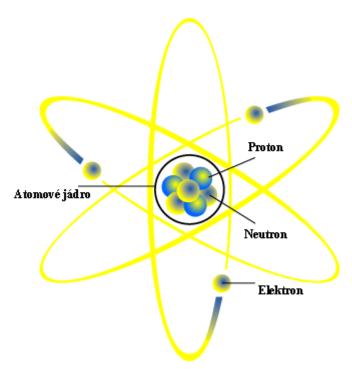
I scored a 4 on AP Biology, much higher than expected. Albert was an effective resource to guide me through AP Biology. Keeping up with it consistently all year as I learned the lesson in class was crucial to reinforcing my understanding and long-term memorization of Biology. After class each day, Albert helped to sink in the ideas that I was taught in the morning.

Lily O., Wake Forest High School









<u>Image Source: Wikimedia Commons</u>

Having grown up in the 21<sup>st</sup> century, you probably know that everything around you is fundamentally made of atoms. The chair you're sitting on, the screen you're looking at, and even the eyes you see with are made up of many different kinds of atoms. But what are atoms? What do they look like? And more importantly, how can I understand atomic structure for my AP Chemistry Exam? In this Ultimate Guide, we're going to give you a little bit of background on each topic to get you excited about it, and then I'm going to give you tips and advice on what you should memorize (or not), how to eliminate wrong answers quickly, and key words that you should use in the long- and short-answer section of the exam.







We will first start our discussion with a brief overview of the wave-like nature electromagnetic radiation. We will then go on to discuss the particle-nature of matter and how the discoveries in the early 20<sup>th</sup> century shaped our understanding of the atomic structure and spectrum of the hydrogen atom. We'll discuss Bohr's model of the atomic structure of the hydrogen atom, and the quantum mechanical model for atomic structure. We will dive into an explanation about the quantum numbers and their physical interpretations, and we will finish up this article with an overview of how atomic structure influences periodicity and periodic trends in the periodic table. Kapische? Let's go!

#### **Electromagnetic Radiation – Essential Knowledge 1.D.3.**

No discussion of atomic structure is complete without first understanding what Electromagnetic Radiation is. An examples of electromagnetic radiation is the visible light that you see coming off your screen and hitting your eyes, giving objects color and visibility. Electromagnetic radiation also makes up the radio waves travelling to our cars and the WI-FI signal going to our phones and computers.

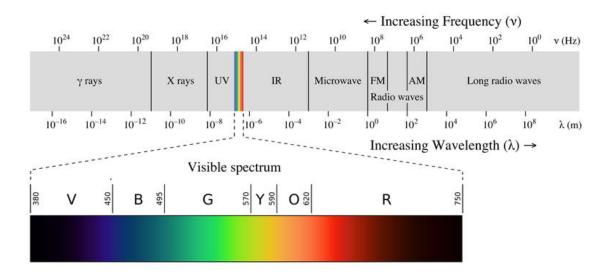


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But clearly, there is a big difference between visible light and your WI-FI signal. What is that difference? All types of electromagnetic radiation can be described in terms of two variables: their wavelength, and their frequency. Wavelength, denoted by the Greek letter lambda ( $\lambda$ ) and measured in meters (m), is the distance between two peaks in a wave. Visible light is an example of shortwavelength electromagnetic radiation, with wavelengths between 400-700 nanometers (nm), or 1 billionth of a meter. Frequency, denoted by the Greek letter nu ( $\nu$ ) and measured in Hertz ( $Hz = s^{-1}$ ), is a measure of how many times per second the wave repeats itself. The higher the frequency of a wave, the higher the energy of the wave. An example you can relate to is that exposure to X-rays ( $\nu = 10^{18} \ Hz$ ) is much more harmful than exposure to FM radio waves ( $\nu = 10^8 \ Hz$ ).

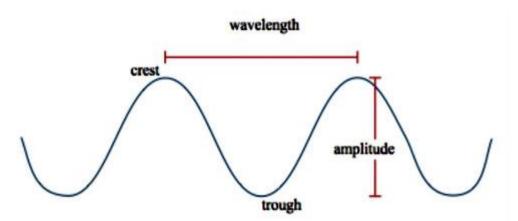


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Another feature of electromagnetic radiation is that all electromagnetic waves travel at the speed of light ( $c = 2.998 \times 10^8 \text{ m s}^{-1}$ ). This means that the product of the wavelength and frequency of an electromagnetic wave are always equal to the speed of light, or:

$$c = \lambda \times v = 2.998 \times 10^8 \text{ m s}^{-1}$$







This equation will be given to you on the AP Exam, so there's no reason to try and memorize it. It implies that frequency and wavelength are *inversely* proportional to each other, meaning that as one variable increases, the other decreases correspondingly. You should have no trouble solving this equation with a simple algebraic rearrangement of variables.

A great tip for quickly eliminating wrong answers on the Multiple Choice and for checking your answers on the Free Response section is to <u>focus on the exponents</u>. Since the product of the variables must have an exponent of  $10^8$  (the speed of light), it makes sense that if the known variable has a large *positive* exponent (e.g.  $\lambda = 8 \times 10^{15} m$ ), the corresponding variable must have a *negative* exponent (in this case,  $v = 3.75 \times 10^{-8} Hz$ ). This approach will help you instantly eliminate at least two wrong answers on the Multiple Choice, and will save you valuable time crunching numbers on the Free Response.

This understanding of the relationship between frequency, wavelength, and the speed of light was one of the fundamental discoveries that paved the way towards an understanding of the atomic nature of matter. Now that we understand the wavelike nature of light, let's move on the particle-like nature of light! Sounds crazy? You don't even know!

#### Nature of Matter - Essential Knowledge 1.B.1, 1.D.3.

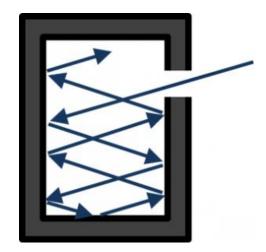
Towards the end of the 19<sup>th</sup> Century, a series of experiments were baffling physicists from around the world and challenging their understanding of the nature of matter. One of them was known as the Blackbody Radiation. A blackbody is an idealized object that absorbs all incoming frequencies of electromagnetic radiation, approximated by a small slit in a large black box.







A blackbody emits electromagnetic radiation at frequencies entirely based upon its temperature, and the classical model of light as waves was unable to account properly for the wavelengths of light being emitted!



**Image Source: Wikimedia Commons** 

To explain these results, German Physicist Max Planck (1858 – 1947), also known as the Father of Quantum Theory, theorized that, instead of matter being able to emit at infinite frequencies of electromagnetic radiation, there was some limit as to the frequency that light could be emitted or absorbed at. In other words, he thought of the emission frequencies coming out of matter as a series of steps rather than a smooth ramp. For everyday objects, energy can take on any arbitrary value. However, Planck theorized that for small objects, the energy being emitted by objects was more like a staircase, where it could only come in discrete packets he called quanta. In other words, the energy released from objects is quantized, a phenomenon which eventually to what we know as the Quantum Theory of Matter. It turns out, the nature of matter is quantized! Planck, through mathematical derivation, arrived at what we now call Planck's Constant (h), which is the smallest unit of Energy that can be gained or lost by atoms, in units of Joules (energy) times second (time), where:

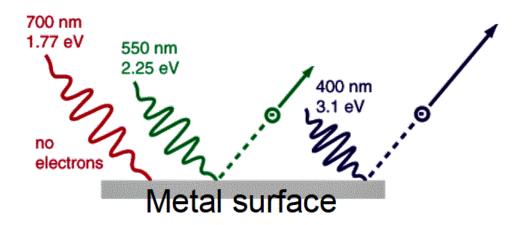
 $h = 6.626 \times 10^{-34} \text{ J s.}$ 







This should seem strange – it's like saying that a car can only travel at specific speeds! Even after his discovery, Planck was unconvinced that this constant was anything other than a theoretical mathematical artifact. It was, in fact, Albert Einstein (1879 – 1955) who was able to explain the importance of this discovery. Many people think that Einstein was given the Nobel Prize in Physics for his works on Special Relativity. In fact, Einstein was awarded the Prize for figuring out the cause for the Photoelectric Effect. This effect was an experimental observation that, when you shone a light on a piece of metal hooked to a current meter, only electromagnetic waves above a certain frequency (regardless of the energy) cause electrons to be released from the surface of the metal.



What made this observation even more interesting was that this was true regardless of the energy the light possessed. Einstein, using Planck's Quantum Theory, hypothesized that the electromagnetic radiation hitting the metal was in fact composed of many small particles, which he called Photons, and the energy of these photons was directly related to the frequency of the electromagnetic wave by the following relationship:

 $E_{photon}$  = hv, where  $h = 6.626 \times 10^{-34} Js$  and the frequency is in units of Hz.







And using the previous relationship we learned about frequency and wavelength, this equation can also be interpreted as,

$$E_{photon} = h\nu = \frac{hc}{\lambda}$$

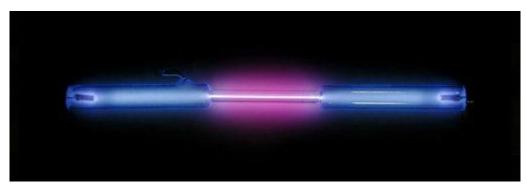
The AP Exam will almost certainly contain some questions about this topic. So let's review some common pitfalls.

Classic expectation: a high enough intensity of light, regardless of frequency, should could electrons to be ejected. WRONG!

Quantum Explanation: Light itself comes in little packets of energy called Photons. At a specific wavelength, photons have a specific amount of energy, and only photons with enough energy, regardless of intensity, can knock out electrons.

#### Atomic Spectrum of Hydrogen – Essential Knowledge 1.D.3.

The final experiment which demonstrated to physicists that the classical explanation of "electromagnetic radiation as waves" was incomplete was the atomic spectrum of Hydrogen. If you put hydrogen gas in a tube and run a lot of electricity through it, it will emit light.



**Image Source: Wikimedia Commons** 







Classical explanation would predict that the light being emitted is a continuous spectrum containing all frequencies of light. However, that is not the case. Hydrogen emits light in what is called a Line Spectra, meaning, light is only emitted at *discrete* wavelengths.

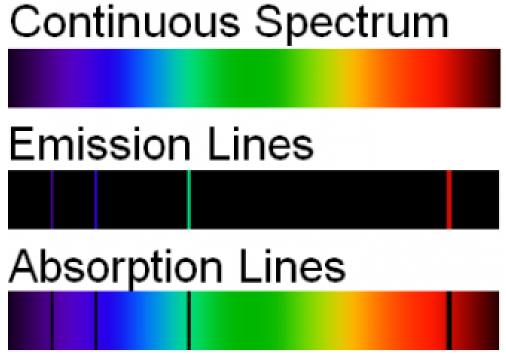


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Sounds familiar? That's because the quantum nature of matter can be used to explain the atomic spectrum of hydrogen! If we assume that hydrogen atoms can only emit photons of quantized energy, with the energy of each photon being,

 $E_{photon}$  = hnv, where n is a positive integer value

We find that the frequencies of emitted light exactly match those calculated by the equation! In fact, the integer *n* is our principal quantum number!







One thing to keep in mind is that on the AP Exam you may be given *either* frequency or wavelength for this calculation, so don't forget to use the relationship previously discussed to convert between them.

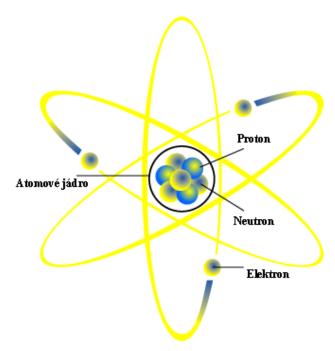


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#### **Bohr Model – Science Practice 1.3, 3.3.**

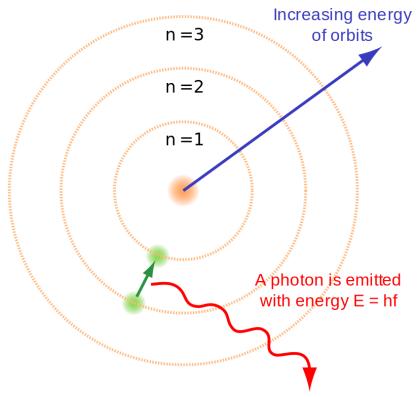
The classical model of atomic structure assumes that the negatively-charged electrons orbit the positively charged nucleus at any arbitrary radius away from the nucleus, like planets in our solar system orbiting around the sun. Danish Physicist Niels Bohr (1885-1962) used the derivation of the principal quantum number of the hydrogen line spectra to revise this Classical Model of the Atom. He proposed that the electrons could only orbit the nucleus at discrete radii that he called Shells, and electrons in shells further away from the nucleus possessed more energy.







He proposed that the line spectrum of hydrogen was caused by the transition of electrons from one shell to another!



**Image Source: Wikimedia Commons** 

While this is certainly an attractive picture, these quantum calculations have shown us that this theory is in fact wrong! In Bohr's model, electrons are still basically particles orbiting the nucleus. For various reasons we will not get into, this assumption simply cannot be true. In 1924, French Physicist Louis de Broglie presented his doctoral thesis (which was only two pages long!!!) proving that light, and in fact ALL particles, are inherently both particles and waves at the same time. This is known as the Wave-Particle Duality and was the breakthrough explanation necessary to explain how light, which clearly acts as a wave, can also act as a particle with quantized energy.

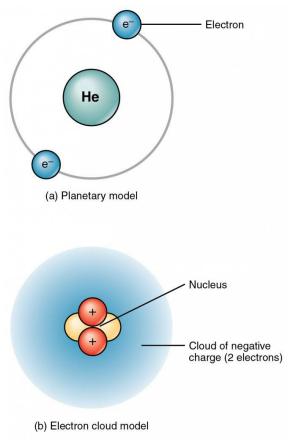






#### Quantum Mechanical Model of the Atom – 1.B.1, 1.C.2.

This leads to a very strange implication: *all objects are inherently fuzzy*. And while macroscopic objects like cars have immeasurably small wavelengths, electrons have wavelengths that *are* measurable. It was for this reason that Erwin Schrödinger (1887 – 1961) proposed a series of mathematical equations called *Wave Mechanics* which showed that all subatomic particles behave according to a set of Quantum mathematical equations called *wave functions*. Rather than orbiting the nucleus in so-called Planetary Motion, electrons actually orbit the nucleus as an *Electron Cloud*. A feature of the electron cloud is that they are in fact *Areas of Probability* for locating electrons (the cutoff is 90% probability).



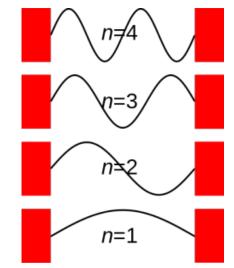
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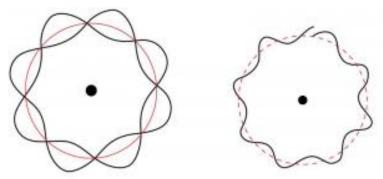




The Quantum Mechanical Model of the Atom treats all electrons as if they orbit the nucleus as a standing wave. An example of a standing wave is a guitar string, which, when plucked, vibrates at a certain harmonic frequency. In the same sense, electrons vibrate around the nucleus at a certain harmonic frequency. An important property of a standing wave is it does not propagate through space, and therefore, must always equal a whole number integer such that the ends meet at both sides. Here are two visual examples, one of a string as a standing wave, the other of a circle as a standing wave.



**Image Source: Wikimedia Commons** 



**Image Source: Wikimedia Commons** 







In the second image on the right, we see an example of an *impossible* standing wave. It is impossible because only waves of certain frequencies match up correctly at each end, and form a complete circle.

<u>Key Fact to Remember:</u> It is these mathematically correct waves, known as *harmonic frequencies*, which correspond to the principal quantum number *n* previously discussed.

#### Quantum Numbers – Essential Knowledge 1.C.2.

The Quantum number n is one of four quantum numbers that are used to describe an electron in an atom. When given all four quantum numbers, we possess all the information necessary to describe atomic structure of an electron in an atom. The quantum numbers of an electron are: Principal Quantum Number (n); quantum of angular momentum (I); the magnetic quantum number  $(m_I)$ ; and the spin quantum number  $(m_S)$ . Don't get confused by the terminology. For the sake of the Exam, try to keep things as simple as possible. You won't be provided with any of this information explicitly, so it is important to understand this information as much as possible. Think about the flow from one quantum number to the next, and most importantly, don't panic!

Table 1. Quantum Numbers for each of the first four shells.

Quantum Numbers for the First Four Shells					
n	1	Orbital Designation	m <sub>l</sub>	Number of Orbitals	
1	0	1s	0	1	
2	0	2s	0	1	
	1	2р	-1, 0, 1	3	







Quantum Numbers for the First Four Shells						
n	1	Orbital Designation	m <sub>l</sub>	Number of Orbitals		
3	0	3s	0	1		
	1	3p	-1, 0, 1	3		
	2	3d	-2, -1, 0, 1, 2	5		
4	0	4s	0	1		
	1	4p	-1, 0, 1	3		
	2	4d	-2, -1, 0, 1, 2	5		
	3	4f	-3, -2, -1, 0, 1, 2, 3	7		

The first quantum number, previously discussed, will tell you the harmonic wave function that corresponds to the electron, and it must be a positive integer value greater than zero. The greater n is, the greater the average radius of the electron is from the nucleus.

This has two important ramifications. First: the higher n is, the further away the electron is from the nucleus (i.e. the larger the circumference of its path), and the higher the energy of the electron is.  $Bigger(n) = Larger\ Energy$ . Second: the higher the quantum number, the  $less\ tightly\ bound$  the electron is, and the easier it is to be removed. That means that in an atom, electrons with the highest principal quantum number are the ones most likely to be knocked out of the atom first!







This effect is due to the *shielding* of the electrons from the positive charge of the nucleus due to successive layers of electron shells, like magnets of like-pole repelling each other.

$$n = Any Positive Integer [1, 2, 3, ...]$$

Angular momentum is a physical property that any orbiting object possesses. For a classical macroscopic object, angular momentum can take on any arbitrary value. However, as per the theme of this Guide, electrons can only possess *quantized* angular momentum. The values of angular momentum that an electron may possess are entirely determined by the principal quantum number n of the electron.

Possible values of Angular Momentum (I): 0 < l < (n - 1).

#### Let's look at an example.

If the electron of a hydrogen atom is in the first shell, what is its principal quantum number and what possible values of angular momentum can it possess?

In this example, the electron is in the <u>first</u> shell, meaning that n = 1.

For n = 1, 0 < l < [(1) -1] à 0 < l < 0; in other words, l can only equal 0.







As you have probably seen before, each value of *I* corresponds to an orbital "name" given in the table below. IT IS IMPORTANT TO REMEMBER THESE NAMES:

Table 2. The given names of each of the common orbitals.

Angular Momentum Value (I)	0	1	2	3
Given Name	S	р	d	f

The third quantum number is called the Magnetic Quantum Number and is denoted  $m_l$ . The easiest way to think about this quantum number is to remember that it dictates  $\underline{M}$ ethod of  $\underline{L}$ eaning, or in regular English, the orientation of the orbital in space. Although the orientation doesn't exactly depend on the value of  $m_l$ , for our purposes the comparison is sufficient. For example, while the sorbital  $(m_l = 0)$  is spherical, meaning no orientation, the p-orbital  $(m_l = -1, 0, 1)$  is composed of three pairs of lobes, each of equal energy and oriented about one of the principal axes x, y, or z.

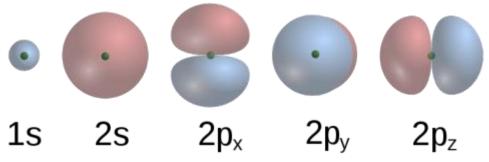


Image Source: Wikimedia Commons







#### Electron Spin - Essential Knowledge 1.C.2.

The final quantum number is called the Electron Spin and is denoted  $m_s$ . Let's go back to the analogy of electrons as planets for a second. In this analogy, the electrons revolve around the nucleus, and the distance, speed, and direction of revolution are determined by the first three quantum numbers. However, there is another type of motion that the planet undergoes; rotation. The planet, or in this case the electron, rotates around itself. This rotation is an intrinsic property not just of electrons, but of all subatomic particles. Without getting into too many details, you'll just have to accept it as a fact that the spin of all electrons is either plus or minus ½. The difference between positive and negative spin is akin to thinking about the earth either facing with the North Pole "Up" or "Down". Let's review the quantum numbers one more time before moving before moving on.

Table 3. A quick review of the quantum numbers and their meaning.

Symbol	Quantum Number	Explanation
n	Principal	Determines electron <u>energy</u> and orbital <u>size</u> .
1	Angular Momentum	Identifies orbital shape.
$m_I$	Magnetic	Identifies orbital <u>orientation</u> .
$m_s$	Spin	Identifies one of two possible spin states.

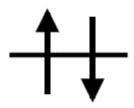






#### Electron Configuration – Essential Knowledge 1.B.2, 1.C.1.

As Chemists, what we need to know is that *no two electrons in an atom may have the same set of four quantum numbers*. This means that only two electrons may occupy a given orbital ( $m_s = \pm \frac{1}{2}$ ). This concept is known as the Pauli Exclusion Principle. We denote the electron with the positive spin as an arrow facing up, and the electron with the negative as an arrow facing down. This is expressed visually as,



Electrons occupy the lowest-energy levels of an atom first. So, when trying to figure out the electron configuration of an atomic structure, we would fill out the lowest energy orbital (1s) before moving on to the next highest orbital (2s) and so on. This observation is known as the Aufbau Principle. Aufbau means "building up" in German, and it refers to the order in which we as chemistry students "build-up" the electrons in an atomic structure. There are many mnemonic devices that help you memorize this diagram, but we find it easiest to memorize the exceptions rather than the rule;

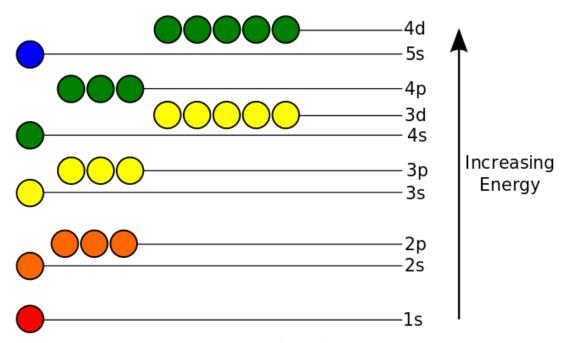
3d is between 4s and 4p 4d is between 5s and 5p For n = 6, the energy goes: 6s < 4f < 5d < 6p.







Another important thing to remember when applying the Aufbau principle is Hund's Rule; that we obtain the lowest energy configuration of an atom by having the maximum number of unpaired electrons in so-called "degenerate" orbitals. Degenerate orbital is another word for orbitals of equal energy, i.e. the three 2p orbitals or the five 3d orbitals. So for an atom with enough electrons to fill five spots in the *d-orbital* (i.e. Manganese, atomic number 25), the lowest energy configuration would be to have each orbital with 1 electron.



<u>Image Source: Wikimedia Commons</u>

With that, we have finished covering the general details of atomic structure! With the information provided hitherto, you should be able to answer any Multiple Choice question on the topic of atomic structure, and to provide a reasonably detailed answer on the Free Response section. With this information at hand, we can now discuss periodic trends in the Periodic Table of the Elements, whose conversation without this quantum knowledge would have been incomplete. Let's begin with a quick historical conversation, and then move on the Periodic Table itself.







#### Periodicity – Essential Knowledge 1.C.1, 2.D.3.

The science of Chemistry emerged as an independent field of science after the experiments of French scientist Antoine Lavoisier (1743-1794), who is most famous for formulating the Law of Conservation of Mass. Among his less widely known accomplishments, however, was his discovery of the chemical constituents of the air, such as Nitrogen and Oxygen. His research on the elements paved the way for Russian Chemist Dmitry Mendeleev (1834-1907), who discovered that if he rearranged the elements according to their mass, he was able to find similarities in their chemical properties. However, he couldn't explain why this relationship existed.

Reihen	Gruppe I.	Gruppe II.	Gruppe IIL	Gruppe IV.	Gruppe V.	Gruppe VL	Gruppe VII.	Gruppe VIII.
eih	l –	_	–	RH <sup>4</sup>	$RH^3$	$\mathbf{R}\mathbf{H}^2$	RH	_
- 22	R2O	RO	$R^2O^3$	RO <sup>2</sup>	R <sup>2</sup> O <sup>5</sup>	$RO^3$	$R^2O^7$	RO <sup>4</sup>
1	H=1							
2	Li=7	Be=9.4	B=11	C=12	N=14	O=16	F=19	
3	Na=23	Mg=24	Al=27.3	Si=28	P=31	S=32	Cl=35.5	
4	K=39	Ca=40	-=44	Ti=48	V=51	Cr=52	Mn=55	Fe=56, Co=59,
								Ni=59, Cu=63.
5	(Cu=63)	Zn=65	-=68	-=72	As=75	Se=78	Br=80	
6	Rb=85	Sr=87	?Yt=88	Zr=90	Nb=94	Mo=96	-=100	Ru=104, Rh=104,
								Pd=106, Ag=108.
7	(Ag=108)	Cd=112	In=113	Sn=118	Sb=122	Te=125	J=127	
8	Cs=133	Ba=137	?Di=138	?Ce=140	_	_	_	
9	(—)	l –	l –	l –	_	_	l –	
10	<b> </b>	_	?Er=178	?La=180	Ta=182	W=184	_	Os=195, Ir=197,
								Pt=198, Au=199.
11	(Au=199)	Hg=200	Tl=204	Pb=207	Bi=208	_	_	
12	_	_	_	Th=231	_	U=240	_	
								l

Image Source: Wikimedia Commons

We now know, however, that what he was seeing was the periodicity in the atomic structure of the elements. For example, all elements in the first column of the periodic table have one electron in their *s-orbital*.



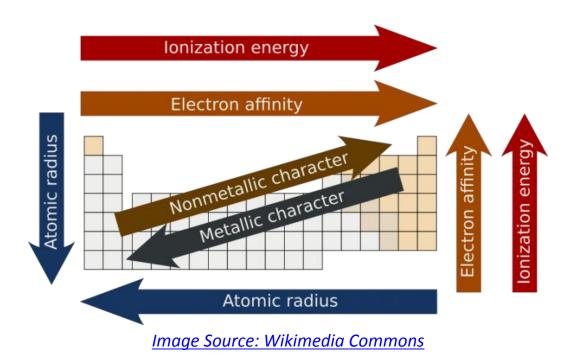




This electron configuration gives the atom certain chemical traits that are clearly distinguishable from chemicals in other columns of the period table. So what Mendeleev discovered was in fact that if we order the elements in order of their valence, or outermost, electrons, we discover elements with recurring chemical properties. This concept is known as *Periodicity*, or *Periodic Trends*.

#### Periodic Trends – Essential Knowledge 1.C.1.

There are other periodic trends besides chemical reactivity. The number and position of valence electrons determines the ionization energy (the energy required to remove an electron from an atom, or to *ionize* it into a +1 positive ion), the electron affinity (how attracted the element is to gaining another electron), atomic radius (the average radius of an atom, measured as half the distance between radii in a covalently bonded diatomic molecule), and metallic character (metals are solid and brittle, nonmetals are gaseous and pliable). The way these periodic trends play out are all neatly summarized in the image below:



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You'll have a Periodic Table on the AP Exam, and I've provided you with one here as well. The important thing is not to memorize *exact* examples, but rather to memorize *trends*. Now, let's review some practice questions about periodicity.

Which element has a larger electron affinity: Fluorine or Cesium?

Fluorine (atomic number 7) is considered to be the element with the largest electron affinity. Cesium, on the other hand, is considered the element with the *least* electron affinity. Therefore, *Fluorine* has the larger electron affinity.

Which element has a larger electron affinity: Iodine or Neon?

THIS IS A TRICK QUESTION. Although you may think that Neon would have a higher electron affinity because it is further up and right of Iodine, in fact Neon is one of the Noble Gasses. Noble Gasses are so-called because they <u>have full</u> <u>valence electron shells</u>. That means that they are <u>highly non-reactive</u>. It is in fact very tough to add or remove electrons from noble gases. Therefore, noble gases are less reactive than almost any other element.

Another note about Noble Gasses; when writing out the valence electrons for an element, let's say Manganese (Mn), you will often see this notation: [Ar]  $4s^2$   $3d^5$ . This notation is used to indicate that the element has the same electron configuration as Argon (Ar), PLUS seven electrons in the fourth shell. Argon, having a complete valence shell, has a complete electron configuration for the first three shells, or;  $1s^2$   $2s^2$   $2p^6$   $3s^2$   $3p^6$ . To save time writing these numbers out, chemists often write [Ar] to indicate those filled electron shells.







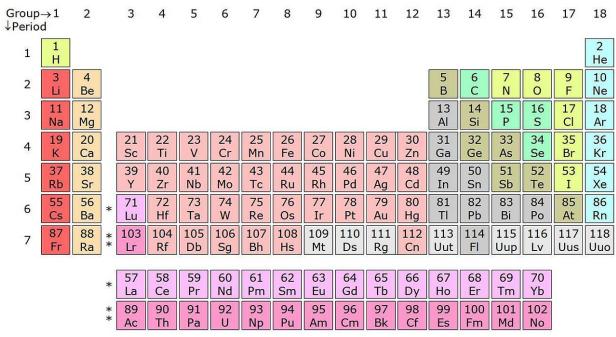


Image Source: Wikimedia Commons

With that discussion about periodicity and periodic trends, we are done! By now you should be fully prepared to answer any question on the Multiple Choice or Free Response sections of your AP Chemistry Exam. Studying chemistry is not an easy task. It requires hours of preparation and study, and we have to understand material from a broad range of disciplines such as Biology, Physics, and Mathematics to be good Chemists. However, you should realize that the most exciting discoveries in Pharmaceuticals, Medicine, Material Science, Space Flight, and more, are all possible due to chemists. Chemistry, after all, is the science of how all matter interacts with each other. And with the knowledge you have, you are prepared to enter an exciting world full of intrigue and discovery!

Did we miss anything? Do you have any questions about a topic we didn't cover? Write us and we will be glad to explain further!

Good luck on your exam!







## The Ultimate Guide to Stoichiometry

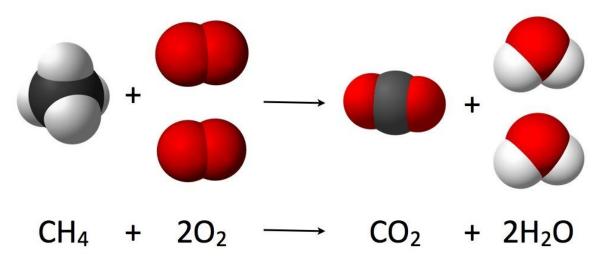


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Stoichiometry is the method of quantitatively relating the changes in substances undergoing a chemical reaction. This idea is present in almost every topic in AP Chemistry, so it is one of the most important areas to study for your exam. Stoichiometry appears to have many forms, but this guide will highlight the core elements of stoichiometry that can be used for solving any stoichiometry problem. To tackle this giant topic, we'll break this ultimate guide for AP Chemistry into five sections.







### The Ultimate Guide to Stoichiometry Cont.

#### **Section 1: Fundamentals of Stoichiometry**

#### **Balancing Equations**

Stoichiometry is based on knowing the quantitative relationships among changing reactants and products in a chemical reaction. This information is most commonly summarized as a balanced chemical equation. Frequently a balanced or unbalanced equation will be provided for you unless it is a reaction type you are required to know. Let's look at the (unbalanced) chemical equation for the combustion of methane,  $CH_{4}$ .

$$CH_4 + O_2 \rightarrow CO_2 + H_2O$$

This equation is unbalanced because there is not the same number of each element on both the reactant and product sides of the chemical equation. In order to perform stoichiometry, we need to balance this reaction. We won't go into great detail here, but remember that when balancing an equation, you are only allowed to change the coefficients in front of the chemical species. Changing subscripts or superscripts doesn't balance the reaction; it creates a different reaction. The balanced equation is given below.

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

This equation is balanced because there are the same number of each element on the reactant side and the product side. You can always check if an equation is balanced by counting all of the elements on each side.







### The Ultimate Guide to Stoichiometry Cont.

This balanced equation gives us the ratios of change for each reactant and product. In words, this particular equation tells us that for every one mole of  $CH_4$  that reacts:

- 2 moles of O<sub>2</sub> will also react
- 1 mole of CO<sub>2</sub> will be produced
- 2 moles of H<sub>2</sub>O will be produced

We use these ratios when doing stoichiometry problems.

#### Mole-to-mole stoichiometry

The simplest stoichiometry problem is going from moles of one chemical species in the balanced chemical equation to moles of another species in the same chemical equation. Let's take a quick look at a couple problems using the combustion of methane, and then we will discuss the general strategy for solving this problem. First, let's ask the question:

"How many moles of water are produced when 2 moles of methane combust?" From the ratios we outlined above, you may be able to determine that if every mole of  $CH_4$  produces two moles of  $H_2O$ , then two moles of  $CH_4$  produces four moles of  $H_2O$ .

Here's the direct calculation we would follow to get to the same answer, 4 moles of water:

$$2\ moles CH_4 imes rac{2\ moles H_2 O}{1\ mole CH_4} = 4\ moles H_2 O$$







Now let's look at another stoichiometry problem using the same balanced equation.

"When 6 moles of water are produced by combustion of methane, how many moles of carbon dioxide are also produced?"

Our mathematical equations will look very similar to the first problem.

$$6 \; molesH_2O imes rac{1 \, mole CO_2}{2 \, molesH_2O} = 3 \; molesCO_2$$

Notice that in each problem we start with the given information, and we multiply by a ratio in fractional form to obtain our answer. The major difficulty in stoichiometry is properly setting up these ratios. The easiest way to make sure the ratio is correct, is to think about each ratio as a step that converts units. Let's go over the last problem in more detailed steps. Actual stoichiometry problems won't need this level of breakdown, but it will help with understanding the fundamentals.

#### In-depth mole-to-mole stoichiometry

We know our starting information given in the last problem, 6 moles of water, and we know that the question is asking for moles of carbon dioxide as our answer. We still need to figure out the exact number of moles of carbon dioxide and what ratio will convert moles of water to moles of carbon dioxide. Let's start building the calculation we will use, and add to it step by step.

$$6 \ moles H_2O \times \frac{??}{??} = ?? \ moles CO_2$$







Now we have to figure out what to put in our ratio. We can think of our ratios as unit conversions with two steps: 1) canceling the old units and 2) replacing them with the new units. To remove old units, we want to multiply by their reciprocal. Let's look at a couple examples.

$$molesH_2O imes rac{1}{molesH_2O} = rac{molesH_2O}{molesH_2O} = 1; rac{1}{molesH_2O} imes molesH_2O = rac{molesH_2O}{molesH_2O} = 1$$

You can see in these examples that with proper setup, we can cancel out any units that we want. Specifically, to cancel a unit in the numerator, we multiply by a ratio with a copy of those units in the denominator. If the units we are removing are in the denominator, we instead multiply by a ratio with a copy of those units in the numerator. For our current problem, we are replacing moles of water in our numerator so we will need moles of water in the denominator of our ratio. Let's add that to our calculation.

$$6 \ moles H_2O imes rac{??}{?? \ moles H_2O} = ?? \ moles CO_2$$

The last step of our unit conversion is to transition to our new units. Luckily this step is pretty straightforward. If the old units were in the numerator, the new units will go in the numerator of the ratio. If the old units were in the denominator, the new units will go in the denominator of the ratio. Applying that to the current problem means that since the moles of water that we are replacing is in the numerator, moles of carbon dioxide should be in the numerator of this ratio.

