5.111: Principles of Chemical Science

Lecturer: Professor Brett McGuire and Professor Mei Hong
Notes by: Andrew Lin

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Introduction

Professor McGuire will be teaching the first half of the course, and Professor Hong will teach the second half. Dr. David Grimes is our course manager, and we'll also have a team of TAs that we'll meet in recitation. We can contact the course staff about anything, but Dr. Grimes is the main point of contact for almost all questions.

Fact 1
Professor McGuire's father was a chemistry professor, who got him started in chemistry from a young age – he now does research in astrochemistry. In other words, he "discovers molecules in space." He joined MIT in the middle of 2020, and this is the first time he's teaching 5.111 in person!

The Canvas website is our main course resource – it contains a Piazza, lecture notes and past videos, assignments, and information about recitations, exams, and office hours. Professor McGuire prefers to use slides rather than writing on the board, especially because a lot of us may be quarantining for a week and can't attend lectures. But we'll make sure not to go faster through the materials just because we don't have to take the time to write out equations – this means that we might have practice problems at the end of lecture or we might end early.

Remark 2. *Professor McGuire also has a script which describes what he'll be talking about on each slide – those are also available on Canvas.*

The main point philosophically of these lectures are to cover big picture ideas, and we should do the remainder of learning outside of class. (And the point of recitations and problem sets is to extend that understanding with applications.)

Attendance is not required for the class, though there will be in-class clicker questions that count for a small fraction of the course points (it's not a problem if we miss a lecture or two, though). Grading will be 300 points from 3 in-class exams, 150 points from the final, 200 points from problem sets, 50 points from the clicker questions, and 50 bonus points from pre-lecture questions (out of a total of 700). Grading is not done on a curve, so there is no limit to the number of As and Bs that will be handed out, and thus we should be highly encouraged to work with other students on problem sets. (Problem sets will mostly have an online and a written component, the latter of which should be uploaded as a PDF file – they'll be due 11pm on Fridays.) Late work is not accepted, and extensions aren't given, but 5.111 is generous about excusing work if we talk to S^3. Finally, exams will be closed notes, but an equation sheet will be provided.

We can always contact the course staff on Canvas or Piazza, though we should make sure to respect everyone's working hours – there will be delays in communication because of this, so it's difficult to guarantee responses sooner than "within two working days." So we should make sure to reach out early if we have a question!

1 January 31, 2022

The goal of this class is to give us all a basic understanding of chemical principles that govern our world, and hopefully get us interested in molecules just like Professor McGuire. We'll begin with a brief history of the topic: **chemistry (the process)** started when the Big Bang made Hydrogen and Helium, and eventually stars started burning those elements to turn them into heavier elements, which forms the material for the next generation of stars. Planets form and orbit around stars, and the chemical bombardment can lead to life.

We can also describe **chemistry (the field)** and its history: **alchemy** used to be considered a real field, in which mixing materials is thought to give us the same material regardless of the ratio in which things are mixed. (For example, salt water is salt water regardless of how much salt is being added to it.) But then some experiments started being performed to test whether this is actually true – Joseph Proust added oxygen to iron, and he found that the amount of rust formed is linearly related with the mass of the oxygen added. (This was known as the **law of definite proportions**.)

Around the same time, John Dalton mixed oxygen and nitrogen together, which can make two different compounds depending on whether the mixing occurs at high or low temperature. It was found that the ratio of oxygen to nitrogen that was consumed was different by a factor of 2 depending on the temperature, and in other experiments similar ratios of whole numbers were found. (This was known as **law of multiple proportions.)** So this motivated the thought that there must be some quantitative building block that is creating these substances, and that breaks alchemy because we can't mix in any quantities that we want. So this gives us the following conclusions which can be thought to begin modern chemistry:

Proposition 3

All matter is made of **atoms**, and such atoms can combine in fixed ratios to form **molecules**.

In particular, there is now a distinction between **mixtures** (like saltwater) and **molecules** (like carbon dioxide) – in the latter case, we can only mix in a fixed proportion. And from these principles, we can start thinking about **stoichiometry** (which comes from the Greek words "stoicheion" and "metron," meaning "element" and "measure"). Basically, we can determine the ratios in which atoms react, because atoms do not get created or destroyed.

Example 4

Consider the following chemical reaction:

$$(?)\ \mathrm{CH_4} + (?)\ \mathrm{O_2} \to (?)\ \mathrm{CO_2} + (?)\ \mathrm{H_2O}.$$

In order to preserve the number of atoms from the left-hand side to the right-hand side, we need to make sure we have the same number of C, H, and O atoms on both sides. If we start with a 1 on the CH_4 term, we need a 1 on the CO_2 term, and then to balance out the Hs and Os, we need 2s on the other two terms. This is the act of **balancing equations**, and those numbers $1, 2, 1, 2$ are called **stoichiometric coefficients**.

Example 5

Consider the following chemical reaction:

$$(?)\ \mathrm{C_2H_4} + (?)\ \mathrm{O_2} \to (?)\ \mathrm{CO_2} + (?)\ \mathrm{H_2O}.$$

We can similarly check that the coefficients $1, 3, 2, 2$ will balance the equation.

Stoichiometry can also tell us about **limiting reactants** – in other words, we can tell which material will run out first if we start with some amount of each reactant. But in the lab, we often work with masses, and thus we need to consider a few more factors:

Example 6

Consider the following chemical reaction:

$$(?)\ \mathrm{CO} + (?)\ \mathrm{H_2} \to (?)\ \mathrm{C_8H_{18}} + (?)\ \mathrm{O_2}.$$

If we start with 10 grams of CO and 5 grams of H_2, which material is the limiting reactant?

First, we can balance the reaction – we start by writing down a 1 somewhere where the "most complicated molecule" is, since scaling doesn't matter. We find that the coefficients should be a multiple of $8, 9, 1, 4$, meaning that we use 8 CO molecules for every 9 H_2 molecules. Since the molecule weight of CO is 28 g/mol (adding up from the periodic table), and the molecular weight of H_2 is 2 g/mol, we have $\frac{10}{28} \approx 0.4$ moles of CO and $\frac{5}{2} = 2.5$ moles of H_2 – when we use them at a ratio of 8 to 9, we'll run out of the CO first, so that is the limiting reactant. So the limiting reactant depends on the species involved, as well as factors related to how equation is balanced.

If we'd like to review any of these materials, we can take a look at the 5.111 Bootcamp on Canvas – it contains the background information we need to succeed in the course that we may or may not remember from high school chemistry.

2 February 2, 2022

Professor McGuire's office hours will be held on Zoom on Mondays from 10-11, where we can come and say hello or ask any questions that we have.

We'll start today by looking more at balancing equations and stoichiometry: consider the chemical equation

$$\mathrm{NaOH} + \mathrm{Ca(OH)_2} + \mathrm{Cl_2} \to \mathrm{Ca(OCl)_2} + \mathrm{NaCl} + \mathrm{H_2O}.$$

This reaction is not balanced, because we have three Cls on the right but only two on the left. So we need to do a bit of work to make it balanced:

$$2\ \mathrm{NaOH} + \mathrm{Ca(OH)_2} + 2\ \mathrm{Cl_2} \to \mathrm{Ca(OCl)_2} + 2\ \mathrm{NaCl} + 2\ \mathrm{H_2O}.$$

Example 7

Suppose we start with 1067 grams of calcium hydroxide, but we have large drums full of sodium hydroxide and chlorine gas (unlimited quantities). How many grams of chlorine gas are used up, and how much bleach (calcium hypochlorite) is produced?

We know that our limiting reactant is then the calcium hydroxide, and to find out the corresponding other quantities we use the molar masses of those molecules by adding up the molar masses of the corresponding elements. (We should remember how to do this from high school chemistry, and if we don't, we should check out the MITx bootcamp.) We find that $\mathrm{Ca(OH)_2}$ has a molar mass of 74.09 g/mol, $\mathrm{Cl_2}$ has a molar mass of 70.91 g/mol, and $\mathrm{Ca(OCl)_2}$ has a molar mass of 142.98 g/mol. So the process is as follows: find how many moles of calcium hydroxide there are in

1067 grams, multiply that number by 2 to get the number of moles of chlorine gas used up, and then convert back to the corresponding number of grams of chlorine gas. Specifically, we can write this out as

$$1067 \text{ g CA(OH)}_2 \times \frac{1 \text{ mol CA(OH)}_2}{74.09 \text{ g CA(OH)}_2} \times \frac{2 \text{ mol Cl}_2}{1 \text{ mol Ca(OH)}_2} \times \frac{70.91 \text{ g Cl}_2}{1 \text{ mol Cl}_2} = 2042 \text{ g Cl}_2.$$

A similar calculation with the other stoichiometric ratios gives us 2059 grams of Ca(OCL)_2. Notice that the only chemistry needed to solve this problem was the **ratios in which the different molecules reacted in** – the rest is dimensional analysis. (Units will often be a way that we can get through a lot of difficult problems in this class!)

Our topic for today is to discuss **atomic structure**: last time, we mentioned that the downfall of alchemy came from the law of definite proportions and the law of multiple proportions. We'll take a look at how atoms were then picked apart in history, in particular noticing that atoms are themselves not indivisible particles.

In the late 1890s, most scientists accepted the existence of atoms as an indivisible unit, and that molecules combined these atoms in fixed ratios. At this time, Newtonian physics was also commonly accepted as a way to understand force and motion, and thus at this point in history scientists thought they understood everything. But there were some experimental results that couldn't be explained by the theories at the time:

Example 8

JJ Thomson was trying to understand the physics of **cathode rays**: the setup is that a vacuum tube is filled with hydrogen gas, and a pair of electrodes was inserted (a positive cathode and a negative anode). When a voltage difference was applied, a cathode ray was emitted, and in fact this caused the tube to glow.

Thomson hypothesized that there could be charged particles inside these tubes, and the way to test this is to apply a perpendicular voltage difference by having a positive and negative plate on opposite sides of the cathode ray. When this was done, the cathode ray was heavily deflected towards the positive plate, which implies that the ray is made up of **negatively charged** particles. But that means that something besides the (neutral) hydrogen gas was being discharged. (And furthermore, a few particles were even being deflected towards the negative plate.)

Thomson tried this experiment with a variety of different gases, and the same result occurred each time – in fact, these cathode rays were deflected in such a way that he could calculate the mass to charge ratio of the particles, and in fact this ratio is the same for all gases! This is a spooky result, because atoms are (at that time) supposed to be the smallest indivisible piece of matter – in a paper in 1897 published in the Philosophical Magazine and Journal of Science, Thomson described that the "subdivision of matter is carried very much further than in the ordinary gaseous state," and in fact there is a common denominator to all matter regardless of the elements! (So in a way, alchemists became closer to being correct, and we're lucky that it didn't catch on that "everything is just mixing together these small particles.")

So the conclusion is as follows: atoms of all elements are made of the same small particles, and these particles must be equal and opposite in charge (based on the experimental results). Furthermore, from Newtonian physics, because the deflection Δx of the beam is proportional to $\frac{q}{m}$ (where q is the charge and m is the mass of the particle), it was found that the mass of the positively charged particle is significantly larger than the mass of the negatively charged particle.

It then makes sense intuitively that the atom is made up of some large, positively charged background, filled with small negatively charged particles. (This was called the **plum pudding model** because Thomson was British – we can think of an oatmeal raisin cookie instead.) While we know that this model is incorrect today, it was a step in the correct direction, and it prompted scientists to think more about atomic structure.

Example 9

A few years later, Ernest Rutherford had been studying radioactive materials, and he found that different particles were emitted by these materials. For example, radium bromide $RaBr_2$ is a very radioactive material (this is bad for us, because our body will grab it and put it into our bones, from which it emits radiation and we potentially get bone cancer) which emites alpha-particles (which we now know are helium nuclei with 2 protons and 2 neutrons). Rutherford then put a thin sheet of gold foil where these

If the plum pudding model is correct, then the gold foil should be made up of a thin diffuse positive background with negative bits, and thus the helium nuclei should barrel through that background easily. And indeed, there were about 120000 alpha particles detected per minute whether the gold foil was there or not. But then Rutherford tried adding a detector in the backwards direction, and he found that about 20 alpha particles were scattered **backwards** by the gold foil (which didn't happen without the gold foil). This was what led to the discovery of the small positive nuclei – it was discovered that atoms are in fact mostly empty space, and the plum pudding model was wrong.

Remark 10. *Rutherford had described that this was the most incredible event that he had experienced in his life, despite being married and having already won a Nobel Prize at that point. Basically, this experiment dramatically changed our perception of the atomic structure – it was found that the radius of the nuclei must be much smaller than the radius of the atom.*

Fact 11

Much later on (within the last few decades), **atomic force microscopy** instruments now allow us to actually probe this atomic scale by bouncing a laser off of a surface. And this actually allows us to see the atoms and bonds between them in certain molecules, even though (as we might learn later on) these bonds really aren't even particles or tubes!

3 February 4, 2022

Problem set 1 is now available for work and submission – Gradescope should be open, and we need to complete it by 11pm next Friday. (But we should start on the problem set early on in case we have any questions for course staff.)

Last time, we started understanding a picture of the atom – scientists were at a point where they understood that atoms were made of a positively charged nucleus and negatively charged electrons, and that allows us to tie everything back to our understanding of physics.

Example 12

Consider a hydrogen atom with a Hydrogen nucleus and a single electron. We know that if we have a positive and negatively charged particle of charge e and $-e$, we have a **Coulomb force**

$$F(r) = -\frac{e^2}{4\pi\varepsilon_0 r^2}$$

between the two particles if they're a distance r apart. (Here, ε_0 is the **permittivity of free space**, which basically makes the units of this equation work out.)

As $r \to \infty$, this force goes to 0, so a faraway electron and nucleus should not interact with each other. But as $r \to 0$, this force goes to infinity, and in fact we have an attractive force between the two particles that should pull them together. We can understand that by using Newtonian mechanics – by Newton's second law, **it seems like we can say**

$$F = ma = m\frac{dv}{dt} = \boxed{m\frac{d^2r}{dt^2} = -\frac{e^2}{4\pi\varepsilon_0 r^2}},$$

so we now have a differential equation that tells us about the evolution $r(t)$ of the distance between the nucleus and electron. The distances that we care about here are on the order of an angstrom (10^{-10} meters), and so if we follow this one-dimensional differential equation, we find that it should take about 100 picoseconds to get from a distance r of 10^{-10} meters to one of 0 meters. But electrons in fact do not crash into our protons in that amount of time, and the question we need to ask is **why the atom isn't collapsing due to this Coulomb force**.

The issue is basically that **quantum mechanics is important at small or large scales** – Newtonian mechanics doesn't describe what happens when we're looking at length scales like those of atoms. The two important facts that we need to know are the following: matter and radiation can be interpreted either as waves or particles (and in fact exhibit properties of both), and light is made of photons.

Fact 13

The word **radiation** can mean different things depending on the context – sometimes we mean "particle radiation," like alpha particles radiating from radioactive particles, and sometimes we mean "electromagnetic radiation," which basically means light. So we need to be careful with our words and understand how it's being used.

The interaction of light with matter is in fact one of the main ways we explore our world at an atomic scale, so we need an understanding of light to understand matter. (And light is in fact the primary way that we've been exploring space, up until just a few years ago.) We won't go into all of the important physics behind light, but at a basic level, electromagnetic radiation has an electric field and magnetic field perpendicular to each other. We'll focus almost exclusively on the electric component in this class, and we'll describe it as an oscillating sine wave. It was thought for a long time that these electric fields were riding on the surface of something called the **aether** – after all, water waves ride on the water, and sound waves ride on the air. This turns out to be false, but it still allows us to make analogies between light waves and other waves, and that's where our vocabulary comes from.

Definition 14

The **amplitude** of a wave is the (signed) distance away from equilibrium for a sine wave, and the **wavelength** λ of a wave is the distance between successive maxima. The **frequency** ν of a traveling wave is the number of cycles per unit time that pass by a given point (often written in units of s^{-1} or Hz).

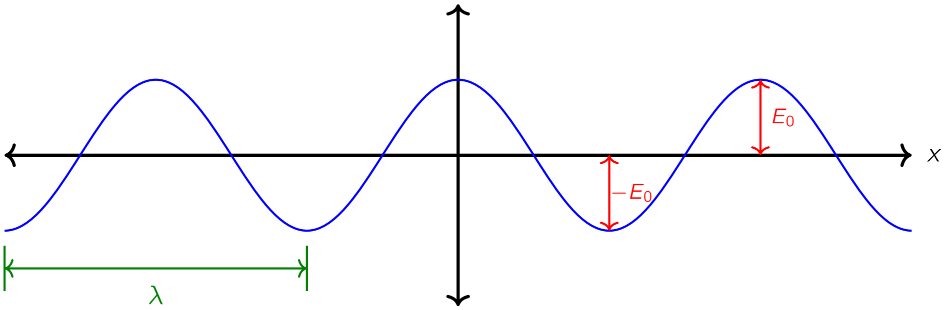
In particular, we have a maximum positive amplitude E_0 for our electric field, and a maximum positive amplitude B_0 for our magnetic field. The equation of a **standing wave** for the electric field then takes the form

$$E(x) = E_0 \cos\left(\frac{2\pi x}{\lambda}\right),$$

while the equation of a **traveling wave** takes a similar form

$$E(x,t) = E_0 \cos\left(\frac{2\pi x}{\lambda} - 2\pi\nu t\right).$$

It's difficult to visualize what this equation really means, especially because it evolves in time, so we often think about a fixed value of x (measuring at a particular location) or fixed value of t (freezing the wave at some particular time). For example, at time $t = 0$, we have the following wave:



We can then define additional quantities which can be important depending on the context in which we're studying waves:

Definition 15

The **period** of a wave is $\frac{1}{\nu}$ (this is basically the time-analogy of the wavelength), and the **intensity** of a wave is the square of its maximum amplitude E_0^2.

Essentially, knowing the wavelength, frequency, and amplitude of a wave tells us everything we need to know about a sine wave. One special property of light waves is that **they always travel at a fixed speed**, and that speed can be written in terms of our defined quantities by thinking about how much time it takes for a wave to move forward by one wavelength:

$$\text{speed} = \frac{\text{distance}}{\text{time}} = \frac{\lambda}{1/\nu} = \lambda\nu \implies \boxed{c = \lambda\nu}.$$

This speed of light has been experimentally calculated to be about 2.998×10^8 m/s – this tells us that it takes about a second for a message from Earth to reach a probe at the Moon, and it takes hours to reach Pluto. (So the fact that we can send messages to satellites in space is pretty impressive!) And this means that knowing either of λ or ν always tells us about the other one as well. The **electromagnetic spectrum** tells us the kinds of (electromagnetic) radiation that are present in different frequencies – radio and microwaves have enough energy to cause rotational motion in atoms, while infrared and some visible light can cause vibrational motion. Above that, we start exciting electrons, and then above that we start putting in a lot of energy into our system.

Example 16

If we take a look at nanocluster.mit.edu, we can see the development of **quantum dots**, which are semiconductor particles that can be designed so that shining UV light at them causes them to emit a particular color. So this is something that can be used for television!

One final fact that we should be aware of is the patterns of **interference**: two waves can constructively or destructively interfere with each other. Specifically, if two waves are of the same frequency and lined up ("in phase"), we get **constructive interference**, where peaks and troughs add together and become larger. But if the waves are offset so that the peaks and troughs are exactly out of alignment, then we can get **destructive interference**. And everything in between can occur as well, and that can all lead to interesting interference patterns that we can learn about in physics!

4 February 7, 2022

We'll discuss the photoelectric effect today, which is a phenomenon that shows that light behaves like a particle (not just like a wave). Since we're taking the "atoms first" approach in 5.111, a lot of the names we've seen in lectures are from "old dead white guys," so it's useful for us to know about unseen identities in chemistry, and we'll occasionally go through a few scientists from Dr. Alec Kroll's slides.

Fact 17

Annie Jump Cannon (1863-1941) is one of the fundamental researchers in astronomy – she was one of the original Harvard Computers (groups of women who did complex analytical calculations for astronomical data), and she developed the system of classification of stars today. She manually classified more than 350000 stars herself! The Annie Jump Cannon award was recently won by Professor Andrea Ghez (who won the 2020 Nobel Prize in Physics for discovering the supermassive black hole) and Professor Ilse Cleeves (who studied the chemical evolution of protoplanetary disks).

Last time, we discussed the wavelength particles of light, but we danced around the topic of energy – we mentioned that X-rays and gamma rays can do a lot of damage to our system if they hit us, but we never really explained how the energy is determined.

Example 18

In the photoelectric effect experiment, incident light is shone on a metal surface, which causes electrons to be ejected from the surface of the metal (which will then be detected by an external detector which can calculate their kinetic energy).

We'll take the classical approach and assume that the kinetic energy of our electron is $\frac{1}{2}mv^2$. We can imagine modeling the surface of the metal as a bunch of beach balls on a pier, and imagine that our light is essentially a water wave with some frequency and some amplitude. Then some of the balls will get bounced up, and in this model the bouncing should depend on the amplitude of the wave (or equivalently its intensity) – in other words, the kinetic energy of the ejected particles should increase with larger amplitude. And we expect the number of electrons ejected to be larger if we have a higher frequency.

It turns out that the following are true:

- Classical physics tells us that the number of ejected electrons should be linear in the frequency ν, and those electrons should have the same energy regardless of ν. But experimentally, it was found that **no electrons are emitted until a certain frequency ν_0 and then after that point the number of electrons emitted is constant**. Additionally, the kinetic energy of the ejected particles is linear in ν beyond ν_0.
- Classical physics tells us that the number of ejected electrons should be constant in the intensity of the light, while the kinetic energy should be linear. But it turns out **the number of electrons emitted is linear in intensity, while the kinetic energy is not affected** (as long as $\nu > \nu_0$ so that electrons are emitted).

In other words, all of the classical predictions were completely incorrect, and it wasn't until Albert Einstein came along that this problem was properly solved. What Einstein did was that he combined the results from photoelectric effect experiments that were done on different metals – the thresholds ν_0 were different, but the **rate of increase of kinetic energy** was the same for all metals. This meant that Einstein could fit a line to the equation $\text{KE} = m\nu + b$, and the slope m turns out to be about $6.626 \times 10^{-34} \text{J} \cdot \text{s}$.