6 
$$molesH_2O \times \frac{??\ molesCO_2}{??\ molesH_2O} = ??\ molesCO_2$$







If you cancel the moles of water on the left side of the equation, you will see that we have moles of carbon dioxide on each side of the equation. Keep in mind that for an equation to be true, both the numbers and the units need to be equivalent on both sides of the equation.

Our last step before just finishing up our arithmetic is deciding what numbers go into our ratio. These numbers will just be the coefficients of our balanced chemical equation.

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

There is a coefficient of one in front of carbon dioxide in the balanced chemical equation, so there will be a one in front of moles of  $CO_2$  in the ratio. These ones can, of course, be omitted since they are being used in multiplication or division. As for water, there is a coefficient of two in front of water in the balanced chemical equation, so there will be a two in front of moles of  $H_2O$  in the ratio. This ratio is mathematically equivalent to saying that one mole of  $CO_2$  is produced per every two moles of water that are produced. This is the same as our earlier verbal statements about these ratios, so we have successfully translated these ideas into mathematics. Putting in these numbers completes our equation for this problem

$$6 \ moles H_2O imes rac{1 \ mole CO_2}{2 \ moles H_3O} = 3 \ moles CO_2$$

As we will see in the following sections, stoichiometry problems never need to be broken down this much, but knowing the process at this level makes it easier to apply stoichiometry to any problem and to properly set up the ratios.







#### **Section 2: Common Unit Conversions in Stoichiometry Problems**

The mole-to-mole problem is at the core of all stoichiometry problems. Anything else that you encounter in stoichiometry problems will just be different types of unit conversions added before or after the mole-to-mole problem. For stoichiometry problems you will generally:

- 1. Convert to moles using the given information
- 2. Perform mole-to-mole stoichiometry
- 3. Convert to the units requested by the question

Various stoichiometry problems can seem completely different, but it is always this same core using different ratios. As we go through problems in the following sections try to recognize the core process repeated in each problem.

#### Mass conversions in stoichiometry

Converting to and from mass is the most common conversion in stoichiometry. Atoms and molecules are too small to count by convenient methods, so we generally rely on mass measurements to quantify how much of a chemical we have. Let's keep using our combustion reaction and work through another example.

How many grams of water is produced when 5 g of methane combust?

Following our general game plan, we will first convert to moles of methane, then use mole-to-mole stoichiometry to get to moles of water, then convert to grams of water.

The first step is converting from grams of methane to moles of methane. We are going to use another ratio to accomplish this.







Using the method from the first section, we know that we want to cancel grams of methane (which is in the numerator of the given) by putting grams of methane in the denominator of our ratio. To transition to moles of methane, we will put moles of methane in the numerator of our ratio.

$$5g\ CH_4 imes rac{??\ molCH_4}{??g\ CH_4} = ??g\ CH_4$$

To find the numbers to use in our ratio, we're going to use the **molar mass**. The molar mass is the mass of one mole of a chemical species. We find this value by adding together the atomic masses (found on the periodic table) of each atom in the chemical species. Methane has 1 carbon, with a molar mass of 12.011 g/mol, and 4 hydrogen atoms, each with a molar mass of 1.008 g/mol. The molar mass of methane is 16.042 g/mol.

$$1 \times 12.01 \frac{q}{mol} + 4 \times 1.008 \frac{q}{mol} = 16.042 \frac{q}{mol} CH_4 = \frac{16.042q}{1mol} CH_4$$

This ratio tells us that 16.042 goes in front of grams in our ratio and 1 goes in front of moles in our ratio. Going through the math yields 0.312 moles of  $CH_4$ .

$$5g~CH_4 imes rac{1molCH_4}{16.042g~CH_4} = 0.312mol~CH_4$$

The next step is the mole-to-mole stoichiometry problem that we've done before.

$$0.312mol\ CH_4 imes rac{2\ mol\ H_2O}{1\ mol\ CH_4} = 0.624mol\ H_2O$$







Our last step is to convert from moles of water to grams of water.

$$0.624mol\ H_2O imes rac{18.02g\ H_2O}{mol\ H_2O} = 11.24g\ H_2O$$

Notice that we cancel moles of water by placing moles of water in the denominator of our ratio and then we transition to grams by putting grams of water in the numerator of our ratio. The numerical values come from the molar mass of water, 18.02 g/mol.

The full equation can be computed all at once:

$$5g~CH_4 imes rac{1molCH_4}{16.042g~CH_4} imes rac{2~molesH_2O}{1~molesCH_4} imes rac{18.02g~H_2O}{molH_2O} = 11.23gH_2O$$

The slight difference in answer comes from rounding errors. When possible, perform all of your math calculations at once, like the last step. You might be wondering if an alternate explanation would be easier:

- 1. Divide grams of methane by molar mass to get moles
- 2. Use the balanced chemical equation to convert to moles of water
- 3. Multiply by molar mass.

These steps work for this particular problem, but you will need to alter this list for every variation of stoichiometry problem. As you encounter more types of stoichiometry, keeping track of each individual procedure will become overwhelming. In the long run, thinking of steps in terms of what you want to accomplish (converting to moles, converting to grams) instead of exactly what you are doing mathematically (dividing by molar mass, multiplying by molar mass) will save you a lot of memorization and deepen your understanding of chemistry.







#### Atoms and molecules in stoichiometry problems

Being able to relate macroscopic properties such as mass to microscopic properties such as the number of atoms or molecules is a fundamental goal of AP Chemistry. The practical relevance of these ideas is also increasing as scientists develop more precise control and understanding of chemical processes.

How many gold atoms can be produced by the reduction of 5 grams of tetrachloroaurate ( $AuCl_4^-$ ) by citrate ( $C_6H_5O_7^{3-}$ ) ions?

$$2AuCl_4^-(aq) + C_6H_5O_7^{3-}(aq) + 2H_2O(l) \longrightarrow 2Au(s)$$

$$+3CH_2O(aq)+3CO_2(g)+8Cl^-(aq)+3H^+(aq)$$

The first step to this problem for this problem is not panicking when you see unfamiliar words in a chemistry problem. No one expects you to know every compound and reaction in existence. You will be given the chemical formulas and chemical equations for uncommon reactions, which is all you need for stoichiometry. As normal, we will first convert to moles of the given, then perform mole-to-mole stoichiometry.

$$5g\ AuCl_4^-(aq) imes rac{1mol\ AuCl_4^-(aq)}{338.779g\ AuCl_4^-(aq)} imes rac{2mol\ Au(s)}{2mol\ AuCl_4^-(aq)} = 0.0148mol\ Au(s)$$

Now we need to convert from moles of gold to atoms of gold. By focusing on the units we need to convert, we know that we need to have moles of gold in the denominator of our next ratio and molecules in the numerator of the ratio.

$$0.0148mol~Au(s) imes rac{??~molecules~of~Au}{??mol~Au} = ???molecules~of~Au$$







To find the numerical values, we use **Avogadro's number**. In the same way that "couple" is a word for two and "dozen" is a word for twelve, Avogadro's number is a way of saying  $6.02 \times 10^{23}$ . More importantly for stoichiometry,  $6.02 \times 10^{23}$  molecules equal one mole of molecules. In other words, the ratio of molecules to moles is  $6.02 \times 10^{23}$  molecules/ mole. We can now plug these numbers into our equation and finish the problem.

$$0.0148mol~Au(s) imes rac{6.022 imes 10^{23} molecules~of~Au}{1mol~Au} = 8.91 imes 10^{21} atoms~of~Au$$

Written at once, our equation is:

Knowing the exact number of atoms and molecules is very important for fields such as nanoscience, so be sure not to think of these calculations as just busy work for AP Chemistry!

#### **Volume in stoichiometry problems**

There are generally three ways that volume appears in stoichiometry problems: density, molarity, and gas laws. We'll tackle gas laws in the next section, but let's work on density and molarity now.

How many milliliters of aluminum metal can be produced by the electrolysis of 18 grams of aluminum oxide? The density of aluminum is  $2.70 \text{ g/cm}^3$ ?







First we need the balanced chemical equation for the reaction.

$$2Al_2O_3 \rightarrow 4Al + 3O_2$$

Next we convert from the units of the given to moles, and then do mole-to-mole stoichiometry.

$$18g~Al_2O_3 \times \frac{1mol~Al_2O_3}{101.96gAl_2O_3} \times \frac{4mol~Al}{2mol~Al_2O_3} = 0.353mol~Al$$

Our last step of converting from moles to the units requested by the question is a little more difficult in this problem. If we had a ratio that related moles and volume directly, we could finish this problem in one step. You might be familiar with molarity (mol/L), but molarity values are usually not readily available for solids. So how do we solve this problem? Notice that the density gives us a ratio that allows us to convert from grams to cubic centimeters (which are equivalent to millimeters) and vice versa. This means that if we can convert to grams, we can use the density to convert from grams to milliliters (cubic centimeters). Luckily, we already know how to convert to mass.

$$0.353mole\ Al imes rac{26.98g\ Al}{1moles\ Al} = 9.52g\ Al$$

Our last step is to use density to finish the problem.

$$9.52g~Al imes rac{1cm^3Al}{2.70gmolesAl} = 3.53cm^3 = 3.53mL$$

The overall equation for this problem is:

$$18gAl_2O_3 imes rac{1molesAl_2O_3}{101.96gAl_2O_3} imes rac{4molesAl}{2molesAl_2O_3} imes rac{26.98gAl}{1molesAl} imes rac{1cm^3Al}{2.70g\,Al} = 3.53cm^3 = 3.53mL\,Al$$







Multiple step conversions come up frequently in more complex problems, and we will see a few more in this guide. Remember that it will just be standard stoichiometry with a step or two before or after.

How many grams of lead (II) chloride forms when 50 mL of 0.35 M lead (II) nitrate reacts completely with excess sodium chloride?

The equation for this reaction is given below.

$$Pb(NO_3)_2(aq) + 2NaCl(aq) \rightarrow PbCl_2(s) + 2NaNO_3(aq)$$

This problem measures the lead (II) chloride using concentration and volume. Molarity (M) is the number of moles per liter of substance (mol/L). While it can technically be used to describe any chemical, it most commonly describes a chemical species dissolved in solution. The first step of this stoichiometry problem, getting to moles of the given, is slightly different than what we've done before. To convert mol/L to moles, we only need to cancel out the liters. Since liters are in the denominator, we will just have liters in the numerator of our ratio. Let's convert the volume given to liters and use this in our ratio.

$$\frac{0.35mol\ Pb(NO_3)_2}{Lsolution} \times 0.050 Lsolution = 0.0175mol\ Pb(NO_3)_2$$

Now that we have moles of lead (II) nitrate, converting to grams of lead (II) chloride is business as usual.

$$0.0175mol\ Pb(NO_3)_2 imes rac{1mol\ PbCl_2}{1mol\ Pb(NO_3)_2} imes rac{278.1g\ PbCl_2}{1moles\ PbCl_2} = 4.87g\ PbCl_2$$

Written out fully

$$\frac{0.35mol\ Pb(NO_3)_2}{Lsolution}\times 0.050L\ solution \times \frac{1mol\ PbCl_2}{1\ moles\ Pb(NO_3)_2} \times \frac{278.1q\ PbCl_2}{1mol\ PbCl_2} = 4.87g\ PbCl_2$$







#### **Section 3: General Problem Types in Stoichiometry**

Stoichiometry is used whenever you need quantitative relationships between different chemicals in the same chemical reaction. There are a few application or problem types that you will need for your AP Chemistry Exam. Because these types of problem are so general, you could encounter them for any type of reaction.

#### **Simple Titrations**

Titrations are used to measure the quantity of a chemical in a sample by taking advantage of the stoichiometry of known reactions. <u>Acid-base</u> titrations are among the most common, so let's use one as an example.

50 mL of 1M solution of sodium hydroxide was necessary to titrate a 100 mL sample of hydrochloric acid. What was the molarity of the hydrochloric acid sample?

In this example we have used an acid-base neutralization reaction to measure the hydrochloric acid. Here's the chemical equation.

$$HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l)$$

In real experiments an indicator is used that will let us know when all of the chemical to be measured is gone. For this neutralization reaction, we would probably use a dye called phenolphthalein, which in this case will change color when all of the hydrochloric acid has reacted. You can look into acid-base chemistry and titrations for more exact details, but for this problem we just need to know that 50 mL of 1M NaOH is needed to fully react with all of the hydrochloric acid in our sample.







Let's use stoichiometry to calculate how much hydrochloric acid was present.

$$50mL imes rac{L}{1000mL} imes rac{1mol\ NaOH}{L} imes rac{1mol\ HCl}{1mol\ NaOH} = 0.05mol\ HCl$$

Since the question asks for a concentration with units of molarity, we need to divide by the volume of our sample.

$$0.05mol~HCl imes rac{1}{100mL} imes rac{1000mL}{1L} = 0.5M~HCl$$

Remember that molarity is defined as moles per liter, so we must convert the volume from milliliters to liters.

One equation that you may see in discussions of acid-base titrations is  $M_AV_A=M_BV_B$  where A stands for acid and B stands for base. This equation may seem simpler, but keep in mind that it only works when the ratio of the chemicals being compared is 1:1. You always need to understand the balanced chemical equation to perform titration calculations. We can use part of a 2002 AP Chemistry free response question to illustrate this point.

Calculate the volume of 0.115 M Ba(OH)<sub>2</sub>(aq) needed to reach the equivalence point when titrated into a 65.0 mL sample of 0.146M HOBr(aq).

$$2HOBr(aq) + Ba(OH)_2(aq) \longrightarrow Ba(BrO)_2(aq) + 2H_2O(l)$$

Using the balanced chemical equation, we can perform a standard stoichiometry calculation. We first convert to moles of the given, then we do mole-to-mole stoichiometry, and we end by converting to the units specified by the problem.

$$0.0650L\ HOBr(aq)solution imes rac{0.146mol\ HOBr(aq)}{1L\ HOBr(aq)solution} imes rac{1mol\ Ba(OH)_2(aq)}{2mol\ HOBr(aq)} imes rac{1L\ HOBr(aq)}{0.115mol\ HOBr(aq)} \ = 0.0413L\ HOBr(aq)$$







Using  $M_AV_A=M_BV_B$  will produce an answer that is off by a factor of two. It is possible to modify this equation based on the chemical coefficients in the balanced chemical equation, but it is much easier to simply reuse the stoichiometry skills that you have to learn anyway.

Titrations are not limited to acid-base reactions, so don't get confused if you see electrochemical or other titrations on your exam. As long as you have a balanced chemical equation, these titrations are straightforward stoichiometry problems from the standpoint of calculations. You will learn more detailed analysis of titrations in the <u>acid-base</u> section of your AP Chemistry course, but keep in mind that is an extension of the ideas covered here, not a replacement.

#### **Limiting Reagent**

Our previous examples have been nice because there was only one starting point given in the problem. But what would we do if there were more than one given? Let's think about this with another stoichiometry problem.

How much copper (II) sulfate can be produced when 12g of copper (II) nitrate is mixed with 15g of sodium sulfate?

As always, we first need a balanced chemical equation.

$$Cu(NO_3)_2 + Na_2SO_4 \longrightarrow CuSO_4 + 2NaNO_3$$

Let's first try performing our standard stoichiometry calculations with each given separately. We will first get to moles of our given, perform mole-to-mole stoichiometry, and then convert to the units requested.

$$\begin{array}{c} 12g \ Cu(NO_3)_2 \times \frac{1mol \ Cu(NO_3)_2}{187.86g \ Cu(NO_3)_2} \times \frac{1mol \ CuSO_4}{1mol \ Cu(NO_3)_2} \times \frac{159.61g \ CuSO_4}{1mol \ CuSO_4} = 10.20g \ CuSO_4 \\ 15g \ Na_2SO_4 \times \frac{1mol \ Na_2SO_4}{142.04g \ Na_2SO_4} \times \frac{1mol \ CuSO_4}{1mol \ Na_2SO_4} \times \frac{159.61g \ CuSO_4}{1mol \ CuSO_4} = 16.86g \ CuSO_4 \end{array}$$







Notice that these two calculations predict different amounts of product. This happens because they are each assuming that all of the given reactants are able to react. This would only occur if the molar ratio of the reactants present is equal to the molar ratios summarized by the balanced chemical equation, which is rarely the case in real-world use. Let's see how much of each reactant we need for the amounts used in the calculations above.

$$12g \ Cu(NO_3)_2 \times \tfrac{1 mol \ Cu(NO_3)_2}{187.86g \ Cu(NO_3)_2} \times \tfrac{1 mol \ Na_2SO_4}{1 mol \ Cu(NO_3)_2} \times \tfrac{142.04g \ Na_2SO_4}{1 mol \ Na_2SO_4} = 9.07g \ Na_2SO_4$$

$$15g\ Na_2SO_4 \times \tfrac{1mol\ Na_2SO_4}{142.04g\ Na_2SO_4} \times \tfrac{1mol\ Cu(NO_3)_2}{1mol\ Na_2SO_4} \times \tfrac{187.86g\ Cu(NO_3)_2}{1mol\ Cu(NO_3)_2} = 19.84g\ Cu(NO_3)_2$$

Now we can see what the issue is. To react all of the sodium sulfate we would need 19.84 g of copper nitrate, but we only have 12 grams. This means that as the reaction progresses, we will run out of copper nitrate before all of the sodium sulfate can react. Likewise, we can see in the first equation that we only need 9.07g of sodium sulfate to react all of the copper nitrate, and the 15 grams that we have is more than enough.

Both of these calculations tell us the same thing: as the reaction progresses, we will run out of copper nitrate before all of the sodium sulfate can react. Because the (relatively) low amount of copper nitrate is limiting how much sodium sulfate can react, we refer to the copper nitrate as the **limiting reagent** in this reaction. Now that we know that copper nitrate determines how much reaction can occur, we also know that copper nitrate is the given we should start with in this problem to get our final answer of 10.20g copper sulfate.

This was a lot of work for one question, but luckily there is a faster way to do limiting reagent problems: compare the number of moles for each of your reactants to moles

$$12g\ Cu(NO_3)_2 imes rac{1mol\ Cu(NO_3)_2}{187.86g\ Cu(NO_3)_2} = 0.0639mol\ Cu(NO_3)_2 \quad 15g\ Na_2SO_4 imes rac{1mol\ Na_2SO_4}{142.04g\ Na_2SO_4}$$







$$= 0.106mol\ Na_2SO_4$$

Remember that our chemical equation tells us that copper nitrate and sodium sulfate react at a 1:1 ratio. We can more clearly see from here that there are not enough moles of copper nitrate to react with the moles of sodium sulfate. But what would happen if the ratio was not 1:1? All we have to do is divide the number of moles by the coefficient from the balanced chemical equation. Let's see this in practice.

How many grams of hydrogen gas is released when 7 grams of magnesium metal reacts with 15g of phosphoric acid?

$$3Mg + 2H_3PO_4 \longrightarrow Mg_3(PO_4)_2 + 3H_2$$

We first need to find our limiting reagent. For each of our reactants, we will convert to moles and then divide the number of moles by the coefficient in the balanced chemical equation.

$$7g\,Mg imes rac{1mol\,Mg}{24.305Mg} = 0.288molMg \Rightarrow rac{0.288molMg}{3} = 0.0960$$

$$15g~H_3PO_4 imes rac{1mol~Mg}{98H_3PO_4} = 0.153mol~H_3PO_4 \Rightarrow rac{0.102mol~H_3PO_4}{2} = 0.0765$$

Since the moles divided by the chemical coefficient is smaller for phosphoric acid, that will be our limiting reagent. It can be difficult to guess or use mental math to find these answer, so be sure to practice this step so it is easy for your AP Chemistry exam. Since phosphoric acid is our limiting reagent, we will use that for our normal stoichiometry problem.

$$15g~H_3PO_4 imes rac{1mol~H_3PO_4}{98H_3PO_4} imes rac{3mol~H_2}{2mol~H_3PO_4} imes rac{2.016g~H_2}{1mol~H_2} = 0.463g~H_2$$







A related question that you may see on your AP exam asks how much of each chemical is present once the reaction goes to completion. We already know that there will be no phosphoric acid remaining because it is our limiting reagent, and we just calculated how much hydrogen gas would be produced. We find the amount of magnesium phosphate in the same way we calculated the mass of hydrogen gas.

$$15g~H_3PO_4 \times \tfrac{1mol~H_3PO_4}{98H_3PO_4} \times \tfrac{1mol~Mg_3(PO_4)_2}{2mol~H_3PO_4} \times \tfrac{262.85g~Mg_3(PO_4)_2}{1mol~Mg_3(PO_4)_2} = 20.12g~Mg_3(PO_4)_2$$

Calculating the excess magnesium is not complex, but it will take one extra step after stoichiometry. As with anything else, the amount in excess (the amount leftover) is equal to the original amount minus how much has been reacted. We use normal stoichiometry to calculate how much magnesium has been used.

$$15g~H_3PO_4 \times \frac{1mol~H_3PO_4}{98H_3PO_4} \times \frac{3mol~Mq}{2mol~H_3PO_4} \times \frac{24.305q~Mg}{1moleMg} = 5.58g~Mg~used$$
 
$$7gMg_{original} - 5.58gMg_{used} = 1.42gMg_{excess}$$

We can now report that there will be 0g of phosphoric acid, 1.42g of magnesium, 0.436g of hydrogen gas, and 20.12g of magnesium phosphate.

#### **Percent Yield**

Another common application of stoichiometry is calculating percent yield. This allows us to know how much of a reaction has actually occurred. This is used in research and industry for determining the efficiency of chemical reactions. The equation for percent yield is:

$$\%yield = rac{actual\ yield}{theoretical\ yield} imes 100$$







This quantity tells what percentage of the total possible reaction has occurred. When percent yield is less than 100% it means that the reaction has produced less than is physically possible. This usually occurs because real reactions are subject to chemical equilibrium, which generally maintains a certain balance between reactants and products. In other cases, the reaction could still be in progress but is so slow that it appears to have stopped.

When percent yield is greater than 100%, it implies that more has been produced than is physically possible. This happens when there are additional unknown chemicals that are being measured along with the products. Common additional chemicals include solvents used during the reaction and products from unexpected side reaction. Let's try a percent yield problem.

What is the percent yield of the reaction above when 10g of iron(III) nitrate and 10g of sodium hydroxide react to form 3g of iron (III) hydroxide?

$$Fe(NO_3)_3 + 3NaOH \longrightarrow Fe(OH)_3 + 3NaNO_3$$

We will need to first find our actual and theoretical yields to find the percent yield. The actual yield is the actual amount produced. The question tells us that 3g of iron (III) hydroxide is produced, so our actual yield is 3g of iron(III) hydroxide. We now have to figure out the theoretical yield of iron(III) hydroxide, which is how much is predicted by stoichiometry. Our first step is to convert to moles of our given. In this case we have two givens, so we have to find our limiting reagent. We do this by converting to moles and dividing by the chemical coefficient from the balanced chemical equation.

$$\begin{array}{c} 10g\ Fe(NO_3)_3 \times \frac{1mol\ Fe(NO_3)_3}{241.86g\ Fe(NO_3)_3} = 0.0413mol\ Fe(NO_3)_3 \Rightarrow \frac{0.0413mol\ Fe(NO_3)_3}{1} = 0.0413 \\ \\ 10g\ NaOH \times \frac{1mol\ NaOH}{39.997g\ NaOH} = 0.250mol\ NaOH \Rightarrow \frac{0.250mol\ NaOH}{3} = 0.0833 \end{array}$$







We can now see that iron(III) nitrate is our limiting reagent because its moles divided by its coefficient is lower than the corresponding value for sodium hydroxide. Most percent yield problems do not require understanding the concept of limiting reagents, but it was necessary in this case to find the theoretical yield. Now we do normal stoichiometry with iron(III) nitrate.

$$10g\ Fe(NO_3)_3 \times \tfrac{1mol\ Fe(NO_3)_3}{241.86g\ Fe(NO_3)_3} \times \tfrac{1mol\ Fe(OH)_3}{1mol\ Fe(NO_3)_3} \times \tfrac{106.867g\ Fe(OH)_3}{1mol\ Fe(OH)_3} = 4.42g\ Fe(OH)_3$$

Now we can use our theoretical yield (4.4.19g) and our actual yield (3g) to calculate the percent yield.

$$\%yield = \frac{3g \, Fe(OH)_3}{4.42g \, Fe(OH)_3} \times 100 = 67.87\%$$

Of course, the answer can also be recorded as 0.6787 (without the % sign). You may come across questions that ask for different parts of the percent yield equation (actual yield and theoretical yield in addition to percent yield). The algebra might be a bit different, but you will always use stoichiometry to figure out the theoretical yield.

#### **Section 4: Application of Stoichiometry to Gasses**

While gasses certainly possess mass, the most convenient ways to measure gasses are by using pressure and volume. We can relate these quantities to moles using the ideal gas law, PV=nRTPV=nRT. Let's see this in action.

If 10mL of 0.5M HCl reacts completely with Na $_2$ CO $_3$ , what volume of carbon dioxide will be released? Assume that the temperature is 25  $^\circ$  C and pressure is 1 atm.







Our balanced chemical equation for this reaction is as follows.

$$Na_2CO_3(aq) + 2HCl(aq) \rightarrow 2NaCl(aq) + H_2O(l) + CO_2(g)$$

First we will convert to moles of our given, and then use mole-to-mole stoichiometry to convert to moles for the desired chemical answer. As we went over in our last problem, we can simply multiply by the volume by the molarity to get the moles for our given.

$$rac{0.5mol\ HCl}{L\ solution} imes 0.050L\ solution imes rac{1mol\ CO_2}{2mol\ HCl} = 0.0125mol\ CO_2$$

Now that we have moles of carbon dioxide, we can use it with the other information given in the problem to calculate the volume of carbon dioxide released.

$$PV=nRT\Rightarrow V=rac{nRT}{P}=rac{0.0125mol\ CO_2 imes 0.0821rac{Latm}{molK} imes 298K}{1atm}=0.306L\ CO_2$$

Remember that when you use the ideal gas law, you must choose the version of the ideal gas constant, R, that matches the units for the pressure, and you must convert temperature to Kelvin units. Let's try a problem with a different reaction.

If the pressure in a sealed 2L flask of pure  $N_2O_4$  is 0.6atm at 30  $^{\circ}$  C, what will the pressure be once all of the  $N_2O_4$ decomposes to  $NO_2$ ? Assume that the temperature remains constant.

$$N_2O_4(g) o 2NO_2(g)$$

Your first instinct might be to use the ideal gas law to convert to moles and to then perform mole-to-mole stoichiometry, but in this case that step is not actually necessary.







Let's see why.

$$0.6atm~N_2O_4 imes rac{2L}{0.0821rac{L~atm}{mol\,K} imes 298K}=0.049mol~N_2O_4$$

$$0.049mol~N_2O_4 \times \frac{2mol~NO_2}{1mol~N_2O_4} = 0.098mol~NO_2$$

$$0.098mol~NO_2 \times \frac{0.0821\frac{Latm}{mol K} \times 298K}{2L} = 1.2atm~NO_2$$

Notice that we multiply by V and divide by RT in the first step, but in the third step we multiply by RT and divide by V! Mathematically, we could get the same answer by ignoring the pressure-mole conversions entirely. This is because moles are directly proportional to pressure so long as the volume and temperature remain constant. When volume and temperature are constant, you can perform pressure-to-pressure stoichiometry using the coefficients of the balanced chemical equation in the same way we do mole-to-mole stoichiometry.

$$0.6atm~P_{N_2O_4} imes rac{2atm~NO_2}{1atm~N_2O_4}=1.2atm~NO_2$$

We get the same answer with a lot less math. Keeping this in mind for you AP exam could save you valuable time. Just remember this only works when pressure and moles are the only changing quantities in the <u>ideal gas law</u>. Temperature and volume must be constant.

#### Partial pressures in stoichiometry problems

There is one more property of gasses that the CollegeBoard loves to use with stoichiometry. That is the relationship between total pressure of a mixture of gasses, and the partial pressure of each individual gas.

$$P_{total} = P_A + P_B + P_C \dots$$







This equation tells us if we ever want to know the total pressure of gasses, all we have to do is add up all of the individual gas pressures. Let's use a question similar to the last one with a different chemical equation to illustrate this point

If the pressure in a sealed 2L flask of pure  $N_2O_5$  is 0.6atm at 45  $^\circ$  C, what will the pressure be once all of the  $NH_3$  decomposes to nitrogen dioxide gas and oxygen gas? Assume that the temperature remains constant.

$$2N_2O_5(g) 
ightarrow 4NO_2(g) + O_2$$

As we just learned, we do not need to switch to moles because we are dealing with all **gasses** and the temperature and volume are not changing. The thing to remember with this problem is that the total pressure is the sum of the partial pressures of each gas. We could do two stoichiometry problems to figure out the partial pressures of both products, and then add them together.

$$0.6atm \ N_2O_5 imes rac{4atm \ NO_2}{2atm \ N_2O_5} = 1.2atm \ NO_2$$

$$0.6atm~N_2O_5 imes rac{1atm~O_2}{2atm~N_2O_5}=0.3atm~O_2$$

$$1.2atm\ NO_2 + 0.3atm\ O_2 = 1.5atm\ total\ pressure$$

A slightly faster method is to convert directly from pressure of the reactions to pressure of the combined products.

$$0.6atm~N_2O_5 imes rac{5atm~products}{2atm~N_2O_5} = 1.5atm~products$$

Either method works fine, so use whichever makes you more comfortable.







Let's look at a more complicated version of the same question.

If the pressure in a sealed 2L flask of pure  $N_2O_5$  is 0.6atm at 45  $^{\circ}$  C, what will the pressure be once half of the NH<sub>3</sub>decomposes to nitrogen dioxide gas and oxygen gas? Assume that the temperature remains constant.

The only difference here is that there will be remaining reactant that we have to consider for our answer. First, let's find the pressure of our products for this problem.

$$0.3atm~N_2O_5 imes rac{5atm~products}{2atm~N_2O_5} = 0.75atm~products$$

Remember that stoichiometry deals with the amount of chemicals **that undergo reaction**. Since only half of the  $N_2O_5$  is reacting, we only used half of it in our calculation. Now that we have the combined pressures of our products, we must find the pressure of our remaining reactants. Since half of our  $N_2O_5$  is remaining, it will contribute 0.3atm to the total pressure.

 $0.3atm\ NO_2 + 0.75atm\ products\ =\ 1.05atm\ total\ pressure$ 

#### **Section 5: Stoichiometry Beyond Atoms and Molecules**

#### **<u>Electrochemistry</u>** in stoichiometry problems

When dealing with <u>electrochemical (redox) reactions</u>, keeping track of electrons can be just as important as keeping track of whole atoms and molecules. Take the following reaction.

$$2Al + 3Cu^{2+} \longrightarrow 2Al^{3+} + 3Cu$$







Here, Al metal is being oxidized by Cu<sup>2+</sup> ions in solution. We can of course use normal stoichiometry to answer questions such as "How many grams of copper can be produced by the oxidation of 5g of aluminum?" By converting to moles of given, doing mole-to-mole stoichiometry and then converting to the desired units of the question. But what if the question asks about charge? Charge is important when determining current in batteries and electrolytic cells, so this conversion is well worth knowing.

How much charge is transferred when 5g of aluminum are transferred?

One way to do this is to break this equation into its two half reactions.

$$Al \longrightarrow Al^{3+} + 3e^{-}$$

$$2e^- + Cu^{2+} \longrightarrow Cu$$

These two reactions show the relationship between electrons transferred and other members of the chemical reaction. The first half reaction shows aluminum metal losing electrons (being oxidized), and the second half reaction shows copper ions gaining electrons (being reduced. The electrons function in the balanced half-reaction in the same way as the chemical species. The top reaction tells us that for every mole of aluminum metal that is oxidized, one mole of Al<sup>3+</sup> is produced and 3 moles of electrons are released. The bottom reaction tells us that every mole of Cu<sup>2+</sup> that is reduced requires 2 moles of electrons and produces one mole of copper metal.

Producing the half reactions for yourself is beyond the scope of the AP Chemistry exam, but they can be found in published tables. These will often be provided on your exam, but if not you can also use oxidation states to figure out the necessary ratios between electrons and other members of the balanced chemical reaction. In this case we are changing from Al to Al<sup>3+</sup> and from Cu<sup>2+</sup> to Cu.







The difference in oxidation state for the aluminum species is three units and the difference for copper is two units. Each electron carries one unit of negative charge, which corresponds to ratios of 3 moles of electrons per mole of aluminum reacted and 2 moles of electrons per mole of copper reacted. This gives the same ratios that we found from our half-reactions. Using either method, we now ratios we can use in mole-to-mole stoichiometry.

Like atoms and molecules, electrons are usually too small and numerous to conveniently count. Instead, we tend to rely on the charge of electrons which can be measured more easily and is often of greater interest. One of the numerical constants on your AP Chemistry <u>equation sheet</u> is Faraday's constant, F, which is equal to 96,485 coulombs per mole of electrons

$$(F = 96485 \frac{C}{mole^-}).$$

We can use this value to convert between moles of electron and charge.

$$5g~Al imes rac{1mol~Al}{26.98g~Al} imes rac{3mol~e^-}{1mol~Al} imes rac{96485C}{1mole^-} = 53642C$$

The first step converts to moles of our given, the second step uses mole-to-mole stoichiometry with electrons, and the last step uses Faraday's constant to convert from moles of electrons to coulombs.

Frequently, instead of working with charge directly, you will perform calculations with current. Current measures how much charge moves through a given region per unit time. The SI unit of current is the ampere (abbreviated by A and usually shortened to "amp") which is a coulomb per second. This unit allow us to convert between charge and time.

How long does it take to produce 10g of aluminum metal by the electrolysis of aluminum oxide if a 30A current is used?







This problem sometimes confuses students because there is an additional math step, but the process of stoichiometry is the same. We will first convert to moles of the given, use mole-to-mole stoichiometry, and then convert to the units requested by the questions.

$$10g~Al imes rac{1mol~Al}{26.98g~Al} imes rac{3mol~e^-}{1mol~Al} imes rac{96485C}{1mol~e^-} imes rac{1s}{30C} = 3576s$$

This problem was actually very similar to our last problem; we just needed to add an extra step to convert to time. Keep in mind that this is often the case with stoichiometry. No matter how complex a stoichiometry problem appears, its core is as simple as any stoichiometry problem you have ever done.

#### Thermochemistry in stoichiometry problems

Most reactions absorb or release some amount of energy as heat as they occur. This heat is proportional to how much reaction has taken place, so it can be related to the amount of reacting chemicals by slightly modifying our stoichiometry. Let's use the combustion of ethanol as an example.

$$C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O \quad \Delta H_{combustion} = -1370.7kJ/mol$$

This time we've included the change in enthalpy for this combustion reaction. Under conditions of constant pressure, enthalpy changes are equal to the heat absorbed or emitted by a reaction or process. There are other properties of enthalpy, but this is the most important one for stoichiometry. The negative sign for the change in enthalpy tells us that heat is being released by this reaction. This means we can rewrite this equation in the following way.

$$C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O + 1370.7kJ$$







In words, this equation tells us that for every 1 mole of ethanol that reacts:

- 3 moles of oxygen also react
- 2 moles of carbon dioxide are produced
- 3 moles of water are produced
- 1370.7kJ of energy is released

Notice that these statements describe ratios that relate the amount of energy released to the amount of reactants consumed or products produced. We can now perform heat-to-mole or mole-to-heat stoichiometry in the same way we perform mole-to-mole stoichiometry. We moved the enthalpy information into the product side of reaction and omitted the negative sign and "/mol". As we work through a problem, we will see why that information is now redundant.

How much heat will be absorbed or released when 20 grams of oxygen are used to combust excess ethanol?

As normal, we will convert to moles of our given and then perform stoichiometry. Since the heat produced is now part of our stoichiometry ratios, we can perform mole-to-heat stoichiometry in the same way as mole-to-mole stoichiometry.

$$20g~O_2 \times \frac{1mol~O_2}{15.999g~O_2} \times \frac{1370.7kJ~released}{1mol~O_2} = 1713.5kJ~released$$

There are a few things to remember here. First, the sign for enthalpy tells us if the reaction absorbs or releases heat. Positive means the reaction is endothermic and absorbs heat. Negative means the reaction is exothermic and releases heat. When we write enthalpy within the chemical reaction, we write the heat on the product side if the reaction is exothermic, and we write the heat on the reactant side if the reaction is endothermic. Since the placement on the product or reactant side communicates endothermic or exothermic, it is unnecessary (and incorrect) to include negative signs within the balanced chemical reaction.







The other thing to remember, is that changes in enthalpy are written for the exact chemical equation that was written. If we doubled all of our coefficients for example, we would also need to double our values for enthalpy.

$$2C_2H_5OH + 6O_2 \rightarrow 4CO_2 + 6H_2O + 2741.4kJ$$

How many grams of ethanol are required to heat 100g of water 30 degrees C? The specific heat of water is 4.184 J/mol K

The other major type of thermochemical stoichiometry problem involves specific heat and temperature change. Here, we are trying to relate heat produced by a chemical reaction with the amount of chemicals in that reaction. In this problem we need to calculate the heat needed produce the temperature change, perform heat-to-mole stoichiometry, and then convert to the units specified by the question. The amount of heat that must be transferred to produce a given temperature change can be calculated with the following equation:

$$q = mc\Delta T$$

Since the water is undergoing the temperature change, we will use water-specific values for the variables in this equation.

$$q = 100g \times 4.184 rac{J}{gK} \times 30K = 12552J$$

Units of  ${}^{\circ}$ C are the same size as kelvins, so we can use either for  $\Delta T$ . (This is the only case where this works, so make sure to convert to K for other types of problems!) Also notice that we just used the mass of water given in the problem. The amount of water produced in the combustion reaction is insignificantly small compared to 100g, so we can safely ignore it.







This equation will tell us how much heat is absorbed by the water. Energy is never created nor destroyed, so we know this heat must come from somewhere. Since the combustion reaction is the only source of heat mentioned, we can assume that all of the heat absorbed by the water, was released by the chemical reaction. Mathematically, this means that the magnitude of q for the water solvent equals the magnitude of q for the reaction.

$$|q_{water}| = |q_{reaction}|$$

From this relationship, we know that 125.52J of heat is released from the combustion reaction. We can now use heat-to-mole stoichiometry to convert from heat to moles of ethanol and then use molar mass to convert to grams of ethanol.

$$12552J \times \frac{1kJ}{1000J} \times \frac{1mol\ C_2H_5OH}{2741.4kJ} \times \frac{46.07g\ C_2H_5OH}{1mol\ C_2H_5OH} = 0.211g\ C_2H_5OH$$

#### **Conclusion**

We have now covered every major incarnation of stoichiometry for your AP Chemistry exam. Stoichiometry is a huge part of AP Chemistry, but hopefully you are starting to see that stoichiometry is just one problem that come up a lot, as opposed to several different problems that just share the same name. With practice, stoichiometry can actually become the most straightforward part of AP Chemistry. Work through some problems in the <a href="Albert.io AP Chemistry">Albert.io AP Chemistry</a> section and remember that stoichiometry problems mainly require us to:

- 1. Convert to moles
- 2. Use mole to mole stoichiometry
- 3. Convert to the desired units

Practice using the ideas of unit conversion and cancellation to guide you through these steps, and you will be able to handle any stoichiometry the CollegeBoard can throw your way.







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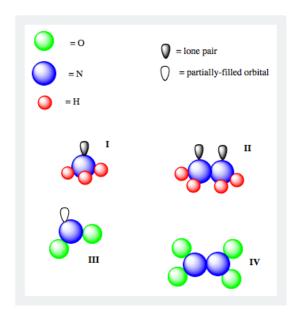
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#### **Introduction to Empirical Formula**

Though it's not quite as useful as a molecular formula, an empirical formula still tells you a lot about the substance, and it's possible to calculate it with much less information. Naturally, the AP Chemistry exam is almost guaranteed to ask you to calculate an empirical formula for at least one substance, if not more. You'll learn how to make these calculations in this section of the AP Chemistry Crash Course. Let's get started!

#### Step 1. Figure Out How Much of Each Element is in the Compound.

Depending on the question, this step can take different forms. For example, let's say that you have a compound composed of nitrogen and oxygen, where nitrogen makes up 30.4% of the compound by mass. We need to have mass of the two elements in grams in order to calculate an empirical formula.







Since we don't know the mass of the sample, we can just simply assume a weight of 100g to make the calculations easier; this means that the compound consists of 30.4g N and (100-30.4) = 69.6g O.

In another case, we might be given the mass of one element in the compound. For example, let's say that we have another compound consisting of only N and O. The total mass of the sample is 65g, and the mass of the nitrogen is 19.8g. Of course, the mass of the oxygen is then (65-19.8) = 45.2g.

#### Step 2. Convert Those Masses into Moles.

Because the empirical formula is based around the ratio of one element's molecules to another element's molecules, grams won't help us much in calculating the empirical formula. Instead, we'll convert the masses into moles, which correspond directly to the actual number of molecules of each element.

Molar mass of N = 14.01g/molMolar mass of O = 16.00g/mol

Compound 1 contains 30.4g of N, which means  $(30.4 \div 14.01) = 2.17$  moles of N, and 69.6g of O, which means  $(69.6 \div 16.00) = 4.35$  moles of O.

Compound 2 contains 19.8g of N, which means  $(19.8 \div 14.01) = 1.41$  moles of N, and 45.2g of O, which means  $(45.2 \div 16.00) = 2.83$  moles of O.

#### **Step 3. Find the Largest Common Divisor.**

Next, we have to use these numbers to calculate an empirical formula. You've never seen a formula that's  $N_{2.17}O_{4.35}$ , right? The coefficients of the elements are always integers.







So, we take the numbers we've been given and try to find the largest common divisor, or in other words, we're trying to make them the smallest integers possible while still keeping the ratio between them the same.

The quickest way to do this is to take the smaller of the numbers and divide all the numbers with it. In the case of Compound 1, we have 2.17mol N and 4.35mol O.  $4.35 \div 2.17 = 2.005$ . This number is very close to 2, so we can assume that the ratio of N to O in the sample was 1:2. This makes the empirical formula NO<sub>3</sub>.

Doing the same with Compound 2, we have 1.41mol N and 2.83mol O.  $2.83 \div 1.41$  = 2.007, which is again very close to 2. So we've discovered that these two compounds are, in fact, the same!

Or are they? To know for sure, we'd have to figure out their molecular formulas...

#### **More Complex Formulas**

 $NO_2$  is a pretty simple formula. However, you may be thrown a far more complicated one. For example, let's say you find out that your sample has 3.39mol C, 5.65mol H, and 2.26mol N (this compound does not exist, by the way).

We start by dividing the two larger numbers by the smallest, 2.26. We get 1.50mol C, 2.50mol H, and 1.00mol N (by definition). Now, all of the coefficients must be integers, so what should we do? We multiply them all by whatever integer factor is necessary.

1.50 needs to be multiplied by 2 to make 3, so we multiply all the numbers by 2 to get 3.00mol C, 5.00mol H, and 2.00mol N.

So, we have calculated an empirical formula of  $C_3H_5N_2$ .







#### **More Examples**

The atomic weight of element X is 100 g/mol. 50.0g of X combines with 32.0g of oxygen. Calculate an empirical formula for the resulting compound.

As you can see, in this problem, we don't need to figure out the masses of the two elements in the compound, since they're listed in the problem. So, we can skip directly to step 2.

We have 50g of X, and X has a molar mass of 100g/mol. So we have  $(50 \div 100) = 0.5$ mol of X.

We have 32.0g of O, and O has a molar mass of 16g/mol. So we have  $(32.0 \div 16) = 2$ mol of O.

Now, we need both of these numbers to be integers. What should we do? It turns out that the method I already outlined in step 3 still works here. We just divide both numbers by the smaller one (0.5). So we then have 1mol of X and 4mol of O, yielding an empirical formula of  $XO_4$ .

Let's do just one more example. This one is a complicated example, which is more like the problems you'll encounter on the free-response section.

A 1.34g sample of a compound containing C and H was burned in an environment with excess oxygen, forming 6.78g  $\rm CO_2$  and 4.59g  $\rm H_2O$ . Calculate an empirical formula of the compound.

Steps 1 and 2 are quite hard in this case. The best thing to do is to first find the number of moles of each of the two compounds ( $CO_2$  and  $H_2O$ ).







The molar mass of  $CO_2$  is (12+32\*2) = 76g/mol. So the reaction produced (6.78  $\div$  76) = 0.089 moles of  $CO_2$ 

The molar mass of  $H_2O$  is (1\*2+32) = 34g/mol. So the reaction produced  $(4.59 \div 34) = 0.135$  moles of  $H_2O$ .

Now, we need to calculate the moles of the elements involved (C and H). O is not important, because the original compound contained no O.

The reaction produced 0.089 moles of  $CO_2$ , which corresponds to 0.089 moles of C.

The reaction produced 0.135 moles of  $H_2O$ , which corresponds to 0.270 moles of  $H_2O$ .

Now we proceed to step 3. We divide both numbers by the smaller one, giving us 1 mole of C and 3.03 moles of H. So, we calculate an empirical formula of CH<sub>3</sub>!

That's all you need to know about how to calculate an empirical formula for the AP Chemistry exam. Good luck and happy studying!

Yes, it is technically possible that the empirical formulas are  $N_{217}O_{435}$  and  $N_{141}O_{283}$ , respectively. However, on the AP Chemistry exam, the empirical formula is probably going to be made up of integers under 10 unless noted otherwise. The slight deviation from 2 is simply due to rounding off.





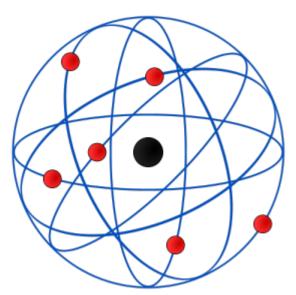


# Quantum Numbers and Theory

#### **Progress of the Atomic Theory**

Before we discuss quantum numbers and theory, we need to briefly review how we arrived at the current atomic theory (Quantum Theory and the Bohr Model).

#### **The Rutherford Model**



**Image Source: Wikimedia Commons** 

Rutherford proposed that an atom was made up of a dense, positive nucleus, surrounded by mostly empty space and negative electrons. Rutherford's model of the atom prevailed for many years until scientists started noticing inconsistencies. Physics established that an electron moving in a curved path around a nucleus must give off energy. As it continuously loses energy, the electron should spiral into the nucleus. Since this does not happen, there needed to be a new model to describe atoms.







#### Quantum Numbers and Theory Cont.

#### **The Bohr Model**

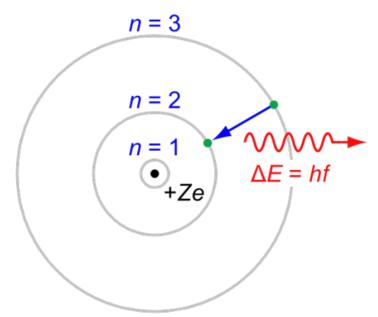


Image Source: Wikimedia Commons

Bohr proposed that the nucleus is in the center with protons and neutrons, and the electrons are around the nucleus, but instead of orbiting in circles, he thought that they exist in distinct energy levels in spheres, accounting for the specific changes in light emitted as electrons gained energy (photons).

Bohr proposed his theory after observing electrons transition between energy states using a hydrogen discharge lamp. The Bohr model states that as an electron moves between energy levels, energy is emitted or absorbed as a photon. This causes a difference in the frequency and wavelength of the light viewed through the element being observed, as electrons absorb or emit photons.

The Bohr model was successful in modeling the activity of a hydrogen atom, but it was not accurate with other atoms. Several changes were made, and in current models electrons still have discrete energies, but they also occupy specific orbitals. These are specifically shaped areas in which an electron may exist, but is not actually visible outside of computer modeling. This has given us our current understanding, explained using quantum numbers and theory.







#### **Quantum Numbers and Theory**

To describe the location of an electron in an element, we utilize quantum numbers and theory. Each electron is described using four different quantum numbers, and no two electrons in the same atom can have the same set of numbers. The numbers indicate the shell, subshell, orbital, and spin of the electron. This tells you all of the characteristics of any given electron in an atom.

Principal Quantum Number	$n = 1, 2, 3, \dots$
Angular Momentum Quantum Number	l = 0,1,2,,n-1
Magnetic Quantum Number	$m_l = -l, -l+1,0,l-1, l$
Spin Quantum Number	$m_s = -1/2, +1, 2$

**Image Source: Wikimedia Commons** 

The first number is the principal quantum number, represented by an n. The principle quantum number tells you what shell the electron is in.

An electron's "n" tells you:

- its approximate distance from the nucleus
- the size of the orbital it is in
- its energy level

The larger n is, the larger the atom is. The values of n are all positive integers, beginning with one, because they represent shells and there will always be at least one shell in an atom. The first of which is n=1 and is the lowest energy shell. According to the quantum theory, this shell is the closest to the nucleus.

When an electron moves from a less stable position to a more stable position, it moves from a higher energy position to a lower energy position, making this a favorable and common change. The wavelength and frequency of the photon emitted depends on the energy change of the electron.







For example, as an electron falls from n=3 to n=2 (a higher energy state to a lower energy state), it emits (releases) red light (photons at 450-495 wavelengths), but when an electron falls from n=6 to n=2, violet light is emitted.

As an electron is excited (from "absorbing" photons or energy), it can jump to a higher energy level, increasing the n value by a whole number. When an electron "emits" energy, it jumps to a lower energy level, decreasing the n value by a whole number. So, n=4 has more energy than n=3. As an electron gains energy, it jumps to a higher energy level, absorbing photons, and increasing n.

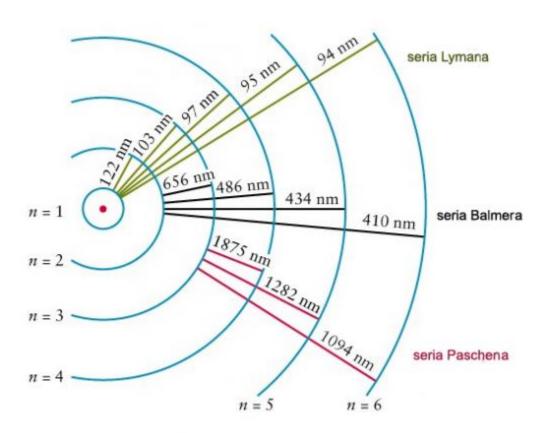


Image Source: Wikimedia Commons

#### **Examples:**

1. If an electron's principal energy level goes from n=5 to n=4, it has moved to a lower energy level, so it has emitted (lost) energy as a photon.



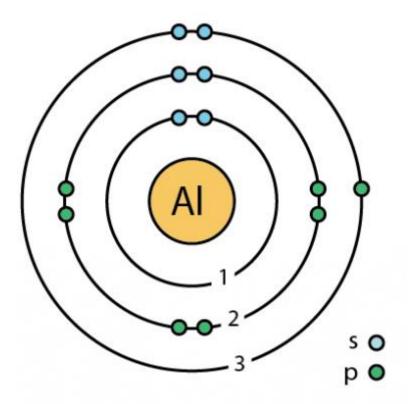




- 2. If you have two atoms, one with n=3 and the other n=4, the atom that is n=4 has more energy, because it has a higher n, and is larger, because atomic radius increases with n.
- 3. When an electron moves from n=2 to n=4, it has moved to a higher energy level, so it is absorbing energy as photons.

**Key Concept**: Electrons exist in specific energy levels called shells. When electrons change energy levels, they absorb or emit energy as photons.

#### **Subshells**



**Image Source: Wikimedia Commons** 







The next part of quantum numbers and theory is the orbital angular momentum quantum number and the idea of subshells. The orbital angular momentum quantum number, I, tells you the subshell in which the electron exists. This tells you the shape of the subshell the electron is in. This is also always a whole number, but ranges from zero to n-1, meaning it can never be larger than n.

n =	1=
1	0
2	0, 1
3	0, 1, 2
4	0, 1, 2, 3

Each I number correlates to a specific subshell. The most common of these subshells are labeled s, p, d, and f.

I	Subshell
0	S
1	р
2	d
3	f







This means that n = 1 has one subshell, an "s"; n=2 has two subshells, one "s" and one "p"; n=3 has three subshells, one s, one p, and one d.

n =	Subshells Present
1	S
2	s, p
3	s, p, d
4	s, p, d, f

The shape of the subshell is determined by its energy level. Every type of subshell (s, p, etc.) has a specific shape.

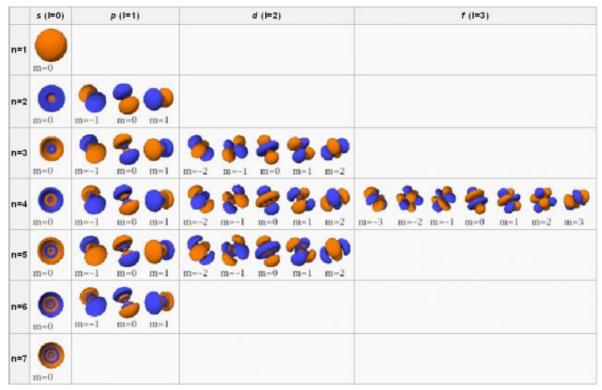
An s orbital is spherical around the nucleus. Think of the inside of a jawbreaker. The center is the nucleus. The next layer around it is the 2s subshell. The next layer is 3s, and so on. A p orbital is shaped like a dumbbell. See the image below for the shapes of each type of orbital in each subshell. All of the orbital shapes in one box combine to form that subshell.







Quantum numbers and theory begin to get very complicated when you try to memorize the shapes. Don't worry about that, just remember that s orbitals are spheres, p orbitals are dumbbells, d orbitals are two balloons connected at the ends by a donut, and f orbitals look like flowers.



**Image Source: Wikimedia Commons** 

To view these, imagine that they are on a three-dimensional plane, as in the image below.

Subshells have names composed of the principle quantum number and the letter of the subshell. If an electron is in the p subshell (l = 1) of the third principle energy shell (n = 3), it is in the 3p subshell.







#### **Examples:**

- 1. If an electron has n=4 and l=0, it is in the 4s subshell.
- 2. If an electron is n=3, it could have three possible subshells: 3s, 3p, and 3d, because l=0, 1, and 2.

**Key Concept**: Every energy level (shell) has subshells, which each has a specific shape.

#### **Orbitals**

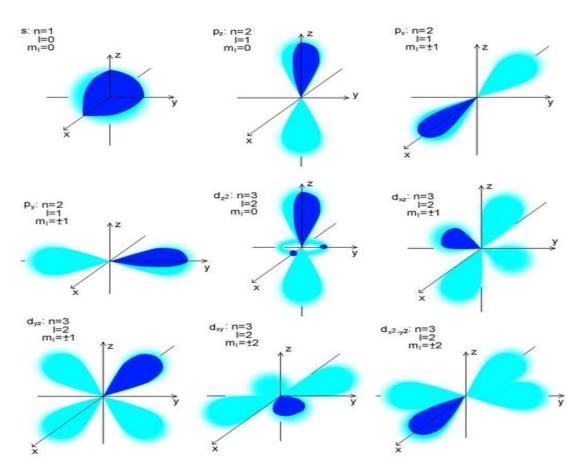


Image Source: Wikimedia Commons







Every subshell has orbitals. The number of orbitals is determined by the size of the subshell. Each subshell of the same type has the same number of orbitals.

The magnetic quantum number, " $m_l$ ", tells you the orbital the electron is in and describes the energy levels in its subshell. The values of " $m_l$ " are again whole numbers, ranging from -l to +l. So if l = 2, the " $m_l$ " values are -2, -1, 0, 1, and 2. This means that when l = 2, there are five possible orbitals for an electron to occupy.

Subshell	T=	Possible m <sub>I</sub> Values	Number of Orbitals
S	0	0	1
р	1	-1, 0, 1	3
d	2	-2, -2, 0, 1, 2	5
f	3	-3, -2, -1, 0, 1, 2, 3	7

**Key Concept**: The number of orbitals is different for each subshell and every subshell of a single type will have the same number of orbitals.

#### **Electron Spins**

Finally, the electron spin quantum number, "m<sub>s</sub>", tells you the electron spin. Who would have guessed?

Each orbital can hold two electrons. The two electrons have opposite spins, which we have arbitrarily called up and down.







This up or down spin is represented by  $+\frac{1}{2}$  and  $-\frac{1}{2}$  or an "up arrow" and "down arrow", as seen below.

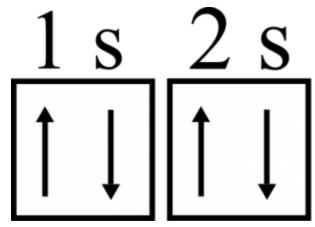
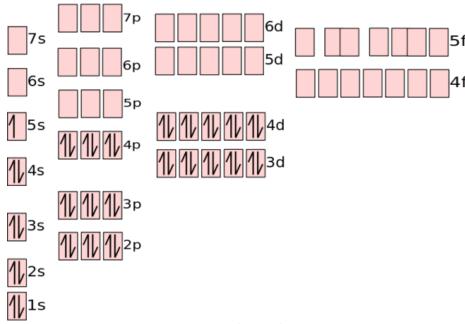


Image Source: Wikimedia Commons

In this image, you also see that the orbital is represented by a box. Each box can hold two electrons. Each subshell has a different number of orbitals, which can be represented by multiple boxes, as seen below:



**Image Source: Wikimedia Commons** 







This is an example of the electron configuration for silver. Notice that each orbital only has two electrons, the s subshell has one orbital, the p has three, the d has five, and the f has seven. This is another way of demonstrating the locations of the electrons in an atom. See the review for electron configuration for more information on this type of diagram.

#### **Example:**

For an electron that is n=2,l=1, and  $m_l=0$ , there are two possible quantum number configurations. Since the magnetic quantum number is given, you only have two options, the positive and negative spins. So the two possible configurations are n=2, l=1,  $m_l=0$ ,  $m_s=1$  and n=2, l=1,  $m_l=0$ ,  $m_s=1$ .

**Key Concept**: Each atomic orbital can hold two electrons with opposite spins.







#### **Ionization Energy**

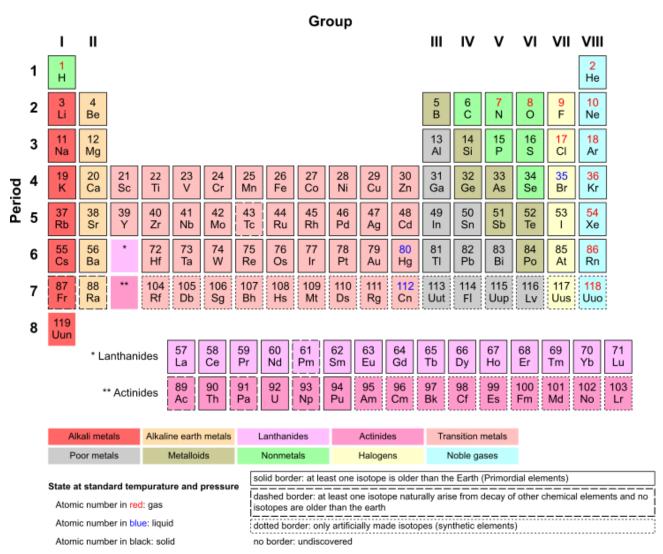


Image Source: Wikimedia Commons

Quantum theory also explains ionization energy. A higher n value indicates a greater distance from the nucleus. The farther an electron is from the nucleus, the smaller the attraction between them. The lower the attraction, the easier it is to remove that electron. Since ionization energy is the energy required to remove an electron, it decreases (ionization is easier) as n increases.







The valence (last or furthest from the nucleus) shell of any atom cannot have more than eight electrons. This is the most stable electron configuration. If an atom has one electron in its valence shell, it will require less energy to remove that one electron than to gain seven electrons to get to a full electron configuration. This means that it will have a low ionization energy and a low electron affinity. As an atom approaches eight valence electrons, its ionization energy increases. Electrons with full valence shells (noble gasses) have incredibly high ionization energies, because they already have a full valence shell.

As you move across the periodic table from left to right, ionization energy increases, because valence electrons increase. This tendency is called a periodic trend. Ionization energy decreases as you move down the periodic table. This is because as you move down the periodic table, the size of the atoms increases. As size increases, the valence electrons are further and further from the nucleus, decreasing their electron affinity and therefore decreasing their ionization energy.

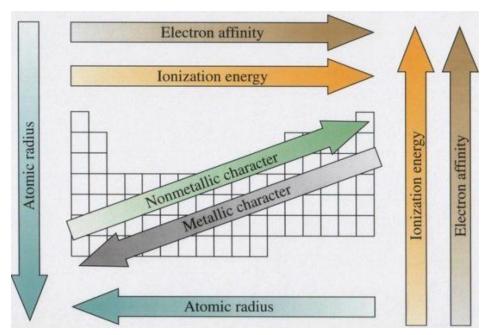


Image Source: Wikimedia Commons







So even though the electrons in barium are in a higher energy level than beryllium, they are further away from the nucleus, meaning they have less affinity for the nucleus. This makes removing an electron take less energy, so barium has a lower ionization energy than beryllium. By the same logic, barium has a lower ionization energy than mercury, because barium has fewer electrons in its valence shell.

#### **Examples:**

- 1. To determine which of two electrons has a higher ionization energy, look at their n values. A higher n means a higher ionization energy. If the n values are the same, then the electron with the higher I or mI value.
- 2. When determining which element has a higher ionization energy, compare their locations on the periodic table. Remember, that ionization energy increases as you go up and to the right on the periodic table. This means that fluorine has a higher ionization energy than lithium; cadmium is higher than barium; chlorine is higher than gold; and silicon is higher than lead.

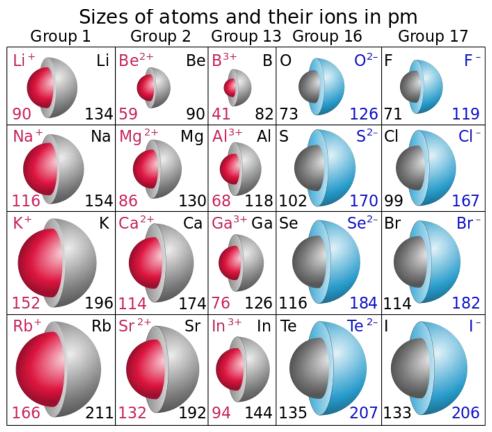
**Key Concept**: Ionization energy tends to increase as you move up and right on the periodic table. This is the same trend as atomic size and electron affinity and the opposite trend as atomic radius.







#### **Atomic Radius Trend**



**Image Source: Wikimedia Commons** 

#### **Conclusion and Summary**

We've covered a lot in this AP Chemistry Crash Course, so let's take a moment to review:

- Each electron can be uniquely identified with four quantum numbers
- The principle quantum number, n, describes the distance from the nucleus. This quantum number can be any whole number greater than or equal to 1.







- The angular momentum quantum number, I, describes the shape of the electron's orbital. The angular momentum quantum number can have a value ranging from 0 to n-1.
   Angular momentum quantum numbers are also labelled with letters.
  - ► I=0 are s orbitals
  - ► I= 1 are p orbitals
  - ► I = 2 are d orbitals
  - ► I = 3 are f orbitals
- The magnetic quantum number, m<sub>I</sub>, describes the orientation of the orbital. This number can be any integer between –I and +I.
- The spin quantum number,  $m_s$ , describes the spin of the electron. This number is either +1/2 (spin up) or -1/2 (spin down)
- The quantum numbers of electrons can be related to the properties of atoms such as ionization energy and the absorption of light.

This covers just about everything you'll need to know about quantum numbers and theory for the AP Chemistry exam. You are guaranteed to see some of this topic on your exam, so be sure to reread this article as much as you need to get up to speed on everything quantum for AP Chemistry.







## The Ideal Gas Law



**Image Source: Wikimedia Commons** 

#### Introduction to The Ideal Gas Law

The Ideal Gas Law summarizes all of the various experiments in the 17<sup>th</sup> and 18<sup>th</sup> century that strove to define the relationships between the different properties of a gas. These relationships can all be explained by the ideal gas law. The ideal gas law is based on three critical assumptions.

1. Gas molecules are single points in space and that they do not take up any volume, which is a good assumption when the volume of gas molecules is far smaller than the volume of the container.







- 2. Second, that any collisions between gas molecules and other gas molecules, or gas molecules and the surface of the container, are perfectly elastic and do not involve the transfer of energy. The second assumption is sound at lower temperatures near room temperature.
- 3. The final assumption is that the heat capacity of a gas does not change as a function of temperature, which is a good approximation at lower temperatures but not higher ones.

#### Gas Laws - Essential Knowledge 2.A.2.

Pressure is generated by the collisions of gas molecules against surfaces. These collisions are what cause pressure. Pressure (P) is defined as the average force per unit area on a container. Atmospheric pressure, also known as Standard Pressure, is the pressure exerted by the air at sea level. It is the defined pressure under which ideal relationships are established. The temperature (T) of a gas is given in units of absolute temperature, the Kelvin scale (after Lord Kelvin). One unit of Kelvin is equal to one degree Celsius ( $1K = 1^{\circ}C$ ). The temperature of a gas is directly proportional to the pressure on the container when the volume is held constant, and this relationship is known as the Gay-Lussac law.

This system of holding one variable constant while changing the other two and looking at their relationship was the way all the gas laws were formulated. Robert Boyle published his observation in 1662 that, when holding the temperature of a gas constant, the pressure and the volume of a gas are inversely related to each other (as one goes up, the other goes down). After many experiments and scientific observations over the following hundred years, the collection of rules was compiled in one equation that related all the various properties of a gas. This equation is called the Ideal Gas Law

$$PV = nRT$$
, where  $R = 0.08206 \frac{Latm}{mol K}$ 







Basically put, the product of the volume (*V*) and pressure (*P*) of an ideal gas, which are inversely proportional to each other, are equal to the product of the number of gas molecules (*n*, usually expressed in molar units) times the absolute temperature in Kelvin (*T*) times a constant of proportionality called the <u>Gas</u> <u>Constant (*R*)</u>. The Gas Constant can be expressed in different units depending on what units the variables are reported on, but its function remains the same: to relate one side of the equation to the other.

This is the <u>keystone</u> equation for <u>Gasses</u> on the AP Chemistry exam. All other laws can be derived from this one. Therefore, take the time to understand really what this means. The most common mistakes AP Chemistry students make is trying to solve for a variable without having units that do not match the gas constant. For example, if you wanted to solve for the pressure of a gas, and you were to input the pressure in degrees Celsius instead of Kelvin, your answer will be wrong. This can also happen if you were to input the pressure in units of Pascal instead of atmospheres, and forgot to change out the gas constant to reflect this change of units. The gas constant can be expressed in many different units, so just make sure that you have selected the version which matches the units in your equation. And don't forget that sometimes the easiest thing to do could be to convert your units rather than taking the time to find a new value of the gas constant.

We will now provide three examples that showcase questions you may be asked to solve on the AP Chemistry Exam.

#### Example 1

What is the volume in liters of a freely expanding container with a pressure of 1 atm which contains 1 mole of oxygen gas at 25  $^{\circ}$  C?

The first thing we will do is rearrange the idea gas law to solve for Pressure

$$V = nRTP^{-1}$$







We will then retrieve the value of the gas constant for units of liters and atmospheres. We will use the AP Chemistry Equation Sheet available on the CollegeBoard website <a href="here">here</a> on page 162.

$$R = 0.08206 Latm mol^{-1}K^{-1}$$

We will then convert the temperature from degrees Celsius to Kelvin.

$$Temperature(K) = 273 + {}^{0}C = 273 + 25 = 298 Kelvin$$

Finally, we will input all of the variables into the ideal gas law and solve for pressure.

$$L = (1 mole) (0.08206 Latm\ mol^{-1} K^{-1}) \left(298 K (1 atm)^{-1}\right)$$

$$L = 24.45L$$

This relates to an important point: one mole of an ideal gas occupies 22.4 L at 273 Kelvin. As we know, gasses expand when they are heated up. So qualitatively this calculation makes sense, we obtained a result which is a little bit larger than the value at 273 K.

#### Gas Pressure – Essential Knowledge 2.A.2, 4.A.1.

According to the ideal gas law, pressure is related to the number of molecules of a gas. One derivation of this is that the total pressure of a gas is in fact composed of *partial pressures* of the different molecules that the gas consists of.

$$P_{total} = P_A + P_B + P_C ...$$







A gas like the air we breathe consists of various constituent molecules of gas such as carbon dioxide  $(CO_2)$ , nitrogen  $(N_2)$ , oxygen  $(O_2)$ , and water  $(H_2O)$ . Even though the air, in general, has a total pressure, we can measure the contribution of the partial pressure of each type of gas molecule to the total pressure. This relationship is another consequence of the kinetic theory of gasses: considering that it is the collisions of each molecule of gas with the wall of the container that provide the total pressure, the amount of pressure exerted by each gas individually is directly proportional to the sum of that particular gas inside the container. This quantity is known as the *molar fraction*.

$$P_A = P_{total} x X_A, where X_A = \frac{moles A}{total moles}$$

#### **Example 2**

In a sealed container at room temperature with a fixed volume of 0.5 L, 16.5 grams of carbon dioxide and 27.0 grams of steam are released during a combustion reaction. Assuming that all the oxygen was used up in the reaction, find the partial pressure of carbon dioxide inside the container.