Einstein actually recognized this value, because it came up in a different context a few years earlier:

Example 19

At the start of the 20th century, Max Planck was trying to understand blackbody radiation, thinking about the intensities and colors of light emitted based on the temperature (we've seen this in action if we've seen metal heated up turning red, then orange, then yellow).

At that point, the **Rayleigh-Jeans law** predicted that the intensity of light at a frequency ν is $\frac{8\pi kT\nu^2}{c^3}$, but that result only works for low frequencies, and if it held for ultraviolet light we would not be able to survive on the surface of the earth! So Planck tried making the assumption that it requires more energy to produce light at higher frequencies, and here's essentially how that works. We can think of light being the wave produced from a harmonic oscillator, for which the potential energy of the oscillator is $\frac{1}{2}k(x-x_0)^2$. Furthermore, we'll assume that each oscillator has **quantized energies** – there was no justification for this at the time, but he just worked with the assumption that the energy for those oscillators would be $E = nh\nu$, where n is an integer, h is some constant, and ν is the frequency of the oscillator. Statistical physics then gives us the modification to the Rayleigh-Jeans equation

$$I(\nu) = \frac{8\pi h\nu^3}{c^3}\frac{1}{e^{h\nu/kT-1}},$$

and it turns out that this equation actually fits the curve of experimental data that we had. Since h was the only free constant here, it could be fit to the data, and this actually arrived at the same $6.626 \times 10^{-34}\,\mathrm{J}\cdot\mathrm{s}$. So something fundamental is going on with the physics here! Returning to the photoelectric effect, we now have the equation for the kinetic energy of the emitted particles

$$\mathrm{KE} = h\nu - h\nu_0,$$

and this gives us the equation for the energy of light: $\boxed{E = h\nu}$. This is actually a pretty big deal – it means that the color of the light actually determines its energy, and it led to the prediction that **light was quantized into individual packets (photons)**. After all, having more energy in the light (experimentally) doesn't displace more electrons – it makes sense to attribute this to the fact that each light particle can only have one interaction with the metal surface once. So intensity just means more photons, and we can now explain the photoelectric effect in more detail:

Definition 20

The **work function** associated to metal surface is the energy associated with the frequency threshold $\phi = h\nu_0$.

This energy ϕ is basically the amount of energy that binds our electron to the metal – as long as an incident photon hits our electron with energy $E_i = h\nu > \phi$, we will pop the electron out into free space, and the electron will take in the additional kinetic energy $E_i - \phi = h\nu - h\nu_0$.

Problem 21

Light with a wavelength $\lambda = 310$ nm is shone on a surface with $\phi = 5.1$ eV (here we have the definition of an **electron-volt**, $1\text{ eV} = 1.602 \times 10^{-19}$ J). What is the maximum kinetic energy of the emitted electrons?

Solution. First, we can compute the energy of the photons in the incident light:

$$E = h\nu = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34}\ \mathrm{J}\cdot\mathrm{s}\cdot 2.998 \times 10^{8}\ \mathrm{m/s}}{310 \times 10^{-9}\ \mathrm{m}} = 6.41 \times 10^{-19}\ \mathrm{J} \approx 4.0\ \mathrm{eV}.$$

Since this energy is lower than the work function, no electrons will be emitted. ☐

5 February 9, 2022

We'll discuss the wave-like properties of electrons today, hopefully ending with some discussion of spectroscopy. One fact that we should remember from physics is that particles have momentum, and anything that's moving has some classical momentum $p = mv$. Last lecture, we discussed that light behaves like a wave, but also like a particle – thus, it makes sense that light must have momentum as well. But photons don't have mass, so Einstein thought about a different formula that doesn't explicitly involve the mass: he posited that the momentum of a photon is given by $\boxed{p = \frac{h}{\lambda}}$, where λ is the wavelength of the light.

Example 22

Arthur Holly Compton came up with an experiment to test this hypothesis: start with a stationary electron in free space, strike it with an x-ray, and measure the frequency of the light before and after the collision.

We know now how frequency and energy are related for photons – since $E = h\nu$ and ν decreased, the light must have lost energy, and in fact that energy was transferred to the electron. (This should look familiar if we've taken 8.01 and thought about billiard ball collisions.) But if we believe in conservation of energy and momentum, the only way for this to have happened is if momentum was indeed transferred, and thus this experiment confirmed that light has momentum of the form that Einstein conjectured.

This sat in the literature for a while until Loius de Broglie was thinking about something to do for his PhD thesis – what he posited was that **if light has particle-like properties, matter must also have wave-like properties** – in other words, this boxed equation should hold for particles as well, meaning that **all particles have some inherent wavelength** $\boxed{\lambda_p = \frac{h}{p}}$ (this is known as the **de Broglie wavelength**). If we try plugging in some typical values of p for everyday objects, such as a baseball traveling through the air, we'll notice that $\lambda = \frac{h}{mv}$ is **extremely small** – for an Adam Wainwright fastball of mass 0.145 kg traveling at 43 m/s, the wavelength is on the order of 10^{-34} m, which is many orders of magnitude smaller than the diameter of an atom. So this de Broglie wavelength is only noticeable on a very different quantum scale from what we're normally used to.

On the other hand, if we do this de Broglie calculation for an electron, which has mass 9×10^{-31} kg and typical speed around 10^5 m/s when trapped in a metal, we find that λ is approximately 70 angstroms. This is now much larger than the size of an atom, so we can experimentally see the impacts of the wave-like nature of the electron, and that's in fact what does occur.

Fact 23

The way that wavelength properties of electrons are observed is through **diffraction patterns** – if we send in a beam of electrons through a thin slit and have the pattern shine on a wall, we see constructive and destructive **interference** create areas of high and low intensity. And a similar diffraction pattern can be seen in light (search up "Airy disk" on Google). JJ Thomson's son, GP Thomson, did in fact perform this experiment in 1927 and observed diffraction from cathode rays. (So the father and son won Nobel Prizes for proving that electrons were particles and waves, respectively.)

So we can now accept that electrons are waves, and if we make that assumption, it turns out that we will start observing some interesting properties:

Example 24

Consider two perfect mirrors separated by a distance L, forming a **resonant cavity**. If we trap a light wave with the correct wavelength $L = \frac{n\lambda}{2}$, it will bounce back and forth between the mirrors forever and reflect back in perfect overlap, causing interference.

We can check mathematically (or watch simulations) that two traveling sine waves to the right and to the left of the same wavelength and amplitude form a **standing wave** – the peaks and troughs stand still. So in this perfect scenario, we have a way of trapping a standing wave inside a box (like this cavity of mirrors), and this only occurs for certain wavelengths of light. So if we take into consideration all of our different equations between kinematic quantities

$$L = \frac{n\lambda}{2}, \quad p = mv = \frac{h}{\lambda}, \quad \text{KE} = \frac{1}{2}mv^2,$$

we find the allowed energies of a particle of mass m trapped inside of a box of length L to be

$$\text{KE} = \frac{1}{2m}(mv)^2 = \frac{1}{2m}p^2 = \frac{1}{2}\frac{h^2}{\lambda^2} = \frac{1}{2m}\frac{h^2n^2}{(2L)^2} = \frac{h^2n^2}{8mL^2}.$$

What's interesting about this is that **electrons must then have discrete energy levels** if they're indeed constrained within a box, and this follows from the wave-like properties of our fundamental particles! Since n cannot be zero (we know that $\lambda = \frac{2L}{n}$), what we're saying is the following:

Proposition 25

A trapped (stable) particle inside a box has a **minimum** energy $E_{\text{min}} = \frac{h^2}{8mL^2}$.

If we think about the energy levels that are formed for a baseball trapped inside a 125 meter long stadium (we're secretly assuming things are one-dimensional here, but the concepts are the same in three dimensions), we find that the kinetic energy of the baseball is $n^2(1.5 \times 10^{-52}$ eV). Since these spacings are actually very tiny, the baseball can basically be at whatever kinetic energy we want, and it'll satisfy the requirements for resonance. **So this is why for macroscopic systems, we don't observe confinement energies**. On the other hand, thinking about electrons inside a 1 angstrom box, we have kinetic energies approximately $40n^2$ eV. So the spacings start mattering at the atomic scale – we can't have electrons choosing their energies freely.

Definition 26

Spectroscopy is the interaction of light with matter, and it can be used to study these kinds of energy levels.

If we consider a simple quantum system like a hydrogen atom and shine light on it, we'll see that the hydrogen atom absorbs certain wavelengths of light. What that means is that the light is transferring its energy to the electrons somehow, just like in the photoelectric effect, but unlike in last lecture **only certain energy levels will actually work** (since we're not freeing electrons from the system anymore). It turns out that this is where the confinement of the hydrogen atom comes into play – **electrons are restricted to a discrete set of energy values**. To understand what those energies are, notice that the energy differences between electron levels must be

$$E_f - E_i = E_{\text{photon}} = h\nu = \frac{hc}{\lambda}.$$

Through experimental values, the result that we end up finding is that

$$h\nu = R\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right),$$

where R is the **Rydberg constant** and is approximately 13.6 eV (though it's different for different atoms). What this means is essentially that **electrons can be in states of energy $\frac{R}{n^2}$** for some positive integer n (this is a **quantum number**). None of this is formal yet, but this does show the basic concept that energy quantization does show up at the atomic scale. And this is how we'll be looking at electrons in the subsequent lectures!

Fact 27

Prompted by quantum mechanics, we'll be describing our particles using a **wavefunction**, denoted $\psi(x)$ in one dimension or $\psi(x, y, z)$ in three dimensions. But that will be discussed more next lecture!

6 February 11, 2022

Fact 28

For today's "chemists we might not know about," we have Dr. Percy Julian, who was the third Black American to obtain a PhD in chemistry (the barriers of education at the time were very restrictive). He was the first person to perform the natural product synthesis of physostigmine, which was a breakthrough drug for glaucoma, and some of his later work laid the foundation for the modern steroid industry (cortisone and corticosteroids), and he was the first Black American chemist elected to the National Academy of Sciences.

Last lecture, we introduced the concept of a wavefunction, which is used to bridge the wave-like and particle-like properties of light.

Example 29

The important property to know about wavefunctions is that a large amplitude $\psi(x)$ means a high chance of seeing the particle near x. So if $\psi(x)$ is localized, we can think of our object as being "particle-like," but if $\psi(x)$ is oscillating through lots of space (de-localized), we can think of it as being more "wave-like." But more generally $\psi(x)$ can have properties of both, and that's what occurs in most systems.

It turns out that the **probability density for the particle's position**, quantum mechanically, is $|\psi(x)|^2$. So if we have a bell-curve-shaped wavefunction for a baseball, where the wavefunction goes to zero but never actually hits it, there is some nonzero probability that when we measure the position of the baseball that it's actually on Mars (or somewhere else very far away) – that probability is just very small if the wavefunction is localized.

Another way to qualitatively represent whether a wavefunction is exhibiting "wave-like" or "particle-like" behavior is to try to **determine its wavelength** or **extract the energy of the system**. It turns out that there's a very specific set of wavefunctions which allow us to actually extract energy – they're wavefunctions that satisfy the time-independent **Schrodinger equation** $\hat{H}\psi = E\psi$. Here $\hat{H}$ is the **Hamiltonian operator**, which performs a certain mathematical operation (differentiation, multiplication, and so on) on a wavefunction and gives us another function.

Example 30

If we have an operator $\hat{B} = 21\frac{\partial}{\partial x}$ (differentiate and multiply by 21), the action of $\hat{B}$ on the wavefunction $\psi_a(x) = 2x$ gives us $\hat{H}\psi_a(x) = 42$. Meanwhile, the action of $\hat{B}$ on $\psi_b(x) = e^x$ gives us $21e^x$, which is a constant times the original function.

We're looking for wavefunctions of the **second type** (like ψ_b) here, where the operator basically just multiplies our original wavefunction by some number. That number ends up being the energy E of our system for the Hamiltonian operator $\hat{H}$, and in particular if we know two of the three of $\hat{H}, E, \psi$, we can figure out the third. Since $\hat{H}$ is just encoding the parameters and physical setup of our system, and E can be found by spectroscopy, that means we can deduce the wavefunction ψ and gather more information about our system.

Definition 31

If we have an operator $\hat{H}$, wavefunction ψ, and number E satisfying $\hat{H}\psi = E\psi$, the wavefunction ψ is called an **eigenfunction** $\hat{H}$, and the energy E is called an **eigenvalue** of $\hat{H}$.

It makes sense now to ask what the Hamiltonian tends to look like, and the idea is that we add together the kinetic and potential energy of the system together.

Example 32

Here's an example of a Hamiltonian in one dimension, where $\hbar = \frac{h}{2\pi}$ is the **reduced Planck's constant**:

$$\hat{H}(x) = -\frac{\hbar^2}{2m}\frac{\partial}{\partial x^2} + \hat{V}(x).$$

Here, the first term encodes the kinetic energy – it's beyond the scope of the class to explain why, but it's worth looking up. And the second term is just multiplication by the potential energy $V(x)$ at a given point. Plugging this back into the time-independent Schrodinger equation, the differential equation that energy eigenfunctions must satisfy is

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2} + \hat{V}(x)\psi(x) + E\psi(x).$$

We won't be asked to solve differential equations in this class – that's for a later physical chemistry class if we are interested – but the tricky part here is to think about the potential energy $\hat{V}(x)$. (And in three dimensions, the equations become more messy, but changing the dimensionality of our wavefunction requires more complicated forms of $\hat{H}$. For example, we use the Laplacian operator ∇^2 instead of the second derivative $\frac{\partial^2}{\partial x^2}$.)

Example 33

We now return to modifying the Bohr and Rutherford models of the atom – we know that they are incorrect models, because particles like electrons exhibit wavelike behavior.

If we're trying to solve for the energies of a hydrogen atom, we can use the **Born-Oppenheimer approximation**, where essentially we assume the nucleus is stationary relative to the electron because of the differences in masses between the two parts of the hydrogen atom, and the potential energy interaction between them is just the Coulomb force

$$\hat{V}(r) = \frac{q_1 q_2}{4\pi\varepsilon_0 r} = \frac{(Ze)(-e)}{4\pi e_0 r} = -\frac{Ze^2}{4\pi\varepsilon_0 r},$$

where e is the electric charge and Z is the [nuclear charge] (the number of protons for the atom). For example, we have $Z = 2$ for He^+ or $Z = 3$ for Li^2+ (the ions coming from the fact that we're assuming there's only one electron for each atom). So if we plug in this $\hat{V}(r)$ into the Schrodinger equation, we find that our goal is to find wavefunctions $\psi(r, \theta, \phi)$ satisfying

$$\boxed{-\frac{\hbar^2}{2m}\nabla^2\psi(r,\theta,\phi) - \frac{Ze^2}{4\pi\varepsilon_0 r}\psi(r,\theta,\phi) = E\psi(r,\theta,\phi)}.$$

Solving this differential equation is difficult, but that's not what our goal is in this class: it turns out the answer is

$$\psi(r, \theta, \phi) = R_{n\ell}(r) Y_\ell^m(\theta, \phi),$$

where the first term is a function of how far the electron is from the nucleus, and the second term is one of the **spherical harmonics**. (We can check our textbook for expressions of each one.) What will be important for us in the next few lectures will be to look at the general qualitative properties of what these look like, but what we should notice is that there are three indices n, ℓ, m, known as **quantum numbers**. Basically, n dictates the energy level of the hydrogen atom, and the ℓ and m indices will encode other information about which state we're in.

7 February 14, 2022

Fact 34

Subrahmanyan Chandreasekhar and Chandrasekhara Veknata Raman were newphew and uncle – they were physicists who both won the Nobel Prize in science. The former established the Chandrasekhar limit, which is the maximum mass a white dwarf can have before becoming a neutron star or black hole. Meanwhile, the latter discovered raman scattering, which is a type of interaction that is partially responsible for the color of the sky.

Last time, we looked into what wavefunctions look like and described the hydrogen atom Hamiltonian and wavefunctions. Let's review how we got here – we started with Dalton and Proust, who gave us the laws of definite and multiple proportions, leading to the discovery of the existence of atoms. Then JJ Thomson found that atoms are made of electrons and protons, while Rutherford found that atoms are mostly empty through the gold foil experiment. Around this time, due to Einstein and Compton, it was found that light exhibits both particle and wave properties, and then de Broglie and GP Thomson found that this was true for particles as well. So the gradual evolution of physics has led us to quantum physics, and for us to understand atoms we must understand wavefunctions.

In that process, we first understood that particles confined to a box have **discrete, quantized energies** (whose corresponding eigenfunctions we can understand by studying standing waves in a resonant cavity). More generally, we can find the eigenfunctions of a system by looking at the Hamiltonian operator $\hat{H}$ and the Schrodinger equation $\hat{H}\psi = E\psi$ – for the hydrogen atom, we found that the (three-dimensional) wavefunctions, in spherical coordinates, look like

$$\psi(r, \theta, \phi) = R_{n\ell}(r) Y_\ell^m(\theta, \phi),$$

where n, ℓ, m are the **quantum numbers** of the state (integers or half-integers). Specifically, there are certain rules that these numbers must follow:

- The **principal quantum number** n can be any positive integer, and this is most related to the distance of the electron away from the nucleus. (This makes sense if n is related to the energy by a factor of $\frac{1}{n^2}$ – just like in the Coulomb interactions, the distance is what affects the energy of the system.)
- The **angular momentum quantum number** ℓ dictates the amount of angular momentum that the electron has within the atom, and it must take one of the values $0, 1, \cdots, n-1$. (Essentially, we should think of these bounds as saying that the angular momentum is nonnegative, but we can only have so much of the total energy dedicated to angular momentum.)
- The **magnetic quantum number** m takes on values between $-\ell$ and ℓ, inclusive, and it basically tells us the fraction of the angular momentum that is projected along the z-axis ($+\ell$ is $+z$, and $-\ell$ is $-z$).

We know that there is always a ground state for any quantum system, which gives us the minimum possible energy of the system. In this case, it's $\psi(1,0,0) = R_{10}(r)Y_0^0(\theta,\phi)$. Remember that the squared magnitude of the wavefunction gives us a probability density of finding the electron at a particular coordinate (r,θ,ϕ), and in fact the shapes these sweep out are going to lead us to the **orbitals** that we might have heard of from high school chemistry. It turns out that we usually refer to $\ell = 0,1,2,3$ as s, p, d, f, so that $\psi(1,0,0)$ is also the **1s** state – we might have heard of the 1s orbital before! And for $\ell = 1$, if $m_\ell = \pm 1$ we have an x- or y-direction (secretly, it's a linear superposition of the two), and if $m_\ell = 0$ then the orbital is pointed in the z-direction. (We won't need to know more than that, but we can look up pictures of orbitals with higher ms ourselves to see what's going on.) We can now explain that there's a lot of different ways to write down the same state, and here's where we mention that **we experimentally flip the signs of the energies of our hydrogen atom states**: the energy of a given state is

$$E_n = -\frac{R}{n^2},$$

where R is the Rydberg.

Example 35

The state $n = 1, \ell = 0, m_\ell = 0$ can also be written with "state label" 100, or with wavefunction $\psi(1,0,0) = \psi_{100}$, or as the 1s orbital. (This state has energy $-R \approx -13.6$ eV.) Similarly, $n = 2, \ell = 1, m_\ell = 0$ can be written with state label 210, wavefunction ψ_{210}, or as the $2\mathrm{p_z}$ orbital (z comes from $m = 0$). (This state has energy $-\frac{R}{4} \approx -3.4$ eV.) Finally, the $21-1$ state is either (a combination of) the $2\mathrm{p_x}$ and $2\mathrm{p_y}$ orbital, and it also has energy $-\frac{R}{4}$, and the 300 state is the 3s orbital, and it has energy $-\frac{R}{9}$.

Definition 36

The principal quantum number n tells us the **shell** that a particular orbital is in, and the angular momentum number ℓ tells us the **subshell**. Finally, the magnetic quantum number m tells us the particular **orbital** of our hydrogen atom state.

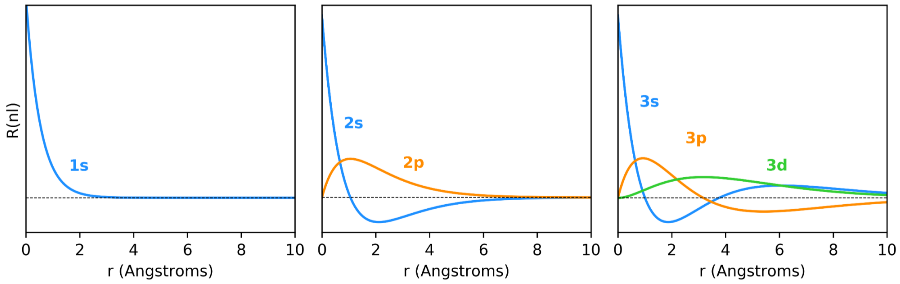
Notice that if we sum up the total number of orbitals for a given n, we get

$$1 + 3 + 5 + \cdots + (2n-1) = n^2.$$

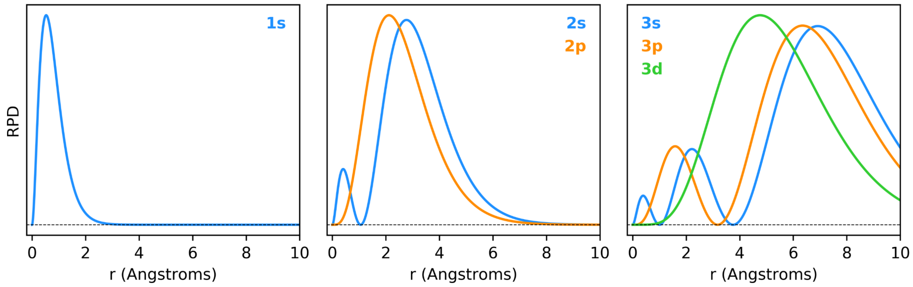
This tells us that in general, if we have a **one-electron** system with some nucleus of Z protons, then there are n^2 **degenerate** (same-energy) orbitals at energy

$$E = -\frac{RZ^2}{n^2}.$$

Visualizing these orbitals is a difficult problem, but Max Born came to the rescue here – he hypothesized (without proof or derivation) that $|\psi|^2$ gives us the probability density of finding the electron in a particular location. And so we can take these solutions to the hydrogen atom and draw them out – below are shown the graphs of $R_{n\ell}$ (taken from lecture) for $Z = 1$:

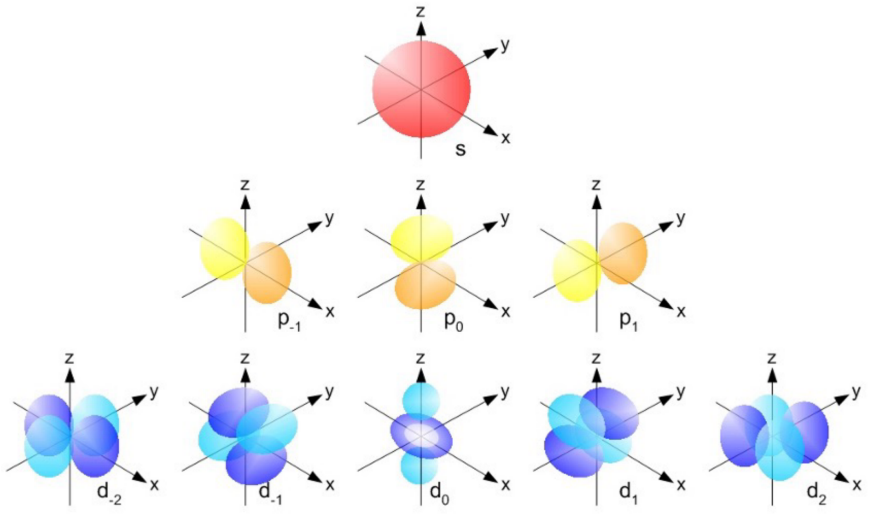


In general, we'll find $n - \ell - 1$ **radial nodes** (places of zero probability density) for the radial portion (that's the degree of the polynomial that's showing up in $R_{n\ell}$), and in particular we'll notice that the probability of finding the atom . But we have to remember that each value of r corresponds to a spherical shell, so to find the radial probability densities we have to multiply by r^2 and square $R_{n\ell}$ (again from lecture):



In particular, we now have probability density zero of finding the electron at distance zero from the proton, which is what we should expect. And furthermore, we can find the most likely location of finding the electron for each of these different orbitals: that radius of maximum probability increases with n but decreases with ℓ (for example, for the 1s orbital, it's the **Bohr radius** $a_0 \approx 0.5291$ Angstroms).

And finally, we can understand the angular portions by graphing the probability density in three dimensions:



This time, we get ℓ **angular nodes** (each node is a tangent plane of zero probability density), and this time we can see why certain orbitals are pointed in certain directions! We'll talk more about orbitals next lecture.

8 February 16, 2022

Fact 37

Ben Barres was a neurobiologist who was largely responsible for understanding the importance of **glial cells** and their role in brain development (forming and eliminating synapses). He was the first openly transgender member of the National Academy of Sciences, and he spent his career advocating for equality and accountability in science.

Last lecture, we discussed one-electron systems and the quantum numbers of the hydrogen atoms. The Schrodinger equation also applies to multi-electron systems, but anything larger than the system we've been talking about in the last few lectures becomes intractable to solve directly from the differential equation – an analytical solution doesn't even exist. But we can make good approximations instead, much like we made the Born-Oppenheimer approximation for the one-electron system.

Fact 38 (Orbital approximation)

We will assume that every electron in an atom occupies its own **hydrogen** atom wavefunction (pretending like it is the only electron that exists).

The idea is that the shapes and nodal structures that we discussed last lecture for hydrogen atom orbitals still hold for each electron, but this time the new orbitals are lower in energy, and the energy depends both on n and on ℓ. In particular, instead of having one energy level for the 1s orbital, another for the 2s, $2\mathrm{p_x}$, $2\mathrm{p_y}$, and $2\mathrm{p_z}$ orbitals, and so on, we now have a different ordering for the energy levels of the orbitals: from lowest (most negative) to highest, the ordering starts

$$1\mathrm{s}, 2\mathrm{s}, \{2\mathrm{p_x}, 2\mathrm{p_y}, 2\mathrm{p_z}\}, 3\mathrm{s}, \{3\mathrm{p_x}, 3\mathrm{p_y}, 3\mathrm{p_z}\}, 4\mathrm{s}, \{3\mathrm{d_{xy}}, \cdots\}, \cdots .$$

The idea is that instead of just having an energy of the form

$$E = -\frac{RZ^2}{n^2} = -\mathrm{IE}_n,$$

where IE_n is the **ionization energy** (that is, how much energy is required to remove the electron from the nucleus and release it to free space), this time (for a more general nucleus) there are two main factors that change the setup from the hydrogen atom:

- We've increased the size of the nucleus and thus increased the value of Z (the atom holds on tighter to the electron),
- The negative charges of the other electrons will repel the electron in various directions, and thus they provide various amounts of **shielding**. In particular, each electron can be very good at shielding (effectively decreasing the nuclear charge by 1), or very bad (effectively doing nothing), or somewhere in between.

Thus, we now have an equation of the form

$$E = -\frac{R\left(Z_{\mathrm{eff}}^{\mathrm{nl}}\right)^2}{n^2} = -\mathrm{IE}_n,$$

where $Z_{\mathrm{eff}}^{\mathrm{nl}}$ (which will be referred to as Z_{eff} in the future) is the **effective nuclear charge** that our electron feels.

Example 39

Helium has two electrons and a nucleus of $Z = 2$, so each electron can theoretically feel Z_{eff} anywhere between 1 (complete shielding) and 2 (no shielding). Notice that the ionization energy in these cases can be anywhere between 13.6 eV and 54.4 eV – it turns out to be 24.6 eV, meaning that the actual value of Z_{eff} is around 1.34 (so the other electron shields about two-thirds of its charge).

This argument now allows us to explain why, for example, 2s orbitals have lower energy than 2p orbitals – looking back at the radial probability distributions from last lecture, we notice that the 2s orbital has a larger probability to be close to the nucleus than the 2p orbital, and thus it is shielding 2p more than the other way around. (And the same argument works to show why 3s has lower energy than 3p, which has lower energy than 3d.)

This allows us to actually think about how electrons are placed into orbitals in a general atom:

Fact 40 (Aufbau principle)

(This name comes from "aufbauprinzip," or "construction principle" in German.) Electrons occupy the lowest energy states available, and there can be at most two electrons per orbital (one of **spin up** and one of **spin down**). Furthermore, **Hund's rule** must be obeyed, which states that we always put only one electron in each available orbital if there are multiple at the same energy, keeping all of those spins in the same direction, and fill in the second electron in each orbital only when that process is finished.

We haven't actually introduced the concept of electron spin yet, and that's what we'll do now. The origin of all of this was the study of **sodium** – George Uhlenbeck and Samuel Goudsmit were looking at the emission of light when electrons jumped between orbitals of sodium. But instead of seeing a single spectrum light at the expected frequency ν, a **doublet** of two lines around ν was seen instead. It turns out this is because there is some other property of the electrons that slightly affects the energies – Uhlenbeck and Goudsmit thought this had to do with magnetic fields, and in fact it turns out there is a **fourth quantum number**, the **spin magnetic quantum number** m_s, which dictates the state of the electron. (There is no classical counterpart of this – we just have to accept it or take 8.04.)

Fact 41

We can visualize an electron as a rotating sphere rotating in one of two directions, and that corresponds to a positive spin ($m_s = \frac{1}{2}$) or negative spin ($m_s = -\frac{1}{2}$), according to the right-hand rule. There is no dependence on the range of values of m_s on n, ℓ, m, but this is still a source of angular momentum and of kinetic energy for our system.)

This is where Wolfgang Pauli comes into the picture: because two different electrons (in different states) must not have identical quantum numbers, we have the following:

Proposition 42 (Pauli exclusion principle)

No orbital can have more than electrons, and if it has two electrons then they must have opposite spins.

We're now ready to see how electron configurations look in some specific examples:

Example 43

If we have oxygen ($Z = 8$), the first electron goes in the 1s orbital and so does the second (we represent this with an arrow up ↑ and an arrow down ↓). The same occurs in the 2s orbital. Finally, we have four electrons to place in the 2p orbitals, and thus by Hund's rule we must have one ↑ in each of those three obitals and an additional ↓ in either $2p_x$, $2p_y$, or $2p_z$, **or** one ↓ in each of those three orbitals and an additional ↑. This gives us the electron configuration $1s^2 2s^2 2p^4$, or alternatively (in full) $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$.

Definition 44

The **core electrons** are the electrons closest to the nucleus, and the **valence electrons** are those farthest from the nucleus. (But there is a gradient between the two ideas.)

Fact 45

We can think of orbitals as the empty seats on a train (where there are two seats per row) – people sit in the rows one at a time, but then eventually two people have to pair up when there are no empty rows left.

9 February 18, 2022

Our first exam is in a week, and we should check the Canvas Course Information document for more details. (It will be in class, and it's closed book and notes other than our given equation sheet.) There is a practice exam and other practice problems posted, and a review session will also be held next Thursday afternoon. We should bring a **calculator which is not an app on our phone or tablet**.

Fact 46

Alma Levant Hayden worked at the National Institutes of Health (NIH) and the Food and Drug Administration (FDA) – she became the Chief of the Spectrophotometer Research Branch at the FDA, and she was likely the first black American scientist to work there. The FDA was big on testing drugs around then because of the thalidomide scandal in the 1960s, and Hayden uncovered the composition of Krebiozen (a fake cancer treatment) using analytical chemistry techniques – it was just mineral oil and creatine.

Our topic of today's lecture is **periodic trends** – we'll look through electron configurations and other patterns between elements. Last lecture, we discussed shielding and how multi-electron systems can change the effective nuclear charge seen by a given electron.

Example 47

An experiment was run to determine ionization energies of various elements – **photoelectron spectroscopy** can in fact show the Aufbau principle in action. The photoelectric effect (for an electron in a metal) works via the equation $\text{KE} = h\nu - \phi$, and thus if we shine light at an electron trapped in an atom, we instead of the equation $\text{KE} = h\nu - \text{IE}$. So our experiment will works as follows: we shine very high-frequency light (X-rays) at an atom and measure the kinetic energy of the electrons that come off, and that gives us the various ionization energies.

For an atom like Carbon, we should then expect to see two electrons at kinetic energy $h\nu - E_{2\text{p}}$, two electrons at kinetic energy $h\nu - \text{E}_{2\text{s}}$, and two electrons at kinetic energy $h\nu - E_{1\text{s}}$ (where E is the (positive) ionization energy, not the (negative) eigenstate energy). So in general, we should see an equal spike at those corresponding energies when we shine our X-rays at a collection of carbon atoms. (And more generally, we should expect spikes at various energies corresponding to 1s, 2s, 2p, 3s, 3p, and so on, in increasing order.)

Remark 48. *We can often use a shorthand for electron configuration, known as the* **noble gas configuration***: since Neon is a noble gas with configuration* $1s^2 2s^2 2p^6$*, we can write the electron configuration of Silicon,* $1s^2 2s^2 2p^6 3s^2 3p^2$*, as* $[Ne]3s^2 3p^2$.

We also have to be careful that electron configurations can change if we have ions: though Cl has configuration $[\text{Ne}]3\text{s}^2 3\text{p}^5$, Cl^+ has configuration $[\text{Ne}]3\text{s}^2 3\text{p}^4$ (we pull out one of the electrons, and it's going to be the one least tightly bound). And in particular, this configuration looks the same as the one for Sulfur – having the same electron configuration is referred to as being **isoelectronic**.

Fact 49 (Exceptions to the Aufbau principle)

The electron configurations for K, Ca, Sc, Ti, V, Cr are (respectively) [Ar]4s, $[\text{Ar}]4\text{s}^2$, $[\text{Ar}]4\text{s}^2 3\text{d}$, $[\text{Ar}]4\text{s}^2 3\text{d}^2$, $[\text{Ar}]4\text{s}^2 3\text{d}^3$, and $[\text{Ar}]4\text{s}^1 3\text{d}^5$. Basically, the 4s orbital turns out to have a lower energy than the 3d orbital, so it is filled first. But then something weird with Hund's rule happens with Chromium – an empty spot was left in 4s and instead goes into 3d. The whole point was to **avoid pairing up electron spins until absolutely necessary**, and it turns out that moving the pair in 4s and having it take the last available orbital in 3d (this is known as **promotion**) is energetically favorable. The same thing occurs when going from Nickel ($[\text{Ar}]4\text{s}^2 3\text{d}^8$) to Copper ($[\text{Ar}]4\text{s}^1 3\text{d}^{10}$), but we aren't changing the number of unpaired electrons here – the point this time is that **atoms like having half-full or full orbitals**.

Other than those exceptions, though, the best way to keep track of the order in which we fill orbitals is to look at the following chart:

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

Then to understand the order that we fill our orbitals in, we draw **downward-left diagonal lines** across the table, and fill the orbitals in order from top to bottom (so first we fill 1s, then 2s, then 2p and 3s, then 3p and 4s, then 3d and 4p and 5s, and so on). But there are more exceptions that come up with ions:

Fact 50

Cations (positive ions formed by removing electrons from elements) tend to remove the s electrons before the d electrons, because a filled s orbital has higher energy for quantum mechanical interaction reasons. And whenever we do this ionization for an atom we always have to see whether there are new promotion opportunities that will increase its stability.

Definition 51

An electronic configuration is **diamagnetic** if all electrons are paired up, and it is **paramagnetic** if there are unpaired electrons.

(This turns out to affect how various substances are attracted, or not, to electric fields.) And now we're ready to look at more general trends across the periodic table:

1. **Ionization energy** (the energy required to remove an electron from its orbital in an atom). Recall that the ionization energy is given by $\frac{R(Z_{\text{eff}})^2}{n^2}$. As we move across the periodic table, the effective nuclear charge should increase, because we're adding more protons and the corresponding electrons only partially shield the nucleus. And as we move down the periodic table, the value of n goes up, and that makes more of an impact than the increase in effective nuclear charge. Thus ionization energy **increases to the right and decreases downward**. But there are always exceptions, such as the elements with half-filled shells.
2. **Electron affinity** (the energy ΔE in the equation $\text{X}^-(\text{g}) + \Delta E \to \text{X}(\text{g}) + \text{e}^-$ – this is the amount of energy required to remove an electron from an anion of that element). In other words, this is the amount of energy by which the system becomes more stable when we add an electron. These trends **are basically the same as above** (elements on the top or right of the periodic table bound their electrons more tightly with the Coulomb force), but again with exceptions.
3. **Electronegativity** (how much a system "wants" another electron). This is a combination of the ionization energy and electron affinity, so **the trend is again basically the same**.
4. **Atomic radius** (the size of the atom, including the electrons – this is a fuzzy definition because everything is quantum mechanical, orbitals aren't all spherical, and there is no defined position). Nevertheless, we can still generally say that the atomic radius **increases down the periodic table** and **decreases to the right** (because the electrons are again more tightly bound).

10 February 22, 2022

Fact 52

Sara Josephine Baker was the first woman to receive a doctorate in public health at NYU. Her work focused on reducing infant mortality and childhood illness in Hell's Kitchen, a slum in New York – she invented an infant formula and methods for treating infants with silver nitrate. She established protocols that eliminated head lice and eye infections in schools, and caught Mary Mallon (a cook who was an asymptomatic carrier of typhoid fever) twice.

Last lecture, we discussed ionization energy (the amount of energy to eject [usually] the most weakly bound electron), electron affinity (the amount of energy needed to remove an electron from an anion to get a neutral species of the atom), and electronegativity (vaguely how much an atom prefers to have an electron added to it, versus giving away the electron) for various elements on the periodic table. We're going to explain now how we can quantify electronegativity more explicitly, following the work of Linus Pauling and Robert Mulliken:

Definition 53 (Mulliken's definition of electronegativity)

The electronegativity χ of an atom is the average of the ionization energy and the electron affinity.

On the other hand, **Pauling's values are the ones used today** – they're difficult to obtain experimentally, but we can look them up in tables because the experiments have been done. To understand this in more detail, we'll have to talk more about **chemical bonds** (formed by two electrons) and how they depend on electronegativity.

Fact 54

We can watch "dogs teaching chemistry" at https://www.youtube.com/watch?v=_M9khs87xQ8 to see some examples of chemical bonds.

The ideas are as follows: a bond is formed by the interactions between two valence electrons from two atoms. If atom 1 is very electronegative and atom 2 is not, then the electron will be essentially taken from atom 2 to atom 1 (not completely, but the electron density is shifted much more strongly towards atom 1), forming an **ionic bond** from Coulomb charges between the anion (partial negative charge) and cation (partial positive charge).

On the other hand, **covalent bonds** are formed when electronegativity is similar among the atoms – the electrons are then essentially equally shared – and **polar covalent bonds** are where the electronegativity is slightly larger for one atom than the other. (The **dipole moment** is a relevant concept for polar covalent bonds, which points in the direction of the more negatively charged atom.)

Definition 55 (Pauling's definition of electronegativity)

Pauling's definition of electronegativity is based on **dissociation energies** (the energy we must put in to remove bonds between two atoms) between bonds. Tthe formula is complicated, but we can look up values in tables. If $\chi < 0.2$, then the bond is covalent, and if $\chi > 2$, then the bond is ionic. In any intermediate region, the bonds are polar covalent.

Example 56

Consider the formation of table salt

$$\mathrm{Na} + \mathrm{Cl} \to \mathrm{NaCl}.$$

Because Na and Cl are on opposite sides of the periodic table (opposite behavior for periodic trends of electronegativity), we will see an ionic bond form.

More specifically, we can think about the reactions

$$\mathrm{Na} \to \mathrm{Na}^+ + \mathrm{e}^-, \quad \mathrm{Cl} + \mathrm{e}^- \to \mathrm{CL}^-.$$

In the first reaction, we are removing the highest-energy electron from Na, so the energy required to make this occur is the **ionization energy of sodium**, which is 494 kJ/mol (we like to do stoichiometry in terms of moles, so we take Avogadro's number into account). And in the second reaction, we're doing the **reverse** of taking an anion and removing its electron, so the energy required for that is the negative of the electron affinity, which is −349 kJ/mol. Thus, the total energy of the reaction

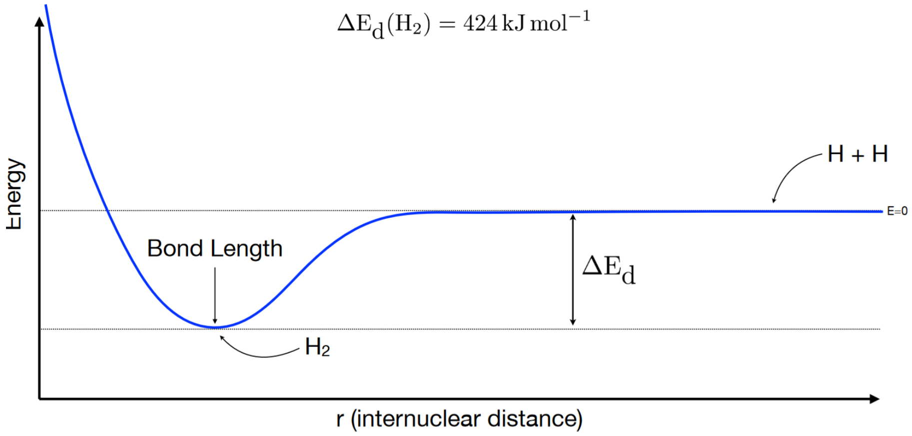
$$\mathrm{Na} + \mathrm{Cl} \to \mathrm{Na}^+ + \mathrm{Cl}^-$$

is 145 kJ/mol (we have to put energy in to make this happen). So forming ions from neutral atoms usually takes energy, but the reason that this actually forms molecules is that from there, we have ions that form a molecule through Coulombic interactions, and that takes energy −589 kJ/mol. Thus, making table salt reduces the energy of the system by −444 kJ/mol – it's a favorable interaction.

Fact 57

The way we arrive at the Coulombic energy −589 kJ/mol is by looking at the Coulomb potential energy $E - \frac{q_1 q_2}{4\pi\varepsilon_0 r}$, plugging in $q_1, q_2 = e, -e$, and letting r be the distance between the Sodium and Chlorine atoms (measured through spectroscopy). Plugging in and canceling units, we find that $E = -9.774 \times 10^{-19}$ J, and then we multiply by Avogadro's number of molecules and convert to kJ to get our answer. **But** the actual energy of forming NaCl is more positive than this (less favorable), because we've ignored repulsive interactions, treated our ions as point charges, and ignored effects due to quantum mechanics.

A useful chart to keep in mind is shown below, which explains the energy (more negative is more favorable) corresponding to various distances between the two atoms: there is no interaction for large distances, the Coulomb interaction makes the bond favorable for medium distances, and uncomfortable overlaps between the atoms cause repulsion for short distances.



Charts like this help us read off how strong bonds are between molecules (how much energy is needed to break them), as well as how far apart they are (the local minimum). This gives us a general trend: the longer the bond length, (usually) the weaker the bond is.

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Fact 58

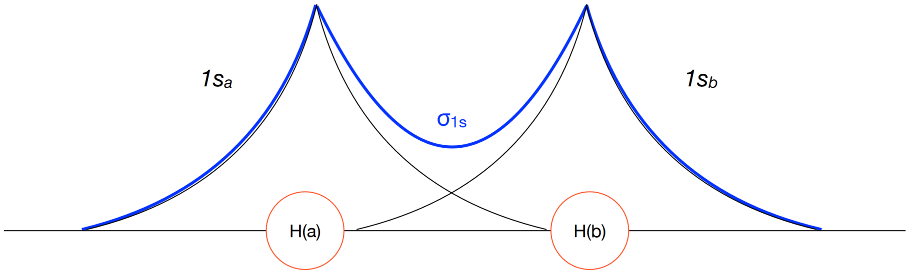
Muhammad ibn Zakariya al-Razi lived around the year 900 – he studied medicine in Baghdad, and he introduced the idea that medicine should be practiced regardless of ability to pay. He rigorously documented symptoms, progression, and treatments of various diseases (without making reference to the supernatural), as well as the reaction of the pupil to light, and he widely declared that contemporary scientists' conclusions should be considered more important than ancient ones. (Much of this was revolutionary at the time!)

Today's lecture is focused on **molecular orbital theory** – these next five or six lectures are all discussing theories of bonding, and there will be some disconnection between the different theories but hopefully everything will wrap up in due time. We've previously mentioned ionic, covalent, and polar covalent bonds, and today we'll take a quantum mechanical approach at understanding those bonds. Specifically, we'll take atomic orbitals and add their wavefunctions together (superposition) to create **molecular orbitals**, and linear algebra will help us understand how bonding and anti-bonding orbitals come from linear combinations of atomic orbitals (LCAO). The key point is that (by linear algebra) we always get as many molecular orbitals as we used atomic orbitals initially.