Our ultimate goal is to find the partial pressure of oxygen in the container. We will need to calculate the total number of gaseous moles in the container, plug in that value for n, then use the ideal gas law to solve for the total pressure in the container. Finally, we will use the equation given above for the molar coefficient  $X_A$  to find the molar coefficient of oxygen in the container, and solve for oxygen's partial pressure.

The number of moles of a gas is equal to its mass divided by its molecular weight. The molecular weight of carbon dioxide can be calculated by adding the molecular weight of two carbon atoms and one oxygen atoms to equal 44.00 g. Steam is gaseous water, and the molecular weight of water is 18.00 g.







Now let us solve for the number of moles of each compound and add the resulting values together.

$$Moles H_20 (n_{water}) = 27.0g/18.00gmol^{-1} = 1.50mol$$

$$Moles\,CO_2\,(n_{carb}) = 5.50g/44.00gmol^{-1} = 0.375mol$$

The total number of moles of gas is the container is therefore.

$$n_{total} = n_{water} + n_{carb} = 1.50mol + 0.375mol = 1.875mol$$

And the molar fraction of carbon dioxide in the container is:

$$x_{carb} = \frac{n_{carb}}{n_{total}} = 0.375 mol / 1.875 mol = 0.200$$

Now we arrange the ideal gas equation to solve for the total pressure in the container:

$$P_{total} = n_{total}RTV^{-1} = (0.375mol)(0.08206Latm mol^{-1}K^{-1})(298K)(0.5L)$$

$$P_{total} = 4.585atm$$

And finally we solve for the partial pressure of carbon dioxide in the container:

$$P_{carb} = P_{total} \times X_{carb} = (4.585atm)(0.200) = 0.917atm$$

This type of secondary analysis, of using the ideal gas law to find a value to solve for a second equation, is very common.







#### Example 3

Natural gas is used to heat up many residential houses. The main component in natural gas is propane. Calculate the number of moles of gas in a 1 L container that initially has a pressure of 500 torr.

The first thing we would need to do in this case is write out and balance the chemical reaction. The combustion of propane will be written out as follows:

$$C_3H_8 + O_2 \leftrightarrow CO_2 + H_2O$$

We can now <u>balance the equation</u> to take into account how many moles of compounds are on each side of the equation. There must be three times as many moles of carbon dioxide as moles of propane since each molecule of propane has three carbon atoms. This reaction will also create four molecules of water for every molecule of propane since propane contains eight hydrogen atoms. The total number of oxygen atoms in three molecules of carbon dioxide and four molecules of water is an even number. Therefore, we do not need to adjust the molar coefficient of propane.

$$C_3H_8 + 5O_2 \leftrightarrow 3CO_2 + 4H_2O$$

We would then calculate the number of moles of oxygen in the container using the ideal gas law, rearranged to solve for n. Since solid compounds to not get included in the **equilibrium expression**, and the question asks for the beginning of the reaction, presumably before the formation of any water or carbon dioxide, the partial pressure of oxygen is just equal to the total pressure of the tank. We will use the ideal gas law flavor of the gas constant in pressure units of torr!

$$n = \frac{RT}{PV} = (62.36 Ltorr \, mol^{-1} K^{-1}) \frac{(298 K)}{(500 torr)(1L)}$$
  $n = 37.17 moles \, O_2$ 







There are many other examples of ways the ideal gas law will be tested on the AP Chemistry exam, and we recommend you try them all! Do you have any questions? Comment below and let us know!

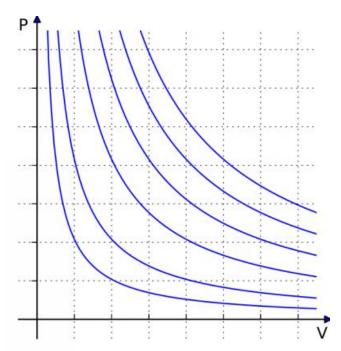






# R Value in Chemistry

The Gas Constant (*R*) (R Value) is a fundamental constant of proportionality in chemistry and physics. It serves as a way to relate the units of energy to units of temperature in physical and chemical analysis. Therefore, the Gas Constant can be expressed in different units depending on what units the variables are reported in. Its function, however, remains the same—to relate two separate scales to one another. Below is a tabular representation of pressure-volume isotherms, of which the gas constant is the constant of proportionality.



**Image Source: Wikimedia Commons** 

Here are the three most common flavors of the Gas Constant as written out on the AP Exam **Equation Sheet**:

$$R = 8.314J \quad mol^{-1}K^{-1}$$

$$R = 0.08206L \quad atm \quad mol^{-1}K^{-1}$$

$$R=62.36Ltorr \quad mol^{-1}K^{-1}$$







The first value is the thermodynamic flavor of the gas constant, useful when dealing with changes in energy such as the standard change in free energy for equilibrium expressions, written as:

$$\Delta G^0 = -RT \quad lnK$$

The second and third values are both expressed in terms of the ideal gas law and are used to relate one side of the ideal gas law equation to the other.

$$PV = nRT$$

The gas constant can also be defined in terms of the Boltzmann constant:

$$R=k_BN_A$$
; where  $k_B$  = Boltzmann's constant,  $N_A$  = Avogadro's number.

The gas constant deals with molar amounts of substances, whereas the Boltzmann constant deals with individual molecules. That is why it is possible to convert from one constant to the other just by using Avogadro's number. This is a useful piece of information to know for your AP Exam!

#### **Example 1**

Given below is the Maxwell-Boltzmann Distribution for the probability distribution of the speeds of gasses. Calculate the Boltzmann constant based on the gas constant with the appropriate units.

$$f(v) = \sqrt{(rac{m}{2\pi kT})^3} 4\pi v^2 e^{-rac{mv^2}{2kT}}$$

To do this, we need to convert from the molar quantity of the gas constant to the particle quality of the Boltzmann constant. Using the equation given above, we rearrange to solve for the Boltzmann constant and plug in the thermodynamic flavor of the gas constant.







We must use the thermodynamic flavor rather than the ideal gas flavor because the units in the expression must come out to the amount of force done per molecule per temperature unit, which is only achieved by using the thermodynamic flavor of the gas constant.

$$kB = R/N_A = (8.314J \quad mol^{-1}K^{-1})/(6.022x10^{23}molecule \quad mol^{-1})$$
  $k_B = 1.381x10^{-23}J/K \cdot molecule$ 

#### Example 2

In a sealed container at room temperature with a fixed volume of 0.5 L, 16.5 grams of carbon dioxide and 27.0 grams of steam are released during a combustion reaction. Assuming that all the oxygen was used up in the reaction, find the partial pressure of carbon dioxide inside the container.

Our ultimate goal is to find the partial pressure of oxygen in the container. We will need to calculate the total number of gaseous moles in the container, plug in that value for *n*, then use the <u>ideal gas law</u> to solve for the total pressure in the container. Finally, we will use the equation given above for the molar coefficient *XA* to find the molar coefficient of oxygen in the container, and solve for oxygen's partial pressure.

The number of moles of a gas is equal to its mass divided by its molecular weight. The molecular weight of carbon dioxide can be calculated by adding the molecular weight of two carbon atoms and one oxygen atoms to equal 44.00 g. Steam is gaseous water, and the molecular weight of water is 18.00 g. Now let us solve for the number of moles of each compound and add the resulting values together.

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 $MolesCO_2(n_{carb}) = 5.50g/44.00gmol^{-1} = 0.375mol$ 







The total number of moles of gas is the container is therefore.

$$n_{total} = n_{water} + n_{carb} = 1.50mol + 0.375mol = 1.875mol$$

And the molar fraction of carbon dioxide in the container is:

$$X_{carb} = n_{carb}/n_{total} = 0.375 mol/1.875 mol = 0.200$$

Now we arrange the ideal gas equation to solve for the total pressure in the container. Most important, we use the ideal gas flavor of the gas constant that also has the units that match the problem! Namely, units of atmospheres for pressure instead of torr.

$$\begin{split} P_{total} &= n_{total} RTV^{-1} = (0.375 mol)(0.08206 L \quad atmmol^{-1} K^{-1})(298 K)(0.5 L) \\ P_{total} &= 4.585 atm \end{split}$$

And finally we solve for the partial pressure of carbon dioxide in the container:

$$P_{carb} = P_{total} \times X_{carb} = (4.585atm)(0.200) = 0.917atm$$

This type of secondary analysis, of using the <u>ideal gas law</u> to find a value to solve for a second equation, is very common.

The most common mistakes AP Chemistry students make is trying to solve for a variable without having units that do not match the gas constant. For example, if you wanted to solve for the pressure of a gas, and you were to input the pressure in degrees Celsius instead of Kelvin, your answer will be wrong. This can also happen if you were to input the pressure in units of Pascal instead of atmospheres, and forgot to change out the gas constant to reflect this change of units. The gas constant can be expressed in many different units, so just make sure that you have selected the version which matches the units in your equation. And don't forget that sometimes the easiest thing to do could be to convert your units rather than taking the time to find a new value of the gas constant.







The gas constant is also used to related the equilibrium state of a reaction at a certain thermodynamic temperature in Kelvin units to the amount of free energy theoretically available if the reaction were to proceed to 100% completion. This purely theoretical calculation allows us to calculate the directionality of a reaction and the amount of energy that will be released or consumed by a reaction depending on its actual condition. Calculating how much free energy is actually available can be done by comparing the standard change in free energy, defined by the compound concentrations at equilibrium, to the actual concentrations of the compounds in the reaction, or the reaction quotient *Q*.

$$\Delta G = \Delta G^o + RT lnQ$$

So when it comes down to it, what separates  $\Delta G$  and  $\Delta G^o$ ? Think about it like this: The standard change in free energy is always a specific value for a chemical reaction at standard temperature and pressure. We can calculate his value for any given chemical reaction by comparing empirical values of any molecules from a table of thermodynamic values. The standard change corresponds to a theoretical process: the complete transformation of reactants into products at STP. The non-standard change in free energy,  $\Delta G$ , represents the total free energies of the products and reactants at any given concentration, as expressed in the reaction quotient  $Q \cdot \Delta G$  varies continuously as the concentrations of products and reactants change, in contrast to  $\Delta G^o$  which is a constant for a given reaction.  $\Delta G$  can be thought of as the "distance" (in free energy) of the non-equilibrium reaction from the equilibrium state, finally reaching zero at equilibrium.

#### Example 3

Natural gas is used to heat up many residential houses. The main component in natural gas is propane. Calculate the amount of free energy when methane combusts in oxygen at 25°C in 1 L tank given the following standard thermodynamic values, then calculate the available free energy at the start of the reaction when the partial pressure of oxygen is 500 torr.







Species	ΔH <sub>fO</sub> (kJ/mol)	Sº (J/K·mol)	ΔG <sub>fo</sub> (kJ/mol)
C <sub>3</sub> H <sub>8</sub> <sup>(g, propane)</sup>	-103.8	269.9	-23.49
CO <sub>2</sub> <sup>g</sup>	-393.509	213.74	-394.359
<i>O</i> <sub>2</sub> <i>g</i>	0	205.138	0
H <sub>2</sub> O <sup>g</sup>	-241.818	188.825	-228.572

The first thing we would need to do in this case is write out and balance the chemical reaction. The combustion of propane will be written out as follows:

$$C_3H_8 + O_2 \leftrightarrow CO_2 + H_2O$$

We can now balance the equation to take into account how many moles of compounds are on each side of the equation. There must be three times as many moles of carbon dioxide as moles of propane since each molecule of propane has three carbon atoms. This reaction will also create four molecules of water for every molecule of propane since propane contains eight hydrogen atoms. The total number of oxygen atoms in three molecules of carbon dioxide and four molecules of water is an even number. Therefore, we do not need to adjust the molar coefficient of propane.

$$C_3H_8 + 5O_2 \leftrightarrow 3CO_2 + 4H_2O$$

To find the standard <u>Gibbs free energy</u>, we must calculate the total change in entropy and multiply that by the temperature in Kelvin. To do so, we will multiply the molar coefficient of the compound from the balanced chemical equation by the thermodynamic value provided above.

$$\Delta S^o = \Sigma S^o products - \Sigma S^o reactants$$







$$\Delta S^o = [(3x213.74) + (4x188.825)] - [(269.9) + (5x205.138)]$$
  
$$\Delta S^o = 100.93 J/K \cdot mol = 0.10093 kJ/K \cdot mol$$

Then convert the units of temperature from degrees Celsius to units Kelvin.

$$Temperature(K) = 25^{\circ}C + 273 = 298K$$

Finally, we will replicate the process outlined for the change in <a href="entropy">entropy</a> and repeat it for finding the standard change in <a href="entropy">enthalpy</a> of the combustion.

$$egin{aligned} \Delta H^o &= \Sigma \Delta H_{f^o} products - \Sigma \Delta H_{f^o} reactants \ \Delta H^o &= \left[ (3x^-393.509) + (4x^-241.818) 
ight] - \left[ (^-103.8) + (5x0) 
ight] \ \Delta H^o &= ^-2,046 \cdot kJ/mol \end{aligned}$$

Now that we have calculated all the necessary variables, we plug the values into the expression for the standard change in free energy.

$$\Delta G^o = \Delta H^o - T \Delta S^o = (-2,046 \cdot kJ/mol) - [(298K)(0.10093J/K \cdot mol)]$$
  
$$\Delta G^o = -2,076 \cdot kJ/mol$$

We would then calculate the number of moles of oxygen in the container using the <u>ideal gas law</u>, rearranged to solve for *n*. We will use the ideal gas law flavor of the gas constant in pressure units of torr!

$$n = RT/PV = (62.36 Ltorr \quad mol^{-1}K^{-1})(298K)/(500torr)(1L)$$
 
$$n = 37.17 moles O_2$$







Then we will plug the concentrations into the reaction quotient and solve for available free energy, and this time, we will use the thermodynamic flavor of the gas constant! Since solid compounds to not get included in the equilibrium expression, and the question asks for the beginning of the reaction, presumably before the formation of any water or carbon dioxide, the reaction quotient *Q* is simply equal to the partial pressure of oxygen.

$$Q=[products]/[reactants]=(0)/(37.17)=0$$
 
$$\Delta G=\Delta G^o+RT\quad lnQ=^-2,076\cdot kJ/mol+(0.008314kJ/K\cdot mol)(298K)ln(0)$$
 
$$Ln(0) = \text{undefined, so}$$
 
$$\Delta G=\Delta G^o$$

<u>Most important to note</u>: at the start of a reaction the theoretical available free energy is equal to the standard change in free energy!







## Le Chatelier's Principle



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Le Chatelier's Principle, despite its intimidating name, is actually a very simple idea and quite important to AP Chemistry. It simply means that if a reaction at equilibrium is disturbed in a way that would shift the balance to one side, the reaction will move to restore the equilibrium.

It's sort of like if you were on a balancing beam with your arms stretched out at your sides, and your friend suddenly tied a weight to your right arm. Two things would happen: first, you would bitterly curse your ex-friend, and second, you would shift your weight over to your left side to counteract the weight on your right arm, thus restoring equilibrium.

Now, in the context of chemical reactions, what kind of disturbances can happen? Essentially, we can change concentration/amount of reactants, pressure/volume, and temperature. We'll go over each of them in turn in this section of the AP Chemistry Crash Course.







#### **Disturbance 1: Concentration/Amount of Reactants**

Fortunately, this is the simplest of the three to understand. In fact, the balancing beam analogy was an example of this disturbance: if we view your right side as reactants and your left side as products, then your friend simply added more reactants, causing you to shift some of your reactants into products.

On a more concrete level, let's look at the Haber Process. Here is the equation:

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

If we increase the amount of hydrogen, we will cause more ammonia ( $NH_3$ ) to be produced, according to Le Chatelier's Principle. Of course, this will also mean a decrease in nitrogen.

If we instead add ammonia, the reverse will be true. More nitrogen and hydrogen will be produced.

On the flip side, you can also cause a shift by taking product or reactant away from the reaction vessel. If you remove ammonia from the system, equilibrium will shift right (toward the products) and result in more ammonia being formed.

#### **Disturbance 2: Pressure/Volume**

Those two terms are combined because, of course, the only way to increase pressure while keeping the amount of gas and temperature constant is to reduce the volume, as specified by the <u>ideal gas law</u>.

Going back to our Haber Process:

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$







Let's say we have this nitrogen-hydrogen-ammonia mixture in a box, and we squeeze the box to increase the pressure. Now, pressure is in itself a component of the equilibrium, so it wants to get back to equilibrium, according to Le Chatelier's Principle. How can we reduce the pressure?

Well, if we look at the equation, we see that there are 4 moles of gas on the left side and only 2 moles of gas on the right side. So, in the extreme cases, if the mixture were all reactants, it would be under twice as much pressure as it would be if it were all products.

So, if we increase the pressure, the equilibrium will shift to relieve the pressure; the equilibrium will shift to the right and we'll have more products.

An increase in pressure causes the reaction to shift toward the side with the fewest moles of gas. Be careful not to include moles of solid or liquid in your determination.

Does that make sense? Pressure is probably the hardest to understand, so if you're struggling, take some extra time. And if you're not struggling, sit back and relax because temperature is actually pretty simple.

#### **Disturbance 3: Temperature**

Guess what? We'll be using the Haber Process again. However, there's a new term to add to the reaction: heat. The reaction is exothermic, which means that heat is produced by the reaction. The exact amount of heat is irrelevant for this part of the discussion, so I'll just write heat.

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 + heat$$







How can we use this additional piece to disturb the equilibrium? Well, heat has essentially become one of our products. So, taking our lesson from the first disturbance method, adding more of a product will drive the equilibrium to the left; taking away some of the product will drive the equilibrium to the right.

So, if we want to get more ammonia, we can simply cool down the container we're using to store the mixture. This cooling will remove the heat, one of the products, and thus will cause more ammonia and heat to be produced, in accordance with Le Chatelier's Principle.

On the other hand, if we instead want to break down ammonia to make nitrogen and hydrogen, we need to increase the ambient temperature. Then we'll have more products and thus we can drive the equilibrium to the left.

Got all the disturbances down? Are you sure? Let's test your knowledge.

#### **Application of Le Chatelier's Principle: Increasing Yield**

We're going to switch to a different reaction just to make this more interesting.

$$H_2 + I_2 \rightleftharpoons 2HI + heat$$

Let's say that this reaction is currently at equilibrium and you have complete control over the container. Now I tell you that I need more hydrogen iodide. What can you do to give me more HI?

Let's go through each disturbance in order and see if any of them will help you.

Disturbance 1: This is the obvious choice. Just add more hydrogen and iodine. The added reactants will push the equilibrium to the right, and I'll have my hydrogen iodide. Yay! So we're done...







#### NOT SO FAST!

It turns out we don't have any more hydrogen and iodine. You're going to have to think of something else...

Disturbance 1 (again): Well, if you can't add hydrogen and iodine, you can at least take out the hydrogen iodide that has formed and give it to me immediately. It'll start going back to equilibrium immediately, but that's my problem, not yours. And once the hydrogen iodide is out of the container, more will be produced.

But no. It turns out I lied about the "complete control" thing. You're not allowed to open the container or tamper with its contents directly. You have to increase the amount of hydrogen iodide some other way.

Disturbance 2: We could still crush the box to increase the pressure, as long as we're very careful not to open it. But wait, will that actually help? Remember that pressure only shifts the equilibrium if the reaction has some way of relieving the pressure. In this particular reaction, there's two moles of gas on each side. Crushing the box won't help us at all.

Disturbance 3: Our last hope. Fortunately, there's heat on one side of the equation, so we know this can work. Heat is a product, so to shift the equilibrium to the left, you need to remove heat. So, you can place the whole container in the freezer.

Hooray! That works! Now you know the basic idea of Le Chatelier's Principle, the three major kinds of disturbances to equilibrium, and how to use those disturbances to increase the yield of a reaction. Good luck on the AP Chemistry exam!







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No discussion of solubility rules is complete without first understanding the notation associated with solubility analysis. Understanding solubility on a deep level requires us to view the topic from a particulate approach, which means we will have to discuss the Kinetic Molecular Theory in detail. This will help you understand how compounds become solvated, on a particle level. Once we understand that, there is no stopping us! Thermodynamics is next, with a general discussion about the effects of temperature on solubility. Then, the *meat* of this article: an in-depth discussion about the solubility equilibrium expression  $K_{sp}$  and what the AP Exam will require of you. Finally, we will wrap up with a discussion of how inter molecular forces can affect the ability of compounds to become solvated!







#### Solubility Notation – Essential Knowledge 6.C.3.

There are some notations which you will probably be familiar with already that we must go over before continuing with this guide.

- We sometimes abbreviate the word "precipitate" as "ppt".
- Solid particles can be designated as (s), i.e. NaCl<sub>(s)</sub>. In a solubility equation, this would equal the precipitate.
- We define soluble products as those who can become solvated in water.
   In molecular notation this would be designated as (aq), which stands for "solvated in aqueous media", i.e., Na+(aq).

In general, the higher the temperature of a system the easier it is for compounds to become solubilized in solution. How come? Well, let us consider the system using the Kinetic Molecular Theory.

#### Total Energy of a System – Essential Knowledge 5.A.1.

Three terms define the total energy of any system.

$$E_{total} = KE + PE + U$$

The first term, kinetic energy (KE), governs the energy an object possesses based on its motion. Macroscopic objects like a moving car have a certain kinetic energy, and microscopic objects like gasses do too. Kinetic energy is a function of the momentum (p) of an object, and momentum is itself a function of the velocity (v) and mass (m) of an object. The greater the mass and the larger the velocity, the greater the momentum, and therefore the greater the kinetic energy. Don't worry about the calculus; that is just a notation thing.

$$KE = \int p = \int mv = \frac{1}{2}mv^2$$







The second term, potential energy (*PE*), is a composite function that describes the energy stored within the system based upon its external conditions. For example, a rock at the top of a mountain has a certain potential energy because it exists inside of a *gravitational field*, and this field gives it the potential to fall. Likewise, a charged ion (i.e. Na<sup>+</sup>) has a certain potential energy inside of an *electric* field. Anytime the word <u>field</u> is mentioned, you can assume that potential energy has something to play in it. Each external force field has its set of equations for potential energy, and we will not be going over them as we speak.

The final term, internal energy (U), is a thermodynamic function that encompasses all the energy associated with the bonds inside of a molecule. The internal energy of a system is affected anytime bonds are made or broken. Absorbing high-energy photons, which cause the electrons in an atom or molecule to jump to a higher-energy state, is also reflected by changes in the internal energy. There are also vibrational and rotational moments in multi-atomic molecules that contribute to the internal energy of a system. Intramolecular forces such as the electric dipole associated with the formation of polar covalent bonds or the magnetic dipole present in aromatic compounds are also classified under changes in internal energy since they are present regardless of external electric or magnetic fields.

To adequately describe the energetic state of a system you need to include all the various functions relating to the variables of kinetic, potential, and internal energy. Many equations compromise the total potential and internal energies of a system, and calculating each one is an <u>incredibly</u> tedious process, if not downright impossible. So, a way to get around this obstacle is only to consider *changes* in a system. When we do so, we need only consider those variables that are *changing* between the beginning and end of our reaction.







#### Kinetic Molecular Theory – Essential Knowledge 2.A.2.

It is easiest to understand the kinetic molecular theory terms of **gasses**. Let's say that we place pure helium gas (monoatomic, He) in a container and that we fix the volume of the container. At room temperature ( $T = 20^{\circ}C$ ), the gas particles exert a certain pressure on the walls of the container (measured by a barometer). As the temperature drops, what we experimentally observe is that the pressure of the gas in the tank drops in a linear fashion. And what Scottish-born William Lord Kelvin did was extrapolate the linear relationship to the point where the pressure of the gas equals zero. The theoretical temperature that he calculated was  $-273^{\circ}C$ .

So what does this mean? Well, let us consider the energetics argument. What is the total energy of the mono atomic helium gas? Its internal energy is negligible: they have no rotational or vibrational modes, nor does it have a molecular dipole. Inter molecular forces are negligible because the gas molecules are so far apart from each other. Neither does it have any potential energy: the helium molecules are not charged, nor do they possess an inherent magnetic dipole. The only energy that these molecules possess is, in fact, *kinetic* energy, the energy of motion. Since  $KE = \frac{1}{2}mv^2$ , if the particles have any energy they are moving. So, what happen at the point where the pressure of the container equals zero? At that point, the gas molecules have no energy and therefore have ceased all movement.

What does this all mean? Bottom line: the temperature of a gas is directly proportional to its temperature! In liquids, the molecules have a significant amount of inter molecular forces which can also absorb energy. However, this basic understanding of heat equaling movement is the reason why all solubility calculations vary as a function of temperature. Standard measurements are therefore always performed at a certain temperature, such as 25°C so that the calculated value is always true for solubilization at that temperature.







#### Thermodynamic Considerations of Solubility – 6.C.3.

Applying the Kinetic Theory of Matter to the topic of solubility, we now realize that particles at higher temperatures are excited to higher states of energy, which frequently means and increased number of collisions between these particles. Increased collisions mean that statistically a molecule of water has a greater chance of hitting one of the ions to be solubilized in a way that causes the ion to become *solubilized*. This applies to any endothermic (heat-absorbing) reaction, which compromises most (but not all) solubilization reactions.

On the other hand, some solvation reactions like that of sodium sulfate are exothermic (heat-releasing) and therefore are less soluble at a higher temperature. A graph of some solubilization constants as a function of temperature is shown below to provide an example.

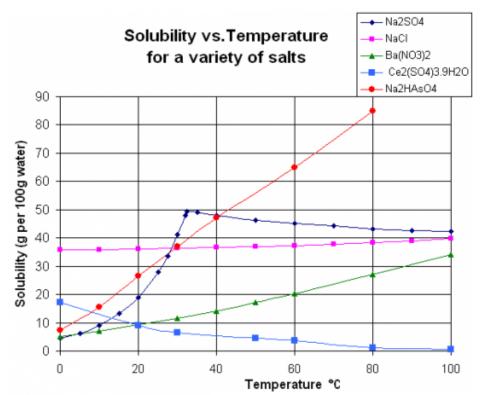


Image Source: Wikimedia Commons







Higher temperature also serves to decrease the attraction between individual water molecules, which are highly attracted to one another. Breaking up the lattice of hydrogen bonds somewhat allows incoming ions to take their place inside the lattice. This can visually be represented as the water molecules around the ion forming a solvation shell.

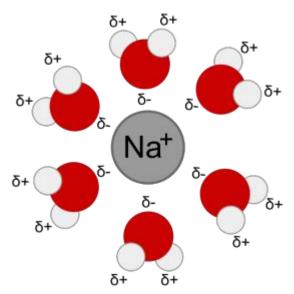


Image Source: Wikimedia Commons

#### The Always Soluble's – Essential Knowledge 6.C.3.

Several salts that are always soluble in water regardless of their composition. All salts which contain the following ions are always soluble:

- Sodium, Na+
- Potassium, K<sup>+</sup>
- Ammonium, NH<sub>4</sub>+
- Nitrate, NO<sub>3</sub><sup>-</sup>







#### **Example:**

Table salt, NaCl, is completely miscible in water, dissociating completely to its constituent sodium and chloride ions.

$$NaCl_{(s)} \leftrightarrow Na^+_{(aq)} + Cl^-_{(aq)}$$

In the past, you were required to memorize a list of compounds or salts and know from memory whether or not the product was soluble in water, or will form a precipitate. Instead, the new AP Chemistry exam stresses the understanding of the solubility equilibrium constant,  $K_{sp}$ . To quote from the <u>AP Chemistry Exam</u> <u>Guide</u> (page 79):

"Memorization of other 'solubility rules' is **beyond the scope** of this course and the AP Exam. **Rationale:** Memorization of solubility rules does not deepen understanding of the big ideas."

Therefore, we will focus the rest of our discussion on the application of the solubility equilibrium constant.

#### **Solubility Equilibrium Constant – Essential Knowledge 6.C.3.**

For the dissolution of a salt, the reaction quotient Q is referred to as the solubility product and  $K_{sp}$  as the solubility-product constant. Why "solubility-product"? Well, let's use an example to show how we calculate the solubility of an ionic substance in water. For the ionic salt silver chloride (AgCl):

$$AgCl_{(s)} \leftrightarrow Ag^+_{(aq)} + Cl^-_{(aq)}$$







Writing out the  $K_{sp}$  of the reaction (solubilization) is the same as writing out any other equilibrium constant: the equilibrium constant is the ratio of products and reactants. For a reaction with the form:

$$aA + bB = cC + dD$$

The equilibrium expression would be written out as follows:

$$K=rac{[A]^a[B]^b}{[C]^c[D]^d}$$

However, in the example above, the only reactant is a solid. Solids are excluded from equilibrium expressions. Therefore, the expression for the example (and for any solubility expressions) simplifies to:

$$K_{sp} = [Ag^+] \times [Cl^-]$$

This is why the solubility equilibrium constant is called the "solubility-product" constant: because the value of  $K_{sp}$  is always equal to the product of the concentrations of the two constituents of the salt. The value of the equilibrium constant is experimentally-derived and will be given to you on the AP Exam from a table of standard solubility products. However, it is up to you to know how to use and apply it.

Using the example above, and given  $K_{sp} = 1.8 \times 10^{-10}$ , find how many grams of silver chloride can be dissolved in one liter of water.

We would write:

$$K_{sp} = 1.8 \times 10^{-10} = [Ag^+] \times [Cl^-]$$







In silver chloride,  $[Ag^+] = [Cl^-]$ , so this can be alternatively written as

$$K_{sp} = 1.8 \times 10^{-10} = [Ag^+]^2$$

Which when square-rooting both sides simplify to:

$$[Ag^+] = 1.34 \times 10^{-5} = [Cl^-]$$

Since equilibrium expressions are written in standard units, the number given above is for moles or compound. And since the concentration of silver chloride equals the concentration of silver and chloride ions, one liter of water will solubilize  $1.34 \times 10^{-5}$  moles of AgCl. The molar mass of silver chloride is found to be 143.32 g/mol using the Periodic Table. So converting to grams:

$$(1.34 \times 10^{-5} mol) \times (143.32 g/mol) = 1.92 \times 10^{-3} g$$

Since equilibrium expressions are written in standard units, the number given above is for moles or compound. And since the concentration of silver chloride equals the concentration of silver and chloride ions, one liter of water will solubilize  $1.34 \times 10^{-5}$  moles of AgCl. The molar mass of silver chloride is found to be 143.32 g/mol using the Periodic Table. So converting to grams:

One liter of water would solvate 1.92 x 10<sup>-3</sup> grams of silver chloride.

This calculation becomes a little more algebra-dependent when you deal with non-binary salts (salts that contain more than one positive and one negative ion). An example is the salt lead bromide (PbBr<sub>2</sub>), which contains two bromide ions for every lead ion.

Given  $K_{sp} = 4.6 \times 10^{-6}$ , find how many moles of lead bromide can be dissolved in 500 mL of water.







We would write:

$$K_{sp} = 4.6 imes 10^{-5} = \left[Pb^{2+}
ight] imes [Cl^-]^2$$

When one mole of lead bromide dissolves, two moles of chloride and one mole of lead ions are formed. This can be represented as:

$$\left[Pb^{2+}
ight]=x$$
 and  $\left[Cl^{-}
ight]=2x.$ 

This variable 'x' is equal to the number of moles of lead bromide being dissolved. We can substitute 'x' into our  $K_{sp}$  expression:

$$K_{sp} = 4.6 imes 10^{-5} = \left[Pb^{2+}
ight]x[Cl^{-}]^{2} = (x)\cdot(2x)^{2}$$

We then solve the equation for 'x':

$$(x) \cdot (2x)^2 = 4.6 \times 10^{-5}$$
  
 $(x) \cdot 4x^2 = 4.6 \times 10^{-5}$   
 $4x^3 = 4.6 \times 10^{-5}$   
 $x^3 = 1.15 \times 10^{-5}$   
 $x = (1.15 \times 10^{-5})^{\frac{1}{3}} = 2.26 \times 10^{-2}$ 

One liter of water will solubilize  $2.26 \times 10^{-2}$  moles of lead bromide. However, the question was for 500 mL of water. So, we need to divide the value we got by half, which gives us  $1.13 \times 10^{-2}$  moles of lead bromide. This method can be used to solve for the molar quantity of a compound which can dissolve in water.

It's also important to note that in some cases  $K_{sp}$  value will be reported in logarithmic units  $(pK_{sp})$ . Writing the constant in logarithmic notation is used for simplicity.







For example,

$$K_{sp}\left(AgCl\right) = 1.8 \times 10^{-10} \grave{a} \log \left(1.8 \times 10^{-10}\right) = -9.74$$
 $K_{sp}\left(PbBr_2\right) = 4.6 \times 10^{-5} \grave{a} \log \left(4.6 \times 10^{-5}\right) = -4.34$ 

We want you to note this important trend in solubility-product constants: the smaller (more negative) the equilibrium constant, the less compound can be dissolved in water. This is true both for the regular and logarithmic form of the constant. Analyzing  $K_{sp}$  values is the new way that the AP Chemistry Exam will test your understanding of Solubility Rules. By being able to predict the favor ability of solvation based on an understanding of the solubility-product constant, this will give you true insight into the deep meaning behind solubility.

#### Application of Le Chatelier's Principle – Essential Knowledge 6.C.3.

When performing solubility experiments, one can notice the decreased solubility of certain compounds in the presence of like compounds. For example, sodium chloride is fully soluble in water. However, if you were to try and solubilize a different sodium salt (such as sodium sulfate, Na<sub>2</sub>SO<sub>4</sub>) or chloride salt (such as silver chloride, AgCl) the solubility of the second salt would be lower than if you tried to solubilize the salt in a solution of pure water. This is due to the phenomena known as the *Common Ion Effect*.

In essence, <u>Le Chatelier's principle</u> predicts that as you change the concentration of a compound on one side of the equilibrium expression, the system will be prompted to adjust for those changes. Using the example above, suppose sodium chloride was dissolved in water as such:

$$NaCl_{(s)} \leftrightarrow Na_{(aq)}^+ + Cl_{(aq)}^-$$







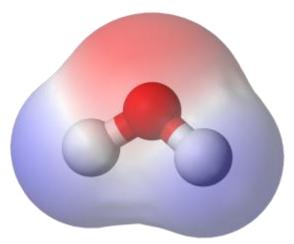
Now, when we go to add silver chloride, instead of the usual reaction quotient Q where the starting concentration of chloride is equal to zero, now the starting concentration of chloride is actually equal to the concentration of dissolved chloride from the NaCl.

$$AgCl_{(s)} \leftrightarrow Ag^+_{(aq)} + \uparrow Cl^-_{(aq)}$$

Le Chatlier's Principle is applied by arguing that less silver chloride will dissolve in the salt solution because there is already a certain amount of chloride in the solution. In other words, as we increase the concentration of one of the compounds in the reversible reaction, the concentration of the compounds on the other side of the reversible reaction must also increase. This is the core of the Common Ion effect, and it is a topic that you will almost certainly encounter qualitatively at least on the AP Chemistry Exam.