Example 59

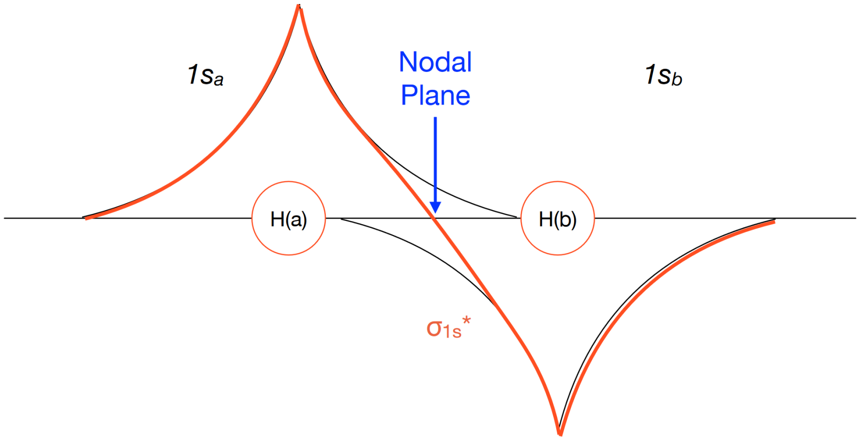
The molecule H_2 is formed by creating a bond between two Hydrogen atoms. We'll start by looking at the 1s orbitals (lowest energy) for each hydrogen, which have real-valued wavefunctions (unlike the other orbitals) that are spherically peaked.

Quantum mechanics allows us to understand how these wavefunctions interfere with each other – by superposition, we can create a molecular orbital by adding the individual wavefunctions (in black) together (result shown in blue):

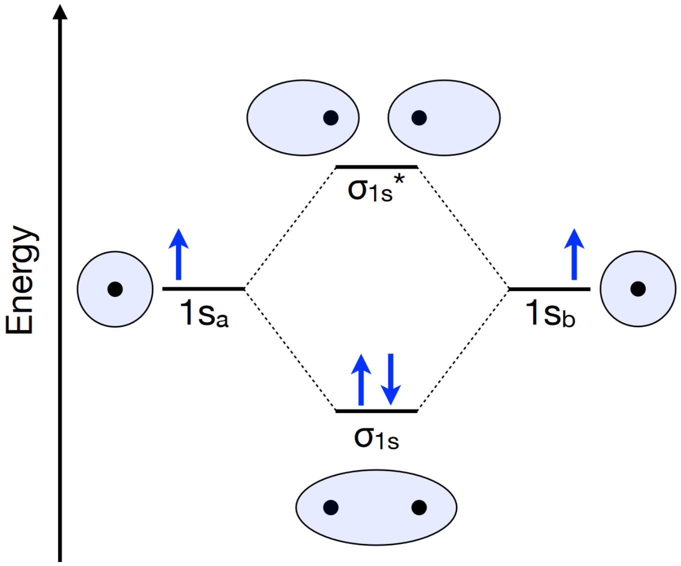


(One important note here is that **we add the wavefunctions, not the probability densities**.) And because electrons in a bonding molecular orbital are attracted to both nuclei, they are more tightly bound and have a lower energy than just being bound by a single nucleus.

But we've mentioned that we should actually have two molecular orbitals – the idea is that we can subtract the wavefunctions instead of adding them, and this actually creates a node in the middle of the two atoms:



This is known as an **anti-bonding** molecular orbital, but we'll talk more about it later. The main point for now is that we have are two molecular orbitals σ_{1s} and σ^*_{1s}, and we now want to think about the energies for our molecular orbitals through a **molecular orbital diagram**:



For each orbital, we also show the probability density function for where the electrons can be found – for both the σ_{1s} and σ_{1s}^* orbitals, we have a **σ molecular orbital**, which is defined to be a molecular orbital cylindrically symmetric orbital about the bond axis with **no nodal plane along that bond axis** (so no issue in this case). And now with this new energy level diagram, we start by placing electrons in the original atomic orbitals, and then we follow the Aufbau principle to place them into the molecular orbitals. (So in this case, both of the two electrons from the two Hydrogen atoms go to σ_{1s}.) We then write down an electron configuration for molecular hydrogen, and it is $(\sigma_{1s})^2$ (the parentheses are required to avoid things like $*$ and 2s conflicting).

Definition 60

The **bond order** calculates the number of bonds formed between two atoms, and it is given by

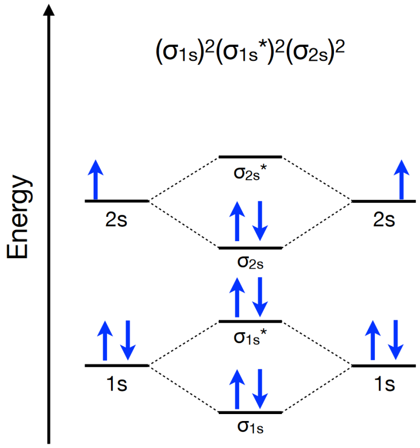
$$\text{BO} = \frac{1}{2}(\text{number of electrons in bonding molecular orbitals} - \text{number of electrons in anti-bonding molecular orbitals}).$$

Indeed, for molecular hydrogen we have a bond order of $\frac{1}{2}(2-0) = 1$.

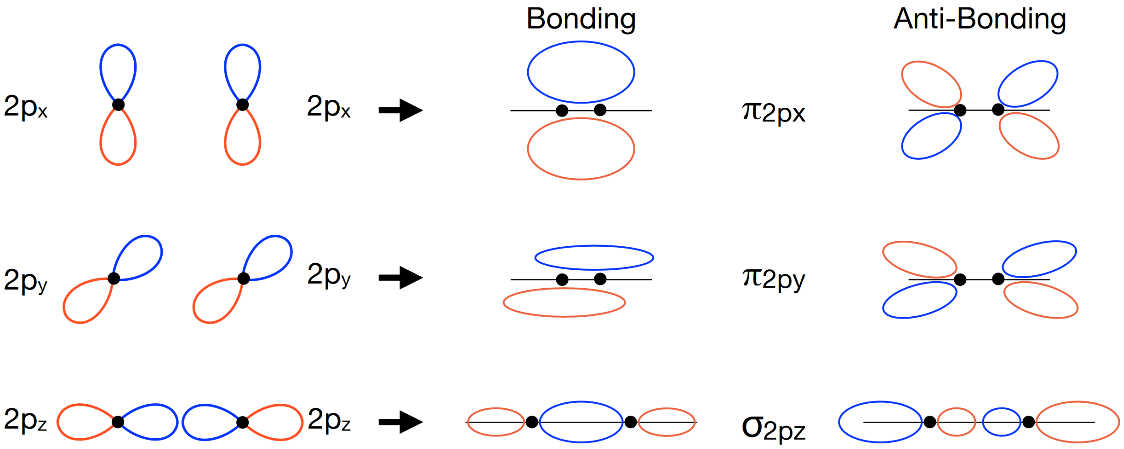
Example 61

Molecular helium He_2 has a similar molecular orbital diagram and electron configuration, except we now fill in all four of the orbitals in the diagram with a spin up and a spin down electron, and the electron configuration becomes $(\sigma_{1s})^2(\sigma_{1s}^*)^2$. Notice that the bond order here is $\frac{1}{2}(2-2) = 0$, so molecular orbital theory predicts that the Helium molecule shouldn't exist. That's basically true – two Helium atoms can come together, but it's only a loose association.

Next, we'll try to think about how to form molecular orbitals for Li_2. This time, we also have to form molecular orbitals for 2s, and they form the analogous σ_{2s} and σ_{2s}^* orbitals.

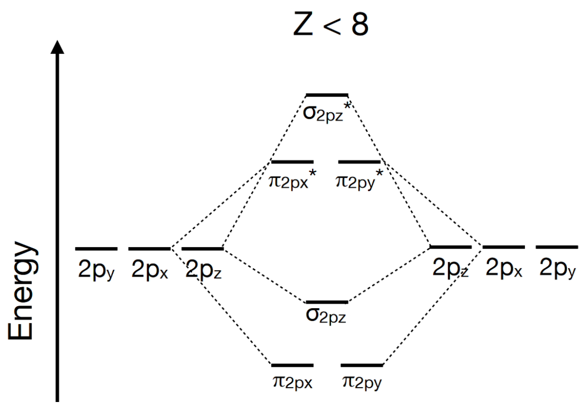


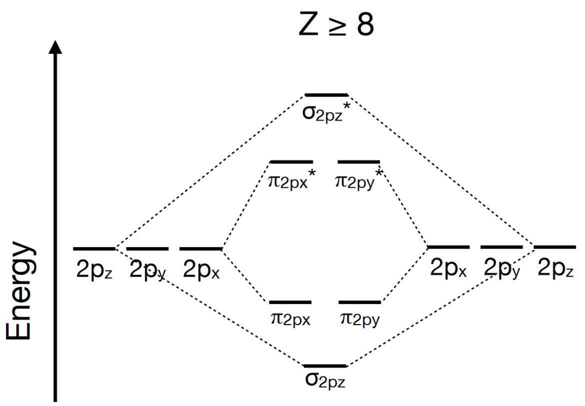
The bond order for dilithium is then $\frac{1}{2}(4-2) = 1$, but a shortcut here is to note that **we only need to look at valence electrons** (because core electrons always have the same number of bonding and anti-bonding orbitals and electrons in those orbitals). So nothing much is changing in this case, but the next step has us looking at **molecular orbitals for the p orbitals**. Now that we have three different p orbitals, we're going to have to start making three-dimensional considerations – in particular, we have degeneracies in energy, and **it now matters whether the orbitals are aligned in the direction of the bond axis or not**. Here's the way the orbitals add together (note that red and blue represent different phases for the wavefunction, and think of the p_y orbital as coming in and out of the page):



Notice that we do actually have nodal planes along the bonding axis for the bonding and anti-bonding orbitals in the first two cases, but we still have a region of enhanced interaction in both cases. So they can't be σ orbitals, and they are instead known as **π molecular orbitals**: we have the π_{2px}, π^*_{2px}, π_{2py}, and π^*_{2py} molecular orbitals. On the other hand, for the last set of orbitals, we get the cylindrically symmetric behavior we expect from orbitals pointing at each other, and we indeed have σ bonding and anti-bonding orbitals there.

So there are two different cases for how these p orbitals can appear on a molecular orbital energy diagram, depending on the value of Z (because of quantum mechanical interactions, and beyond the scope of this class). The diagram below explains the situation (and leaves off the 1s and 2s molecular orbitals, though they are still there):





Notice that the σ anti-bonding orbitals are higher energy than the π anti-bonding orbitals in both cases, but the σ bonding orbitals are higher in energy for $Z < 8$ and lower for $Z \geq 8$.

Fact 62

If both atoms in a molecule are the same (homonuclear diatomic), we should keep these ordering rules in mind for where σ_{2pz} fits into the energy levels. On the other hand, if the two atoms are different (heteronuclear diatomic), we use the $Z < 8$ ordering if both atoms have $Z < 8$, and the situation is much more complicated otherwise and we won't discuss it.

Example 63

If we want to find out the electron configuration for C_2, we completely fill the 1s and 2s molecular orbitals, and then (following the left diagram) the remaining four electrons must go into the orbitals remaining of lowest energy. We eventually end up with an electron configuration of $(\sigma_{1s})^2(\sigma_{1s}^*)^2(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2px})^2(\pi_{2py})^2$.

Definition 64

The **HOMO (highest occupied molecular orbital)** is the molecular orbital of highest energy with electrons, and the **LUMO (lowest unoccupied molecular orbital)** is the molecular orbital of lowest energy without electrons.

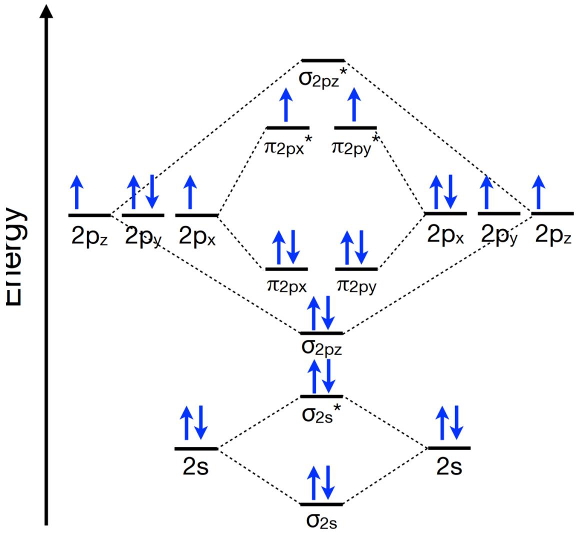
These come up when discussing reactivity of molecules, so they do play a big role in how orbitals influence chemical reactions!

12 March 2, 2022

(We'll skip "Scientists You Might Not Know" today because the lecture is a bit longer than usual.) Today, we'll be talking about hybrid orbitals, and we'll start by taking a look at last lecture's material:

Example 65

Below is shown the electron configuration for O_2 (filled using the Aufbau principle). Recall that this is the diagram for $Z \geq 8$ only.

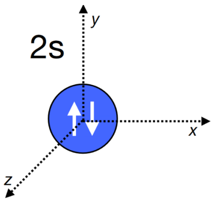


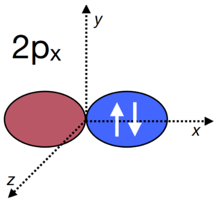
The bond order is then (just looking at the valence electrons) $\frac{1}{2}(6-2) = \boxed{2}$ because we have 6 bonding electrons and 2 anti-bonding electrons in the 2p orbitals, and because there are unpaired electrons molecular oxygen is **paramagnetic** (unlike Nitrogen, which is diamagnetic). The idea is that diamagnetic molecules will be very weakly repelled by a magnetic field, while paramagnetic molecules will be attracted to magnetic fields (we can check the video here for more).

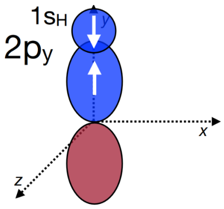
We're now ready to look at more complicated molecules that come up in our daily lives:

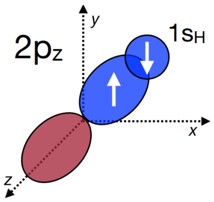
Example 66

A water molecule H_2O has a central Oxygen atom of electron configuration $[He]2s^2 2p^4$ – if we assign two of the electrons to p_x and one each to p_y and p_z, we can then imagine that the hydrogen atoms each bond to one of the unpaired electrons.









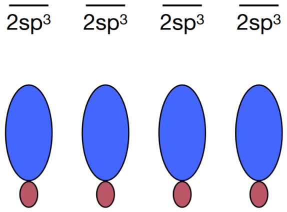
To create those orbitals, we must create a bonding (add wavefunctions together) and anti-bonding (subtract them) orbital, and this creates a σ and a σ^* orbital in both the y and z p orbitals. So from what we've described, we should see a bond along the y and along the z orbitals, meaning there is a 90 degree bond angle of two single bonds. (The actual value is 104.5 degrees, and we'll understand that more as the lecture goes on.)

Example 67

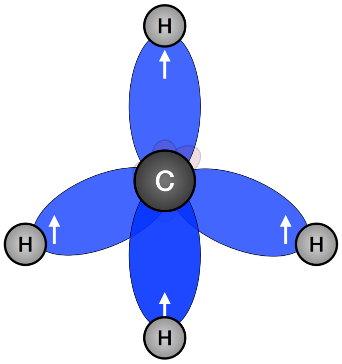
Methane has a formula of CH_4, and this time the configuration $[He]2s^2 2p^2$ is a bit more complicated – we don't have four unpaired electrons in the Carbon atom, and experimentally we know that the bonds are indeed not planar for methane. So molecular orbital theory has failed to describe this molecule.

The complication now is that our **orbitals have been approximations**, except for the hydrogen atom where there is only a single electron. We've been approximating multi-electron atomic orbitals as hydrogen atom orbitals but with a different Z_{eff}, and this approximation only goes so far. So what we're going to discuss now is **hybridization**, the act of combining orbitals in different ways.

Returning to the Carbon atom and methane, we need to find ways to form orbitals that aren't just pointed along the x, y, or z directions. Since we need to have four electrons to pair with the four Hydrogen atoms, we first promote one of the electrons in 2s into the $2p_z$ orbitals, and then we combine our four ordinary orbitals into four hybrid orbitals (named sp^3 because they come from combining one s orbital and three p orbitals):



So we now have four hybrid orbitals which can point in the directions of a tetrahedron, and they will be each 109.5 degrees apart from each other, and the molecule CH_4 now looks as shown below (we can imagine each electron from a Hydrogen atom paired with the corresponding atom in the sp^3 orbital in Carbon):



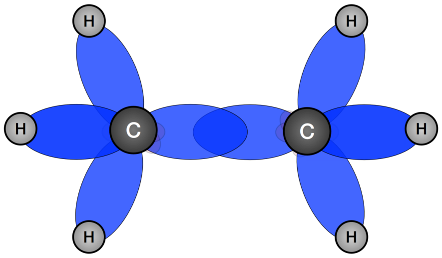
Each of the four bonding axes now point in a different direction, and because they are cylindrically symmetric around that axis and have no nodal plane **along** that axis, they are each a σ orbital. Specifically, we'll denote the one formed by methane by

$$\sigma(\mathrm{C2sp}^3, \mathrm{H1s})$$

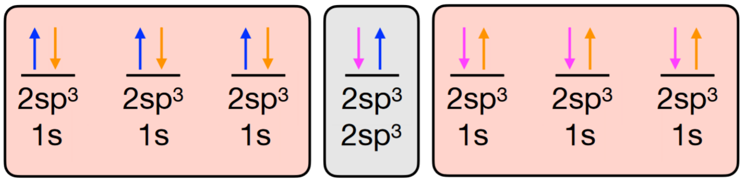
(because it was a σ bond formed by adding a $\mathrm{C2sp}^3$ and a H1s orbital together).

Example 68

Ethane has chemical formula C_2H_6, and we can form the molecule as follows: hybridize the orbitals of carbon, form a single bond between the two carbons, and attach a hydrogen atom to each of the remaining sp^3 orbitals, as shown below:



We then form a single $\sigma(\mathrm{C2sp}^3, \mathrm{C2sp}^3)$ bond, as well as six $\sigma(\mathrm{C2sp}^3, \mathrm{H1s})$ bonds, and the electronic configuration is shown as below.

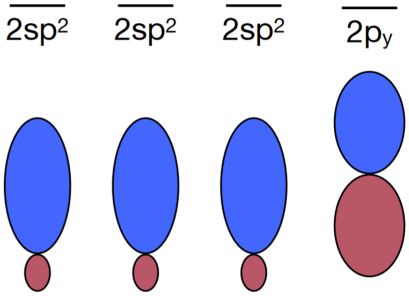


As a note, though, **we should not color the different electrons**, because electrons are indistinguishable and we can't tell which electron came from which during a bond.

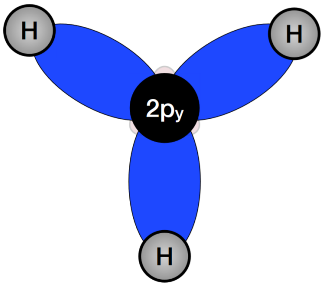
More generally, we don't have to make four hybrid orbitals with the s and p orbitals that we have:

Example 69

Suppose we want to make the molecule BH_3. Since Boron has electron configuration $[He]2s^2 2p^1$, we promote the 2s electron to $2p_z$ (for example), and we bring together the 2s, $2p_x$, and $2p_z$ orbitals to create three $2sp^2$ orbitals.

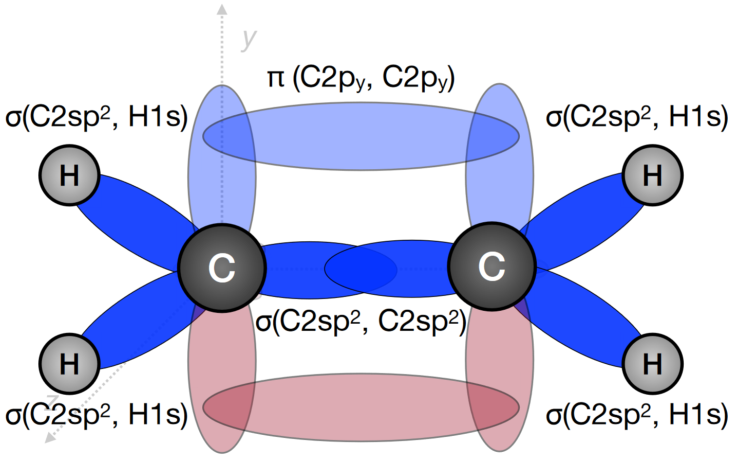


This time, because there are no electrons in the $2p_y$ orbital, we get a trigonal planar shape for the bonds (120 degrees between them, all in the same plane). This forms three bonds that we label as $\sigma(\text{B}2\text{sp}^2, \text{H}1\text{s})$, shown below.



Example 70

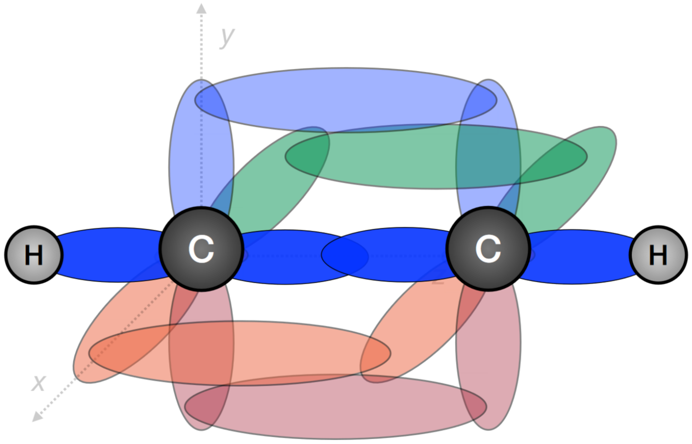
If we next consider ethylene, which has a chemical formula of C_2H_4, we must form a double bond between the two Carbon atoms so that all electrons are paired up, and in this case we only hybridize into sp^2 orbitals. The diagram for that is shown below.



The more faintly colored orbitals give us a π bond (the second bond between the Carbon atoms has a nodal plane. And because of the existence of this pi bond, **we can't twist** the Hydrogen atoms bonded to the Carbon atoms separately without snapping the pi bond.

Example 71

A final case to consider is a molecule like acetylene, C_2H_2, in which we must form a triple bond between the Carbon atoms to pair up all electrons. This time we hybridize just one p orbital on each Carbon atom to produce two sp orbitals, and the final diagram is shown below.

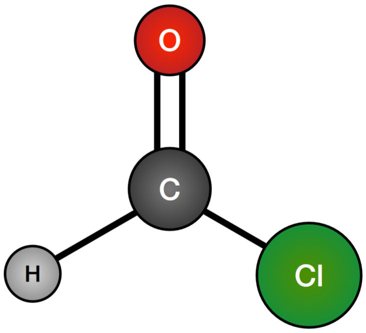


The idea is that the unpaired electrons again form π bonds, so we have a single $\sigma(\mathrm{C2sp}, \mathrm{C2sp})$ bond, two $\sigma(\mathrm{C2sp}, \mathrm{H1s})$ bonds (one for each Carbon atom), one $\pi(\mathrm{C2p_y}, \mathrm{C2p_y})$ bond (along the y axis), and one $\pi(\mathrm{C2p_x}, \mathrm{C2p_x})$ bond (along the x axis). It's important to note that **the choice of hybridization depends on how the orbitals must combine** to make bonds possible! And of course, we need to describe how we actually make the choices for the geometric structure of the molecules, but we won't get to that for another two lectures.

Fact 72

One important note is that atoms that are at the extremes of molecules (for example, the hydrogen atoms in many of our examples above) bonded to only one other atom by a single **do not hybridize** their orbitals. So far, all of our terminal atoms have been Hydrogens, but we'll now look at an example where this is not the case.

If we now look at the molecule (formyl chloride) shown below, we can think about the hybrid orbitals formed:



Essentially, the single bond between the Carbon and Hydrogen atom give us a $\sigma(\text{C2sp}^2, \text{H1s})$ orbital (because the 120 degree angles tell us that Carbon hybridized its orbitals into three sp^2 orbitals), and the single bond between the Carbon and Chlorine atom give us a $\sigma(\text{C2sp}^2, \text{Cl3p}_\text{z})$ (no hybridization on the Chlorine atom; z chosen arbitrarily). After that, the double bond formed by the C and O atoms give us a $\sigma(\text{C2sp}^2, \text{O2sp}^2)$ bond between the hybridized orbitals, as well as a $\pi(\text{C2p}_\text{y}, \text{O2p}_\text{y})$ bond between the remaining non-hybridized orbitals. And next lecture, we'll explain why we needed to make an sp^2 orbital out of the Oxygen atom too!

Fact 73

It's important to remember that **we are not forming anti-bonding orbitals** anymore – for example, if we form a molecular orbital between an sp^3 orbital of Carbon and an s orbital of Hydrogen, then the two electrons forming the bond both go into the bonding oribtal and nothing else happens. For more electrons, the situation becomes more complicated, but that's outside the scope of this course!

13 March 4, 2022

Today's lecture will focus on **shapes of molecules** coming from hybrid orbitals and extra electrons that aren't part of bonds.

Fact 74

Emmy Noether was a mathematician who developed Noether's theorem (describing whether physical quantities are conserved) while she was teaching at the University of Erlangen without pay for a decade. She then later taught at Göttingen (until she was kicked out by the Nazis) and then in the United States. Many call her the "most important woman in mathematics." After her death, Einstein's praised her as the "most significant mathematical genius" in a letter to the editor of the New York Times.

Molecular shapes matter a lot because they have significant biological and material science applications, and also because (relevant to Professor McGuire) they can be detected in space by looking at the rotational spectra (because rotating molecules takes less energy than electronic transitions). It turns out that this spectrum (that is, the frequencies of light given off) can be described using a quantum number via

$$\nu = 2B(J+1)$$

where $B = \frac{h}{8\pi^2 cI}$ takes the role of Rydberg's constant and is different for every molecule (because it depends on the moment of inertia $I = \mu r^2$). So what goes into this first-order approximation of the rotational frequencies of a molecule is just the masses and distances between molecules, and this gives us a unique fingerprint for each molecule that can be used to look out into space. (Professor McGuire likes to look into the region TMC-1 using a giant telescope, and we do indeed see patterns of lines that fit particular molecules!)

The topic of today's lecture is **VSEPR** (pronounced "ves-per"), which stands for Valence Shell Electron Pair Repulsion. VSEPR tells us about a few foundational principles for determining molecular shapes:

- Valence electron pairs (either two electrons that are in a lone pair configuration, or two electrons forming a bond) repel each other.
- The shape of the molecule around the central atom **minimizes** the repulsion (that is, as separated as possible).

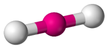
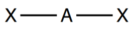
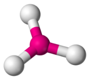
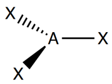
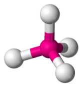
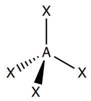
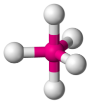
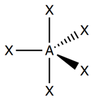
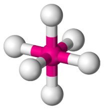
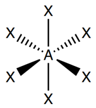
Definition 75

In VSEPR nomenclature, we will denote a central atom with A, a bonding atom with X, and a lone pair of electrons with E. The **steric number (SN)** is the number of atoms bonded to the central atom, plus the number of lone pairs of electrons.

"Steric" means "effect of size on something," and we'll now see how the steric number affects molecular shape by looking at the following table:

Formula	SN	Structure	Hybridization	Angle	Example
AX_2	2	Linear	sp	180°	CO_2
AX_3	3	Trigonal planar	sp^2	120°	BH_3
AX_4	4	Tetrahedral	sp^3	109.5°	CH_4
AX_5	5	Trigonal bipyramidal	sp^3d	90° and 120°	PF_5
AX_6	6	Octahedral	sp^3d^2	90°	SF_6

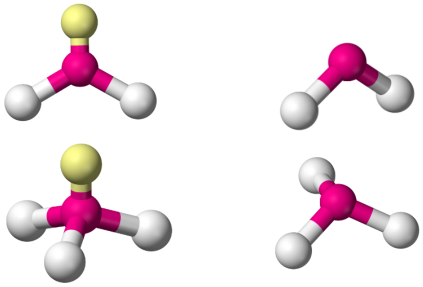
In these five examples above, we have no electron pairs, so each of the bonds is arranged in a way that separates the bonds as much as possible. (And the minimum hybridization occurs because making hybrid orbitals takes energy.) We won't have to know any of the specific examples, but we do need to be able to draw (somewhat) the geometry for each of these cases. And we usually draw using the chemical notation shown below, rather than with a ball-and-stick model (note that dashed wedges go into the screen, and solid wedges come out of the screen):

SN	Structure	Structure
2		
3		
4		
5		
6		

We're now ready to think about **lone pairs**, like we discussed with H_2O last lecture – these are valence electrons that are paired with each other and not involved in the bonding. Each of these pairs adds to the steric number and thus affects the geometry, and the idea is that we get very similar shapes to before but without bonds on the lone pairs. (Furthermore, the bond length is shorter for the lone pairs, and thus **lone pairs repel a bit more than bonds**.)

Formula	**SN**	**Structure**	**Hybridization**	**Angle**	**Example**
AX_2E	3	Bent	$< 120°$	SO_2	
AX_3E	4	Trigonal pyramid	$< 109.5°$	NH_3	
AX_2E_2	4	Bent	$< 109.5°$	H_2O	
AX_4E	5	See-saw	$< 90°$, $< 120°$	SF_4	

Below are shown the structure for AX_2E and AX_3E – on the left, lone pairs are shown in yellow, and on the right, lone pairs are omitted. (And the same logic works for the other molecules as well – we basically take a tetrahedral, trigonal bipyramidal, or octahedral structure and remove some of the pairs, squishing together the remaining ones to decrease the bond angle.)



We'll finish with a few more complicated examples (we should try to draw each of these out and understand how they work), where again we are responsible for knowing all of these different structures:

Formula	**SN**	**Structure**	**Hybridization**	**Angle**	**Example**
AX_3E_2	5	T-shaped	$< 90°$	ClF_3	
AX_2E_3	5	Linear	180°	I_3^-	
AX_5E	6	Square pyramidal	$< 90°$	BrF_5	
AX_4E_2	6	Square planar	90°	XeF_4	

Example 76

We can tell how much "squish" occurs in bond angles between molecules based on atomic size. For example, because PH_3's lone pair is farther away from the nucleus than NH_3's lone pair (and thus larger), even though both of those molecules have a trigonal pyramidal structure, we will get larger bond angles for NH_3. Furthermore, the bond angle for a tetrahedral molecule like CH_4 will be larger than the bond angle for any trigonal pyramidal structure.

Next lecture, we'll start thinking about Lewis structures and how to actually determine when we'll have lone pairs!

14 March 7, 2022

Our next exam will be next Wednesday during class (cover material up until next lecture). Just like for exam 1, practice exams and other problems are already posted on MITx.

Fact 77
Juan Carlos Finlay got his medical degree and held some prestigious positions in Cuba, until he was tasked with studying the causes of yellow fever. He discovered that outbreaks coincided with mosquito season, and he was the first person to suggest that mosquitos were a disease vector (suggesting mosquito control as a way to deal with yellow fever). Those measures were then implemented by Walter Reed while working on the Panama Canal (who now gets all of the credit, except in Cuba, where the highest scientific honor is named the Carlos J. Finaly National Order of Merit).

Today, we'll continue discussing bonding and molecular structure by taking a look at **Lewis structures**. As a reminder, molecular orbital theory failed to reproduce structure in polyatomic molecules, and that's why we discussed hybrid orbitals and VSEPR theory for explaining those shapes. The issue is that we have to know the number of bonds between the atoms first, and that's what we'll discuss today.

Fact 78
Gilbert Lewis (a Massachusetts native) is the inventor of Lewis structures – he published a paper with his theory in 1916, which is while quantum mechanics was still being understood (and in fact he might not have been aware of it). And this theory still works today – it's the one we use in modern chemical practice. It doesn't include quantum mechanics, so there are a few errors, but for almost all situations it gives us what we need. Lewis was nominated for a Nobel Prize 41 times but never won it.

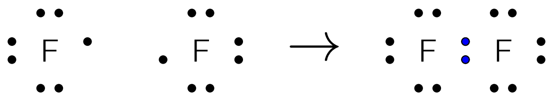
Here are the key concepts:

1. Bonds are formed between atoms so that elecrons are shared to create full valence shells.
2. (Octet rule) Electrons are distributed so that atoms are (almost always) surrounded by eight valence electrons.
3. We represent electrons with dots around elements.

(The number 8 comes from the fact that, for example, the maximum number of electrons we can fill at the $n = 2$ level is $2s^2 2p^6$.)

Example 79
Consider molecular fluorine (F_2), where we bring together two Fluorine atoms (each with seven valence electrons) to form a molecule.

Originally, each Fluorine atom only has seven electrons, but if we bring them together we can get a full octet around each one:



The two electrons that are between the two Fluorine atoms are then the **bonding electrons**, and the other electrons are the **lone pair electrons**.

Fact 80
Because there is no 1p orbital, Hydrogen can achieve stability with just two electrons.

Now that we understand the general concept, we'll talk about a foolproof method for generating Lewis structures:

1. Draw a **skeleton structure** (we'll see what this looks like soon). Hydrogen and Fluorine are always **terminal atoms**, and usually the element with the lowest ionization energy goes in the middle of the structure.
2. Count the total number of valence electrons, taking into account whether the molecule is a negative or positive ion.
3. Count how many electrons are needed to give all atoms a full valence shell (usually 8, except 2 for Hydrogen).
4. The number of bonding electrons is the difference between (3) and (2).
5. Assign two bonding electrons to each bond in our skeleton structure. If any bonding electrons remain, add double or triple bonds.
6. Assign the remaining valence electrons in pairs to complete octets.
7. Determine formal charge (discussed later on in this lecture).

Example 81

Hydrogen cyanide is a molecule with an H, C, and N atom – we'll construct the Lewis structure for it now.

The central atom for HCN is C (because it has the lowest ionization energy), and thus the skeleton structure has C in the middle, H on one side of C, and N on the other side. We have a total of $1+4+5 = 10$ valence electrons, and we need $2+8+8 = 18$ total electrons to get full valence, so we need $18-10 = 8$ bonding electrons (so 4 bonds).

We can now only form one bond between H and C, so we need to form 3 bonds between C and N. Drawing in the bonding and valence electrons gives us the following diagram (**where we've replaced pairs of bonding electrons with lines connecting the atoms**):

$$\mathrm{H} - \mathrm{C} \equiv \mathrm{N}\,\colon$$

Example 82

The cyanide anion contains a C and an N atom, and it has a charge of -1.

Counting valence electrons, we have $4+5+1 = 10$ (the extra 1 comes from the negative charge), and we need $8+8 = 16$ electrons for full valence. Thus, we have 6 bonding electrons and thus three bonds, and we place the remaining electrons to complete the octets. Since we have an ion, we also have to mark in the charge:

$$[\colon\mathrm{C} \equiv \mathrm{N}\colon]^{-}$$

We're now ready to discuss how **formal charge** comes into the picture – it is meant to measure how much an atom has gained or lost electrons while forming covalent bonds. In particular, **we want to make sure each atom in the molecule is as close to a formal charge of zero as possible**.

Definition 83

The formal charge on an atom is

$$\mathrm{FC} = \mathrm{V} - \mathrm{L} - 0.5\mathrm{B},$$

where V is the number of valence electrons, L is the number of lone pair electrons, and B is the number of bonding electrons for the atom.

Notice that the sum of all formal charges on a molecule will equal the overall charge of that molecule, just by counting the total number of electrons that contribute to the formal charges (each bond of two electrons contributes -1 to each atom in the bond). So for example, HCN should have a total formal charge of 0, and CN^- should have a total formal charge of 1.

Example 84

The formal charge on Carbon in CN^- is $4-2-3=-1$, and the formal charge on Nitrogen is $5-2-3=0$. (This is reasonable – we have $-1+0=-1$, and the charges are pretty close to 0.)

Fact 85

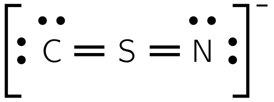
When we choose between different ways to draw a Lewis structure, structures with the lowest absolute values of formal charges will be the most stable.

Example 86

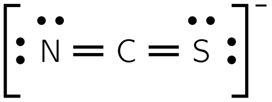
Consider the thiocyanate ion, containing one C, S, and N atom and with a charge of -1. The ionization energies (from highest to smallest) are N, C, S, so the central atom looks like it should be S.

However, formal charge will tell us the actual answer. Below are shown the three possible Lewis structures for the three different skeleton structures, along with their formal charges:

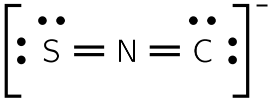
Structure A



Structure B



Structure C



The formal charges for N, C, and S in the three potential structures (respectively) are $(-1,-2,2)$ for structure A, (-1, 0, 0) for structure B, and (1, -2, 0) for structure C. In all three cases, the sum of the formal charges is -1, but Structure B has the most 0s and ± 1s, so that is the most stable structure and in fact the correct answer.

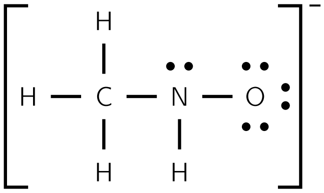
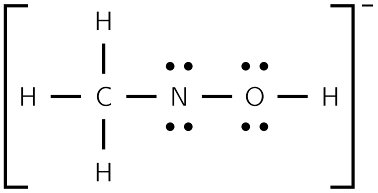
Fact 87

If two different structures for an atom have the same distribution of absolute values of formal charges, then we should make sure the **most electronegative atom** has the negative formal charge.

Example 88

Consider the molecule CH_3NHO^-. The CH_3 is called a **methyl group**, and it is always terminal, so we just need to figure out the ordering of the other molecules. Since this is a "chain molecule," we usually write the atoms in order, except terminal atoms (like H) might depend on formal charges.

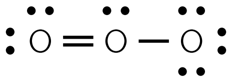
Below are shown two different structures, one bonding the fourth H atom to O and one bonding it to N. (Correspondingly, we have a formal charge of -1 on the Oxygen on the left, but on the Nitrogen on the right.) And because Oyxgen is more electronegative, the left structure is more stable.

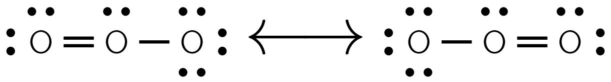
We'll finish by discussing the concept of **resonance**:

Example 89

Ozone has chemical formula O_3, and it has two different possible structures if we follow the rules of drawing Lewis structures above (we have 18 valence electrons and 24 needed for full valence, so we need 3 bonds, meaning we draw a double bond and a single bond).



The key point is that we could draw the double bond on the left or on the right – these are entirely equivalent, and in either case we have a $+1$ formal charge in the middle and 0 and -1 formal charges on the sides. It turns out that the bond order in Ozone is about 1.5 – **there are two equivalent bonds, and that's something Lewis structures cannot reproduce.** This is denoted with the notation below:



(We should be particularly careful to use this particular resonance arrow – other arrows will come up when we start talking about equilibrium, acids and bases, and so on!) The key point is that resonance structures have the **same arrangement of atoms**, only a different arrangement of electrons. So if we have a different skeleton structure, like for CH_3NO^-, that gives us two different molecules ("structural isomers"), not two resonance structures. And next lecture, we'll look at more complicated scenarios and important exceptions to these rules.

15 March 9, 2022

We'll continue looking at Lewis structures today, understanding how they break and how we can sometimes fix them. (This is our last lecture of knowledge for Exam 2.)

Fact 90

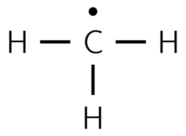
David Unaipon is a member of the Ngarrindjeri people, and he is credited for breaking the stereotypes of Indigenous Australians within Australian society. He was a preacher, author, and inventor (considered the "Australian Leonardo da Vinci"), and he invented the mechanism for modern mechanical sheep shears (though never given credit for it).

Last lecture, every structure we were given had an even number of valence electrons, but sometimes that won't occur in molecules.

Example 91

Consider the molecule CH_3 – we know that we need to have a central atom of Carbon and three surrounding Hydrogen atoms. We then have $4 + 1 + 1 + 1 = 7$ total valence electrons, but we need 14 total and we can only form three total bonds because Hydrogen can only form one bond each.

We then have only one electron left, and that gives us one unpaired electron hanging out:

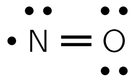


Then everything checks out – we have the right number of electrons, and everything has a formal charge of 0. So this is where the octet rule breaks:

Fact 92

If we have an odd number of valence electrons, we cannot have all atoms form an octet, because the octet rule pairs electrons up. But Lewis structures still function in this case, and we call these molecules with unparied electrons **radical species**. Radicals tend to be very reactive because the electron "wants" to pair up and form a bond.

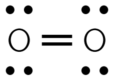
Radicals turn out to be very important in biology, because they can damage our DNA. For example, nitric oxide (NO) has the following Lewis structure:



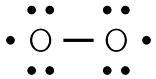
Remark 93. *NO in fact activates guanylate cyclase (GC) in the human body, which is a signaling molecule that converts GTP to cGMP, and this leads us to* **vasodilation**. *But cGMP is degraded by the enzyme PDE 5, which stops vasodilation (decreasing blood pressure), and this is how Viagra was developed.*

Example 94

Next, we can think about molecular oxygen O_2 (another weird exception): we've drawn the Lewis structure below for it following our rules (which has no formal charges, and it has the correct number of valence electrons).



But we already talked about molecular oxygen with molecular orbital theory – we mentioned that there are unpaired spins and we have paramagnetism. **So the Lewis structure is not actually correct – experiments tell us that we have a biradical two unpaired electrons, and the diagram looks as below:**



We'll continue to discuss weird exception cases:

Fact 95

The atoms B and Al can be stable with an incomplete octet.

Example 96

The molecule BF_3 has 32 total electrons for full valence and only $3+7+7+7 = 24$ electrons, so it seems like we want to form 4 bonds between the Bs and Fs. But this gives us a formal charge of -1 on the B and a formal charge of 1 on the F, and in fact experimentally there are only single bonds between each B and F (giving us all zero formal charges).

We'll now move on to a topic that we haven't really talked about in about two weeks, which is the **influence of d orbitals**. This is connected to the concept of **valence shell expansion**:

Fact 97

Elements with $n \geq 3$ have d orbitals, so more than eight electrons may fit around a central atom. This most commonly occurs if we have a large central atom and small electronegative atoms bonded to it.

Example 98

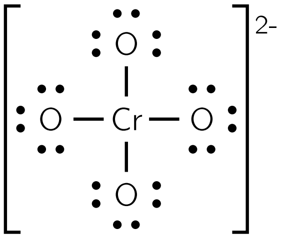
The molecule PCl_5 has P as its central atom and a bond from each Cl atom to the central P. Our ordinary Lewis rules would require 48 electrons and 40 for full valence, which only allows for 4 bonds and thus we can't actually connect the molecule together. So instead, Phosphorus expands its octet, hybridizing in a d orbital, and we arrive at our final structure (with six lone pair electrons on each Chlorine atom and five total single bonds).

Example 99

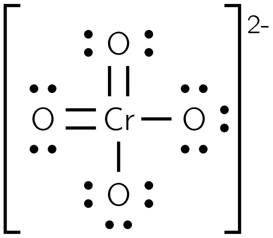
On the other hand, the molecule CCl_5 does not work, because the energy required to mix in a 3d orbital (much higher energy than the valence orbitals of Carbon) to create an expanded octet for C is a huge cost and is not outweighed by the energy from bonding. So it is a general rule that **we never make five bonds with Carbon**.

Example 100

The anion CrO_4^{2-} contains Cr (the atom with the special property that it has electron configuration $[Ar]4s^1 3d^5$ because of the half-filled orbital special stability). But this doesn't matter for Lewis structures – there are six valence electrons from Cr, so we get a total of $6+6+6+6+6+2 = 32$ valence electrons. We need 40 to form full octets, so we need to form 4 bonds, and that gives us the following structure:



But this gives us a $+2$ formal charge on the Chromium and a -1 formal charge on the Oxygens, which is not very good. And experimentally, we find that we do not in fact have single bonds everywhere, and we can improve the formal charge by rearranging the bonds slightly:



This then gives us two -1 formal charges on two of the Oyxgens and 0s everywhere else, and this is the best we can do with an anion of charge $2-$. And this is only possible because **Chromium can expand its octet** because it's lower down on the periodic table.