#### Molecular Polarity – Essential 2.B.1, 2.B.2, 2.C.1.

When two atoms share a covalent bond but have different electronegativities (0.5 <  $e^-<$  2.0) the electrons in the bonds are shared unequally, and the molecular becomes *polar*. Below is a heat map of electron density, a standard method of displaying bond polarity. The red region is representative of areas with high electron density, and blue represents low density.



<u>Image Source: Wikimedia Commons</u>



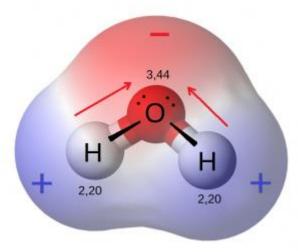




The polarity of a molecule directly relates to the manner in which compounds are solvated by water in solution. It can be challenging to predict molecular polarity. Diatomic molecules of the same element are always non polar. Likewise, carbohydrates are generally non polar. Any molecule with mirror planes of inversion cannot be polar because polarity is by definition determined by an uneven distribution of charges. Even molecules that are symmetrical about an uneven axis such as boron trifluoride (BF<sub>3</sub>) which has a trigonal planar is non polar, because the overall distribution of charges is symmetrical.

#### **Hydrogen Bonding – Essential Knowledge 2.B.2.**

A type of inter molecular bonding is the hydrogen bond, which is a specific type of inter molecular bonding. Below we've shown an image of the electron density of a molecule of water, which consists of one oxygen atom bonded to two hydrogen atoms. Oxygen ( $e^- = 3.44$ ) has a much higher <u>electronegativity</u> than hydrogen ( $e^- = 2.20$ ), and therefore the electrons are more attracted to the oxygen atom and spend more time closer to its nucleus. This results in the formation of a polar bond.



**Image Source: Wikimedia Commons** 







Now the water molecule, which is surrounded by other similar molecule, has both a positive and negative partial charge. In a solution of water, the partially positive hydrogen atoms attract the partial negative charge of other oxygen atoms in nearby water molecules, and vice versa. This creates a unique network of weak electrostatic interactions which are aptly named hydrogen bonds.

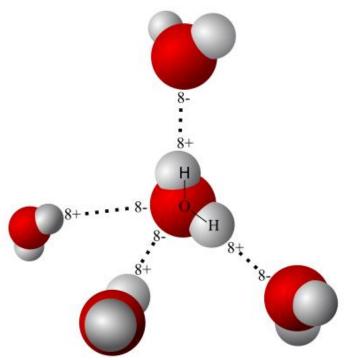


Image Source: Wikimedia Commons

Unlike the other inter molecular forces, hydrogen bonds are relatively strong though still weaker than ionic and covalent bonds. They are also important because of the sheer number of them in solutions of polar protic (hydrogen-containing) molecules like H<sub>2</sub>O: they are the main contributor to the physical effect of surface tension in water.

One important final point: hydrogen bonds only exist in protic molecules that are polar. Carbohydrates, which consist of molecules composed of many carbonhydrogen bonds (as the name implies), do not possess any polarity, and therefore cannot for hydrogen bonds. That is why oils do not dissolve in water!







#### Effects of pH on Solubility – Essential Knowledge 6.C.3.

The pH of a solution is a measure of the concentration of protons ( $H^+$  ions), where the most concentrated protonated solution has pH = 0, and the least protonated (most basic) solution has pH = 14. There is a larger discussion about what constituted an acid and a base, but for now, we will keep the discussion around the Arrhenius definition of acids and bases ( $H^+$  and  $OH^-$  ions).

How does the pH of a solution affect the solubility of a compound? Well, some compounds are neutral at some pH and charge-containing at others. For example, ammonia ( $NH_3$ ) is neutral at basic pH, but, as the concentration of  $H^+$  increases, ammonia becomes charged and turns into ammonium ( $NH_4^+$ ). Due to the electrostatic interaction between the positive ammonium ion and the partial negative charge of the polar water molecules, ammonium is much more soluble in water than ammonia!

And with that, we are done! You now know everything there is to know about solubility rules for the AP Chemistry Exam! How did we do? Did we miss anything? If you want to know anything more, or have more specific questions about this topic, write us and let us know! We always appreciate hearing from you, our reader.

Good luck!









*Image Source: Wikimedia Commons* 

Hi, guys! Welcome to another of our *Ultimate AP Chemistry Guide* series! This time, we're going to teach you all about *electrochemistry*. We'll start off with a quick overview of what electrochemical reactions are. Then we'll go over the terms "oxidation" and "reduction", what redox reactions are, and how to balance them. Once you can define those terms without even thinking twice, you will learn how electrochemical reactions can be described in terms of free energy change, and how those calculations tie in with other thermodynamic equations. We will then outline the conditions under which a voltaic cell is created, and how it functions. Finally, we will briefly cover the topic of corrosion, and how metals can be protected from it.







Let's go back to basics for a second. Follow me along here.

**Question:** What is a chemical reaction?

**Answer:** A chemical reaction occurs when two substances (reactants) interact with each other and undergo a chemical transformation to become other substances, generally with different properties than they had before (products). Chemical reactions can be described, among other things, in terms of their **stoichiometry** and of their free energy change ( $\Delta G^{\circ}$ ). So, too, can electrochemical reactions. In much the same way as chemical reactions, electrochemical reactions are defined in terms of products being made from reactants. The main difference between a standard chemical reaction and an electrochemical reaction is (no surprise): **ELECTRONS** ( $e^{-}$ ).

#### **Electrochemistry – Essential Knowledge 3.C.3.**

Electrochemical reactions, as the name implies, classify chemical reactions that involve the flow of electricity. In other words, they involve the movement of electrons from one substance to another. This movement of electrons is more commonly referred to as an *electrical current*. Current is measured in units of Amperes (amp), where one amp of current is the movement of one coulomb of electric charge per second ( $A = C s^{-1}$ ). The flow of electrons can be described as a pair of corresponding reactions: oxidation and reduction.

The term "Oxidation State" is a measure of the number of electrons relative to the number of protons in an atom. An atom in the "ground state" has an equal number of electrons and protons, and therefore we say it has an oxidation number of 0. The term oxidation state can be confusing because the first thing you think about is the word "Oxygen." This nomenclature is not a coincidence.

The term "oxidation" was coined by French Chemist Antoine Lavoisier (1743-1794), who discovered chemical reactions which caused molecules to bind to oxygen, or, become oxidized.







Many years later other chemists figured out that when atoms bonded together in a molecule through covalent bonds, the more electronegative atom "grabs" more of the electrons, and they quantified this relationship as a change in the oxidation state of an atom. Let's use an example to help make heads and tails of this topic.



**Image Source: Wikimedia Commons** 

#### Redox Reactions - Essential Knowledge 3.C.3, 6.A.1.

Rusting is a type of redox reaction where solid iron reacts with molecular oxygen to form *Iron (III) Oxide*. When the iron becomes oxidized (i.e. when oxygen adds to it) the oxidation state of iron changes from the ground state (0) to +3. So as we see, when compounds become oxidized their oxidation number increases. Another way to think about the oxidation state is that in this reaction, oxygen steals some of the electrons off of iron to become more stable, and therefore it "gains" positive charge. On the other hand, when molecular oxygen reacts with  $Fe_{(s)}$ its oxidation state changes from the ground state (0) to -2, so the oxidation state of the reduced molecule becomes more negative. In other words, oxygen gains electrons in this reaction and acquires a net negative charge. These types of reactions are known as *Oxidation-Reduction Reactions*, or *Redox*.







While a Redox Reactions is technically one single reaction, it can be split into a pair of concurrent reactions. When added together, the oxidation and reduction *half-reactions* add up to a complete chemical reaction. When writing out half-reactions, we include the number of electrons being moved to help us see the flow of electrons in the reaction. But where do the electrons go? Well, in the same way that the number of atoms in a reaction have to balance across the reaction using **stoichiometry**, the charge of all the species have to balance across the reaction. Let's use the rusting of iron to explain this concept.

First let's write the balanced stoichiometric reaction of rusting iron, considering that the final product is  $Fe_2O_3$ :

$$Fe_{(s)} + O_{2(g)} = Fe_2O_{3(s)} - > 4Fe_{(s)} + 3O_{2(g)} = 2Fe_2O_{3(s)}$$

Now, let's divide this equation into its oxidation and reduction portions. How do we know what number to assign the oxidation state of each atom? Well, elements in their ground state have a defined oxidation state of zero. As far as the products, we know what for the charges to be balanced, the net electrical charge on both sides must be equal. So, if the sum of the charges on the left is zero, the sum of charges on the right must be zero as well.

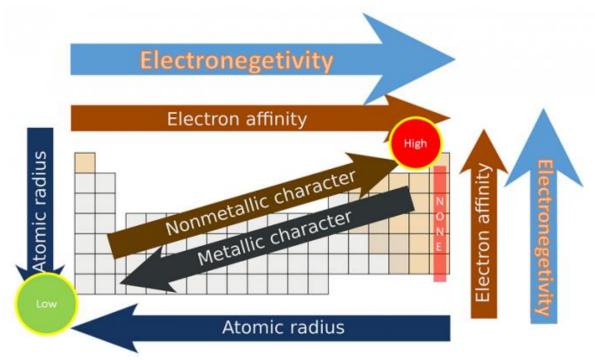






#### **Electronegativity – Essential Knowledge 2.C.1.**

Now to know what oxidation state to assign oxygen and iron, you have to consider the <u>electronegativities</u> of the atoms involved. Let's remind us of the trend in periodic behavior:



**Image Source: Wikimedia Commons** 

The most electronegative atom is fluorine (Z = 7, top right), and the least electronegative atom is francium (Z = 87, bottom left). The oxidation state of a molecule directly relates to the manner in which the covalent bond is shared between bonded atoms. The more electronegative atom attracts the electrons more strongly to its nucleus because of the added stability this arrangement gives to the molecule (*electron configuration reminder:* a full shell is more stable than a partially-filled shell). Therefore, the electron spends more time revolving around the more electronegative atom. We designate this relationship by assigning the most electronegative atom a negative oxidation state, to indicate that the electrons "belong" to it, whereas we show the less electronegative atom has "lost" electrons and therefore has a positive oxidation state.



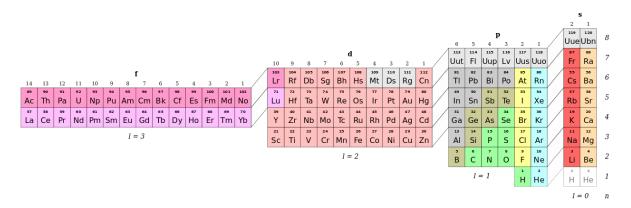




#### **Electron Configuration – Essential Knowledge 1.B.2.**

But where do the electrons come from? And where do they go? Well, as we know, chemicals are all fundamentally made up of atoms. Atoms, in turn, are classified by the number of protons in their nucleus, which determines the total positive charge of each element. And when the atom has an equal number of electrons orbiting the nucleus, the atom has a net neutral charge. However, the stability of an element is not determined by whether or not it has a neutral charge. In fact, the stability of an element has more to do with its *electron configuration*.

Atoms, like glasses, do not like being half empty or half full. Rather, they prefer having an electron configuration which results in them having either full or empty orbitals. Determining which orbitals electrons inhabit is done by "building up" the atom's valence electrons (Aufbau principle). In most cases, however, the most stable version of an element is not one where the number of electrons equals the number of protons. Rather, it is energetically-favorable for elements to either gain or lose electrons to become more stable.



**Image Source: Wikimedia Commons** 

Going back to our balanced stoichiometric reaction,  $4Fe_{(s)} + 3O_{2(g)} = 2Fe_2O_{3(s)}$ ; we will first assign oxidation states to all the elements, and then write out the individual half-reactions it is composed of (oxidation of iron and reduction of oxygen). You will also learn some general tips about how to assign oxidation numbers. *Are you ready?* Let's hit it!







#### Oxidation States - Essential Knowledge 3.B.3.

Assigning oxidation number can be a big issue for many students because there are millions of chemical compounds each with their own identities. The information overload can cause you to panic, especially during the AP Exam when it is more crucial for you to stay calm. So we're going to teach you a great method to remember how to assign oxidation states that you'll be able to use on the AP Exam. It involves using the *periodic table*, which you get for free!

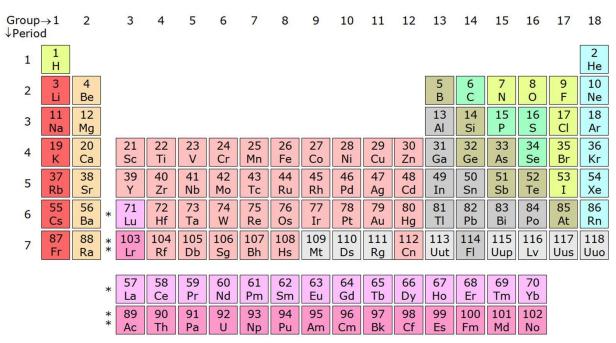


Image Source: Wikimedia Commons

As we previously discussed, oxidation state relates to <u>electronegativity</u>, and it also relates to electron configuration. Therefore, think about the periodic table when we go through these rules, and memorize them in *terms* of the table.







When you finish applying these rules, assign the remaining oxidation states in the compound by keeping in mind that the sum of all oxidation state numbers must equal the net charge on the molecule.

#	Chemical Species	Oxidation State	Exceptions
1	Elemental Form	0	
2	Monoatomic lons	Ionic Charge	
3	Group 1A, 2A Metals	+1, +2	
4	Oxygen	-2	Except in peroxides and F <sub>2</sub> O
5	Hydrogen	+1	Except in metal hydrides where it is -1
6	Fluorine	-1	
7	Cl, Br, I	-1	Except in compounds with O or F
8	Groups 7A, 6A, 5A	-1, -2, -3	*in binary compounds with metals

So what do we mean when we say "keep the periodic table in mind"?







Let's take a look at Rule 3: "Group 1A, 2A Metals -+1, +2". The *reason* for this rule is that alkali and alkaline earth metals are much more stable without any electrons in their outlying s-orbital, and they tend to lose those electrons to form more stable ions. Looking at the periodic table shows you this relationship visually. In the ground state, those metals will have outlying electrons, which is energetically unfavorable. The same line of reasons can be used for rules 6 & 8, where we can see how the position of these elements can affect the number of electrons they lose to become stable.

Rule 7 makes sense when considering the difference in electronegativities between the halogens (Group 7A). Electronegativity *decreases* as you go down a group, and the most electronegative atoms are assigned the negative oxidation state. Since fluorine is the most electronegative element, followed by oxygen, any compounds formed between fluorine/oxygen and another halogen will cause a positive oxidation state to be placed on the halogen. In every other case, however, the halogens will be the most electronegative atoms, so they will have an oxidation state of -1.

So, apply the rules, then assign the remaining oxidation states based on "the sum of oxidation states equals the net charge". Let's practice assigning oxidation numbers to our rusting iron example. The balanced chemical reaction is:

$$4Fe_{(s)} + 3O_{2(g)} = 2Fe_2O_{3(s)}$$

Rule 1:  $Fe_{(s)} \& O_{2(a)}$  have an oxidation state of zero.

Rule 4: Oxygen's oxidation state is -2

To get the oxidation state of Fe, get the total number of atoms of each element in the compound and balance it to equal the net charge on the compound.







We're done! You now possess all the knowledge necessary to assign oxidation states correctly. Armed with this knowledge, we will now balance the redox reaction of iron rusting and generalize that example to <a href="mailto:balancing redox">balancing redox</a> equations in general.

#### Balancing Redox Equations – Essential Knowledge 3.B.3, 3.C.3, 6.A.1.

Since we now know the oxidation states of the products and reactants, we can split the balanced reaction up into its constituent oxidation and reduction reactions. You designate the oxidation state by writing it as if it were an electric charge on the element. The balanced oxidation half-reaction would look like this:

$$4Fe_{(s)} = 4Fe^{3+-->>}Fe_{(s)} = Fe^{3+}$$

And the balanced reduction half-reaction would look like this:

$$3O_{2(g)} = 6O^{2---->>}O_{2(g)} = 2O^{2-}$$

The same rules for balancing the electric charge across the reaction apply to half reactions as well. Once oxidized, iron has an oxidation state of 3+. We indicate that the iron atom loses three electrons to balance this positive charge. This is written as:

$$Fe_{(s)} = Fe^{3+} + 3e^{-}$$

Now the net charge on both sides of the equation is zero, and the reaction is balanced. The reduction half-reaction would look like this once accounting for the electrons:

$$4e^- + O_{2(g)} = 2O^{2-}$$







Notice that we wrote the electrons in on the reactant side of the equation in this case to balance it out, because it was the products that had the charge on them. This is generally the case for reduction half-reactions.



Image Source: Wikimedia Commons

We now have the two balanced half-reactions rusting. What do we do with this information? Well, we now *add* the two reactions together and balance *that!* The goal here is to multiply each half-reaction by the least common denominator of the electrons on each side, so that when we add the reactions together, the electrons *cancel out*.

$$4 \times [Fe_{(s)}] = [Fe^{3+} + 3e^{-}] \times 4$$

$$3 \times [4e^{-} + O_{2(g)}] = [2O^{2-}] \times 3$$

$$4Fe_{(s)} = 4Fe^{3+} + 12e^{-}$$

$$12e^{-} + 3O_{2(g)} = 6O^{2-}$$

$$4Fe_{(s)} + 3O_{2(g)} = 4Fe^{3+} + 6O^{2-} = 2Fe_{2}O_{3}$$







The final product of this reaction,  $Fe_2O_3$ , or Iron (III) Oxide, is rust. There are other electrochemical reactions that, besides electrons, also produce protons (H+), which you also have to balance until they cancel out. We will see examples of that later. In the meantime, let's look at the process one more time step-by-step to make sure we got it right.

- 1) Balance the chemical reaction.
- 2) Assign oxidation states to all elements.
- 3) Write out the two redox half reactions.
- 4) Balance the charge on each half reaction by adding electrons.
- 5) Add the two half reaction together to arrive at your final balanced electrochemical reaction.

#### Free Energy – Essential Knowledge 5.E.3, 5.E.4, 6.D.1.

We have finished learning about how to classify an electrochemical reaction stoichiometrically. Now we will find out how to classify it in thermodynamic terms. Namely, how the electrical component can be incorporated into discussions of free energy change ( $\Delta G^o$ ). Free energy is a measure of the potential energy of a molecule. When substances go from reactants to products, they undergo a free energy change called noted as  $\Delta G^o$ .

Here is the main equation relating to electrochemistry that will be provided to you on the AP Chemistry Exam **Equation Sheet**:

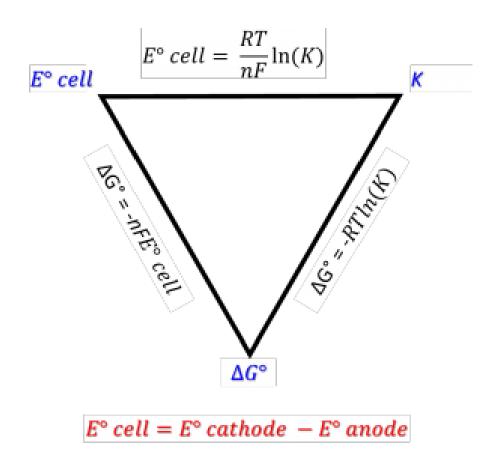
 $\Delta G^{\circ}$  = - n F E°<sub>cell</sub>; where F = Faraday's Constant = 96,485 coulombs (mol e<sup>-</sup>)<sup>-1</sup>, E° = Standard Reduction Potential n = number of moles of electrons







The  $E^o_{cell}$ , or standard reduction potential, is an experimentally-determined value of the electrical potential in volts (V) across the two half reactions. The standard reduction potential for the hydrolysis of hydrogen gas into protons and electrons is defined as 0. Since n must be a positive integer and F is a constant, any values of  $E^o_{cell}$  that are positive will give a negative  $\Delta G^o$ , so the reaction spontaneous in the direction it is written. On the other hand, if  $E^o_{cell}$  is negative, then  $\Delta G^o$  is positive, and the reaction as written becomes unfavorable and non-spontaneous.



Although we won't get into it, keep this diagram in mind when trying to figure out the relationship between free energy, standard reduction potential, and the equilibrium concentration of products and reactants in a reaction. The bolded equation in red will be discussed next up!

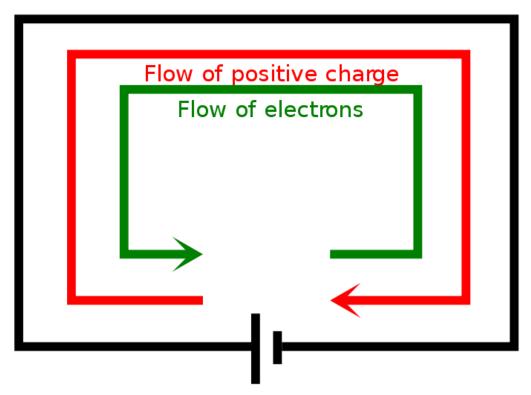






#### Standard Reduction Potential – Essential Knowledge 3.C.3.

Let's remind us what a positive voltage means with this diagram below:



**Image Source: Wikimedia Commons** 

As you see, having a positive value for  $E^o_{cell}$  means that the electrons are flowing in the opposite direction. It's important to remember that  $E^o_{cell}$  measures the potential across the reactions going from *right* to *left*. Half reactions with a negative  $E^o_{cell}$  value are spontaneous in the direction they are written since a negative value of  $E^o_{cell}$  results in a negative  $\Delta G^o$ . This is a common pitfall for many **AP Chem students**: The flow of electrons is opposite that of the movement of charge, and the voltage measures the flow of charge.







#### Standard Reduction Potential

Oxidant	<b>=</b>	Reductant	E° (V)
2 Cl <sup>-</sup>	$\rightleftharpoons$	Cl <sub>2(g)</sub> + 2 e <sup>-</sup>	-1.36
$Ag_{(s)}$	$\rightleftharpoons$	Ag+ + e-	-0.7996
4 OH <sup>-</sup> (aq)	=	$O_{2(g)} + 2 H_2 O + 4 e^-$	-0.401
$Cu_{(s)}$	=	Cu <sup>2+</sup> + 2 <i>e</i> <sup>-</sup>	-0.337
$Ag_{(s)} + CI^-$	=	AgCl(s) + e <sup>-</sup>	-0.22233
$H_{2(g)}$	=	2 H <sup>+</sup> + 2 e <sup>-</sup>	0
Fe <sub>(s)</sub>	=	Fe <sup>3+</sup> + 3 <i>e</i> <sup>-</sup>	+0.04
Fe <sub>(s)</sub>	=	Fe <sup>2+</sup> + 2 e <sup>-</sup>	+0.44
$Zn_{(s)}$	$\rightleftharpoons$	Zn <sup>2+</sup> + 2 e <sup>-</sup>	+0.7618
$Al_{(s)}$	=	Al <sup>3+</sup> + 3 e <sup>-</sup>	+1.662

It is possible, however, to "flip" the equations around. If we wanted to know the standard reduction potential for the opposite reaction of that tabulated, we could flip the reactants and products and  $E^o_{cell}$  for the reaction would be equal and opposite that of the original reaction. For example, if we wanted to know  $E^o_{cell}$  for Iron III ( $Fe^{3+}$ ) reducing to solid iron ( $Fe_{(s)}$ ) all we have to do is write the reaction going the opposite way. In this case,  $Fe^{3+} + 3e^- = Fe_{(s)}$  would have  $E^o_{cell} = -0.04$ .

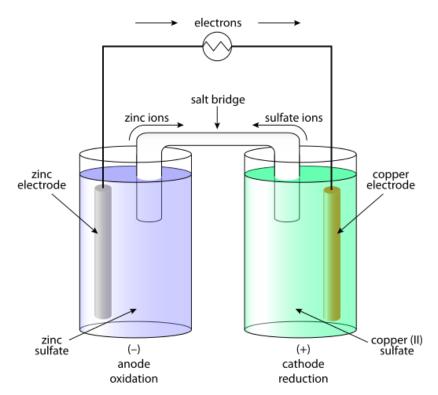






#### Voltaic Cells – Essential Knowledge 3.C.3.

Electrochemical reactions that are spontaneous can be used to generate an electric current. Voltaic (or galvanic) cells host each of the redox half reactions in different containers called half cells. The *half cells* are formed by including a metal in two different oxidation states, usually a solid *electrode* and an aqueous metal ion. The electrons generated from a spontaneous oxidation reaction such as zinc metal to zinc II ions are coupled to a favorable reduction reaction like the solidifying of copper II ions into copper metal.



**Image Source: Wikipedia Commons** 

The electrodes in each half cell are connected to allow electron flow. As electrons flow from the oxidized to the reduced metal, positive charge accumulates at the oxidized electrode and negative charge at the reduced one. To balance this accumulated charge, positive and negative ions flow into the cells from a *salt bridge* that connects the two half reactions.







A salt bridge is essentially an aqueous circuit filled with both positive and negative ions, which can flow freely from into each cell, and balance the accumulated charge.

#### Things to keep in mind:

- Electrons move from the *anode* to the *cathode*.
- The overall voltage in a voltaic cell is *negative*, opposite the flow of  $e^-$ .

#### **Corrosion – Essential Knowledge 3.C.3.**

The last topic we're going to consider before moving on to free response mastery is *corrosion*. Corrosion is a type of electrochemical reaction where pure metal reacts with and is oxidized by oxygen and water to form metal complexes which are brittle. The atom with the smaller (more negative)  $E^o_{reduction}$  will be oxidized in this reaction. An example of this is the rusting of iron, which is the reaction we have been using as an example thus far. Metals can be protected from corrosion by coating them with another metal which is a more potent reducing agent. Another term for this metal is a *sacrificial anode* since the coating is oxidized to protect the underlying vulnerable. Many times the sacrificial metal is *zinc* because it is a strong reducing agent (very likely to lose electrons for stability).

And with that, we're done! The topic of electrochemistry sure isn't an easy one. Many bits and pieces have to be digested, and you can't memorize *everything* for your exam. So remember what we've taught you: use the freebies you are given (Periodic Table, <u>Equation Sheet</u>) to help you assign oxidation states and predict reactions based on free energy changes. And above all, take a deep breath and *Go for it!* 







## How to Balance Redox Reactions



Image Source: Wikimedia Commons

Redox reactions are a very important part of the AP Chemistry exam, and they can be quite challenging. I know that I personally spent more time on understanding redox reaction than on any other concept on the test. I'll try to make it a little easier for you than it was for me.

So, first things first. What is a redox reaction? A redox reaction is simply a reaction in which one element is reduced (gains electrons) and another is oxidized (loses electrons). Here's a handy mnemonic to help you remember that: OIL RIG. Oxidation is losing (electrons), reduction is gaining (electrons).







#### How to Balance Redox Reactions Cont.

A good way to tell if a reaction is a redox reaction is if an element changes oxidation states (for example,  $Cu^+$  becomes Cu) or if an element acquires an oxygen atom or two (hence the name oxidation).

Enough about redox reactions themselves. How do you balance a redox reaction? It's actually fairly simple; there are just a set of steps you need to take and rules you need to follow.

When balancing a redox reaction, you need to know the half-reactions of the reactants. As implied by the name, two half reactions can be added to get a total net reaction. For example, this equation:

$$Cu^+(aq)+Fe(s) o Fe^{3+}(aq)+Cu(s)$$

Splits into these two half-reactions:

$$Fe(s) 
ightarrow Fe^{3+}(aq)$$

$$Cu^+(aq) o Cu(s)$$

Although the potentials of the half-reactions must be found for certain redox reaction calculations, balancing a redox reaction requires none of that.

#### **Balancing a Redox Reaction**

Balancing a redox reaction is actually a fairly simple problem, because you're given the direction of the reaction. You don't have to figure out what's happening, just how it's happening. We'll demonstrate this in the neutral solution example. There are also specific rules for aqueous reactions in acidic or basic conditions, in addition to the rules for neutral conditions.







#### How to Balance Redox Reactions Cont.

The **Half Equation Method** is used to balance redox reactions. This method separates the equation into two half-equations, one for oxidation and another for reduction. Here are the steps involved in the Half Equation Method for a redox reaction in a neutral solution:

- 1. Calculate the charges on each side. Balance them by adding electrons  $(e^-)$  to the more positive side. (One handy tip:  $e^-$  and  $H^+$  are usually found on the same side.)
- 2. The  $e^-$  on each side should be equal. If they are not, multiply one or the other of the half reactions by an integer to make them equal. If this does not make sense, just continue reading; the examples should make it clear.
- 3. Add the half-equations together, canceling out the electrons to form one balanced equation. Common terms should also be canceled out.
- 4. Check the equation to ensure that it is balanced.

Those are the basic steps for how to balance a redox reaction in a neutral solution. Now, let's take a look at a basic example of balancing a redox equation in a neutral solution before we move on to the more complex situation in acidic and basic solutions.

Balance this redox equation:

$$Cu^+(aq) + Fe(s) \rightarrow Fe^{3+}(aq) + Cu(s)$$

First, we split the equation into two half-reactions. The substance getting reduced will have electrons in its reactants, and the substance getting oxidized will have electrons in its products.

$$Fe(s) \rightarrow Fe^{3+}(aq)$$

$$Cu^+(aq) o Cu(s)$$







In this particular case, we can see that *Fe* loses electrons (becoming more positive), while *Cu* gains an electron (becoming less positive). As you can see, this is all clearly laid out in the information given to us: *Fe* becomes more positive, and *Cu* becomes less positive. Isn't that nice? So, the half-reactions are:

$$Fe(s) 
ightarrow Fe^{3+}(aq) + 3e^{-}$$

$$Cu^+(aq) + e^- o Cu(s)$$

Now, if we were to put these two reactions together, we'd have a net gain of 2 electrons. That won't work, so we multiply the bottom equation by 3 to balance the top one's electrons.

$$Fe(s) 
ightarrow Fe^{3+}(aq) + 3e^{-}3Cu^+(aq) + 3e^- 
ightarrow 3Cu(s)$$

Now we can add them together:

$$Fe(s) + 3Cu^{+}(aq) + 3e^{-} \rightarrow Fe^{3+}(aq) + 3Cu(s) + 3e^{-}$$

The electrons cancel each other, and we are left with a balanced reaction:

$$Fe(s) + 3Cu^+(aq) \rightarrow Fe^{3+}(aq) + 3Cu(s)$$

Sounds good? Sounds simple? Good, because there's more ground to be covered here.







#### **Balancing Redox Equations in Acidic and Basic Solutions**

The neutral steps are the same, but there are several new steps to be noted.

- 1. Balance all the elements in the equation other than O and H.
- 2. Balance the oxygen atoms by adding water  $(H_2O)$  molecules to the other side of the equation. This works because water has one O.
- 3. Balance the hydrogen atoms (including those added in step 2 to balance the oxygen atom) by adding  $H^+$  ions to the opposite side of the equation.
- 4. Calculate the charges on each side. Balance them by adding electrons ( $e^-$ ) to the more positive side. (One handy tip:  $e^-$  and  $H^+$  are usually found on the same side.)
- 5. The  $e^-$  on each side should be equal. If they are not, multiply one or the other of the half reactions by an integer to make them equal. If this does not make sense, just continue reading; the examples should make it clear.
- 6. Add the half-equations together, canceling out the electrons to form one balanced equation. Common terms should also be canceled out.
- 7. (Only for reactions in basic solutions) Add a number of  $OH^-$  to both sides equal to the number of  $H^+$  in the reaction, and combine the  $H^+$  and  $OH^-$  together to make  $H_2$ . If that doesn't make sense, just continue to the example.
- 8. Check the equation to ensure that it is balanced.

Got it? Let's try an example. This one is in an acidic solution.

$$Cr_2O_7^{2-}(aq) + HNO_2(aq) \rightarrow Cr^{3+}(aq) + NO_3^{-}(aq)$$







Separate it into two half-reactions:

$$Cr_2O_7^{2-}(aq) o Cr^{3+}(aq)$$

$$HNO_2(aq) o NO_3^-(aq)$$

Balance all elements other than H or O. In this case, we only need to balance Cr:

$$Cr_2O_7^{2-}(aq) 
ightarrow 2Cr^{3+}(aq)$$

$$HNO_2(aq) o NO_3^-(aq)$$

Balance all Os with  $H_2O$  on the other side:

$$Cr_2O_7^{2-}(aq) o 2Cr^{3+}(aq) + 7H_2O(l)$$

$$HNO_2(aq) + H_2O(l) \rightarrow NO_3^-(aq)$$

Balance all hydrogens by adding  $H^+$  to the other side:

$$Cr_2O_7^{2-}(aq)+14H^+(aq) o 2Cr^{3+}(aq)+7H_2O(l)$$

$$HNO_2(aq) + H_2O(l) \rightarrow NO_3^-(aq) + 3H^+(aq)$$

Balance the charges on both sides. For the first half-reaction, the charge on the left is +12 and the charge on the right is +6, so we need 6 electrons on the left side. For the second half-reaction, the charge on the left is 0 and the charge on the right is +2, so we need 2 electrons on the right side:

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$$

$$HNO_2(aq) + H_2O(l) 
ightarrow NO_3^-(aq) + 3H^+(aq) + 2e^-$$







Now, there are too many electrons on the first half-reaction, so we need to multiply the second half-reaction by 3 to compensate:

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$$
  
 $3HNO_2(aq) + 3H_2O(l) \rightarrow 3NO_3^-(aq) + 9H^+(aq) + 6e^-$ 

Now we just add them together and cancel the electrons and any common terms (in this case,  $9H^+$  and  $3H_2O$ ):

$$Cr_2O_7^{2-}(aq) + 5H^+(aq) + 3HNO_2(aq) \rightarrow 2Cr^{3+}(aq) + 4H_2O(l) + 3NO_3^-(aq)$$

There you have it, a redox reaction in an acidic solution! Now let's do one in a basic solution.

$$Ag(s) + Zn^{2+}(aq) o Ag_2O(aq) + Zn(s)$$

Separate it into two half-reactions:

$$Ag(s) o Ag_2O(aq)$$

$$Zn^{2+}(aq) o Zn(s)$$

Balance all elements other than H or O. In this case, we only need to balance Ag:

$$2Ag(s) o Ag_2O(aq)$$

$$Zn^{2+}(aq) o Zn(s)$$

Balance all O's with  $H_2O$  on the other side:

$$2Ag(s) + H_2O(l) \rightarrow Ag_2O(aq)$$

$$Zn^{2+}(aq) o Zn(s)$$







Balance all hydrogens by adding  $H^+$  to the other side:

$$2Ag(s)+H_2O(l)
ightarrow Ag_2O(aq)+2H^+(aq) \ Zn^{2+}(aq)
ightarrow Zn(s)$$

Balance the charges on both sides. For the first half-reaction, the charge on the left is 0 and the charge on the right is +2, so we need 2 electrons on the right side. For the second half-reaction, the charge on the left is +2 and the charge on the right is 0, so we need 2 electrons on the left side:

$$2Ag(s)+H_2O(l)
ightarrow Ag_2O(aq)+2H^+(aq)+2e^- \ Zn^{2+}(aq)+2e^-
ightarrow Zn(s)$$

Next we would balance the electrons, but the electrons are already balanced. So, we just add the two half-reactions together:

$$2Ag(s) + H_2O(l) + Zn^{2+}(ag) + 2e^- \rightarrow Ag_2O(ag) + 2H^+(ag) + Zn(s) + 2e^-$$

The electrons cancel, and there are no other common terms to cancel:

$$2Ag(s)+Zn^{2+}(aq)+H_2O(l)
ightarrow Ag_2O(aq)+Zn(s)+2H^+(aq)$$

We can't have  $H^+$  in a basic solution, so we add  $OH^-$  to both sides to turn the  $H^+$  into water:

$$2Ag(s) + Zn^{2+}(aq) + H_2O(l) + 2OH^-(aq) o Ag_2O(aq) + Zn(s) + 2H_2O(l)$$

Cancel one H<sub>2</sub>O

$$2Ag(s) + Zn^{2+}(aq) + 2OH^{-}(aq) \rightarrow Ag_2O(aq) + Zn(s) + H_2O(l)$$







That makes sense? Just remember, in a basic solution, you can't have any  $H^+$  left over, while in an acidic solution, you can't have any  $OH^-$  left over.