16 March 11, 2022

Remark 101. *I was not able to attend this lecture in person, but these notes are transcribed from lecture slide and the posted lecture script.*

Today's lecture will not be on next week's exam, but it will be important material going forward – we'll discuss interactions between atoms and molecules other than the usual two-electron bonds.

Fact 102

Dorothy Mary Crowfoot Hodgkin was the third woman to graduate from Oxford with a first-class honors degree. After getting a PhD from Cambridge, she spent most of her career doing research and teaching at Oxford (in particular teaching Margaret Thatcher), and she was an accomplished X-ray crystallographer who determined the structure of a steroid, of penicillin, of vitamin B12 (yielding a Nobel prize), and of insulin.

So far in this class, we've gone a long way in understanding how our world works at the chemical level: a series of experiments moved our understanding from being based in alchemy to being studied with quantum mechanics. Specifically, Dalton and Proust explained the laws of definite and multiple proportions, Marie Curie and Rutherford experimented with the makeup of atoms, JJ Thomson and GP Thomson proved the existence and wave/particle-like nature of electrons, Goudsmit and Uhlenbeck discovered electron spin, and Planck and Einstein arrived at Planck's constant in the process of understanding quantization. Schrodinger then completed the story by connecting everything with the Schrodinger equation.

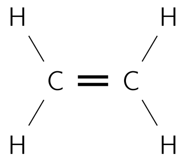
Unfortunately, doing the math becomes complicated, so we make approximations like modeling atoms with an effective nuclear charge Z_{eff} (which gives rise to periodic trends). And once we have multiple atoms which form molecules, we start understanding the different kinds of bonds that can be formed (though we'll see some more today), and furthermore how we can understand the molecular structure of these objects using molecular orbital theory, hybridization, VSEPR, and Lewis structures.

We'll do a quick example of a problem from the problem set to review some of these concepts:

Example 103

We'll run through the Lewis structure for Ethylene, C_2H_4.

We start with the skeleton structure: the two Carbon atoms must be in the middle because Hydrogen atoms are always terminal, and to form full octets we should have two hydrogens on each Carbon. We have 12 valence electrons and $8 + 8 + 2 + 2 + 2 + 2 = 24$ needed to form full shells, so we need to make 6 bonds. Four of them are made to the hydrogen atoms, so we have a double bond between the two Carbon atoms.



This uses up all of the electrons, and we have no lone pairs, so we can now move to looking at this molecule in more detail. The formal charge on all atoms is 0 (because there are as many bonds as valence electrons), and this is good because it means our molecule is stable from the formal charge perspective. (In addition, there are no resonance structures because of symmetry.) Looking at hybridization, we know that Hydrogen does not hybridize, and because there is a steric number of 3 around each Carbon we need sp^2 hybridization (and thus trigonal planar / 120 degree bond angles) for each one. Finally, this means that we have four $\sigma(C2sp^2, H1s)$ bonds between the Carbons and Hydrogens, and we need a $\sigma(C2sp^2, C2sp^2)$ bond and a $\pi(C2p_y, C2p_y)$ bond to complete the double bond (the choice of which p orbital is arbitrary and just defines the axis of the molecule).

Of course, we needed to go through all of the logic of how the bonds worked to figure out the geometric structure (we just drew them as 120 degree bonds ahead of time because we had the foresight). But in general, our Lewis structures should represent the correct angles of the molecule, and we should be able to do this faster and faster with more practice.

We're now ready to talk about "new bonds" that molecules can form, and we'll start with a familiar one:

Example 104

The geometric molecular structure of H_2O (water) is bent, with polar covalent bonds pulling electrons closer to the oxygen than to the hydrogen. In particular, because the molecule is bent, the oxygen will develop a slightly negative charge from the electron density pulled in.

We indicate this charge with a δ^- on the Oxygen (and a δ^+ on the Hydrogens). Notably, the molecule is still neutrally charged overall, but **if we bring water molecules together**, the δ^+ and δ^- charges will attract, particularly because there are lone pairs on the side of the Oxygen atom away from the Hydrogens.

Fact 105

Hydrogen bonds are marked with dashed lines, and while they are not actually traditional bonds (there are no pairs of electrons forming bonding orbitals, and there are no filled valence shells), there is some energy gained in bringing the polar molecules together.

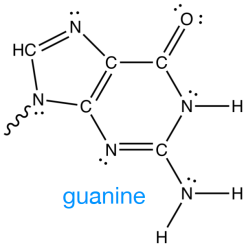
Quantitatively, an O-H bond in water has an energy of -465 kJ/mol, with a bond length of 0.96 Angstroms. On the other hand, a hydrogen bond is at a distance of about 2 Angstroms and only has an energy of about -21 kJ/mol. So we have a stable situation which comes up in a lot of real situations (for example, networks of hydrogen explain how solutions dissolve in liquids). Specifically, because water has a dipole moment (pointing from the δ^+ to the δ^- charge), it can interact with other molecules in asymmetric ways, such as Coulomb interactions and hydrogen bonding.

Fact 106

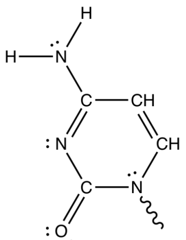
The phrase "like dissolves like" can be rephrased as "polar things like to dissolve polar things" – the idea is that asymmetric charges can interact in favorable ways. And it's also true that nonpolar molecules mix better with other nonpolar molecules (for instance, water and oil don't like to mix, and the fact that soap has both polar and nonpolar ends allows it to dissolve many more substances).

Hydrogen bonding can in fact occur whenever we have an O-H, F-H, or N-H bond in a molecule. For example, in Professor McGuire's PhD thesis work, he studies ice on the surface of interstellar dust. If water is frozen at very cold temperatures, it gets stuck in a particular orientation without getting the chance to form hydrogen bonds. But then heating it up to about 150 Kelvin allows the water molecules to rearrange (though not melt) into crystals with vast hydrogen bonding networks. And spectroscopy is able to detect when this occurs, which has useful applications to detecting temperatures around new stars.

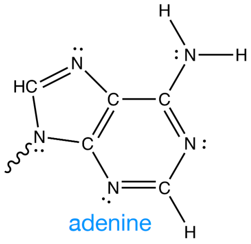
For a more familiar example, we can think about DNA. The four base pairs (adenine, cytosine, thymine, and guanine) are shown below:



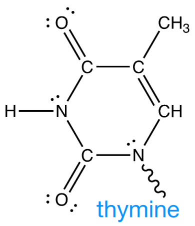
guanine



cytosine



adenine



thymine

In particular, we can form three hydrogen bonds between guanine and cytosine (left-right on the picture), and similarly we can form two hydrogen bonds between adenine and thymine (not the hydrogen at the bottom, because the C-H bond isn't polar enough). And this gives us a lot of structure in DNA – it's what keeps the two halves of the double helix together.

From here, we'll move on to three other types of molecular interactions, but they are based on the same principles as with hydrogen bonds:

Fact 107

Two polar molecules (that is, two molecules which have dipole moments) that aren't quite polar enough for hydrogen bonding can still induce **dipole-dipole** (also known as electrostatic) interactions.

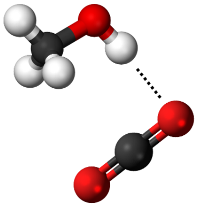
For example, formaldehyde (CH_2O) gets a partial negative charge on the O and a partial positive charge on the C because of the C-O bond (with a dipole moment pointing towards the Oxygen atom). We have no hydrogen bonding because the Hydrogen atoms are bonded to the Carbon atom, but we do get interaction between formaldehyde molecules, aligning in such a way that partial positive and partial negative charges get the maximum favorable Coulombic interaction. Again, these give **weaker interactions** than hydrogen bonds, but they're still pretty strong compared to what we'll talk about next.

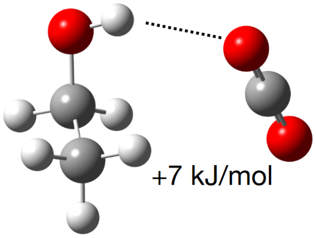
Example 108

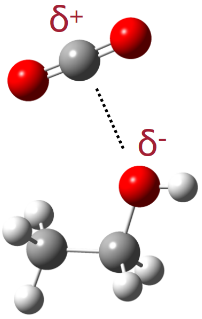
One motivation for understanding interactions between polar and non-polar molecules is in trying to **decaffeinate coffee**. In the 1900s, this was done using ammonia and benzene (which are chemicals that are very bad for us), but we want to find something that is less toxic and environmentally friendly.

Water is an example of a molecule that dissolves caffeine (that's why we brew coffee), but it's not what we use because it also removes the coffee flavor. Instead, supercritical carbon dioxide is used – we'll talk more about critical points in the second half of this course, but the idea is that it acts like both a liquid and a gas. Carbon dioxide has a slight negative charge on the Oxygen molecules and a slight positive charge on the Carbon molecules, but it is only a good way to dissolve caffeine if we combine it with an **enhancer** such as methanol or ethanol. What happens is that methanol forms a hydrogen bonding network which can include CO_2, and that polar network dissolves caffeine even at low temperatures (so that the flavor stays).

However, we don't want to taste methanol, so instead we can try using ethanol. And the idea is that Ethanol and CO_2 can interact as shown below on the right. Basically, the partially positive charge on the Carbon atom in CO_2 attracts the partially negative charge (the lone pair electrons) on the Oxygen in ethanol – this is weak but still favorable. And (compared to the hydrogen bonding structure on the left) it turns out these interactions are more favorable than the hydrogen bonds – in fact, because of the way the electron clouds line up, the hydrogen bond between CO_2 and ethanol isn't even favorable.







Professor McGuire actually figured out what was happening here using spectroscopy tools – with the picture on the right, the electrons on the Oxygen atom in ethanol **caused the double bonds in CO_2 to bend**, creating a polar CO_2 molecule, and that's what we mean by having an **induced-dipole interaction**.

We'll finish by talking about **van der Waals interactions** (also known as **London dispersion force interactions** or **induced-dipole induced-dipole interactions**):

Example 109

If we consider two argon atoms that are near each other, we expect their shapes to be completely symmetric. However, remembering that orbitals represent probabilities rather than completely evenly distributed charge, we know that **random fluctuations** will create slight dipole moments.

That's what van der Waals forces are about – these slight dipoles can then induce slight dipoles in other nearby nonpolar molecules, which creates barely-stable complexes.

Summarizing everything together, **from strongest to weakest**, we find that various ways that atoms and molecules can interact with are as follows:

- Regular molecular bonds,
- Hydrogen bonds,
- Dipole-dipole interactions, followed (barely) by induced-dipole interactions,
- Dispersion interactions.

17 March 14, 2022

Fact 110

Tu Youyou is a Chinese pharmaceutical chemist and malariologist – she was fascinated by medical treatments after contracting tuberculosis as a teenager. She took a course looking at traditional Chinese medicine from a chemical perspective, which led her to research treatment for malaria. In particular, she led her institute's research team for Project 523 (a drug-discovery program) during the Vietnam War, and then later discovered artemisinin and refined its extraction and purification. This is now the **standard for treatment in malaria**, and this work won her the Nobel Prize in 2015.

Today's lecture will begin our discussion of **thermodynamics** – we've been building up everything at the microscopic level in this class so far, tearing apart bonds and making new ones.

Definition 111

Thermodynamics discusses whether energy is released or consumed in a reaction, which explains whether a reaction happens spontaneously. On the other hand, **kinetics** explains how quickly the reaction happens and whether energy is needed to make it happen.

Example 112

Graphite and diamond are two structures of carbon, and graphite is more stable than diamond by about 3 kJ/mol (so that is a thermodynamics argument). But "diamonds are forever," and we don't see diamonds crumbling in our hands – while the conversion to graphite is spontaneous, the reason this doesn't happen comes from kinetics.

Back in lecture 10, we discussed the energetics of breaking and forming bonds – the diagram following Fact 57 explains that we can read off the bond dissociation energy (which explains how much energy is released when we form a bond between atoms). But that breaking and forming of energy is not actually the only associated energy:

Definition 113

The **bond enthalpy** of a bond ΔH_B is the change in heat that comes from a **dissociation** of a bond (when we measure at constant pressure). Specifically,

$$\Delta H = \Delta U + \Delta(PV),$$

where U is the internal energy of the system and PV is the pressure-volume energy.

For most bonds, at a fixed pressure, ΔV is very small (the volume changes by only a fall amount). Specifically, ΔH and ΔU differ by only about 1-2 percent for gasses and basically 0 percent for liquids and solids. But we'll still use

ΔH going forward, and this is because it's **more accessible experimentally** (it's easier to measure heat than actual energy associated with a bond).

Fact 114

The existence of a bond means that there is some positive bond dissociation energy, and the $\Delta(PV)$ term will not make a difference to the sign of ΔH. So **it always takes energy** (heat) **to break a bond** – in other words, bond breaking is **endothermic** (absorbing heat), while bond formation is **exothermic** (giving off heat).

We often tabulate bond enthalpies not with ΔH_B but with the **standard bond enthalpy** ΔH_B° (that is, the standard bond enthalpy at a pressure of 1 bar, which is close to 1 atm but not exactly – bar is the right unit because it is an SI unit). For example, the energy for breaking a C-H bond in CH_4, C_2H_6, CHF_3, $CHCl_3$, and $CHBr_3$ is 438, 410, 429, 380, and 377 kJ/mol, respectively – even though we have a bond between Carbon and Hydrogen in each case, the difference is that we can have different bonding interactions, changes to molecular shape, and so on. So references will usually list the **mean bond enthalpy** instead of all of these (potentially infinitely many) molecules – for a C-H bond, we usually list 413 kJ/mol (which is close but not the same as a lot of the numbers above).

Bond enthalpies will then be used to calculate the **overall enthalpy** of a reaction in which multiple bonds are broken and formed.

Definition 115

The enthalpy of a reaction at standard pressure (1 bar), denoted ΔH_r°, is the heat required to make the reaction happen.

Example 116

Consider the photosynthesis reaction $6\ CO_2 + 6\ H_2O \to C_6H_{12}\ O_6 + 6\ O_2$. Light is required for this reaction to happen – plants absorb energy from the sun – so it took energy to make these bonds, and thus the reaction is endothermic and ΔH_r° is positive (in fact 2816 kJ/mol). On the other hand, cellular respiration is the reverse reaction and is exothermic – it's what we use in our body to burn sugar and produce energy.

It then seems that if we have sugar exposed to air, we should expect lots of energy to be released (and thus the sugar should heat up and explode).

Fact 117

Professor McGuire did a "live demo" in class, passing out Hershey's Kisses in class and having us unwrap them. But our hands did not get overly hot, and that's because **the reaction is slow without enzymes to catalyze it** (there is a high activation energy). And we'll discuss the effects of kinetics later on in this course.

We can now think about how to actually calculate the reaction enthalpy, which is

$$\Delta H_r^\circ = \sum_i \Delta H_{B,i}^\circ(\text{reactants}) - \sum_j \Delta H_{B,j}^\circ(\text{products}),$$

where the first term indicates the sum of the bond enthalpies of the reactants (that is, the energy required to break bonds), and the second term indicates the sum of the bond enthalpies of the products (that is, the energy gained by forming additional bonds). So for example, if the bonds are stronger in the final products than in the reactants, we should have a **negative** ΔH_r° and the reaction should be **exothermic**.

Example 118

Let's calculate the ΔH_r° for photosynthesis. To do this, we need to know the set of all bonds broken and formed.

It turns out that we have 7 C-H bonds, 5 O-H bonds, 5 C-O bonds, 5 C-C bonds, and 1 C-O double bond in glucose. Combining that with the 6 O-O double bonds in the six O_2 molecules tells us all of the reactants, and then the carbon dioxides and waters in the products give us 12 C-O double bonds and 12 O-H single bonds. So if we add up contributions from all of these terms and look up the bond enthalpies in a table, we end up with $\Delta H_r^\circ = -2639$ kJ/mol. That's not quite the right answer as measured by experimental results (we're off by 6 percent), because the mean bond enthalpies are often off by up to about 8 percent. Indeed, even all seven of the C-H bonds in glucose have different bond enthalpies!

So our process for calculating is okay but is kind of painful and inaccurate – a better way is to use the **standard heat of formation**:

Definition 119

The **standard heat of formation** ΔH_f° is equal to ΔH_r° of a reaction which **forms** a mole of the compound from pure elements in their most stable form, at standard state (1 bar and 298 Kelvin).

In particular, because the standard heat of formation measures energies for forming molecules rather than breaking the bonds, we now have the equation

$$\boxed{\Delta H_r^\circ = \sum_i \Delta H_{f,i}^\circ(\text{products}) - \sum_j \Delta H_{f,j}^\circ(\text{reactants})}$$

(this time adding the products' heat of formation and subtracting the reactants', rather than vice versa). We can now calculate the reaction enthalpy using ΔH_f° instead. First, we calculate the ΔH_f° for water, which is the reaction enthalpy of the equation

$$H_2(g) + \frac{1}{2}O_2(g) \to H_2O(\ell).$$

(This is the equation that forms 1 mole of water from the purest forms of elemental hydrogen and oxygen.) These numbers are tabulated as well – it turns out that (experimentally) ΔH_r° is -285.83 kJ/mol. Similarly, the reaction

$$C_{gr}(s) + O_2(g) \to CO_2((g)$$

(taking graphite and oxygen gas and forming carbon dioxide gas) turns out to have a standard heat of formation of -393.5 kJ/mol. The standard heat of formation of O_2 is just 0 kJ/mol (because we're already in the most stable state), and the standard heat of formation of glucose (from combining 3 moles of oxygen gas, 6 moles of graphite, and 6 moles of hydrogen gas) is -1260 kJ/mol. Thus, we find that

$$\Delta H_r^\circ = 6\Delta H_f \circ (CO_2) + 6\Delta H_f \circ (H_2O) - (1\Delta H_f^\circ(C_6H_{12}O_6) + 6\Delta H_f^\circ(O_2)) = -2816\text{kJ/mol}.$$

This time, there are no averages or approximations – all energies of formation are experimentally derived, and this accounts for all of the pressure-volume change. So this method will give us the actually correct experimental value of the enthalpy of the reaction.

Proposition 120 (Hess's Law)

If we add two or more chemical equations together and yield a combined chemical equation, the corresponding ΔH_r°s add as well.

(The idea is that terms on the left and right side of the chemical reaction will cancel out, because the energy of forming and breaking those molecules will be opposite each other.) And that's in fact the reason why we can use the boxed equation above for finding ΔH_r°, and we'll see this kind of argument used when we add and subtract further chemical equations from each other!

18 March 18, 2022

Fact 121

Lise Mietner is an Austrian-Swedish physicist who received her PhD in physics evaluated by Boltzmann. She was the second woman ever to earn a PhD in physics and became the first full female professor of physics. Along with Otto Hahn, she discovered protactinium and nuclear fission (though only Hahn was awarded the Nobel Prize, because of bias, political turmoil, and other reasons). Einstein called her the "German Marie Curie," and we now name an element (meitnerium) after her.

If we're interested in other scientists we might know, we can search up "Half-Arsed History" by Riley Knight (particularly episodes 34, 80, 87, 91, 142, and 149 for scientists)

Today's lecture will introduce **spontaneous change**, but first we need to introduce another definition:

Definition 122

Informally, the **entropy** S of a system measures its disorder – ΔS, the change in entropy, is positive when the system becomes more disordered and negative when it becomes more ordered.

For example, the entropy S decreases when we tidy up a messy backyard into a nice garden, and it increases when kids come home from school and mess up toys in their room. But now we can think about a more chemically-motivated example:

Example 123

When ice melts into water on a hot day, we have $\Delta S > 0$, because we've changed the state of matter. Originally, we had water molecules stuck in place, either in a crystalline shape or otherwise stuck. But then once we melt the ice, those water molecules can basically move around anywhere.

Another way to increase entropy is if we imagine having some nitrogen gas confined to a small container and then allowed it to expand to the rest of the room. (There are essentially "more possibilities" for different ways the molecule can roam around.)

We can now think about how entropy affects reactions: consider the reaction of sodium bicarbonate with acetic acid (which is what we often use to form a "baking soda volcano"):

$$\mathrm{NaHCO_3\ (s) + CH_3COOH\ (aq) \to NaCh_3COO\ (aq) + H_2O\ (\ell) + CO_2\ (g).}$$

This reaction has a positive ΔS, because we have created carbon dioxide gas – gas is disorderly, because it can roam freely (unlike solids and solutions). And in general, notice that in all of the examples we've seen so far, **leaving a system on its own will increase entropy** (we're never going to get spontaneously from a state of disorder to a state of order).

Definition 124

A reaction is **spontaneous** if it proceeds in the forward direction without need for outside intervention.

For example, recall that burning glucose gave us an exothermic process (though slow if we don't have an enzyme) – it turns out that is a spontaneous reaction, and we previously calculated that ΔH_r° is negative. And similarly, creating rust out of iron and oxygen is a spontaneous reaction, and it has a negative ΔH_r°. Let's now do more specific examples: it turns out the spontaneous reaction

$$2\text{H}_2\text{O}_2\ (\ell) \to 2\text{H}_2\text{O}\ (\ell) + \text{O}_2\ (\text{g})$$

has a ΔH of -209 kJ/mol, and we have a positive ΔS (132 J/(mol · K)) primarily because of the mole of gas produced. **But on the other hand**, we have the spontaneous reaction

$$3\text{H}_2\ (\text{g}) + \text{N}_2\ (\text{g}) \to 2\text{NH}_3\ (\text{g})$$

which has a negative ΔH **but a negative** ΔS (because there's fewer moles of gas that can move around), So the trends about ΔH and ΔS aren't agreeing with each other, and we need to know what's going on.

It turns out each of $\Delta H, \Delta S$, and ΔU has some influence on whether the reaction is spontaneous:

Definition 125

The **Gibbs free energy** is defined as $\Delta G = \Delta H - T\Delta S$.

It turns out that ΔG is **negative if the reaction is spontaneous**, zero if we're at equilibrium, and positive if not spontaneous. We'll talk more about equilibrium later on, but what's good is that we can calculate the balance between enthalpy and entropy to see whether a reaction is spontaneous.

Fact 126

We've previously calculated that for burning glucose, $\Delta H_r^\circ = -2816$ kJ/mol by calculating the sum of the standard $\Delta H_{f,i}^\circ$s for the products, and subtracting **from that** the sum of the $\Delta H_{f,i}^\circ$s for the reactants. The same kind of formula works if we're trying to calculate the standard entropy, and values for different common molecules can be found in tables along with that for enthalpy.

Example 127

Looking up the values of S_i° for our products and reactants, we find that $\Delta S_r^\circ = 259.06$ J/(mol · K) (note that this is in joules and not kilojoules, and that we have an extra Kelvin in the denominator). So regardless of the value of T, this reaction is always spontaneous because ΔH and $-T\Delta S$ are both negative.

Example 128

On the other hand, if we look at the reaction that melts ice into water, we can find that $\Delta H_r^\circ = 6.01$ kJ/mol and $\Delta S_r^\circ = 22.0$ J/(mol ·K). The cutoff for which $\Delta G = \Delta H - T\Delta S = 0$ is exactly at $T = 273.15$ K, and indeed a glass of ice water can coexist for a long time at 0 degrees Celsius.

We can also account for the fact that ice melts at different temperatures by noting that ΔH_r° and ΔS_r° are calculated here at **standard pressure** – those values do change depending on the pressure of the system.

Example 129

When we bake a cake, the activity of rising agents (like baking powder or baking soda) is different depending on the temperature of our oven. We can understand that by analyzing the decomposition reaction 2NaHCO_3 (s) $\rightarrow$ Na_2CO_3 (s) + CO_2 (g) + H_2O (g) (the carbon dioxide is what creates air pockets and the fluffy texture of a cake).

We can search up the ΔH_f° heats of formation for each of these products and reactants. From left to right, they're $-950.81, -1130.68, -393.51, -241.82$ kJ/mol respectively, and thus calculating gives us $\Delta H_r^\circ = 135.61$ kJ/mol for the reaction. On the other hand, the standard entropy values of these molecules are $101.70, 134.98, 213.63, 188.72$ J/(mol · K), which gives us $\Delta S_r^\circ = 333.93$ J/(mol · K). We then find that ΔG_r° is positive at room temperature (so that baking soda doesn't vaporize in our cabinets), but ΔG_r° becomes negative starting around 406 Kelvin, which is around 270 degrees Fahrenheit. So that's the point at which baking soda starts to make an effect on our cake!

But there's a better way to calculate ΔG than doing that complicated calculation – it turns out that calculations for ΔG_f° of formation are done for common products and reactants. For example, consider this reaction that we talked about even back on the first day of class:

$$3\ \text{NO (g)} \rightarrow \text{N}_2\text{O (g)} + \text{NO}_2\ \text{(g)}$$

We're told that the ΔG_f°s at 25 degrees Celsius are $86.55, 104.18$, and 51.29 for these three molecules, so we find that $\Delta G_r^\circ = 104.18 + 51.29 - 3(86.55) = -104.18$ kJ/mol. And after spring break, we'll see how these values can be useful as we discuss more properties of equilibrium and reactions!

19 March 28, 2022

Professor Mei Hong will teach the second half of this course – so far in 5.111, we've studied atomic structure and the periodic table through tools of quantum mechanics, and then we thought a bit about chemical bonding and thermodynamics. In the rest of this course, we'll discuss reaction equilibrium, acid base and oxidation-reduction reactions, transition metals, and chemical reaction kinetics.

Fact 130

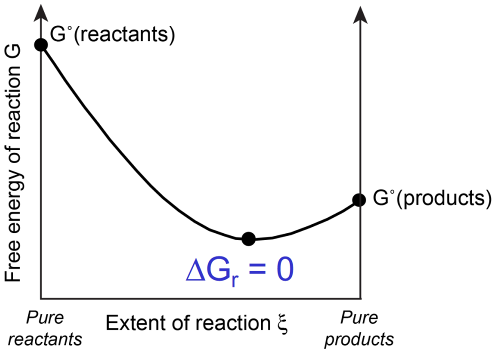
Professor Hong's lab studies biological systems (like proteins and carbohydrates), using NMR spectroscopy to deduce facts about protein dynamics and structures, particularly related to infectious and neurodegenerative diseases.

We'll start by thinking about **chemical equilibrium** today. We often write chemical reactions as only moving in one direction, but when we think about equilibrium, we now want to think about the arrow being directional – reactants can form products, but products can dissociate back into reactants as well. The idea is that chemical reactions don't keep happening in one direction until completion – instead, if the **rates of forward and reverse reactions are equal**, then there is no net change in composition and it looks like we have reached a stable equilibrium. We often denote reactions with the $\rightleftharpoons$ symbol instead of the $\rightarrow$ symbol for this reason.

Example 131

Consider the ammonia synthesis equation $N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$. The Gibbs free energy G tells us the direction of chemical reaction (proceeding to the right if $\Delta G < 0$), and we're now going to talk about how to use these ideas to determine the equilibrium composition of these different compounds.

Recall that we define $G = H - TS$, where H is the enthalpy and S is the entropy of the reaction (so that the change in Gibbs free energy for a reaction at fixed temperature is $\Delta G = \Delta H - T\Delta S$). Conceptually, the diagram below shows the free energy across different extents of the reaction (the **reaction coordinate** is all the way to the left if we only have reactants, and it's all the way to the right if we only have products):



The idea is that **if we start with pure reactants, going downhill decreases the Gibbs free energy**, so the reaction will proceed spontaneously until we get to the minimum point marked with a $\Delta G_r = 0$. On the other hand, if we start with pure products, the reverse reaction will be spontaneous instead, so in either case we will tend towards reaction. This motivates the following definition:

Definition 132

Let ξ be the reaction coordinate. The slope of the Gibbs energy at a constant temperature T and pressure P is

$$\Delta G_r = \left(\frac{\partial G}{\partial \xi}\right)_{T,P}.$$

In particular, ΔG_r is negative on the left and positive on the right.

Our sketch above showed G having a minimum, and this indeed always qualitatively happens for any reaction – essentially what's happening is that **more disorder occurs** when we have a mixture of reactants and products, so the higher entropy lowers the Gibbs free energy $H - TS$ (this is known as **entropy of mixing**). This then leads to the following numerical consideration:

Theorem 133
The Gibbs energy of the reaction is given by

$$\Delta G_r + \Delta G_r^\circ + RT \ln Q,$$

where ΔG_r° is the difference in Gibbs energy of formation at standard states (pure, at pressure 1 bar for gasses, 25 degrees Celsius), Q is the **reaction quotient**, R is the ideal gas constant, and T is the absolute temperature.

This **reaction quotient** is the important quantity for us to study now, and it basically takes into consideration the relative concentrations of the reactants and products:

Definition 134
For a gas-phase reaction, if we have a reaction of the form $a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D}$ (where a, b, c, d are stoichiometric coefficients and A, B, C, D are molecules), then we have

$$Q = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b},$$

where P_A, P_B, P_C, P_D indicate the partial pressure in units of 1 bar as reference. On the other hand, for a solution reaction, we have

$$Q = \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b},$$

where [A], [B], [C], [D] indicate the numerical molarities of the various products and reactants.

In particular, at equilibrium, because $\Delta G_r = 0$, we have

$$0 = \Delta G_r^\circ + RT \ln Q \implies Q = e^{-\Delta G_r^\circ/(RT)}.$$

At equilibrium, we denote the reaction quotient (that is, the equilibrium constant) by K or K_{eq}.

Definition 135
For any reaction and at any fixed temperature T, the equilibrium constant is given by the equation

$$\Delta G_r^\circ = -RT \ln K_{\text{eq}}.$$

In other words, we calculate the equilibrium constant by looking at pressure or molar concentrations at equilibrium. And we have the **law of mass action** – **regardless of initial concentration**, the reaction will proceed forward or backward until this K_{eq} is reached. But notice that the values of [A], [B], [C], [D] aren't fixed and can depend on the total amount of reactants and products that we start with.

Proposition 136
Notice that in an expression like $\frac{[\text{C}]^c[\text{D}]^d}{[\text{A}]^a[\text{B}]^b}$, moving forward increases the numerator and decreases the denominator, and vice versa. So K_{eq} is more than 1 when we have more products than reactants at equilibrium, and it is less than 1 when we have more reactants than products.

Plugging this back into our equation, we can calculate the ΔG_r (slope of the Gibbs energy as a function of the reaction coordinate) by substituting back in:

$$\Delta G_r = -RT \ln K_{\text{eq}} + RT \ln Q = RT \ln \frac{Q}{K_{\text{eq}}}.$$

So for any reaction, if we're given the K_{eq}, and we know the molarities or pressures from the reactants and products, we can compare Q to K_{eq}. If $Q < K$, ΔG_r is negative, and the reaction will proceed generally in the forward direction. On the other hand, if $Q > K$, ΔG_r is positive, and reverse reaction will primarily occur.

Example 137

Thinking back to our ammonia synthesis equation $N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g)$, suppose we know that $K_{\text{eq}} = 1.9 \times 10^{-4}$ at 400 degrees Celsius (the temperature for a nitrogen fixation reaction industrially), and suppose that the pressures from nitrogen, hydrogen, and ammonia are 5.5, 2.2, and 1.1 bar. Then the reaction quotient $Q = \frac{1.1^2}{2.2^3 \cdot 5.5} = 2.1 \times 10^{-2}$ is large compared to the equilibrium constant K_{eq}, so "there are too many reactants" and the reaction will proceed in the reverse direction.

We'll now have to do a more complicated calculation:

Problem 138

Consider the reaction $2\ NO_2(g) \rightleftharpoons N_2O_4(g)$. Suppose that $\Delta G_r^\circ = -4.76$ kJ/mol, so that $K_{\text{eq}} = 6.84$ at 298 Kelvin (room temperature). If we start with 1 bar of NO_2 as reactant and no products, how much $N_2O_4(g)$ do we expect?

Initially, we know that the partial pressure from NO_2 is 1 bar, and the partial pressure from N_2O_4 is 0 bar. Thus, as the reaction proceeds, the partial pressures from the reactants and pressures will be $1 - 2x$ and x, respectively (since 2 moles of reactants give us 1 mole of products). (We may have heard of this from high school chemistry as the "ICE table".) We then have an equilibrium constant which must satisfy

$$K_{\text{eq}} = 6.84 = \frac{P_{N_2O_4}}{(P_{NO_2})^2} = \frac{x}{(1-2x)^2}.$$

(Notice that the initial reaction quotient is $\frac{1}{0^2} = \infty$, and as the reaction proceeds forward the quotient decreases.) Solving this requires solving a quadratic equation, and we find that $x = 0.381$ bar, so the partial pressure from N_2O_4 is 0.381 bar and the partial pressure from NO_2 is 0.238 bar – in other words, as the reaction proceeds, the total pressure of the gas has decreased.

Now that we've discussed the numerical details of the equilibrium constant, we can look again at the equation

$$\Delta G_r^\circ = -RT \ln K_{\text{eq}} \implies K_{\text{eq}} = e^{-\Delta G_r^\circ/(RT)}$$

(remember that ΔG_r° is something we can look up in thermodynamic tables). In particular, if ΔG_r° is **very negative** (the reaction is spontaneous at standard conditions), then K_{eq} will be large. This should make sense conceptually to us: both ΔG_r° being negative and K_{eq} being large indicate that the "minimum point" for G is heavily shifted towards the products (the right of the diagram), so that at standard conditions the reaction proceeds forward.

Example 139

The thermal decomposition of baking soda (sodium bicarbonate) has ΔG_r° equal to 36 kJ/mol at room temperature (corresponding to $K_{\text{eq}} = 4.9 \times 10^{-7}$ and -15 kJ/mol at 450 Kelvin (corresponding to $K_{\text{eq}} = 55$). So that's why we can make cookies when the temperature is higher, and we should notice that K_{eq} is **extremely** temperature-dependent.

Finally, notice that if we have a reaction at equilibrium and then remove some of the products, that decreases the reaction quotient Q (since the terms in the numerator decreased). Thus $Q < K$, and the reaction will shift towards the right. And we'll see more of this discussion of changes to reactions under external stress next lecture!

Fact 140

The first two Nobel Prizes in chemistry were actually awarded because of chemical equilibrium research – van't Hoff "discovered the laws of chemical dynamics and osmotic pressure in solutions," and Ostwald understood the "fundamental principles governing chemical equilibria and rates of reaction."

20 March 30, 2022

Fact 141

Class started today by watching the video Chemists Know.

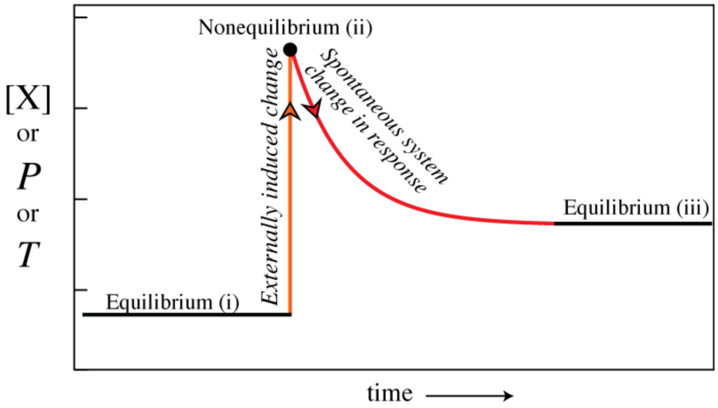
Last lecture, we analyzed chemical equilibrium from the point of view of ΔG_r, which we can essentially think of as the slope of the Gibbs free energy G as a function of the reaction coordinate ξ. Specifically, we found that $\Delta G_r = \Delta G_r^\circ + RT \ln Q$, where Q is the reaction quotient (molarities or pressures of products in the numerator and reactants in the denominator, with exponents given by stoichiometric coefficient.) The law of mass action basically says that we always end up with a reaction quotient Q of K_{eq}.

Today, we'll analyze Le Chatelier's principle, which explains how conditions like pressure, volume, and temperature will change the equilibrium composition of a reaction. And once we understand the influence of temperature T, ew'll try to figure out how to calculate K_{eq} at temperatures other than the standard 298.15 K that we find in thermodynamic tables.

Proposition 142 (Le Chatelier's principle)

If a system is instantaneously changed from an initial equilibrium (i) to a new equilibrium (ii), then the system will adjust so that the new equilibrium partially offsets that change.

The diagram below gives a schematic of what we should imagine, where the disruption or change can be a change in pressure, temperature, or concentration of a reactant or product. Indeed, we see that the new equilibrium has shifted towards the direction of the change, but the approach to equilibrium is in the opposite direction of the spontaneous change:



Example 143

Suppose we have the reaction $N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g)$, and we add some additional hydrogen gas after reaching equilibrium. Then the new equilibrium partial pressure of hydrogen gas should be higher than before (like in the diagram above), and the other reactants and products will adjust based on which way the reaction proceeds (forward in this case, so we have less N_2 and more NH_3). And because we have the same reaction, the law of mass action tells us that K_{eq} **should still be the same**, even though the partial pressures of individual terms have changed. (Another way of thinking of this is that when we added hydrogen, we increased the denominator of the reaction quotient Q, so the reaction needs to proceed forward to reach equilibrium again.)

We'll now think about other external changes which we can't reason about so directly:

Fact 144

If we decrease the volume of a gaseous reaction (and don't change the temperature), then the pressure exerted by the mixture will increase (because the ideal gas law tells us that $PV = nRT$ should be constant). Thus, Le Chatelier's principle should have the system **reduce** the pressure by creating fewer gas molecules.

Example 145

Consider the reaction $2\ P_2(g) \rightleftharpoons P_4(g)$ inside an enclosed vessel. If we compress the vessel, then because the forward reaction gives us fewer gas molecules colliding with the wall, Le Chatelier's principle tells us that pressure will be reduced by having the reaction shift to (proceed towards) the right. Similarly, if we expand the vessel, then the reaction will shift to the left.

More quantitatively, if the volume is cut in half, then we expect the pressure to double, which means that the partial pressures of P_{P_4} and P_{P_2} have both increased by a factor of 2. Thus Q has gotten smaller (because the numerator has increased by a factor of 2, while the denominator has increased by a factor of 4), and $\Delta G_r = RT \ln \frac{Q}{K}$ is now **negative**. So the reaction will indeed move forward.

Example 146

Now suppose that we add an inert (non-interacting) gas to our container in the reaction above, which keeps the temperature and volume constant but increases the total pressure. Then because the **partial** pressures in the expression for the reaction quotient Q do not change, so there is no change to the equilibrium at all. On the other hand, if we add an inert gas while keeping the total pressure constant, we must have expanded the container and thus reducing the partial pressures, requiring the reaction to shift to the left.

However, none of the examples above have changed the equilibrium constant K_{eq} itself, because the temperature has not changed (remember that the law of mass action says that at any given fixed temperature, ΔG_r does not change). Let's now see how Le Chatelier's principle applies for temperature changes:

Fact 147

Increasing the temperature of an equilibrium mixture causes the reaction to shift to **absorb some of that heat**. In particular, for an exothermic reaction (where heat is released, so that the molecules have cooled down), raising the temperature causes the reaction to shift backwards, and for an endothermic reaction (where heat is taken in, so that molecules gain heat), raising the temperature causes the reaction to shift forward.

Example 148

Consider the reaction $2\text{ SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{ SO}_3(\text{g})$, where $\Delta H_r^\circ = -197.8$ kJ/mol. Because this reaction releases heat to the environment, if heat is added to the system, the reaction should shift to the left.

We can now take a more mathematical look at this conceptual thinking to understand how the equilibrium constant depends on temperature: recall that we've derived the equations

$$\Delta G^\circ = -RT \ln K_{\text{eq}} = \Delta H^\circ - T\Delta S^\circ \implies \ln K_{\text{eq}} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}.$$

Notice that there is **no temperature-dependence** on the entropy term – if we assume that ΔH° and ΔS° themselves are independent of temperature, which is a reasonable assumption to make, then the dependence of the equilibrium constant is proportional to $e^{-\Delta H^\circ/(RT)}$ and also to $e^{\Delta S^\circ/R}$. So if we look at the same reaction at two temperatures T_1 and T_2, we find that the equilibrium constants K_1 and K_2 at those two temperatures satisfy the following equation:

Proposition 149 (Van't Hoff equation)

The equilibrium constants K_1 and K_2 for a reaction at temperatures T_1 and T_2 satisfy

$$\ln \frac{K_2}{K_1} = -\frac{\Delta H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right).$$

Indeed, we can check that if we have an exothermic reaction (with $\Delta H^\circ < 0$), then increasing the temperature to $T_2 > T_1$ makes the right-hand side negative, which makes $\frac{K_2}{K_1} < 1 \implies K_2 < K_1$. In other words, increasing temperature gives us **fewer products** at equilibrium, which is indeed what we qualitatively argued above. (And we can do a similar check for other cases: if $\Delta H^\circ > 0$ so that we have an endothermic reaction, the right-hand side will be positive for an increase in temperature, so that $K_2 > K_1$. So the reaction will shift towards the products.)

As an application, we can now think about using this type of principle to **maximize the yield** of a reaction:

Example 150

Thinking back at the Haber-Bosch process $N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g)$, which has $\Delta H_r^\circ = -92.2$ kJ/mol at room temperature, it turns out that $\Delta G_r^\circ = -32.9$ kJ/mol at room temperature. So this reaction does produce ammonia favorably, but unfortunately the kinetics are slow at room temperature. It turns out the compromise temperature that is usually used to produce ammonia is 500° Celsius, where we have $\Delta G_r^\circ = 61.6$ kJ/mol but the kinetics are fast enough. In order to still drive this reaction towards products, we can decrease the volume of the vessel in which the process occurs, or we can remove products as they are being made to continually shift the reaction in the direction that we want.

Example 151

Hemoglobin is a molecule that carries oxygen through the blood through the reaction $\text{Hb (aq)} + O_2\text{(aq)} \rightleftharpoons HbO_2\text{(aq)}$. The partial pressure of oxygen is lower when we go to higher altitudes (from about 0.2 atm to 0.14 atm when we go from sea level to 9840 ft – 0.14 atm is considered almost dangerous for human level), so at high levels the body will produce more hemoglobin (adapation over a few months) to re-establish equilibrium and produce enough HbO_2.

21 April 1, 2022

Fact 152

We'll be starting Scientists You might Not Know again, looking at Barbara McClintock, an American geneticist. She studied gene expression in maize, creating the first genetic map in 1931, and she was the one who suggested the ideas of genetic recombination and crossover during meiosis. It took until the 1970s for her work on controlling genetic elements of maize ("lac operons" are the relevant words here) in the 1950s to be understood, and she won the Nobel Prize in 1983 for it.

Last lecture, we mentioned that external perturbations to equilibrium make reactions shift to offset (minimize) that perturbation. We looked in particular at changes in pressure, volume, and temperature for gaseous reactions, and we also understood the temperature dependence of the equilibrium constant K_{eq} from the van't Hoff equation.

Today, we'll shift to thinking about some aspects of aqueous reactions, namely **solubility, acids, and bases**.

Definition 153

A **solution** is a homogeneous mixture (of solids, liquids, and gases).

Example include a seawater (a mixture of water and dozens of salts), blood (many proteins and small molecules in water), air (nitrogen, carbon dioxide, and other gases), or brass (copper and zinc in a solid solution). But we'll mostly think about liquid-state solutions in this class, and we're curious about when solutions can be formed (particularly solubility of solids and gases in liquids). We call the base liquid the **solvent** and the other materials dissolved in it the **solute**.

Fact 154

Solvation (dissolving a solute into a solvent) occurs spontaneously if the solvent-solute attraction is stronger than the solute-solute and solvent-solvent interactions.

For example, if we have an **ionic compound** (containing a cation and an anion), the polarity of water molecules will pry the ions away from each other, and the hydrogen atoms will favor interaction with the anions and oxygen atoms favor interactions with cations, creating an **ion-dipole interaction**. On the other hand, if we look at a **non-ionic compound** like glucose, there are many potential hydrogen bond donors and acceptors, and we get a favorable **hydrogen-bonding interaction**. (So that's why salt and sugar both dissolve in water.)