That's how you balance a redox reaction! Whew. That was a lot of information. If you have any questions, let us know in the comments. Good luck with your AP Chemistry exam; I hope this crash course helps you!







# Identifying Acids and Bases

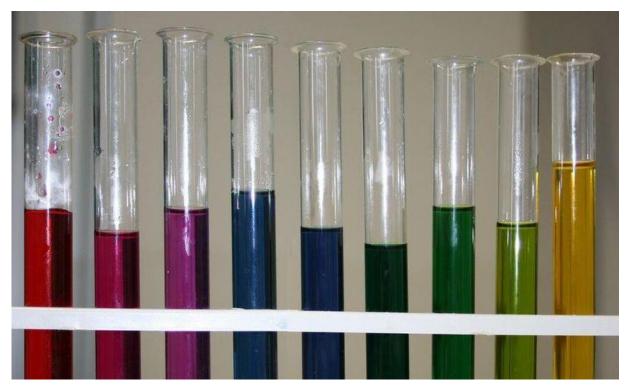


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#### **Acids and Bases Definitions**

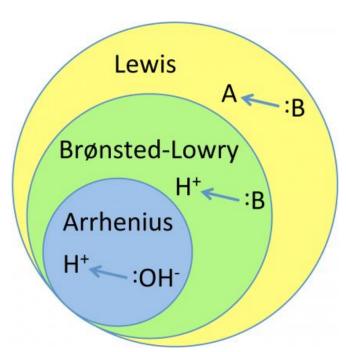
This AP Chemistry crash course review will go over the fundamentals of acids and bases in chemistry and their applications to the AP Chemistry exam. There are three definitions of what constitutes an acid and a base. Each of these definitions is useful for different purposes.







- **1. Arrhenius Definition**: Acids are compounds that increase the concentration of protons ( $H^+$ ) in an aqueous solution. Bases are compounds that increase the concentration of hydroxide ions ( $OH^-$ ) in an aqueous solution. When acids and bases react they undergo a *neutralization* reaction, the product of which is a salt and water.
- **2. Brønsted-Lowry Definition**: Acids are compounds that donate hydrogen atoms  $(H^+)$ , and bases are compounds that accept hydrogen atoms. Acids donate their hydrogen and become conjugate bases, and bases react with protons to form conjugate acids. Acids and bases that dissociate completely are called *Strong acids and bases*, and those that only partially dissociate are called *Weak acids and bases* and form equilibrium mixtures in solution.
- **3. Lewis Definition**: Acids are compounds that can accept an incoming electron pair, and bases are compounds that donate electron pairs to other compounds.



Images Source: Wikimedia Commons







The three definitions of acids or bases are more generalized as we go from top to bottom. The Arrhenius definition only encompasses compounds that increase the concentration of hydrogen ion and hydroxide moieties in an aqueous solution. The Brønsted-Lowry definition encompasses all compounds that are capable of donating hydrogen atoms to one another, regardless of the solvent they reside in; this definition encompasses those compounds that are classified as acids or bases in the Arrhenius definition, such as acetic acid. The Lewis takes way the necessity for hydrogen ions and instead defines acids in bases in terms of electron pairs; this applies to any compounds that are acids and bases under either the Arrhenius or the Brønsted-Lowry definition. The main point to remember is that all three definitions of acids and bases are internally consistent with each other.

The first topic that must be covered in any discussion about acids and bases is how we measure a solutions' acidity. The acidity of a solution is most commonly measured on the pH scale. The pH of a solution is a measure of the concentrated of hydrogen ions  $(H^+)$ , or protons) in solution. To be exact, the pH of a solution is the negative log of the concentration of protons in solution.

$$pH = -\log\left[H^+\right]$$

The pH scale ranges from 0 to 14 for reasons we will discuss below. Before we get there, another useful scale to know is the pOH scale. The pOH of a solution is a measure of the concentration of hydroxide ions  $(OH^-)$  in solution, also in the negative log form.

$$pOH = -\log\left[OH^{-}\right]$$

The *pH* and *pOH* scales are related to each other due to the equilibrium that exists between hydrogen ions and hydroxide in solution. For a given solution, the sum of the *pH* and *pOH* of the solution must always equal 14.

$$pH + pOH = 14$$







To understand why this relationship must be true we have to review in more detail the term acid and base as defined in the Brønsted-Lowry definition. The Brønsted-Lowry definition considers acids to be any protonated compound capable of donating its protons; these species are represented by the figure *AH*, where "A" is the fundamental compound and "H" is the donated proton. A base is defined as any species that can accept a donated proton. The deprotonated base is represented by the symbol "B". When a protonated acid comes in contact with a base, the acid donates the proton to the base, thus protonating the base and itself become deprotonated. This can be represented by the chemical expression below:

$$AH + B \leftrightarrow A - +BH +$$

And the equilibrium expression for the reaction would be:

$$K = \frac{[AH][B]}{[A]^-[BH]^+}$$

One of the most important consequences of the Brønsted-Lowry definition is that a deprotonated acid can regain its donated proton, and a protonated base can become deprotonated once more. We call the deprotonated acid species the *conjugate base* because of its ability to function as a proton acceptor (Brønsted-Lowry base). The protonated base then becomes a *conjugate acid* because of its ability to donate protons. The two species exist in an equilibrium mixture represented by the expression above. The only exception to this rule are the seven so-called "strong" acids and eight strong bases whose conjugate acids and bases are so weak that their dissociation in water is not considered to be reversible.

How does this tie into the pH of a solution? Well, in aqueous media the hydrogen ion is also known as hydronium, since in reality protons dissolved in water form weak bonds to the solvent water molecules. This relationship is represented by the molecule known as the hydronium ion,  $H_3O^+$ .







The Brønsted-Lowry definition enumerates that water molecules are *amphoteric* species, meaning that they can act both as an acid or a base. The reaction that illustrates this is the grabbing of a proton from one water molecule by another water molecule, resulting in the formation of a hydronium  $H_3O^+$  and hydroxide  $(OH^-)$  ion:

$$2H_2O \leftrightarrow OH^- + H_3O^+$$

And the reaction is represented by the equilibrium expression below, where w stands for water.

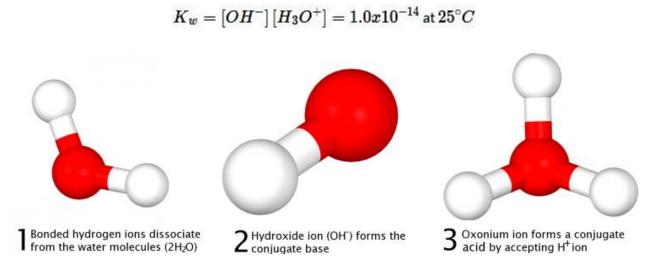


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Hydronium is, therefore, the conjugate acid of water, and hydroxide the conjugate base, and both species are in equilibrium with each other. The concentration of water in water does not appear as part of the equilibrium expression, and so what we are left with are the concentrations of the two product molecules  $OH^-$  and  $H_3O^2$ . Because the dissociation constant ( $K_w$ ) of water is always equal to  $1.0x10^{-14}$ , the addition of the pH and pOH of a solution must always equal the negative log of that value, which is 14. That is how we explain the relationship between pH and pOH in solution.







#### Example 1

What is the concentration of hydronium ion in a 0.500 L aqueous solution of 1 M sodium hydroxide (NaOH)?

Sodium hydroxide is one of the strong bases and therefore dissociated fully in aqueous solution.

$$NaOH \rightarrow Na^{+} + OH^{-}$$

To find the concentration of hydronium ion, we will need to take advantage of the relationship between *pH* and *pOH* of a solution. We begin by calculating the molar amount of sodium hydroxide in the aqueous solution using the unit cancellation method:

We will then calculate the *pOH* of the solution.

$$pOH = -log [OH^{-}] = 0.3010$$

Note that the final number of significant figures has changed. This is because when we take the log of a number, the number of significant figures represents the number of decimal places that must be shown in the logarithm. The reverse is true when going the other direction: the number of decimal places in the log equals the number of significant figures in the number.

We then rearrange the relationship between *pH* and *pOH* so solve for the *pH* of the solution.

$$pH + pOH = 14 \rightarrow pH = 14 - pOH = 14 - (0.301) = 13.699$$







Finally, we rearrange the equation for pH to solve for the hydronium ion concentration.

$$pH = -log \, [H_3O^+] o [H_3O^+] = 10^{-pH} = 10^{-(13.699)} = 2.00x10^{-14} mol H_3O^\pm$$

Qualitatively this answer makes sense because we expect to have an extremely low concentration of hydronium ions in a basic solution of sodium hydroxide.

One feature of conjugate acids and bases is that they are always weaker than their original counterparts. What does this mean? An acid has a certain ability to donate its proton based on the stability of the fundamental acidic species A, and a base has a certain ability to accept protons based on its ability to stabilize the incoming positive charge. Compounds with pi-systems such as carboxylic acids and aromatic systems are generally stronger acids and bases due to their ability to delocalize the electric charge on the molecule.

A Brønsted acid forms an equilibrium mixture when dissolved in water. The water molecule acts as a base, accepting the donated proton from the acid, and becomes the conjugate acid hydronium ion. The acid turns into its deprotonated conjugate base.

$$HA + H_2O \leftrightarrow H_3O^+ + A^-$$

In this way, Brønsted-Lowry acids are consistent with the Arrhenius definition of an acid because they increase the concentration of  $H_3O^+$  in an aqueous solution. The <u>equilibrium expression</u> for this reaction is called the acid dissociation constant and is designated ( $K_a$ ). The larger the value of  $K_a$  the stronger the acid is. Most weak acids have a dissociation constant in the range of  $10^{-2}$  to  $10^{-14}$ .

$$K_a = rac{[H_3O^+][A^-]}{[HA]}$$







The acid dissociation constant is a measure of how fully an acid dissociated upon solvation in water. It is a useful measure for the "strength" of an acid, i.e. its ability to stabilize its conjugate base. The acid dissociation constant is often reported as in the negative logarithmic form  $(pK_a)$ , similar to how pH is reported. The smaller the value of  $(pK_a)$  the stronger the acid is. Most weak acids have a  $(pK_a)$  between 2 to 14.

$$pK_a = -log(K_a)$$

A Brønsted base forms the same equilibrium mixture when dissolved in water, except that here water acts as an acid, donating a proton to becomes the conjugate base hydroxide. This is consistent with the Arrhenius definition of a base, i.e. increasing the concentration of hydroxide ions in aqueous solution. The chemical reaction is expressed as:

$$B + H_2O \leftrightarrow OH^- + BH^+$$

The <u>equilibrium expression</u> for this reaction is called the Base Dissociation Constant and is designated  $K_b$ . It is a measure of how strongly a base grabs up protons in solution and a good estimate of the strength of a base. The larger the value of  $K_b$  is, the stronger the base is. Base dissociation constants are also reported as the negative log of  $K_b$ , and this value is called the  $pK_b$ . The smaller the value of  $pK_b$  is, the stronger the base is.

$$K_b = rac{[OH^-][BH^+]}{[B]}$$







#### **Example 2**

A given monoprotic acid is dissolved in one liter of water. The acid has a dissociation constant equal to  $2 \times 10^{-5}$ . Calculate the pH of the solution at Equilibrium if 0.100 moles of the acid are dissolved.

Solving this problem requires us to use ICE tables. For those of you who don't remember, ICE stands for Initial [Condition], Change, and End[ing Condition]. ICE tables are a common way to solve for equilibrium problems. We write out the balanced chemical equation at the top of the table, then write the initial concentrations of all reagents, the change in their concentration, and the final concentration. The change is usually represented by the variable 'xx'. For the dissociation of an acid in water:

Equation	HA +	$H_2O \leftrightarrow$	H <sub>3</sub> O <sup>+</sup> +	A <sup>-</sup>
Initial	0.100 mol		1 x 10 <sup>-7</sup>	0
Change	-x		+x	+x
End	0.100 - x		1 x 10 <sup>-7</sup> + x	x

Please note that the equilibrium constant of pure water with hydroxide and hydronium is equal to  $1 \times 10^{-14}$ , so the starting concentration of hydronium (and hydroxide) ions in a solution of pure water is always equal to  $1 \times 10^{-7}$ .

At this point we substitute the End values into the equilibrium expression for acid dissociation:

$$K_a = \frac{(1 \cdot 10^{-7} - x)(x)}{(0.100 - x)}$$







There is a simplifying assumption that we can make if we satisfy certain criteria. In order to avoid calculations involving the quadratic equation, which are both time consuming and tedious, we can make as simple calculation to determine if the value of x in the denominator can be removed. For the simplifying assumption to be true, the initial concentration of the acid divided by the dissociation constant of the acid must be greater than 500. In this case,

$$0.100/(2x10^{-5}) = 2,500 >> 500$$

We can, therefore, make the simplifying assumption that x in the denominator is negligible. The expression can be further simplified by assuming that the value of x is much greater than the starting concentration of hydronium ion. The final concentration of hydronium in solution can then be simplified simply to 'x'. The equilibrium expression then becomes:

$$K_a = \frac{(x^2)}{(0.100)}$$

Substituting in the value for  $K_a$  allows us to solve for x.

$$K_a = 2x10^{-5} = x^2/0.100$$
  $x = \left(2x10^{-6}\right)^{\frac{1}{2}} = 1.41x10^{-3}mol$ 

At this point, we go back and check that our assumption that the value of x is much greater than the starting concentration of hydronium ion by dividing our value by the starting concentration. If the number is greater than 500 than our assumption was good; if not, the assumption is incorrect, and we must go back and consider the hydronium ions initially present in the solution. In this case;

$$1.41x10^{-3}/1x10^{-7} = \sim 14,000 >> 500$$







And so our assumption stands. Now to solve the final piece of the puzzle, we substitute the value of x for the concentration of hydronium ions in the pH equation, and arrive at the pH of the acidic solution:

$$pH = -log(1.41x10^{-3}) = 2.851$$

The final equation we will learn relating to acids and bases is the Henderson-Hasselbalch equation, which directly relates the pH of a solution to the  $pK_a$  of an acid. This equation is useful for calculating the fraction of protonated and deprotonated species of a given acid in a solution of a given pH.

$$pH = pK_a + \log rac{[H^-]}{[HA]}$$

It makes sense as the concentration of hydronium ions rise in a solution, the acid is less and less likely to become deprotonated by the solvent, and therefore a greater fraction of the acid will exist in the protonated form. The same is true for the reverse. This calculation can also be performed using the base dissociation constant together with the *pOH* of a solution.

Finally, let us note that the product of the base and acid dissociation constants of a given compound and its conjugate pair is always equal to  $K_w$  due to the equilibrium that exists between hydronium and hydroxide in aqueous solution.

$$K_w = K_a \times K_b = 1x10^{-14}$$

And because of this relationship, the sum of the  $pK_a$  and  $pK_b$  of an acid or base and its conjugate pair is always equal to 14.







## Enthalpy vs. Entropy

When you get to the thermodynamics section of AP Chemistry, one of the hardest things to remember is the definition of enthalpy vs. entropy. This tutorial explains the theory behind enthalpy and entropy using the laws of thermodynamics. Then we will talk about the definition of enthalpy and how to calculate it, using enthalpy practice questions. Once you have a firm hold on the definition of enthalpy, we will discuss entropy and look at entropy practice questions. Finally, we will revisit the topic of <u>Gibbs free energy</u>, of which you should already have a decent understanding, and how it relates to enthalpy vs. entropy.

#### Laws of Thermodynamics and Enthalpy vs. Entropy

#### There are three laws of thermodynamics:

- 1. The first law of thermodynamics is the theory of conservation of energy. It states that energy cannot be created or destroyed, only transferred between types of energy, such as heat and work.
- 2. The second law states that the entropy of the universe is always increasing. This means that the entropy of a closed or isolated system will always increase over time. This law explains that concentrated energy has a tendency to become dispersed energy in the form of random thermal motion.
- 3. This random motion, this entropy, is represented by "S", and is a measure of the energy that is unable to do work. Its units are the change in energy (ΔE per degree = (Joules / Kelvin). Any time that entropy is called random, disorganized, diffuse, dissipated, chaotic, etc., what is being indicated is the random molecular motion in a system that is unable to be harnessed to do work.







When we do so, we only need to consider those variables that are changing between the beginning and end of our reaction.

$$S_{universe} = increases$$
 or  $\Delta S_{universe} > 0$ 

Since we know that natural systems will all increase in entropy over time, we know that changes that cause an increase in total entropy will be spontaneous. We also know that there will never be a spontaneous decrease in entropy. Just like when you pour water on sand, it disperses randomly, so energy disperses randomly.

The third law states that the entropy of a perfect crystal (a crystal in which the molecules are in perfect alignment) approaches zero as temperature approaches absolute zero.

Okay, so this law seems pointless, right? Actually, this law tells us that the entropy of a substance can be calculated at any temperature that is above 0kay. It also explains how the entropy of a system can be higher than zero when the enthalpy and <u>Gibbs free energy</u> are both zero. This allows us to calculate an absolute entropy for molecules, not just a change in entropy.

#### **Enthalpy vs. Entropy**

Enthalpy = heat energy in a closed system. Entropy = energy in a closed system that is unavailable to do work

#### **Enthalpy**

The enthalpy of a reaction is the heat energy it contains. Enthalpy is represented by "H" in equations. The most important law when looking at enthalpy is Hess's Law: The enthalpy change accompanying a chemical change is independent of the way in which the chemical change occurs.







When we do so, we only need to consider those variables that are changing between the beginning and end of our reaction.

$$S_{universe} = increases$$
 or  $\Delta S_{universe} > 0$ 

This means that if you convert reactants into products, the overall enthalpy change is the same whether you do it in one step or multiple steps. This means that even with an intermediary compound, the change in enthalpy is equal to the sum of the change in enthalpy of the products minus the sum of the change in enthalpy of the reactants. This equation is Hess's Law.

$$\Delta H^o = \sum n \Delta H^o_{products} - \sum n \Delta H^o_{reactants}$$

The third law of thermodynamics allows us to calculate absolute entropy, but NOT absolute enthalpy. We cannot calculate absolute enthalpy values because enthalpy does not approach 0 as temperature approaches absolute zero. We can only calculate the enthalpy of a substance relative to other substances. So we use pre-calculated "enthalpy of formation" values to calculate the enthalpy change of a reaction and "absolute entropy" values to calculate entropy.

#### **Example**

Calculate the standard enthalpy of combustion for the following reaction using the enthalpy values below.

$$\begin{split} 2C_2H_5OH_{(l)} + 7O_{2(g)} & o 4CO_{2(g)} + 6H_2O_{(l)} \\ \Delta H^oforCO_{2(g)} &= -393.5 \\ \Delta H^oforH_2O_{(g)} &= -286 \\ \Delta H^oforC_2H_5OH_{(l)} &= -278 \\ \Delta H^oforO_{2(g)} &= 0 \end{split}$$







This problem can be solved in four easy steps.

**Step 1**: Arrange the molecules and coefficients from the chemical reaction into the equation for calculating change in entropy.

The "n" in the equation is the coefficient or number of moles of the molecule from the chemical reaction.

$$egin{aligned} \Delta H^o &= [(4mol)(\Delta H^o for CO_{2(g)}) + (6mol)(\Delta H^o for H_2O_{(g)}) \ &- [(2mol)(\Delta H^o for C_2H_5OH_{(l)}) + (7mol)(\Delta H^o for O_{2(g)})] \end{aligned}$$

**Step 2**: Find the enthalpy of each molecule.

For this type of equation, the enthalpy values will be given to you either in a table on a separate piece of paper or with the question. In this case, the enthalpy values are given with the question.

**Step 3**: Place the enthalpy values in the equation.

$$\Delta H^o = [(4mol)(-393.5kJ/mol) + (6mol)(-286kJ/mol)]$$
$$-[(2mol)(-278kJ/mol) + (7mol)(0kJ/mol)]$$

**Step 4**: Solve the equation.

$$\Delta H^o = [-1574kJ + (-1716kJ)] - [-556kJ + 0kJ]$$

$$\Delta H^o = -3290kJ - (-556kJ)$$

$$\Delta H^o = -3290kJ + 556kJ = -2734kJ$$







#### **Entropy**

The entropy of a system is the amount of disorder it contains.

Ways to predict the entropy of a system:

- 1. Entropy increases as disorder or randomness increases, so the more random a system is, the higher its entropy.
- 2. When undergoing a phase change from solid to liquid and liquid to gas, the entropy of a substance always increases.
- 3. Except with carbonates, when a solid or liquid is dissolved in a solvent, the entropy of the substance increases. Carbonates actually increase the order of a system when dissolved in water.
- 4. Entropy increases when a gas molecule escapes from a solvent.
- 5. As molecular complexity increases (NaCl vs MgCl<sub>2</sub>), entropy generally increases, due to the increase in moving electrons.
- 6. Reactions in which the moles of a particle increases often increase in entropy.

To calculate the standard change in entropy of a reaction, you subtract the sum of the entropies of the reactants from the sum of the entropies of the reactants.

$$\Delta S^o = \sum n \Delta S^o_{products} - \sum n \Delta S^o_{reactants}$$

Also, entropy changes are different for condensation and vaporization. The change in entropy is calculated using the change in enthalpy and the temperature. The formulas necessary for each of these calculations are:

$$\Delta S_{condensation} = rac{-n\Delta H_{vaporization}}{T_{boil}} \, \Delta S_{vaporization} = rac{n\Delta H_{vaporization}}{T_{boil}}$$







All of the formulas we have looked at so far have been used to calculate the enthalpy of the system. To calculate the enthalpy of the surroundings, the following formula must be used, which takes negative one times the change in enthalpy of the reaction divided by the temperature.

$$\Delta S_{surr} = rac{-\Delta H_{ren}}{T}$$

Then, to calculate the total change in entropy of the universe, add the change in entropy of the reaction to the change in entropy of the surroundings, utilizing the following formula.

$$\Delta S_{universe} = \Delta S_{rrn} + \Delta S_{surr}$$

#### **Example Entropy Problems**

#### **Example 1**

One mole of solid calcium carbonate decomposes to form solid calcium oxide and carbon dioxide gas. What is the standard entropy change of this reaction, given the absolute entropies for each compound below?

$$CaCO_{3(s)} 
ightarrow CaO_{(s)} + CO_{2(g)}$$
  $\Delta S^o of CaO_{(s)} = 39.8 J/mol K$   $\Delta S^o of CO_{2(g)} = 213.7 J/mol K$   $\Delta S^o of CaCO_{3(s)} = 92.9 J/mol K$ 

There are four simple steps you can follow to solve this type of problem.







There are four simple steps you can follow to solve this type of problem.

**Step 1**: Arrange the molecules and coefficients from the chemical reaction into the equation for calculating change in entropy.

The "n" in the equation is the coefficient or number of moles of the molecule from the chemical reaction.

$$\Delta S^o = [(1mol)(\Delta S^o for CaO_{(s)}) + (1mol)(\Delta S^o for CO_{2(g)})] - [(1mol)(\Delta S^o for CaCO_{3(s)})]$$

**Step 2**: Find the absolute entropy of each molecule in a table. For this type of equation, the entropy values will be given to you either on a separate piece of paper or with the question. In this case, the entropy values are given with the question.

**Step 3**: Place the absolute entropy values in the equation.

$$\Delta S^o = [(1mol)(39.8J/molK) + (1mol)(213.7J/molK)] - [(1mol)(92.9J/molK)]$$

Step 4: Solve the equation.

$$\Delta S^o = (39.8J/K + 213.7J/K) - 92.9J/K$$

$$\Delta S^o = 253.5J/K - 92.9J/K$$

$$\Delta S^o = 160.6J/K$$







#### **Example 2**

What is the change in entropy when two moles of carbon monoxide condense at -191.4°C? The heat of vaporization of CO is 6.04 kJ/mol.

**Step 1**: Make sure all variables have the correct units.

Temperature should be in Kelvin and change in enthalpy in J/mol.

$$n=2molCO$$
 
$$T_{boil}=(-191.4^{\circ}C+273.15)=81.75K$$
 
$$\Delta H_{vaporization}=\frac{6.04kJ}{mol}\times\frac{1000J}{1kJ}=6040J/mol$$

**Step 2**: Place the variables into the formula, including the number of moles of your molecule.

$$\Delta S_{condensation} = rac{-n\Delta H_{vaporization}}{T_{boil}} \ \Delta S_{condensation} = rac{-(2mol)(6040J/mol)}{81.75K}$$

**Step 3**: Solve the Equation

$$\Delta S_{condensation} = \frac{-(2mol)(6040J/mol)}{81.75K} = \frac{-12080J}{81.75K} = -147.77J/K$$







#### Gibbs Free Energy, Entropy, and Enthalpy

Remember from learning about <u>Gibbs free energy</u>, that the change in free energy is equal to the sum of the free energy of the products minus the sum of the free energy of the reactants.

$$\Delta G^o = \sum n \Delta G^o_{fproducts} - \sum n \Delta G^o_{freactants}$$

Notice that this is very close to the equation used to calculate  $\Delta H^{o}$  and  $\Delta S^{o}$ .

To review, let's discuss the relationship between Gibbs free energy, entropy, and enthalpy.

Gibbs free energy is represented by "G" and is found with the following equation.

$$G^{\circ} = H^{\circ} - TS^{\circ}$$

Since we are looking at the *changes* in energy, we need to account for that in our equation:

$$\Delta G^{\circ} = \Delta H^{\circ} - \Delta T S^{\circ}$$

When using this equation, we almost always are calculating a change during *constant temperature*:

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$$

and we also almost always calculate changes in standard state conditions:

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$$







Using this equation, we can now calculate change in free energy from change in enthalpy and entropy values, as demonstrated in this example.

#### **Example**

In the decomposition of calcium carbonate, what is the change in free energy?

We have already calculated the change in entropy in the previous example. Using a similar equation, we can calculate the change in enthalpy.

$$\begin{split} \Delta H^o &= \sum n \Delta H^o_{products} - \sum n \Delta H^o_{reactants} \\ \Delta H^o &= [(1mol)(\Delta H^o for CaO_{(s)}) + (1mol)(\Delta H^o for CO_{2(g)})] - [(1mol)(\Delta H^o for CaCO_{3(s)})] \\ \Delta H^o &= [(1mol)(-635.3kJ/mol) + (1mol)(-393.5kJ/mol)] - [(1mol)(-1207.0kJ/mol)] \\ \Delta H^o &= [(-635.3kJ/mol) + (-393.5kJ/mol)] - [(-1207.0kJ/mol)] \\ \Delta H^o &= -758.8kJ/mol + 1207.0kJ/mol = 178.2kJ \end{split}$$

Though entropy is recorded in J/K, free energy's standard units are kJ. Always make sure to convert entropy from J to kJ BEFORE calculating Gibbs free energy!

$$\Delta S^o = \frac{160.6J}{K} \times \frac{1kJ}{1000J} = 0.1606$$

Now we can use the new equation relating the two to Gibbs free energy. Thermodynamic standard temperature (298.15 K or 25°C) is used for T.

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} = 178.2kJ - (298.15Ktimes0.1606kJ) = 130.3kJ$$







#### Wrapping Up Enthalpy vs. Entropy

The definition of enthalpy vs. entropy should be much clearer now. If you have any other questions or comments about enthalpy vs. entropy, please let us know in the comments below! If you would like more practice with enthalpy vs. entropy problems, we have included more practice problems and their answers below.

#### **Enthalpy Practice Problems**

1. The standard enthalpy of formation of AgNO<sub>3(s)</sub> is -123.02 kJ/mol. What is the standard enthalpy of formation of AgNO<sub>2(s)</sub>, given the following reaction?

$$AgNO_{3(s)} 
ightarrow AgNO_{2(s)} + \frac{1}{2}O_{2(g)}$$

2. Given the following standard enthalpies of formation, calculate the heat of combustion per mole of gaseous water formed during the combustion of ethane gas.

$$2C_2H_{6(l)}+7O_{2(g)} o 4CO_{2(g)}+6H_2O_{(g)}$$
 $C_2H_{6(g)}$  -84.68
 $O_{2(g)}$  zero
 $CO_{2(g)}$  -393.5
 $H_2O_{(g)}$  -241.8







#### **Entropy Practice Problems**

- 1. Which of these substances should have a higher entropy? Answer without calculating and assume that there is one mole of each substance at 25°C and 1 bar.
  - 1. Hg(I) or CO(g)
  - 2. CH<sub>3</sub>OH(I) or CH<sub>3</sub>CH<sub>2</sub>OH(I)
  - 3. KI(s) or CaS(s)<
- 2. Predict the sign of the entropy change for the following reaction and use the given entropy values to calculate the change in enthalpy of the reaction at 25°

$$egin{aligned} 2H_{2(g)} + O_{2(g)} & o 2H_2O_{(g)} \ \Delta S^o of H_2O_{(g)} &= 188.8 J/molK \ \Delta S^o of H_2(g) &= 130.7 J/molK \ \Delta S^o of O_2(g) &= 205.1 J/molK \end{aligned}$$

#### **Combined Practice Problems**

- 1. Hydrogen and oxygen react to form water vapor with a  $\Delta S_{rxn}$ = -88.99 J/K. What are the entropy changes of the surroundings and the universe at 25°C?
- 2. Calculate the free energy change for the following reaction at 25°C from the change in enthalpy of the reaction and the change in entropy of the reaction. (Remember to check the enthalpy vs. entropy section if you need clarification.)

$$CO_{(g)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{2(g)}$$







#### **Enthalpy Practice Problems Key**

1. The standard enthalpy of formation of AgNO<sub>3(s)</sub> is -123.02 kJ/mol. What is the standard enthalpy of formation of AgNO<sub>2(s)</sub>, given the following reaction?

$$AgNO_{3(s)}
ightarrow AgNO_{2(s)}+rac{1}{2}O_{2(g)}$$
a. -44.35 kJ

2. Given the following standard enthalpies of formation, calculate the heat of combustion per mole of gaseous water formed during the combustion of ethane gas.

#### **Entropy Practice Problems Answer Key**

- 1. Which of these substances should have a higher entropy? Answer without calculating and assume that there is one mole of each substance at 25°C and 1 bar.
- a. Since the motion of molecules in a gas are more random than the motion of molecules in a liquid, carbon monoxide gas has a higher entropy than liquid mercury.
- b. More complex molecules have more ways of distributing their energy (electrons) at a given temperature, so the larger molecule (liquid ethanol,  $CH_3CH_2OH(I)$ ) has a higher entropy than the liquid methanol.
- c. There is more of an attraction between the ions in calcium sulfide than in potassium iodide. As the attraction between ions decreases, the entropy will increase, because movement between ions will be easier. Therefore, potassium iodide will have a higher entropy.







2. Predict the sign of the entropy change for the following reaction and use the given entropy values to calculate the change in enthalpy of the reaction at 25°

a. -88.9 J/K

#### **Combined Practice Problems Answer Key**

1. Hydrogen and oxygen react to form water vapor with a  $\Delta$ Srxn= -88.99 J/K. What are the entropy changes of the surroundings and the universe at 25°C?

d. Since the  $\Delta$ Suniv is greater than zero, the reaction is spontaneous.

2. Calculate the free energy change for the following reaction at 25°C from the change in enthalpy of the reaction and the change in entropy of the reaction. (Remember to check the enthalpy vs. entropy section if you need clarification.)

$$CO_{(g)}+rac{1}{2}O_{2(g)}
ightarrow CO_{2(g)}$$

a. ΔHrxn = -283.0 kJ/mol

b. ΔSrxn = -86.6 J/mol K

c.  $\Delta$ Grxn = -257 kJ/mol







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## Gibbs Free Energy

Example:

$$A + B \longrightarrow C + D$$

Bood: 100 200 400 90

Brongled 300 KCAI

(emorgy absorbed) (emorgy released)

 $\Delta G = 450 - 300 = 150 FCAI$ 
 $BEP > BER : \Delta G = \Theta$ 
 $\therefore \Delta G = -150 FCAI$ 

**Image Source: Wikimedia Commons** 

To adequately describe the energetic state of a system you need to include all the various functions relating to the variables of kinetic, potential, and internal energy. Many equations compromise the total potential and internal energies of a system, and calculating each one is an <u>incredibly</u> tedious process, if not downright impossible. So, a way to get around this obstacle is only to consider *changes* in a system.







## Gibbs Free Energy Cont.

When we do so, we only need to consider those variables that are changing between the beginning and end of our reaction.

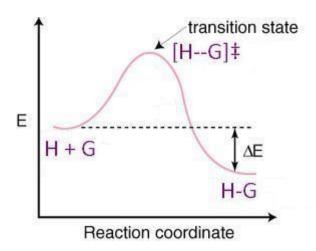


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## Thermodynamic Expression for Free Energy – Essential Knowledge 5.E.2.

The Gibbs Free Energy is a relative value that serves as a benchmark for calculating how much energy a reaction will consume to proceed, or generate while proceeding. Gibbs Free Energy change, or delta  $G(\Delta G)$  in short, is a thermodynamic calculation based on the changes in **Entropy and Enthalpy** of a system. Since these parameters are functions of temperature, they fall under the topic of thermodynamics. When these parameters are calculated under standard conditions (STP), they are referred to as standard changes in free energy, enthalpy, or entropy, respectively. The changes in each of these quantities are represented mathematically below.

$$egin{aligned} \Delta S^o &= \Sigma S^o \ products$$
 -  $\Sigma S^o \ reactants \end{aligned}$   $\Delta H^o &= \Sigma \Delta H_{f^o} \ products$  -  $\Sigma \Delta H_{f^o} \ reactants \end{aligned}$   $\Delta G^o &= \Sigma \Delta G_{f^o} \ products$  -  $\Sigma \Delta G_{f^o} \ reactants \end{aligned}$ 







## Gibbs Free Energy Cont.

The standard change in any of the thermodynamic properties is calculated based on the sum of the property in the products minus the sum of the property in the reactants.

There are three different flavors of the equation for calculating the standard Gibbs Free Energy of a system. Standard entropy, enthalpy, and free energy constants are all related to each other by the expression below, where the absolute temperature *T* is in units of Kelvin. The standard change in entropy and enthalpy are both experimental values that would be provided for you on the AP Exam questions.

$$\Delta G^o = \Delta H^o - T\Delta S^o$$

A negative change in delta energy means that energy is released from the system to the surroundings, and the reaction is therefore overall favorable. Therefore, reactions with a negative standard change in enthalpy and a positive standard change in entropy will always be thermodynamically favorable (i.e. spontaneous) at STP. Conversely, reactions that have a positive standard change in enthalpy and a negative standard change in entropy will always require a net input of energy from their surroundings, and will, therefore, be thermodynamically unfavorable (i.e. non-spontaneous) at STP.

When both the standard change in entropy and enthalpy have the same sign, the favorability of the reaction depends on the temperature at which the reaction takes place and the difference in values between the two variables. For example, a reaction with a very large positive standard change in enthalpy and only a small positive standard change in entropy will only be favorable at very high temperatures. The reverse is true for reactions with a small negative standard change in enthalpy but a large positive standard change in entropy.







## Gibbs Free Energy Cont.

#### Qualitatively this can be summed up as

Value of Δ <i>H</i> °	Value of ΔS°	Favorability
$\Delta H^o < 0$	$\Delta S^o < 0$	Spontaneous at low T
Δ <i>H</i> ° > 0	$\Delta S^o > 0$	Spontaneous at high T
Δ <i>H</i> ° < 0	$\Delta S^o > 0$	Always spontaneous
Δ <i>H</i> ° > 0	$\Delta S^o < 0$	Never spontaneous

A multiple choice question on the AP Exam might look something like this:

#### **Example 1**

Natural gas is used to heat up many residential houses. The main component in natural gas is propane. Calculate the amount of free energy when methane combusts in oxygen at 25  $^\circ$  C, given the following standard thermodynamic values.

Species	ΔH <sub>fo</sub> (Kj/mol)	S°(J/K·mol)	$\Delta G_{fo}(kJ/mol)$
$C_3H_8(g,propane)$	-103.8	269.9	-23.49
CO <sub>2</sub> (g)	-393.509	213.74	-394.359
$O_2(g)$	0	205.138	0
H <sub>2</sub> O(g)	-241.818	188.825	-228.572







The first thing we would need to do in this case is write out and balance the chemical reaction. The combustion of propane will be written out as follows:

$$C_3H_8 + O_2 \leftrightarrow CO_2 + H_2O$$

We can now <u>balance the equation</u> to take into account how many moles of compounds are on each side of the equation. There must be three times as many moles of carbon dioxide as moles of propane since each molecule of propane has three carbon atoms. This reaction will also create four molecules of water for every molecule of propane since propane contains eight hydrogen atoms. The total number of oxygen atoms in three molecules of carbon dioxide and four molecules of water is an even number. Therefore, we do not need to adjust the molar coefficient of propane.

$$C_3H_8 + 5O_2 \leftrightarrow 3CO_2 + 4H_2O$$

To find the Gibbs free energy, we must calculate the total change in entropy and multiply that by the temperature in Kelvin. To do so, we will multiply the molar coefficient of the compound from the balanced chemical equation by the thermodynamic value provided above.

$$\Delta S^o = \Sigma S^o \, products$$
 -  $\Sigma S^o \, reactants$    
  $\Delta S^o = [(3 imes 213.74) + (4 imes 188.825)] - [(269.9) + (5 imes 205.138)]$    
  $\Delta S^o = 100.93 J/K \cdot mol$ 

Then convert the units of temperature from degrees Celsius to units Kelvin.

$$Temperature(K) = 25^{\circ}C + 273 = 298K$$







Finally, we will replicate the process outlined for the change in entropy and repeat it for finding the standard change in enthalpy of the combustion.

$$egin{aligned} \Delta H^o &= \Sigma \Delta H_{f^o} \ products - \Sigma \Delta H_{f^o} \ reactants \ \Delta H^o &= [(3 imes^-509) + (4 imes^-241.818)] - [(^-103.8) + (5 imes 0)] \ \Delta H^o &= ^-2,046\cdot kJ/mol \end{aligned}$$

Now that we have calculated all the necessary variables, we plug the values into the expression for the standard change in free energy. BUT WAIT! We have to make sure that all the units to match... in this case, we will convert the units of standard change in entropy to kilo Joules.

$$\Delta G^o = \Delta H^o - T\Delta S^o = (-2,046 \cdot kJ/mol) - [(298K)(0.10093J/K \cdot mol)]$$
  
 $\Delta G^o = -2,076 \cdot kJ/mol$ 

The big takeaway here is to remember to *multiply* the standard thermodynamic value by the molar coefficient of the compound as determined by the balanced chemical equation.

#### Equilibrium Expression - Essential Knowledge 3.A.2.

The expression for free energy can take on two other forms, depending on the context. If we are dealing with equilibrium problems, then the equilibrium expression for free energy will be used, where *R* is the **Gas constant**, and *K* is the **equilibrium expression** for a chemical reaction.

$$\Delta G^o = -RT \ln K$$







As you may recall, equilibrium is like the energetic low-point in the system, and can be expressed as a fraction of the theoretical concentrations of products and reactants when the reaction has reached this low point.

$$O_2(g) + C_6H_{12}O_6(s) = CO_2(g) + H_2O(g) + q$$

Above is the unbalanced reaction for the combustion of glucose in oxygen to water and carbon dioxide. Balancing this reaction is no different than balancing any other reactions: we place the compounds side by side, determine how many moles of each reactant would be required for the reaction to go to completion, and how many moles of the product would be generated. In this case, we know that carbon-containing products will be generated in multiples of six, and hydrogen-containing products in multiples of twelve. Using the lowest-possible multiple, we find that the reaction balances simply to:

$$6O_2(g) + C_6H_{12}O_6(s) = 6CO_2(g) + 6H_2O(g) + q$$

We will then use the balanced reaction to write out the equilibrium expression. For a reaction in the form:

$$aA + bB = cC + dD$$

The general scheme for writing out the equilibrium expression, including the molar amounts of each compound, is shown below. The concentration of each gaseous compound is expressed as the partial pressure,  $P_A$ . If we know the total pressure at which the reaction is taking place, we can then calculate the molar fraction of the gas in the air or vice versa.

$$K = rac{[A]^a[B]^b}{[C]^c[D]^d}$$







#### **Electrochemical Free Energy – Essential Knowledge 6.D.1.**

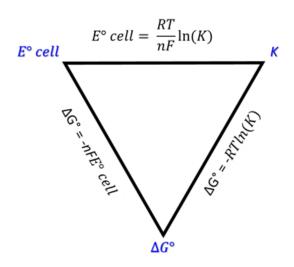
If on the other hand, the topic is <u>electrochemistry</u>, then the Nernst Equation should be substituted into the expression, and the value of Faraday's constant (F) and the standard reduction potential of the cell ( $E^o$ ) should be used. The amount of free energy, in this case, depends on the number of moles of the compound in solution and is represented by the letter n.

$$\Delta G^o$$
 =  $-nFE^o_{cell}$ ; where  $F$  = Faraday's Constant =  $96,48596,485coulombs/mol~e^-$ ,

 $e^{o}$  = Standard Reduction Potential

n = number of moles of electrons

The  $E^{o}_{cell}$ , or standard reduction potential, is an experimentally-determined value of the electrical potential in volts (V) across the two half reactions. The standard reduction potential for the hydrolysis of hydrogen gas into protons and electrons is defined as 0. Since n must be a positive integer and F is a constant, any values of  $E^{o}_{cell}$  that are positive will give a negative  $\Delta G^{o}$ , so the reaction spontaneous in the direction it is written. On the other hand, if  $E^{o}_{cell}$  is negative, then  $\Delta G^{o}$  is positive, and the reaction as written becomes unfavorable and non-spontaneous.



 $E^{\circ}$  cell =  $E^{\circ}$  cathode -  $E^{\circ}$  anode







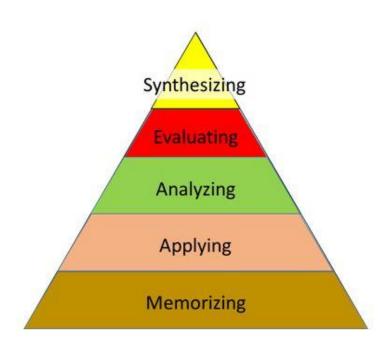
Keep this diagram in mind when trying to figure out the relationship between free energy, standard reduction potential, and the equilibrium concentration of products and reactants in a reaction. It's important to remember that  $E^o_{cell}$  measures the potential across the reactions going from right to left. Half reactions with a negative  $E^o_{cell}$  value are spontaneous in the direction they are written since a negative value of  $E^o_{cell}$  results in a negative  $\Delta G^o$ .







Let's walk through the AP Chemistry Equation Sheet. As you probably know, the Equation Sheet is a tool given to students on the exam so that they do not have to spend as much time memorizing. Instead, the Equation Sheet frees up your head space for higher order thinking. These are the most important tasks of applying, analyzing, evaluating, and synthesizing information. This is known as Bloom's Taxonomy on the Cognitive Domain:



This article will guide you through each and every one of the equations present on the Equation Sheet, how they are used, where you can expect to see them, and we will give an example for each equation present. For reference, the full Equation Sheet can be found <a href="here">here</a> on the CollegeBoard website on pages 161-162.







First we will start by listing all the equations in order, and then we will expand on each one in the section below.

#### Calculating the Half-Life of a Reaction.

Equation	Description/Use	
$c=\lambda x \ v=2.998 imes 10^8 ms^{-1}$	Calculating wavelength or frequency of electromagnetic waves.	
$E_{photon} = hv$ , where $h = 6.626  imes 10^{-34} Js$ and the frequency is in units $Hz$ .	Calculating the energy of a photon of light	
$K_c = rac{[A]^a[B]^b}{[C]^c[D]^d}$	Equilibrium calculations based on molar concentration of compounds in aqueous solution	
$K_p=rac{(P_A)^a(P_B)^b}{(P_C)^c(P_D)^d}$	Equilibrium calculations based on partial pressure of gases in a sealed container.	
$Kw = [OH^-][H_3O^+] = 1.0 imes 10^{-14}$ at $45^0C$	Relating concentration of hydronium and hydroxide ions for pH calculations.	
$pH=-log\left[H^{+} ight]pOH=-log\left[0H^{-} ight]$	Calculating pH/pOH based on hydronium/hydroxide ion concentrations.	
14 = pH + pOH	Relating values of pH and pOH to one another.	
$K_a = rac{[H^+][A^-]}{[HA]}  K_b = rac{[OH^-][HB^+]}{[B]}$	Calculating the dissociation constant of an acid or base in solution.	







Equation	Description/Use
$pK_a = -logK_a  pK_b = -logK_b$	Converting from dissociation constants of acids and bases to the negative logarithmic form of the dissociation constants.
$pH = pK_a + \lograc{[H^-]}{[HA]}$	The Henderson-Hasselbalch equation, used for finding the concentrations of protonated and non-protonated acid species in a solution of a certain pH.
$ln[A]_t - ln[A]_0 = -kt rac{1}{[A]_t} - rac{1}{[A]_0} = kt$	Finding the concentration of a decaying substance based on the time that has elapsed and the rate of decomposition.
$t_{rac{1}{2}}=rac{0.693}{k}$	Calculating the half-life of a reaction.
PV = nRT; where $P$ = pressure; $V$ = volume;	The ideal gas law, used for making calculations using or solving for different parameters of a gas, using the ideal gas assumptions.
n = number of moles;	
$\it R$ = gas constant, and;	
T = temperature in Kelvin.	
1 Comperatore in Nervin.	







Equation	Description/Use
$P_{total} = P_A + P_B + P_C \dots$	Finding the partial pressure of a gas and relating that to the concentration of that gas in a sealed container.
$P_A = P_{total} x X_A, where X_A = rac{moles A}{total moles}$	Determining the amount in moles of a gas based on its partial pressure.
$N=mM^{-1}$	Converting from moles to grams based on the molecular weight of the compound.
$K = ^{0}C + 273$	Converting from degrees Celsius to Kelvin units.
$D=mV^{-1}$	Relationship between mass, density, and volume.
KE per molecule – $rac{1}{2}mv^2$	The kinetic energy of an ideal gas, which can be a useful reminder for equations regarding the Boltzmann Distribution and kinetic gas theory.
A = abc	Calculations relating the optical scattering of light to the concentration of a compound in solution.
$q=mc\Delta T$	Calculating the heat released or gained by an object during a change in temperature.
$\Delta S^0 = \Sigma S^0 products - \Sigma S^0 reactants$	Finding the standard change in entropy in a chemical reaction.







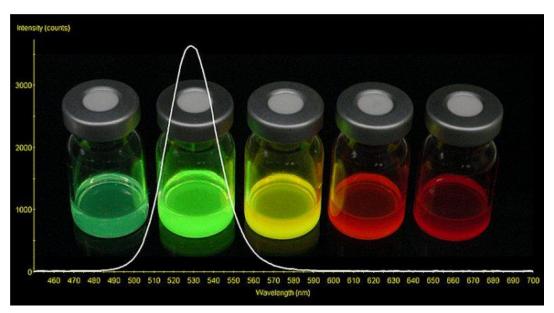
Equation	Description/Use
$\Delta H^0 = \Sigma \Delta H_{f^0} products - \Sigma \Delta H_{f^0} reactants$	Finding the standard change in enthalpy of formation in a chemical reaction.
$\Delta G^{0} = \Sigma \Delta G_{f^{O}} products - \Sigma \Delta G_{f^{O}} reactants$	Finding the standard change in Gibbs Free Energy in a chemical reaction.
$\Delta G^0 = \Delta H^0 - T \Delta S^0$	The thermodynamic flavor of calculating the standard change in free energy is used when dealing with thermodynamic quantities such as entropy and enthalpy.
$\Delta G^0 = -RT \; lnK$	The equilibrium flavor for calculating the standard change in free energy for a chemical reaction in equilibrium.
$\Delta G^0 = -nFE^0$	The electrochemical flavor of the Gibbs free energy expression for calculating the change in free energy for a chemical reaction of a standard electrochemical cell, based on the number of moles of electrons moving during the reaction.
$I = qt^{-1}$	Used for relating the moles of electrons traveling.







Each section of the Equation Sheet comes with its set of definitions. Some of the definitions are redundant and easy; others are not. Pay close attention to them! Getting confused on the meaning of a variable is one of the silliest ways to lose points on the Exam because it is *entirely and completely avoidable*. We will be denoting all equations in this article by a bullet point, •.



**Image Source: Wikimedia Commons** 

#### **Atomic Structure**

Having grown up in the 21<sup>st</sup> century, you probably know that everything around you is fundamentally made of atoms. The chair you're sitting on, the screen you're looking at, and even the eyes you see with are made up of many different kinds of atoms. But what are atoms? What do they look like? And more importantly, how can I understand atomic structure for my AP Chemistry Exam?







No discussion of <u>atomic structure</u> is complete without first understanding what Electromagnetic Radiation is. All types of electromagnetic radiation can be described in terms of two variables: their wavelength, and their frequency. Wavelength, denoted by the Greek letter lambda ( $\lambda$ ) and measured in meters (m), is the distance between two peaks in a wave. Visible light is an example of shortwavelength electromagnetic radiation, with wavelengths between 400-700 nanometers (nm), or 1 billionth of a meter. Frequency, denoted by the Greek letter nu ( $\nu$ ) and measured in Hertz ( $Hz=s^{-1}$ ), is a measure of how many times per second the wave repeats itself. The higher the frequency of a wave, the higher the energy of the wave. An example you can relate to is that exposure to X-rays ( $\nu=10^{18}Hz$ ) is much more harmful than exposure to FM radio waves ( $\nu=10^{8}Hz$ ).

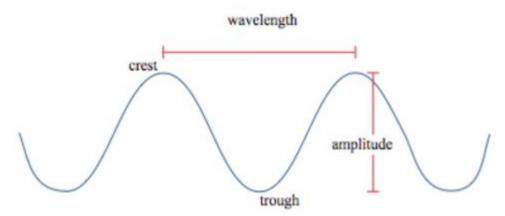


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Another feature of electromagnetic radiation is that all electromagnetic waves travel at the speed of light (c=2.998 × 10<sup>8</sup> ms<sup>-1</sup>). This means that the product of the wavelength and frequency of an electromagnetic wave are always equal to the speed of light, or:

$$c = \lambda xv = 2.998 \times 10^8 ms^{-1}$$

This equation implies that frequency and wavelength are *inversely proportional* to each other, meaning that as one variable increases, the other decreases correspondingly.







You should have no trouble solving this equation with a simple algebraic rearrangement of variables.

German Physicist Max Planck (1858 – 1947), also known as the Father of Quantum Theory, theorized that, instead of matter being able to emit at infinite frequencies of electromagnetic radiation, there was some limit as to the frequency that light could be emitted or absorbed at. In other words, he thought of the emission frequencies coming out of matter as a series of steps rather than a smooth ramp. For everyday objects, energy can take on any arbitrary value. However, Planck theorized that for small objects, the energy being emitted by objects was more like a staircase, where it could only come in discrete packets he called *quanta*. In other words, the energy released from objects is *quantized*, a phenomenon which eventually to what we know as the Quantum Theory of Matter. It turns out, the nature of matter is quantized! Planck, through mathematical derivation, arrived at what we now call Planck's Constant (h), which is the smallest unit of Energy that can be gained or lost by atoms, in units of Joules (energy) times second (time), where:

$$h=6.626 imes 10^{-34} Js$$
, or Planck's Constant

Albert Einstein (1879 – 1955)was given the Nobel Prize in Physics for figuring out that the energy of these photons was directly related to the frequency of the electromagnetic wave by the following relationship:

$$E_{vhoton} = hv$$
, where  $h = 6.626 \times 10^{-34} Js$  and the frequency is in units of  $Hz$ .

Using the previous relationship we learned about frequency and wavelength, this equation can also be interpreted as,

$$E_{photon} = h 
u = rac{hc}{\lambda}$$







#### **Equilibrium**

As you may recall, equilibrium (K) is like the energetic low-point in the system, and can be expressed as a fraction of the theoretical concentrations of products and reactants when the reaction has reached this low point. The reaction quotient (Q), on the other hand, is the actual concentration of product and reactant molecules in a solution in real time, which deviate significantly from equilibrium but provide us a mathematical way to calculate the driving force of the reaction (beyond the scope of this discussion).

There are several different forms of the equilibrium expression, and they all mean the same thing. However, they are each designated by a different subscript.

We identify equilibrium values based on a chemical reaction given solely in molar concentrations as  $K_c$ . For a chemical reaction of the form

$$aA + bB = cC + dD$$

The equilibrium expression is written out as:

$$K_c = rac{[A]^a[B]^b}{[C]^c[D]^d}$$

The gas pressure is used to describe the concentration of chemicals in a system in equilibrium in the following manner:

$$K_p = \frac{(P_A)^a (P_B)^b}{(P_C)^c (P_D)^d}$$







The second subsection of the Equilibrium section deals with equations related to pH. The pH of a solution is a measure of the concentrated of hydrogen ions ( $H^+$ , or protons) in solution. The hydrogen ion is also known as hydronium in aqueous media since in reality the proton remains bonded to a water molecule to form the hydronium ion  $H_3O^+$ . In aqueous media, the hydronium ion concentration is in equilibrium with the concentration of water molecules ( $H_2O$ ) and hydroxide ions ( $OH^-$ ).

The dissociation reaction  $H_2O \longleftrightarrow OH^- + H_3O^+$  is represented by the equilibrium expression below, where w stands for water.

$$K_w = [OH^-][H_3O^+] = 1.0 \times 10^{-14} \, \mathrm{at} \, 25^0 C$$

The concentration of water in water does not appear as part of the equilibrium expression, and so what we are left are the concentrations of the two product molecules. What this equation allows us to do is directly relate the concentration of base to concentration of acid in water! This also implies that as the concentration of base goes down, the concentration of acid increases, and vice versa.

The pH of a solution is therefore defined as the negative log of the hydronium ion concentration, whereas the pOH is defined as the negative log of the hydroxide ion concentration.

$$pH = -log [H^+]$$
  
 $pOH = -log [OH^-]$ 

And because the dissociation constant (Kw) of water is always equal to  $1.0 \times 10^{-14}$ , the addition of the pH and pOH of a solution must always equal the negative log of that value, which is 14:







And because the dissociation constant (Kw) of water is always equal to  $1.0 \times 10^{-14}$ , the addition of the pH and pOH of a solution must always equal the negative log of that value, which is 14:

$$14 = pH + pOH$$

The more general expression for any acid or base is as follows, where *HA* stands for the acidic species with the proton still attached, and *HB*<sup>+</sup> stands for the positive basic species with the proton still attached.

$$K_a = rac{[H^+][A^-]}{[HA]} \ K_b = rac{[OH^-][HB^+]}{[B]}$$

We relate the pH of a solution to the  $pK_a$  (negative log of an acid dissociation constant) of an acid to find the relative concentrations of the protonated and non-protonated species of the acid in a solution of a given pH. This is known as the Henderson-Hasselbalch equation. A similar calculation can be performed for a base using the pOH of the solution and the  $pK_b$  (base dissociation constant) of the base.

$$egin{aligned} pK_a &= -logK_a \ \\ pK_b &= -logK_b \ \\ pH &= pK_a + \log rac{[H^-]}{[HA]} \end{aligned}$$

Please note that these calculations are only relevant for weak <u>acids and bases</u>. Strong acids and bases dissociate entirely in water and therefore are not in equilibrium with their non-solvated species.







#### **Kinetics**

Kinetics is most basically the study of the change of concentration of a reagent during a reaction in which it is consumed. An example of a kinetic reaction is the radioactive decay of uranium. Another example is the metabolism of a drug by the human body once it is ingested. Kinetics are measured as the change from starting concentration [A]O to a final concentration at time t,  $[A]_t$ . Every kinetic reaction has a particular rate constant k which determines the rate at which the initial concentration decays. The half-life  $t_{\frac{1}{2}}$  is a useful parameter that is often used as a sort of measuring point for the speed of the kinetic reaction. Since all of these calculations are based on calculus (namely, integration), the natural log is used to equalize the starting and ending concentration to each other, for reasons that are outside the scope of this discussion.

$$\begin{split} & \ln[A]_t - \ln[A]_0 = -kt \\ & \frac{1}{[A]_t} - \frac{1}{[A]_0} = kt \\ & t_{\frac{1}{4}} = \frac{0.693}{k} \end{split}$$

Equations 2 is just a derivation of Equation 1 by using one of the laws of transforming logarithms, so they are somewhat redundant. You may be asked to calculate the final concentration of a reagent after a given amount of time in a reaction, in which case you will use algebra to rearrange either of these reactions to find the final answer.







#### Gasses, Liquids, and Solutions

All the different gas laws can be compiled into one equation called the <u>Ideal Gas</u> Law:

$$PV = nRT$$
 ; where -

P = pressure;

V = volume:

n = number of moles;

R = gas constant, and;

T = temperature in Kelvin.

According to the ideal gas law, pressure is related to the number of molecules of gas. Therefore, concentrations of gases are reported as *partial pressures*, where:

$$P_{total} = P_A + P_B + P_C...$$

A gas like the air we breathe consists of various constituent molecules of gas such as carbon dioxide  $(CO_2)$ , nitrogen  $(N_2)$ , oxygen  $(O_2)$ , and water  $(H_2O)$ . Even though the air, in general, has a total pressure, we can measure the contribution of the partial pressure of each type of gas molecule to the total pressure. This relationship is another consequence of the kinetic theory of gasses: considering that it is the collisions of each molecule of gas with the wall of the container that provide the total pressure, the amount of pressure exerted by each gas individually is directly proportional to the sum of that particular gas inside the container. This quantity is known as the *molar fraction*.

$$P_A = P_{total} x X_A, where X_A = \frac{moles A}{total moles}$$







Converting from moles to mass (m) is easily achieved by obtaining the molar mass M of a compound:

$$N = mM^{-1}$$

And of course, since Kelvin units and degrees Celsius are on the same scale, converting between one and the other is very easy:

$$K = {}^{0}C = +273$$

The density of an object is defined as the mass of the object divided by the volume of the object. One kilogram of water in one liter of volume has a density of 1.000:

$$D = mV^{-1}$$

According to the Kinetic Molecular Theory, each molecule of gas in an ideal gas has a kinetic energy equal to one-half its mass times its velocity squared:

$$KE$$
 per molecule =  $\frac{1}{9}mv^2$ 

Molarity is defined as the number of moles of *solute* per liter of *solution*. The solute is the reagent being dissolved. One thing to note is that one thousandth of a molar unit (millimolar, mM) is equal to one millimole of a compound in one *liter* of solution. Meaning, if you dissolve one mmol of a compound in one mL of solution, the molarity of the solution is 1 Molar! This can be *very* confusing even for Chemistry graduate students, so we suggest you practice this and always confirm your units when performing these calculations on the fly.







The final equation in this section has to do with Beer's Law, or Molar Absorptivity. The absorbance (A) of a solution can be defined as the molar absorptivity constant (a) of a compound times the path length (b) of the cuvette in centimeters times the concentration of the compound in solution (c). The standard path length in almost every experimental procedure is 1 cm. The molar absorptivity is a value unique to each chemical.

$$A = abc$$

Given a certain absorbance and molar absorptivity value, you can calculate the concentration of a compound in solution.

#### Thermochemistry/Electrochemistry

The first equation we will deal with in this section is the chemical definition of heat. Heat in this context refers to the energy transferred to or from an object of a certain mass (m) with a given specific heat capacity (c) as the temperature of the object changes  $(\Delta T, \text{ in Kelvin})$ :

$$q = mc\Delta T$$

The Equation Sheet will provide you general definitions for the standard change in entropy, enthalpy, and free energy, though it is up to you to know the correct context.

$$egin{aligned} \Delta S^0 &= \Sigma S^0 products - \Sigma S^0 reactants \ \ \Delta H^0 &= \Sigma \Delta H_{f^0} products - \Sigma \Delta H_{f^0} reactants \ \ \ \Delta G^0 &= \Sigma \Delta G_{f^0} products - \Sigma \Delta G_{f^0} reactants \end{aligned}$$







Standard entropy, enthalpy, and free energy constants are all related to each other by the expression below, where the absolute temperature T is in units of Kelvin.

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

The expression for free energy can take on two other forms, depending on the context. If we are dealing with equilibrium problems, then the equilibrium expression for free energy will be used, where *R* is the **Gas constant**, and *K* is the **equilibrium constant**:

$$\Delta G^0 = RT \ln K$$

If on the other hand, the topic is <u>electrochemistry</u>, then the Nernst Equation should be substituted into the expression, and the value of Faraday's constant (F) and the standard reduction potential of the cell ( $E^0$ ) should be used. The amount of free energy, in this case, depends on the number of moles of the compound in solution and is represented by the letter n.

$$\Delta G^0 = -nFE^0$$

The final equation on the Equation Sheet relates directly to electrochemistry and is the chemical method of representing the value of the electrical current. The current in units of amperes (A) is a measure of the amount of electrical charge (q) passing through a given point over a certain amount of seconds (t).

$$I = qt^{-1}$$





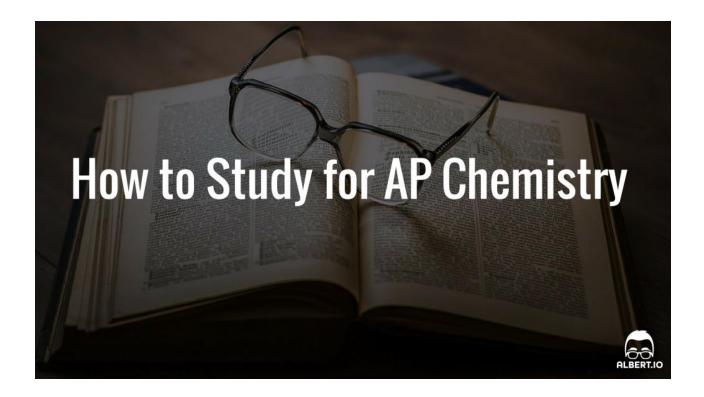


And with that, we are done! We hope that this Guide will give you the edge you need in succeeding on the AP Chemistry Exam. The Equation Sheet is a powerful tool. It not only saves you the task of memorizing certain equations, but it also allows you to more clearly recall other equations and relationships not explicitly mentioned on it. The best piece of advice we can give you about the equation sheet is this: Do not hesitate to write on the equation sheet early on in the test so you can remember all of these obscure unwritten relationships when the time comes!









AP Chemistry requires a mishmash of math, reasoning, and memorization, so it can be difficult just figuring out how to study for AP Chemistry. We feel your pain, so we decided to help out with this how-to guide for studying AP Chemistry.

There's a lot to cover in AP Chemistry (two semester's worth of college-level chemistry), and this article is going to set you on the right track to study smart for AP Chemistry.







#### What's on the AP Chemistry Exam?

#### **AP Chemistry Exam Format**

The CollegeBoard will assess your mastery of chemistry with an exam at the end of the course, so determining how to study for AP Chemistry requires understanding the format of the test. You will have 3 hours and 15 minutes to complete two sections. The first section (90 minutes) focuses on discrete answers to questions in the form of 60 multiple choice questions. There will be math, but no calculators are allowed on this first part. The second section (105 minutes) requires writing out answers in the form of 3 long and 4 short response questions.

#### **Learning Objectives in AP Chemistry**

Knowing the test structure will help you think about how to pace yourself during the AP Chemistry exam, but most of your focus should be on studying the actual chemical content of the exam. There are many topics in AP Chemistry, and you will need some tool or checklist to make sure that you are studying everything.

The most specific list of AP Chemistry topics are the *learning objectives* of AP Chemistry. These objective are listed in the AP Chemistry Course and Exam Description and briefly summarize everything there is to know for the AP Chemistry exam. For example, learning objective 1.17 states: "The student is able to express the law of conservation of mass quantitatively and qualitatively using symbolic representations and particulate drawings. This means that you should be able to create and analyze sketches that correctly describe chemical reactions at the atomic level. Here's an example from the CollegeBoard.

Of the 4 diagrams below, can you identify the best depiction of oxygen gas reacting with hydrogen gas to form water vapor? To answer this question, you must know the molecular form of hydrogen and oxygen gasses and recognize that there should be two hydrogen gas  $(H_2)$  molecules for each oxygen gas  $(O_2)$  molecule. Only option C correctly displays all of this information.







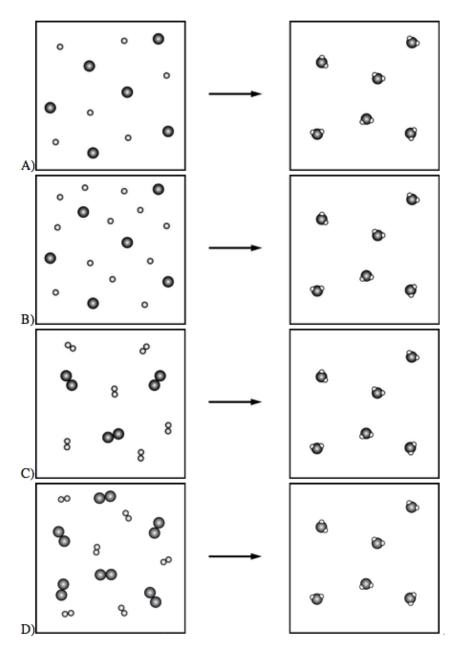


Image Source: CollegeBoard

Think of the learning objectives as a checklist while you study. It will help you keep track and not forget an important topic. There is no reason to memorize any part of the learning objectives, but save a copy that you can consult when necessary. If you cannot demonstrate mastery of any of the learning objectives, it is definitely an area you should study.







#### **Essential Knowledge Statements**

In addition to making a handy checklist, the learning objectives are also the best entry point for more detailed information and organization within the AP Chemistry curriculum. Each learning objective is composed of exactly one essential knowledge statement and one or more science practices. Here is an example of what the essential knowledge statements have to offer.

Learning objective 1.17 also tells us to reference essential knowledge 1.E.1 (as well as Science Practice 1.5) which states: "Physical and chemical processes can be depicted symbolically; when this is done, the illustration must conserve all atoms of all types." This general statement is further outlined with sub-points. You probably don't need to read the whole statement right now, but keep in mind that organizing similar topics into groups will maximize the efficiency of your studying. There are, however, some special notes included with the essential knowledge that are definitely worth a look.

#### **Exclusion Statement**

Exclusion statements tell you what *won't* be on the exam. For example, in regards to <u>electrochemistry</u>, the CollegeBoard states that: "The Nernst equation is **beyond** the scope of this course and the AP Exam." Watching out for statements like this can save you a lot of time, but make sure to read the accompanying rationale as well. The given rationale, in this case, is "Qualitative reasoning about the effects of concentration on cell potential is part of the course. However, inclusion of algorithmic calculations was not viewed as the best way to deepen understanding of the big ideas." This rationale helps refine what is and is not included in the exclusion statement. While it is true that you don't have to worry about knowing the Nernst equation or performing calculations with it, you do need to know the qualitative trend between concentration and cell potential. There's no way to learn everything about chemistry in one class (or one lifetime!) so use the essential knowledge statements and their content notes to focus your studies and spend your time wisely.







#### Math on the AP Chemistry Exam

Don't let the ban on calculators in the multiple choice section fool you —there is quite a bit of math everywhere on the AP Chemistry exam. You probably won't have numerically complex questions, but you will need to perform calculations and use a great deal of math sense. Here are a couple of examples from the CollegeBoard to show you what I mean.

$$K(s) + \frac{1}{2} Cl_2(g) \rightarrow KCl(s)$$
  $\Delta H^{\circ} = -437 \text{ kJ/mol}_{rss}$ 

What remains in the reaction vessel after equal masses of K(s) and  $Cl_2(g)$  have reacted until either one or both of the reactants have been completely consumed?

- (A) KCl only
- (B) KCl and K only
- (C) KCl and Cl<sub>2</sub> only
- (D) KCl, K, and Cl,

Image Source: CollegeBoard

You're not being asked for specific masses for the chemicals in the vessel after the reaction, but you still need to compare the exact molar masses for potassium (39.10 g/mol) and chlorine gas (70.90 g/mol) to get the correct answer. Trying to simplify math by approximating the molar mass of chlorine gas as twice as large as potassium, will lead to answer A. Only by considering the exact molar masses will you notice that all of the potassium metal will be consumed, and chlorine gas will be in excess at the end of the reaction. When we also consider the potassium chloride product, we can see that the answer is C.







A sample of  $N_2O_5$  was placed in an evacuated container, and the reaction represented above occurred. The value of  $P_{N_2O_5}$ , the partial pressure of  $N_2O_5(g)$ , was measured during the reaction and recorded in the table below.

Time (min)	P <sub>N2O5</sub> (atm)	$ln(P_{ m N_2O_3})$	$\frac{1}{P_{\rm N_2O_5}}$ (atm <sup>-1</sup> )
0	150	5.0	0.0067
100	75	4.3	0.013
200	38	3.6	0.027
300	19	2.9	0.053

Which of the following correctly describes the reaction?

- (A) The decomposition of N<sub>2</sub>O<sub>5</sub> is a zero-order reaction.
- (B) The decomposition of N<sub>2</sub>O<sub>5</sub> is a first-order reaction.
- (C) The decomposition of N<sub>2</sub>O<sub>5</sub> is a second-order reaction.
- (D) The overall reaction order is 3.

Image Source: CollegeBoard

In this case, there are no calculations needed per se, but it is necessary to identify numerical trends. The most general method for solving this problem is to determine which column of data makes a straight line when graphed as a function of time. You could sketch a graph for each column, but a faster way is to notice that only the natural log of the pressure is changing by the same amount every 100 seconds. Only a linear graph would have this property, so you can tell that the middle column of data will make a straight line without needing to graph. When the natural log of pressure v time is linear, that signifies that the reaction is first order reaction (B).

Make sure that you always ask yourself how mathematical reasoning can be applied to any topic. You can focus on learning objectives that include science practices 2 and 6 to develop the mathematical and data analysis skills required for the AP Chemistry exam.







#### **Gathering Your Resources for the AP Chemistry Exam**

Now that you know what you will be studying, the next step is collecting the tools and resources that will help you study best. In addition to your textbooks, there are also many web articles, tutorial videos, and practice questions available online. It can take some searching to find good information that fits the AP Chemistry curriculum (remember to check the essential knowledge and exclusion statements), but you can likely find resources that fit your learning style. Here's a starter list of resources.

#### **CollegeBoard Materials for AP Chemistry**

<u>AP Chemistry Course and Exam Description</u> – Complete curriculum guide with sample problems. Also includes:

- AP Chemistry Equation and Formulas This list will be provided for you with your exam. Don't assume that being given equations means they don't need to be studied. Make sure that you know what all the variables mean and what situations require these equations.
- Periodic Table Some periodic tables include more information than others, so you want to be accustomed to what will and won't be provided on the periodic table issued by the CollegeBoard.

<u>Past Free Response Question</u> – These are a great resource for becoming familiar with the written portions of the exam.

#### **Videos**

<u>Bozeman Science</u> – These videos are organized in the same way as the AP Chemistry curriculum and covers major topics in each of the Big Ideas.

<u>Khan Academy</u> – These videos are not directly tied to the AP Chemistry curriculum, but still cover many of the same topics.







#### **Albert.io AP Chemistry Posts**

We also have a large catalog of AP Chemistry posts that cover core content, study guides, book reviews, and more. You can browse all of the posts <a href="here">here</a>, but here are a couple of popular examples:

- The Best AP Chemistry Review Books of 2016
- One Month AP Chemistry Study Guide This post provides a sample AP
   Chemistry study guide that you can modify to fit into any time frame. This
   free guide is a great for refreshing key concepts that show up frequently
   on the exam

#### **Testing Yourself Before the AP Chemistry Exam**

Because the CollegeBoard places a heavy emphasis on skills in AP Chemistry, you will have to do a fair amount of practice questions and tests in addition to reading textbooks and notes or watching videos. Old free response questions can be found on the CollegeBoard's <a href="website">website</a>; multiple choice questions can be found in review books, Albert.io's <a href="AP Chemistry section">AP Chemistry section</a> and other online sources. The exam has gone through changes over time, so try to find recent examples if possible. Older exams are still useful, but make sure the content fits the current AP Chemistry curriculum.

#### **Conditions**

The goals of your studies include both learning content and becoming accustomed to real exam conditions. The current multiple choice section gives you 90 minutes to answer 90 questions, so try to replicate that at some point during your studies. You may find it easier to relax these conditions during your first study sessions. If you have access to more than one practice exam, you can use the first for general studying, and save the rest for timed practice. You should always have at least a general idea of how long it takes to answer a given number of questions, but a time limit may not be helpful for the first practice test.







You will eventually want to be able to answer multiple choice questions in a minute or less (on average), but it might be best to focus first on answering questions correctly and then focus on answering questions quickly and correctly.

#### **Accuracy**

Take note of which questions you answered correctly and incorrectly, as well as which questions were more difficult to answer. If any of your correct answers were guesses (which you should always do when you do not know the answer; the AP Chemistry exam does not penalize incorrect answers.), those questions require further study as well. It is also helpful to note if the questions *felt* easy or difficult. If a question was difficult, it may require further study even if you answered it correctly. If you incorrectly answered a question that felt was easy, that may reflect insufficient test-taking skills or a fundamental misunderstanding of the topic at hand. Remember that the goal of studying is not just learning but also developing confidence in your knowledge.

#### **Timing**

It is also important to know how long it takes to answer questions. In addition to preparing you for a timed exam, timing yourself can give insight into your comprehension of chemistry. If you had to reread the question repeatedly or had to try several strategies before finding the correct one, you need to study the topic more.

Some questions just take more time, and extra studying won't change that. Learn to recognize these questions by sight. Each multiple choice question is worth the same, so there is no downside to answering the easiest questions first and returning to the harder questions at the end. Just be sure to record your answers carefully if you are skipping questions.







#### **Analyzing Your Results**

Knowing what topics and question types give you trouble will help you revise and optimize your study plans. Categorizing your mistakes is a great way to identify the trends that can help focus your studies. For the AP Chemistry exam, we recommend categorizing your questions using (at least) the following methods:

#### 1. State why you answered specific questions incorrectly.

It's not always fun to focus on your mistakes, but mistakes and failure often teach more than success. Try summarizing the main issue in one phrase or sentence. For example, "I couldn't remember if 3d orbitals were filled before or after 4s orbitals," "I had a hard time picturing all the ions in solution" and "I confused endothermic with exothermic" are all simple descriptions of why a question was answered incorrectly. If you notice that similar issues occur frequently, that will identify an area to revisit.

For example, if you frequently could not find the relationship between physical properties, go over your <u>equation sheet</u> and focus on which quantities are directly and inversely proportional and try using flash cards to remember trends that aren't summarized in equations. If you "couldn't remember how to convert from moles reacted to electrons transferred" or "divided by molar mass instead of multiplying" then you definitely want to practice a lot of <u>stoichiometry</u> problems. The statements generated by this method do not always yield large patterns, but it's guaranteed to give you a few things to consider.

#### 2. Categorize strengths and weaknesses by content areas.

As mentioned above, the learning objectives are specific pieces of chemistry curriculum which can be categorized as part of particular essential knowledge. These essential knowledge statements are grouped by "Enduring Understanding" statements, which in turn are grouped into the four "Big Ideas" of AP Chemistry.







For example, if you were studying how intermolecular forces control the properties of liquids and solids, that topic falls under Essential Knowledge 2.B.3 "Intermolecular forces play a key role in determining the properties of substances, including biological structure and interactions." More broadly, this fits into Enduring understanding 2.B which focuses on forces between particles influence macroscopic properties. Finally, the CollegeBoard categorizes all of this as part of Big Idea #2 which covers how chemical and physical properties are explained by microscopic structure.

You should not make any attempt to memorize these classifications (you have enough to study), but this organization will make it easier to keep track of all of the topics that you need to study, and it will give you some ideas as to the types of connections the CollegeBoard wants you to make. Take note of which sections are giving you trouble and which ones you understand well.

#### 3. Categorize strengths and weaknesses by science practices.

One thing to keep in mind as you study is that the AP exam does not just focus on accumulated knowledge but also what you can do with this knowledge. These skills are summarized by the CollegeBoard as *science practices*, and can be found in the AP Chemistry Course and Exam Description. There are seven science practices outlined by the CollegeBoard, and you want to be able to apply these practices within each domain (topic) in AP Chemistry. Try to identify both the topics and the science practices in the questions you try, and keep track of strengths and weaknesses in science practices. As you study through topics, apply as many of the science practices to the topic at hand as possible, and pay special attention to your weakest one or two science practices. Science practices that require visualizing chemistry at the atomic scale or analyzing data are featured heavily on the AP Chemistry exam,







#### 4. Note format of questions and answers

Some AP Chemistry questions have unusual prompts or answer choices. For example, there are multiple-choice questions that require numerical calculations, but the answer choices are not numerical values. Other questions require choosing a response that includes a specific answer and the correct rationale. The content of these questions will be covered in your course and studies, but the structure of the questions themselves may require deliberate study. If you have a hard time with a question but feel you understand the underlying material, think about alternative ways to phrase the question or answer choices that would be easier. Then compare your simplified version to the test question.

#### **Adjusting Your Strategies for the AP Chemistry Exam**

Knowing your strengths and weaknesses can help you to refine your study habits. Many students only focus on their weak areas, but understanding both strengths and weaknesses is essential for optimal studying. Here are a few tips for using your strengths and weaknesses to your advantage.

#### 1. Improve stronger areas as well as weaker areas.

The point-value of questions is not dependent on the difficulty of the topic. For efficient studying, your strongest topics have the advantage of being easier to learn and work with, whereas your weaker have more room for improvement. You will want to balance your studies among easy and difficult topics to maximize performance. After studying two or three weak sections, review a strong section. This ensures that you spend most of your time on bolstering weak areas while perfecting strong areas.







#### 2. Relate strong content areas to weak ones.

All topics in chemistry are related in some way. If you find how difficult topics are similar to easy topics, you will master the material more efficiently. For example, if you can easily calculate how much heat is released when ethanol undergoes combustion, but you always mess up electrolysis problems, consider how similar these two ideas are. Both cases can be thought of as extensions to <a href="stoichiometry">stoichiometry</a> problems, especially if you imagine how heat and electrons can be represented in a balanced chemical equation or half reaction.

Making these kinds of connections are especially important in the AP Chemistry exam. Many of the questions are grouped into sections that all refer to the same image, reaction, or data. Each question requires you to demonstrate mastery over a different learning objective applied to the same reference. Making these connections while you study will make these types of questions much easier to handle during the actual exam.

#### 3. Use strong science practices to train weak content areas and vice versa.

Your strongest science practices likely correspond to strong thinking and learning skills. You can use these skills to learn difficult or unfamiliar material. For example, imagine that you excel at using visual representations and models (Science Practice 1), but you have difficulties grasping why atoms in the same row of the periodic table get smaller as we travel from left to right (even though the number of protons and electrons increases). You can draw a diagram of each element in a row of the periodic table and place the correct number of electrons into orbits like in the Bohr model. You will see that adding electrons doesn't make the atom any bigger since they are occupying the same shell. In fact, the additional protons will create a stronger attractive force that pulls the electrons in closer.

Likewise, the science practices are most easily studied when applied to a particular content area. Attempting to strengthen weak practices while applying them to content that you are less confident with will be difficult to analyze.







It will not be clear if a problem is related to the science practice or the content area. Start with your best content area so you can focus primarily on the science practice. When you feel more comfortable, try applying the practice to progressively weaker topics.

#### **Wrapping Up**

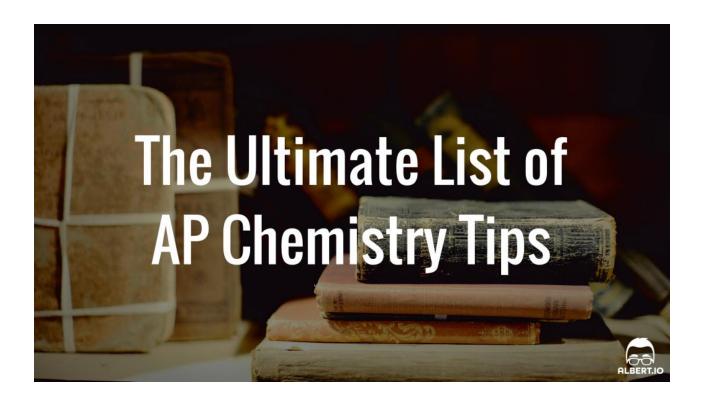
Using these ideas will greatly help in preparing for your AP Chemistry exam. At this point, you might be wondering how you will find time to plan all this studying and actually study! Luckily, you don't have to handle everything by yourself. Albert.io's AP Chemistry section already categorizes every question based on the curriculum set by the CollegeBoard, so all you have to do is pick your section and get to work. Take a look for yourself. Albert Chemistry questions meet and exceed the difficulty of the AP Chemistry exam, so they are a great place to start your studies.

**Start your AP Chemistry Prep today!** 









In this article, we will discuss some AP Chemistry Tips. Scoring a 4 or 5 on the AP Chemistry exam can seem impossible. From <u>stoichiometric calculations</u> to thermodynamics and from chemical reactions to <u>atomic structure</u>, chemistry can seem like a mystery. If you're taking AP Chemistry you probably have a solid science and math background and a real interest in the subject. Luckily, that's already half the battle! Whether your goal is to earn college credit, challenge yourself, or just learn more about the subject, AP Chemistry will be a great experience, but not without its difficulties.

It can help to look at past AP score distributions to gauge the level of difficulty of the exam. On the 2015 AP Chemistry Exam, only 8.4% of test takers earned the coveted score of 5.







(Fun fact: only 3 students out of 150,000 earned a perfect score!). 15.2% earned a score of 4, 28.1% earned a score of 3, 25.5% earned a score of 2, and 22.8% earned a score of 1. This means that only around half of all exam takers received a passing score of 3 or above. The other half only earned a 1 or 2. This can seem intimidating as you're starting your AP Chemistry journey, but it's important to realize that you get out what you put in. If you make a commitment to study your hardest and study the right things, you should be on track to earn a great score!

This list of 50 AP Chemistry tips will give you everything you need to know to get your best possible score on the exam, from study techniques to tips from real AP teachers, and from things to avoid studying to how to change your way of thinking. Let's get started!

#### **Overall How to Study for AP Chemistry Tips**

- **1. Know the format of the exam.** Don't be confused about the format of the AP Chemistry exam; you may have found conflicting information online. That's because the exam's format completely changed starting with the 2015 exam. Let's get it straight: the AP Chem exam is a total of 3 hours and 15 minutes long, with a 90-minute multiple-choice section and a 105-minute free-response section. Each section counts for half of your score, so they are both equally important to study for. The multiple-choice section has 60 questions, and the free-response section consists of a mix of 7 short or long essay questions. We'll go into greater detail on the individual sections later on.
- **2. Buy a review book.** Investing in a good AP Chemistry review book is absolutely essential. Why do you need a review book? Well, review books contain only the most important information, written concisely and organized into important topics. Textbooks, on the other hand, throw so much information at you that there's no way you can get through it all a second time efficiently and actually understand everything you've read. AP review books are often written by AP teachers and other AP professionals.







They know the exam format in and out and know the most critical information you need to know for the exam. Most also come with diagnostic exams and practice exams. For AP Chemistry review books, be sure to get a version published after 2014. Try Barron's, the Princeton Review, or 5 Steps to a 5.

- **3. Know what is NOT included on the exam.** There are a few concepts and ideas that are considered to be beyond the scope of the AP Chemistry exam. This means that you will not have to know them for the test. Don't spend very much time, if any at all, studying the following ideas. Keep in mind, though, that these concepts may still be useful as background knowledge.
  - Memorization of exceptions to the Aufbau principle
  - Assignment of **quantum numbers** to electrons
  - Phase diagrams
  - Colligative properties
  - Calculations of molality, percent by mass, and percent by volume
  - Knowledge of specific types of crystal structures
  - The use of formal charge to explain why certain molecules do not obey the octet rule
  - The study of the specific varieties of crystal lattices for ionic compounds
  - Learning how to defend Lewis models based on assumptions about the limitations of the models
  - Lewis acid-base concepts
  - Language of reducing agent and oxidizing agent
  - Labeling an electrode as positive or negative
  - The Nernst equation
  - Calculations involving the Arrhenius equation
  - Numerical computation of the concentration of each species present in the titration curve for polyprotic acids







- Computing the *change* in pH resulting from the addition of an acid or a base to a buffer
- The production of the Henderson-Hasselbalch equation by algebraic manipulation of the relevant **equilibrium constant** expression
- · Computations of solubility as a function of pH
- Extensive Organic Chemistry
- Molecular Orbital Theory
- Nuclear Chemistry

Source: CollegeBoard's AP Chemistry Course and Exam Description

- **4. Learn to draw connections between concepts.** Most chemistry tests you've taken up to this point have probably been mostly based on recalling facts and calculations that you've had to memorize. The AP Chemistry exam is a little different. Instead of relying on rote memorization, the exam focuses on connections between concepts and the analysis of data using information you've learned. That being said, spend less time trying to memorize facts and more time on inquiry-based learning and reasoning skills. Learn to apply concepts to certain situations, learn how to use calculations, and most importantly, learn how to make connections between everything you're learning in your chemistry class.
- **5. Familiarize yourself with the Big Ideas.** The CollegeBoard uses Big Ideas to guide the creation of AP exams and to show students what is important to understand, expand on, and analyze. By developing a deep understanding of the following AP Chemistry Big Ideas, you are setting yourself up for success on the exam. The Big Ideas, according to the CollegeBoard, are:
  - The chemical elements are the building blocks of matter, which can be understood in terms of the arrangements of atoms.







- Chemical and physical properties of materials can be explained by the structure and the arrangement of atoms, ions, or molecules and the forces between them.
- Changes in matter involve the rearrangement and/or reorganization of atoms and/or the transfer of electrons.
- Rates of chemical reactions are determined by details of the molecular collisions.
- The laws of thermodynamics describe the essential role of energy and explain and predict the direction of changes in matter.
- Bonds or attractions that can be formed can be broken. These two
  processes are in constant competition, sensitive to initial conditions and
  external forces or changes.

Source: CollegeBoard's AP Chemistry Course and Exam Description

- **6. Know about calculator rules and formula sheets.** On the AP Chem exam, you will be allowed to use a scientific calculator during the FRQ section, but not during the multiple-choice section. Additionally, you will be given a periodic table of elements and a **formula sheet** to use during the entire exam. Keep in mind that the formula sheet you'll be given does not contain every equation you may need. For example, the sheet will not include equations that are derived by combining others on the sheet. It's also important to realize that because you are given a formula sheet, you will not be awarded points for simply writing down the correct equation as your answer.
- 7. Watch Bozeman Science videos. If you are a visual learner, or if you need a break from reading page after page of a chemistry textbook, give <a href="Bozeman">Bozeman</a>
  <a href="Science">Science</a> videos a try. Mr. Anderson, the creator of the videos, explains the chemistry concepts you need to know for the exam in a clear, concise, and friendly way. He also includes slideshows and concept maps for each of his videos to help explain things further.







The great thing about watching chemistry videos is that you can rewind if you missed something or need it explained again, pause if you need to digest something before moving on, and even fast-forward if you already have an understanding of a certain topic. Make sure to actively watch these videos, meaning take notes, draw diagrams, or keep a running vocabulary list as you watch.

- **8. Do the chemistry problem of the day.** Ideally, you will dedicate a portion of your day, *every single day* of the week to studying for AP Chemistry. But life happens, and this isn't always an option for every student. Still, it's important to make chemistry a part of your day, even if it's only for 5 minutes. Make it a habit to answer the chemistry **Problem of the Day**. You can even sign up to have the daily problems sent to your email inbox every day, that way you won't forget. Many of the questions are modeled after real AP Chemistry multiple-choice questions.
- **9. Follow chemistry social media accounts.** If you spend a lot of time online, make AP Chemistry a part of your online life, too! Follow <u>@ChemistryWorld</u> on Twitter, explore AP Chemistry on <u>Pinterest</u>, 'like' <u>Chemistry lovers</u> on Facebook, or use the social media platform you enjoy the most and find something chemistry-related that you can interact with. AP Chemistry is all about making chemistry a part of your life, so what better way to do this than through social media!
- **10. Make detailed flashcards.** One of the most helpful self-study techniques is making flashcards. The act of writing out detailed and informative flashcards is helpful because using your own words, drawing diagrams, and using mnemonic devices that only *you* know, cements the ideas in your mind. Attempt to make flashcards for every term on **this list**. Make sure to write the definitions in your own words so that you actually understand what you're putting down.

Unfortunately, it's impossible to make your own flashcards on absolutely every chemistry term. If you tried, you'd probably spend the entire year making flashcards and not have enough time to actually study them!







For times when you're bored, don't know what to study, or are tired of looking through your own flashcards, try visiting <u>Study Stack</u>. They have literally hundreds and hundreds of chemistry flashcards organized into different categories. They act like real flashcards that you can flip over and add to "Know" and "Don't Know" piles. Make use of this resource!

- **11. Form a study group.** Studying alone can get tedious and boring, and you may find yourself getting distracted more easily. Get a group of your classmates together and meet once or twice a week to go over the latest chemistry concepts you've been learning in class. You may find that hearing a concept explained by one of your peers makes it easier to understand. If one of your friends is having difficulty with a certain formula, explaining it to them in your own words can also help cement the idea in *your* brain.
- **12. Rewrite your notes.** You should be taking good notes during class lectures, when you're reading your textbooks and review books, and while you're watching chemistry videos. What should you do with these notes after you've written them? Rewrite them! It may seem redundant to rewrite notes, but it not only makes your notes neater and easier to read and use as a study tool, but it actually helps the information to sink in.

#### **Start your AP Chemistry Prep today**

#### **AP Chemistry Multiple-Choice Review Tips**

**1. Know the types of multiple-choice questions.** On the AP Chem exam, you will have 90 minutes to answer 60 multiple-choice questions. These consist of either discrete questions or question sets. Discrete questions are stand-alone questions with four answer choices. Question sets are based on graphs, experiments, a set of data, or another stimulus given to you at the beginning of the question set and also have four answer choices.







**2. Know what the multiple-choice questions look like.** Many of the AP Chem multiple-choice questions can be pretty involved. You'll need to analyze diagrams, graphs, images, and charts of data, to arrive at your answers, while other questions will include a paragraph to base your answers on. Let's take a look at a few examples.

**The first example** is based on information given to you in paragraph form. This is an example of a discrete stand-alone question, since there is only one question based on the given data.

A 100g sample of a metal was heated to 100 degrees Celsius and then quickly transferred to an insulated container holding 100g of water at 22 degrees Celsius. The temperature of the water rose to reach a final temperature of 35 degrees Celsius. Which of the following can be concluded?

- (A) The metal temperature changed more than the water temperature did; therefore the metal lost more thermal energy than the water gained.
- (B) The metal temperature changed more than the water temperature did, but the metal lost the same amount of thermal energy as the water gained.
- (C) The metal temperature changed more than the water temperature did; therefore the heat capacity of the metal must be greater than the heat capacity of the water.
- (D) The final temperature is less than the average starting temperature of the metal and the water; therefore the total energy of the metal and water decreased.







**The next example** is a question set, which includes multiple questions based on one table of data. **Questions 8–10** refer to three gases in identical rigid containers under the conditions given in the table below.

Container	A	В	С
Gas	Methane	Ethane	Butane
Formula	CH <sub>4</sub>	$C_2H_6$	$C_4H_{10}$
Molar mass (g/mol)	16	30	58
Temperature (°C)	27	27	27
Pressure (atm)	2.0	4.0	2.0

- 8. The average kinetic energy of the gas molecules is
  - (A) greatest in container A
- (B) greatest in container B
- (C) greatest in container C
- (D) the same in all three container
- 9. The density of the gas, in g/L, is
  - (A) greatest in container A
- (B) greatest in container B
- (C) greatest in container C
- (D) the same in all three containers
- 10. If the pressure of each gas is increased at constant temperature until condensation occurs, which gas will condense at the lowest pressure?
  - (A) Methane

(B) Ethane

(C) Butane

(D) All the gases will condense at the same pressure.

Source: CollegeBoard AP Chemistry Course Description







It's important to note that the emphasis of AP Chemistry multiple-choice questions is not on fact recalling, but on analyzing data given to you using your indepth knowledge of chemistry concepts.

- **3. Know the calculator policy.** Calculators are NOT allowed on the multiple-choice section of the AP Chemistry exam. That being said, there are still going to be math-based questions. However, these calculations will only require simple arithmetic and can be done quickly, either mentally or on paper. Some questions only require estimation, so brush up on your estimation skills as well.
- **4. Use standard multiple-choice test taking strategies.** When in doubt, fall back on some standard multiple-choice test-taking strategies.

For the AP Chem exam:

- Answer ALL questions (there is no penalty for wrong answers)
- Examine each question for a maximum of 40 seconds
- Watch out for reverse questions that include the word "EXCEPT"
- Make educated guesses using the process of elimination
- Read the questions before looking at the given data
- **5. Don't underestimate the power of practice!** In order to get a firm understanding of how to answer sometimes-complicated AP Chem multiple-choice questions, you need to practice regularly. You can find sample questions from the **CollegeBoard's AP Chemistry Course Description**, **review books**, a variety of online resources, and at **Albert.io**. Answer a few questions everyday, making note of the questions you struggle with.

**Start your AP Chemistry Prep today** 







#### **AP Chemistry Free-Response Tips**

**1. Know the FRQ format.** On the AP Chemistry exam, you will have 90 minutes to answer 7 essay questions, broken down like this:

	Long Free-Response	Short Free-Response
How many?	3	4
How much time?	16 minutes for each	10 minutes for each

The Long-Free Response questions are exactly what they sound like: long, multipart questions. Each of these questions will often be based off of one set of data. The Short-Free Response questions are shorter and may contain single or multipart questions.

- **2. Understand the skills you need.** According to the CollegeBoard, the 7 essay questions will assess a few essential skills. These include:
  - Experimental design
  - Quantitative/qualitative translation
  - Analysis of authentic lab data and observations to identify patterns or explain phenomena
  - Creation or analysis of atomic and molecular views to explain observations
  - The ability to follow a logical/analytical pathway to solve a problem
  - Manipulation and interpretation of data
  - Making predictions and justifying phenomena
  - Using mathematical processes to explain concepts







- **3.** Be clear and specific. Your goal on the AP Chemistry exam is to prove that you have a deep understanding of chemistry concepts. That's why you absolutely must communicate as clearly and as precisely as you can. Avoid vague, unclear, and flowery language. Inject details, examples, and evidence in your answer. Do not restate the question in your answer and do not ramble. If a sentence adds nothing to your answer, do not include it.
- **4. Use appropriate scientific language.** Do not make the mistake of using improper terms to describe important concepts. For example, do not refer to an atom as a "molecule" or to an intermolecular force as a "bond." Make sure you know how to use proper chemistry symbols and notation. This includes the correct use of superscripts and subscripts, parentheses versus brackets, mol versus m, etc.
- **5. Pay attention to units and significant figures.** In order to receive full credit on FRQ responses, make sure to include units and correct significant figures in your final answer. If the question does not specify, write your answer to the same number of sig figs as the weakest piece of data.
- **6. Understand that calculators, formula sheets, and periodic tables alone are not enough to answer questions.** Some AP Chem students have the misconception that their calculator and formula sheets are "cheat sheets," meaning they don't really have to study their math skills since everything is given to them. Yes, you can store equations in your calculator and yes, a formula sheet and periodic table will be given to you on the exam, but these tools are no substitute for actually understanding the material. You need to know how to apply these given formulas to specific problems and this can often involve multiple steps and multiple formulas that build upon each other. The goal of the AP Chemistry exam is to test your mathematical reasoning and quantitative skills, so you can't get away with just winging it on test day. It's also important to note that you will not receive credit for referencing positions on the periodic table or for simply writing the correct formula on your answer sheet.







- **7. Check if your numerical answers are logical.** Since you can use your calculator on the FRQ portion of the exam, it can be easy to punch numbers into your calculator too quickly, make a typing mistake you don't notice, and come up with a completely wrong answer. Try and combat this by making sure your final answer seems reasonable. For example, there are no negative **equilibrium constants**, Kelvin temperatures, or bond energies. If your answer is negative, does it make sense in this case? Don't lose points based on carelessness.
- **8. Attempt every part of the problem.** Most free-response questions have multiple parts. If you can't answer part "c" of a question, don't fret; you could still get points for parts "a," "b," and "d." Even if your numbers are off because you can't get question "c," good reasoning could still get you partial credit.
- **9. Know how to connect and apply math to key terms.** For the AP Chemistry exam, you need to know your vocabulary and definitions, but you also must know how to do math problems associated with these terms. As an example, take the term *lattice energy.* It's important to know what this term means, but it's also important to know how to apply it in calculations. For example, a question might ask you to calculate the lattice energy of a given crystal lattice composed of sodium and chlorine in a one-to-one ratio.
- **10. Answer in complete sentences.** Since this is the AP Chemistry exam, not the AP Language and Composition exam, you should *not* write your answers in the typical five-paragraph essay format. AP Chem FRQs require that you answer the question and nothing more. This means that you should not add sentences that contribute nothing to your answer or include flowery, vague terms. Still, this is an AP exam, and you should write in complete sentences. Never use bulleted lists and never just list as many things as you can.
- **11. Show all your work.** For questions that involve math and calculations, be sure to include *all* the steps you took to arrive at your answer, even if some of the steps seem obvious. Some questions might give you more points for showing your steps than for giving the correct final answer.







- **12. Know these essential chemical calculations.** You should know the following problem types and calculations inside and out before taking the AP Chem exam:
  - Percentage composition
  - Empirical formulas from experimental data
  - Molecular formulas from empirical formulas
  - Mole fractions
  - Molar solutions
  - Kinetics calculations
  - Gas laws
  - Stoichiometric relations
  - Titration calculations
  - Faraday's laws of electrolysis
  - Standard electrode potentials
  - **Equilibrium constants**
  - Thermodynamic calculations
- **13.** Write down the values given to you and their units. It can sometimes be difficult to figure out which formula to use for free-response questions that involve math. To combat this, write out all the values and their units that are given to you in the question. From there, you should have a clearer picture of (1) what the question is asking you to do, and (2) which formula you should use to arrive at the answer.







#### **Tips by AP Chemistry Teachers**

- 1. "one" with your calculator. Since you don't have to erase your calculator's memory before the exam, go over the AP Chemistry Formula Sheet and program constants into your calculator. This makes calculating math problems faster, more efficient, and minimizes misfires on the keyboard of your calculator. Learn how to scroll back through your last several actions to see where your mistakes lie. Becoming really familiar and comfortable with your calculator is extremely important. Thanks to Ms. Rene M. at the University of Texas at Arlington for the tips!
- **2. Get very comfortable with the Periodic Table.** The Periodic Table is important for the AP Chemistry exam because it provides so much information. Focus on groups 1-8A, know what they are, how to find the number of valence electrons and bonds that an element can form by its group number, and learn other periodic trends. The Periodic Table is key to getting a full grasp of chemistry.
- **3. Know your variables and units.** You need to know what variables and units to use for each FRQ so that you know which equation you should use. For example, take the <u>ideal gas law</u>. In order to solve for any of the variables, you will need to know that:

```
PV = nRT
```

P = pressure (atm)

V = volume (liters)

N = moles

R = gas constant = 0.08206 atm\*L/K\*mol

T = temperature (Kelvin)

If you use the wrong variable, such as Celsius instead of Kelvin, you would get the answer wrong. Thanks to Ms. Jennifer L. for the tips!







- **4. Ace the basics**. Know the basic stuff forwards and backwards. Having a good chemistry foundation is essential to fully understand the harder stuff. Be able to recite ions and compounds in your sleep. Know about Nomenclature, Solubility Rules, Patterns of Chemical Reactivity, etc. Thanks to Mr. K. for the tip!
- **5. Don't read the textbook like you would a novel.** Textbooks can sometimes feel like information overload. That's why you should read in small sections, about 15-20 minutes at a time. Study the pictures and diagrams and keep a running list of important vocabulary words. Take frequent study breaks to prevent burnout. Thanks to Mr. S. for the tips!
- **6. Read all of the FRQ questions before you start to answer them.** Reading all the questions first helps you determine which questions you're the most comfortable and confident answering. Solve the questions in a sequence that is easiest and most effective for you. Thanks to Dr. H. at Trinity Valley School for the tip!
- **7.** It is not necessary to simplify all numerical expressions. In most cases, answers like sin 40° or ln 2, or answers that contain symbols for irrational numbers will suffice. Thanks to Mrs. B. at Edwardsville High School for the tips!
- **8. Attempt every FRQ, regardless of whether you know the answer or not.** Did you know that you could get point for logical answers, even if they aren't right? This means you have nothing to lose. Give every question a try. Thanks to Ms. Nikki W. for the tip!
- **9. Learn by doing.** Working several problems over the course of a few months is the best way to learn chemistry! The more problems you do, the easier they become. Thanks to the Hazelwood School District for the tip!
- **10. You must PRACTICE!** Practice solving problems in small groups, share problem solving strategies with your classmates, and practice at home. The more you practice solving problems the more success you will have on the AP exam.







#### **Tips From Past AP Chemistry Students**

- **1. Use mnemonic devices.** Since you need to memorize lots of concepts and terms, mnemonic devices will be your best friend on the AP Chem exam. For example, for <u>redox reactions</u>, I remembered OILRIG (oxidation is losing and reduction is gaining) to remember how electrons are transferred in a reaction. Thanks to Kimberly T. for the tip!
- **2. Know how to explain how you arrived at your answer.** The AP Chem exam is all about justification and explanation. For example, "what is the partial pressure of CO<sub>2</sub> when equilibrium is established? Explain how you arrived at your answer." FRQs require you to use logic and explain your thought process.
- **3. Memorize it NOW.** If you need to memorize something (mono and polyatomic ions, solubility rules) memorize it ASAP. Don't put off memorizing concepts because it will just make it harder as you keep building upon the material you're learning throughout the year.
- **4. Study solved examples in the textbook.** Do not gloss over solved problems in your textbook. Study them as a priority and do not stop studying the concept until you completely understand it without having to look at the solution.
- **5. It's boring, but read your textbook!** Even though your AP Chemistry textbook may be really boring, make sure you read each chapter! It makes concepts so much easier to understand. You can't really get away with not reading it.
- **6. Know the different reaction types and how to find their products.** Practicing reactions is crucial.







- **7. Read the AP Chemistry Course Description.** You can download it from <u>CollegeBoard</u>. It really works. It has multiple-choice questions and FRQs that are exactly like the exam.
- **8. Know how to manipulate formulas.** Sometimes, FRQs are worded in ways that seem unfamiliar. You may think that you don't know which formula to apply. That's why you need to practice manipulating formulas and equations in different ways.
- **9. Drawing graphs can be helpful.** Even if the question doesn't ask you to draw a graph, drawing a graph can help jog your memory and put your thought process on paper. It may make solutions more obvious when you can actually see them on paper.
- **10. Do full practice exams.** Your teacher probably has access to full AP Chemistry practice exams. They are essential to understanding what the exam will really be like and how you should adjust your thinking.

#### Are you a teacher or a student? Do you have an awesome tip? Let us know!

AP Chemistry is going to be a challenging class and a difficult exam, there's no doubt about it. But if you're reading this, you've probably already made the commitment to working your hardest and performing the best you possibly can on the exam. Memorizing facts for the AP Chem exam is not as important as it used to be, but it is still useful to memorize certain formulas and concepts. Know how to perform the essential chemistry calculations and understand how to derive and combine different equations from the formulas given to you on the exam. Brush up on your math skills, become extremely comfortable with your calculator, and know how to analyze, manipulate, and connect chemistry terms and concepts. Overall, as long as you stay dedicated to AP Chemistry, use the study techniques given to you here, and know what to expect on exam day, you're on your way to a great score on the AP Chem exam! Good luck!







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