Fact 155

In general, **like dissolves like** – polar liquids like water are good solvents for ionic and polar compounds, while nonpolar liquids like hexane are good solvents for nonpolar compounds.

We can now remind ourselves of the different kinds of molecular interactions at play for different kinds of mixtures (ion-dipole, dipole-dipole, hydrogen bonding, and dispersion):

Example 156

Salt and water mix because of ion-dipole interactions, alcohols and water mix because dipole-dipole interaction and hydrogen bonding, and CCl_4 and benzene mix pretty well because of dispersion interactions.

Fact 157

Stronger interactions between solvents and solutes lead to higher **solubility**.

Example 158

Isoprene (natural rubber) is a nonpolar molecule, so it is much less soluble than glucose in water. Furthermore, sodium chloride (table salt) is even more soluble because of the stronger ion-dipole interactions. On the other hand, this ranking is reversed if we want solubility in a nonpolar substance like *n*-hexane.

To get a more quantitative statement about how much dissolution is possible, we say that a solution is **saturated** when there is undissolved solute remaining because the solvent has dissolved all that it can. In such a situation, the dissolved and undissolved solute are actually in dynamic equilibrium (some molecules are going into the solution phase, while others are exiting it; at equilibrium these rates are the same and the composition doesn't change).

Definition 159

The **molar solubility** is the molar concentration (in moles per liter, also denoted M) of a solute in a saturated solution.

We can speak about "equilibrium constants" for dissolving a solid into a solvent, but the concentration of the solid does not factor into the **equilibrium solubility product** K_{SP}.

Example 160

If we have the reaction $BaSO_4((s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$, starting with just solid $BaSO_4$, at equilibrium we'll have a molarity s (moles per liter) of each aqueous ion. Thus, we find that

$$K_{SP} = [Ba^{2+}][SO_4^{2-}] = s^2.$$

These solubility products are in thermodynamic tables – in this case it's about 1.1×10^{-10}, so we find that $s = 1.05 \times 10^{-5}$ M (only a miniscule amount of dissolution).

Example 161

On the other hand, consider a reaction like $Ag_2CO_3(s) \rightleftharpoons 2Ag^+(aq) + CO_3^{2-}(aq)$. Since each mole of silver carbonate gives us 2 moles of Ag^+ and 1 mole of CO_3^{2-}, we have $K_{SP} = (2s)^2 \cdot s = 4s^3$ if the reaction proceeds forward with a molarity of s. (In particular, **notice that the factor of** 2 **factors into the solubility product in two ways!)**

Just like in our reaction quotient considerations, we can do the same thinking process comparing Q to K_{SP}: the reaction is **unsaturated, saturated, or supersaturated** depending on whether Q is less than, equal to, or more than the equilibrium solubility product. (And supersaturation can occur, because changing temperature can affect the solubility of a solute in a solvent. So we can temporarily get more products and change the temperature back to create a temporary supersaturated state.)

Thinking more about thermodynamic quantities, the entropic component ΔS° of dissolving a solid is typically favorable. But to calculate ΔH° for the solution, we measure the situation **calometrically** by measuring the amount of heat absorbed or released at a constant pressure. (If heat is released, that means ΔH° is negative, and if heat is absorbed, then ΔH° is positive.) And for example, in an instant cold pack, dissolving NH_4Cl or NH_4NO_3 gives us a positive ΔH° (endothermic reaction).

So to determine spontaneity, we need to calculate $\Delta G_{sol} = \Delta H_{sol} - T\Delta S_{sol}$. We mentioned that entropy generally increases when we dissolve a solid (more disorder), we expect that the dissolving of a substance will become more favorable at higher temperatures. (In particular, dissolution will always be spontaneous if $\Delta H_{sol} < 0$, and otherwise we require $T\Delta S > \Delta H_{sol}$ for spontaneity.)

We'll now talk about general **solubility trends**, specifically looking at salts in aqueous solutions.

Fact 162

Anions and cations are not very soluble if they are more than monovalent (such as S^{2-} or CO_3^{2-}), except for SO_4^{2-}. Sodium, potassium, and ammonium salts are soluble, while silver, lead, or mercury salts are quite insoluble. And more generally, K_{SP} tells us about the solubility (higher means more soluble).

Example 163

If we consider the salts NaCl and AgCl, their K_{SP} values are 38 and 1.8×10^{-10}, respectively. This means that the standard Gibbs energy ΔG°_{sol} is very negative for NaCl and very positive for AgCl.

To understand this, we should note that whenever we have an ionic compound, we need to break apart the solid lattice structure into gaseous ions (which has a positive **lattice enthalpy**) and then hydrate those ions into aqueous state (which has a negative **enthalpy of hydration**). It turns out that the lattice enthalpy and enthalpy of hydration are 787 kJ/mol and -783 kJ/mol overall, so $\Delta H^\circ_{\text{sol}}$ is 4 kJ/mol overall; adding this to the $T\Delta S^\circ$ of -10 kJ/mol at room temperature gives us an overall spontaneous reaction. But for AgCl, the enthalpies of the partial reactions are 916 kJ/mol and -850 kJ/mol, so overall the ΔG° for that dissolution is much more possible.

Fact 164

It turns out that substances tend to dissolve more quickly at higher temperature, but not necessarily that they are more soluble. In particular, solids are generally more soluble at higher temperature, while gases are less soluble (gas molecules are more disordered in the gas phase).

This leads us to **Henry's law**, which tells us that the **solubility of a gas in aqueous solution is directly proportional to its partial pressure**. (Basically, what's happening is that the pressure is proportional to the rate at which gas molecules hit the surface of the solvent.) We can write this as

$$s = k_H P,$$

where k_H is **Henry's constant** (depending on the particular gas and also on the temperature at which we are dissolving).

Example 165

Oxygen solubility in water is given by $k_{O_2} = 1.3 \times 10^{-13}$ mol/(L atm). At Bear Lake in the Rocky Mountain National Park, the partial pressure of oxygen is about 0.14 atm, so the molar concentration of oxygen in the lake (by multiplication) is about 0.18×10^{-3} M. It turns out that aquatic life can exist with an oxygen concentration of 0.13×10^{-3} M, so there is fish in that lake.

We'll now get started with acid-base chemistry, which we'll dive into next week as an application of chemical equilibrium. We may remember that pH is a measure of how acidic a substance is, and there are many different definitions of acidity:

Definition 166

An **Arrhenius acid** is a substance that increases the H^+ (hydrogen ion) concentration in water, and an **Arrhenius base** is a substance that increases the OH^- (hydroxide) concentration.

Schematically, the reaction going on with an acid is that

$$\text{AH (aq)} + \text{H}_2\text{O } (\ell) \to \text{H}_3\text{O}^+\text{(aq)} + \text{A}^-\text{(aq)},$$

creating more hydrogen ions, and the reaction for a base is that

$$\text{BOH (aq)} \to \text{B}^+\text{(aq)} + \text{OH}^-\text{(aq)},$$

creating more hydroxide ions.

Definition 167

A **Brønsted-Lowry acid** donates a proton H^+, while a **Brønsted-Lowry base** accepts a proton H^+ (these are not restricted to aqueous solutions).

Definition 168

Acids and bases also have **conjugate bases and acids** (respectively), corresponding to removing (donating) or adding (accepting) a H^+ ion.

Based on this, we'll think more about acid-base neutralization and other related concepts next week!

22 April 4, 2022

We'll discuss pH and other aspects of acid-base chemistry today, understanding strengths of acids and bases and how weak acids and weak bases reach aqueous equilibria.

Fact 169

Marie Maynard Daly was an American biochemist who was the first African-American woman to receive a PhD in chemistry (in 1947 from Columbia). She studied cholesterol and its effect on the heart, sugar on the arteries, and age on the cardiovascular system, as well as histones (which are proteins important for gene expression), nucleic acid structure (determining the base composition of DNA).

Last lecture, we introduced the definition of Arrhenius and Brønsted-Lowry acids: for example, HCl is an acid because we donate a proton via the equation $\mathrm{HCl\ (g) + H_2O\ (\ell) \to H_3O^+(aq) + Cl^-(aq)}$, and similarly $\mathrm{NH_3}$ is a base because it reacts with water via the equation $\mathrm{NH_3(aq) + H_2O(\ell) \to NH_4^+(aq) + OH^-(aq)}$. Combining these two reactions gives us an **acid-base neutralization reaction**

$$\mathrm{HCl\ (g) + NH_3(g) \to NH_4^+(s) + Cl^-(s)}.$$

We'll now apply this to something that is not a strong acid: acetic acid (in vinegar) is the compound $\mathrm{CH_3COOH}$, which reacts with water to create a hydronium ion ($\mathrm{H_3O}$) and acetate:

$$\mathrm{CH_3COOH(aq) + H_2O(\ell) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)}$$

We can then think $\mathrm{CH_3COO^-}$ as the **conjugate base** of the original acid $\mathrm{CH_3COOH}$ (formed when an acid donates a $\mathrm{H^+}$), and we can think of $\mathrm{H_3O^+}$ as the **conjugate acid** of $\mathrm{H_2O}$ (formed when we accept a $\mathrm{H^+}$).

Let's now look at another equation, coming from taking carbonic acid and removing one of its protons: we can proceed through either of the two reactions

$$\mathrm{HCO_3^-(aq) + H_2O(\ell) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq)}.$$

$$\mathrm{HCO_3^-(aq) + H_2O(\ell) \rightleftharpoons H_2CO_3(aq) + OH^-(aq)}.$$

This is an example of an **amphoteric** molecule, which can be either an acid or a base depending on the conditions of the reaction.

We'll now introduce a third definition of acids and bases, but which we will not use much in the rest of the course:

Definition 170

A **Lewis acid** is a species that accepts lone-pair **electrons**, and a **Lewis base** is a species that donates lone-pair electrons.

In particular, this gives us definitions of acids even if there are not hydrogen ions: for example, BF_3 and NH_3 can react and combine, in which BF_3 accepts the lone pair of electrons from NH_3. So BF_3 is a Lewis acid, and NH_3 is a Lewis base.

Fact 171

Water is amphoteric, because protons can be transferred between water molecules – this makes water a central story in much of what we're going to talk about. Specifically, consider the equation

$$H_2O(\ell) + H_2O(\ell) \rightleftharpoons H_3O^+(aq) + OH^-(aq).$$

The first water molecule on the left-hand side is then an acid corresponding to the the hydroxide ion OH^-, and the second molecule is then a base corresponding to the hydronium ion H_3O^+.

It makes sense to then ask about the equilibrium constant for this reaction (known as **water autoprotolysis)**: specifically, if we have a glass of water, we may want to know what fraction of the molecules exist as H_2O versus hydronium versus hydroxide. In this case, the equilibrium constant is $K_{eq} = [H_3O^+][OH^-]$ (water doesn't show up because it's the base liquid), and it turns out that $\Delta G^\circ = 79.89$ kJ/mol. Remembering that $\Delta G^\circ = -RT \ln K_{eq}$, we should expect the equilibrium constant to be very small, and indeed plugging in the numbers gives us $\boxed{K_{eq} = 1.0 \times 10^{-14}}$ at room temperature. If we just have a plain glass of water, we know that the concentrations of H_3O^+ and OH^- must be equal, we find that the concentration is 10^{-7} M – in other words, we have about 1 water molecule in tens of millions that is actually ionized, which is tiny.

This motivates a log-based scale for keeping track of ionization:

Definition 172

The **pH** and **pOH** of a water-based solution are given by (note that we take **base 10 log**)

$$\text{pH} = -\log[H_3O^+], \quad \text{pOH} = -\log[OH^-].$$

We can also define $\text{p}K_w = -\log K_w$ for the water autoprotolysis reaction (which is 14 at room temperature).

In particular, after taking a logarithm of the equilibrium constant reaction, we have the relation

$$\text{pH} + \text{pOH} = 14.0$$

at room temperature. And in any aqueous phase acid-base chemistry question, that equation above must always hold, even if there are other reactions at play.

Proposition 173

If the concentration of hydronium ion of a solution satisfies $[H_3O^+] > 10^{-7}$, then the pH is lower than 7 and the solution is acidic. Similarly, decreasing the concentration of H_3O gives us a pH higher than 7 and a basic solution.

Fact 174

Orange juice has a pH of between 2 and 3, coffee has a pH around 5, and blood has a pH around 7.4. On the other hand, ammonia and bleach are very basic and have pH around 12.

The classical reference points are that 1 M of HCl and NaOH have pH of 0 and 14, respectively, because they completely dissociate into ions – that's what we call a **strong acid**. But there are other acids that are weaker, and we can think about that with the following concept:

Definition 175

The **acid dissociation constant** for an acid AH undergoing the reaction $AH(aq) + H_2O(\ell) \rightleftharpoons H_3O^+(aq) + A(aq)$ is given by the "equilibrium constant"

$$K_a = \frac{[H_3O^+][A]}{[AH]}.$$

For example, $K_a = 1.76 \times 10^{-5}$ for acetic acid, so only a small fraction of acetic acid molecules will donate the proton, meaning that acetic acid is a **weak acid** (far from being completely dissociated). On the other hand, HCl has a K_a of about 1×10^7 – generally a K_a larger than 1 indicates a strong acid.

Definition 176

We also define a log scale for the acid dissociation constants:

$$pK_a = -\log K_a.$$

In particular, a large value of pK_a means that K_a is pretty small, so there is not much dissociation and the acid is quite weak. (And we can often find pK_a values in textbooks – super strong acids have negative values of K_a, such as HI, HBr, $HClO_4$, and HCl. The reference point is that H_3O^+ has a pKa of zero.)

Definition 177

The **base ionization constant** for an acid B undergoing the reaction $B(aq) + H_2O(\ell) \rightleftharpoons BH(aq) + OH^-(aq)$ is given by the "equilibrium constant"

$$K_b = \frac{[BH][OH^-]}{[B]}.$$

We also define $pK_b = -\log K_b$.

For example, for the base ammonia NH_3, K_b is about 1.8×10^{-5}, so we have a weak base, and a large value of pK_b means we have a **weak** base. (So this is not the same as the pH scale – small values indicate strong dissociation / ionization for both acids and for bases.) In particular, if we look at an equation like

$$HA\ (aq) + H_2O(\ell) \rightleftharpoons H_3O^+(aq) + A^-(aq),$$

which is the dissociation reaction for the acid HA, we can realize that for a strong acid like HCl, the reaction will proceed very far forward and the reverse reaction will not occur very strongly. So Cl^- is a very weak conjugate base. More quantitiatively, realizing that if we look at the K_a and K_b reactions for a conjugate acid AH and base A, we have

$$K_a K_b = \frac{[H_3O^+][A]}{[AH]} \cdot \frac{[AH][OH^-]}{[A]} = [H_3O^+][OH^-] = K_w.$$

So taking logs again, we find that

$$\boxed{pK_a + pK_b = pK_w = 14.0}$$

at room temperature. So this gives us a quantitative way of explaining why a weaker acid leads to a stronger base and vice versa – it's not possible for an acid/base and its conjguate base/acid to both be strong (and have a negative pK_a and pK_b).

We'll now walk through and start to describe **different types** of acid-base problems, in which we take a K_a or K_b value and try to determine the pH:

1. **Weak acid in water**: as an example, consider ascorbic acid (Vitamin C), which has a K_a of 8.0×10^{-5}. Suppose we're asked to calculate the pH when we dissolve 500 mg of Vitamin C in 100 mL of water. The acid dissociation reaction is then $HC_6H_7O_6(aq) + H_2O(\ell) \rightleftharpoons H_3O^+ + C_6H_7O_6^-(aq)$. The initial molarity can be calculated by stoichiometry to be 0.0284 M – if the reaction proceeds forward with x M, we end up with

$$K_a = 8.0 \times 10^{-5} = \frac{x^2}{0.0284 - x}$$

(just by thinking about the equilibrum constant definition). This looks like a quadratic equation, but we can often make a simplifying assumption that $0.0284 - x \approx 0.0284$ (assuming that x is small). So the equation then simplifies to

$$8.0 \times 10^{-5} = \frac{x^2}{0.0284} \implies x = 0.00151,$$

and that tells us the concentration of H_3O^+ and thus $\text{pH} = -\log x = 2.82$. And the main rule is that **if the dissociate is less than 5 percent, the approximation is valid enough** – since x is a bit more than 5 percent of 0.0284, it's not a great approximation we'll try to get a more exact answer with the full quadratic equation. We then find that $x = 0.00147$ instead, and that gives instead that $\text{pH} \approx 2.83$ instead.

In particular, there are situations where the ionization is much more than 5%, and we can be more precise about when they occur: if we're trying to solve the equation

$$K_a = \frac{x^2}{F - x} \implies x^2 + K_a x - K_a f = 0 \implies x = \frac{1}{2}(-K_a \pm \sqrt{K_a^2 + 4K_a F}),$$

and if F is comparable to the size of K_a, then x will also be on the order of K_a. In fact, we get 62 percent dissociation if $F = K_a$ exactly, even if we have a weak acid! So the key point here is that **even with a weak acid, we can have a "strong weak acid" that is very dissociated when it is very dilute.**

2. **Weak base in water**: for example, consider NH_3 which has a K_b of 1.8×10^{-5}. If we have a 0.15 M NH_3 solution, then after the reaction has proceeded forward by x M, we have

$$K_b = 1.8 \times 10^{-5} = \frac{x^2}{0.15 - x}.$$

Making the approximation that $0.15 - x \approx 0.15$ (we can be pretty confident that this is fine because the initial concentration is much larger than K_b), $x = 0.00164$, and this is indeed the case. We then find that $\text{pOH} = -\log x = 2.79$, so the pH of the solution is $14.00 - 2.79 = 11.21$. (The key difference is the role that x plays here!)

The remaining kinds of acid-base problems will be discussed next time!

23 April 6, 2022

Fact 178

Chien-Shiung Wu ("Madame Wu") is a Chinese-American physicist who conducted the Wu experiment, which famously (and shockingly) proved that parity is not a conserved quantity in physics. Her theoretical physics colleagues (but unfortunately not her) won the 1957 Nobel Prize in Physics, but she later won the very first Wolf Prize in physics in 1978. In her career, she also established the existence of quantum entanglement and the nature of beta decay.

Today, we'll discuss how to calculate **pH of salt solutions and buffers** using acid-base neutralization reactions. We showed last time that the water auto-ionization reaction has an equilibrium constant of $K_w = 1.0 \times 10^{-14}$, and shifting to a log scale we defined pH, pOH, $\mathrm{p}K_w$, $\mathrm{p}K_a$, and $\mathrm{p}K_b$ in various contexts (such that $\mathrm{pH} + \mathrm{pOH} = \mathrm{p}K_a + \mathrm{p}K_b = \mathrm{p}K_w = 14$). In particular, this means that conjugate acids and bases cannot both be strong.

Last time, we finished by calculating the pH of a single weak acid or weak base by itself, either by approximation or by solving a quadratic equation. Today, we'll start looking at having both an acid and a base in a single mixture:

Fact 179

In equations like $\mathrm{HCl} + \mathrm{NaOH} \to \mathrm{NaCl} + \mathrm{H_2O}$, NaCl is a **salt** formed by the neutralization of an acid by a base.

If we have a strong acid and a strong base that are neutralizing, we always have a neutral pH for the salt (after all, Na^+ and Cl^- are very weak conjugate bases and acids, so this salt does not perturb the water on an ionization level). On the other hand, if we form a salt with a weak acid and a weak base, we usually do **not** have a neutral pH because the situation depends on the extent of the ionization. Indeed, a weak acid HA reacts with water to form its conjugate base A^- and a hydronium ion $\mathrm{H_3O}^+$, and that conjugate base has its own equilibrium reaction

$$\mathrm{A}^-(\mathrm{aq}) + \mathrm{H_2O}(\ell) \rightleftharpoons \mathrm{HA}(\mathrm{aq}) + \mathrm{OH}^-(\mathrm{aq}).$$

So if salts contain conjugate bases of **weak** acids, we get more basic solutions, and similarly salts with conjugate bases of weak bases give us more acidic solutions. And if a salt contains both, then the picture becomes more complicated and we won't discuss that case in this class. We can now start making conclusions:

Example 180

Consider **ammonium chloride** $\mathrm{NH_4Cl}$, which is commonly used in many labs. Dissolving this in water, ammonium is conjugate to ammonia ($\mathrm{NH_3}$), a weak base, but chloride is conjugate to hydrochloric acid (HCl), a strong acid. So Cl^- is very weak (neutral), but $\mathrm{NH_4}$ donates its protons, so we get an overall acidic solution.

Similarly, sodium acetate would be basic because acetic acid ($\mathrm{CH_3COOH}$) is a weak acid but sodium hydroxide (NaOH) is a strong base.

Example 181

Let's compute the pH of an ammonium chloride solution, given that the $\mathrm{p}K_b$ of ammonia is 4.75. The relevant equation here is $\mathrm{NH_4^+}(\mathrm{aq}) + \mathrm{H_2O}(\ell) \rightleftharpoons \mathrm{NH_3}(\mathrm{aq}) + \mathrm{H_3O^+}(\mathrm{aq})$ (since chloride does not perturb the water balance).

The usual calculation from last lecture: works here since $\mathrm{NH_4^+}$ is on the left-hand side and we're really doing a reaction of the conjugate acid with water, we must first calculate

$$\mathrm{p}K_a(\mathrm{NH_4^+}) = 14 - \mathrm{p}K_b(\mathrm{NH_3}) = 9.25 \implies K_a = 10^{-9.25}$$

and then we can use the equilibrium constant calculation:

$$\frac{x^2}{0.15 - x} = 10^{-9.25} \implies [H_3O^+] \approx 9.18 \times 10^{-6}.$$

This value of x is small enough that our approximation is valid, and then taking a log gives us $pH = -\log_{10}(9.18 \times 10^{-6}) \approx 5.04$. So indeed ammonium chloride is acidic. (As reference, it turns out that the pH of a 0.15 M ammonia solution is 11.2.)

Fact 182

A demonstration of an acid-base neutralization reaction was shown to us in class: a graduated cylinder contains sodium hydroxide (basic), with an indicator which turns purple when the solution is basic and red when it is acidic. The idea is basically to **titrate** a 0.2 M HCl solution (acidic) into it, which will neutralize sodium hydroxide. But because it takes time for the acid to diffuse through the cylinder, we see an **acid-base rainbow** effect.

To get a more interesting chemical equilibrium situation, though, we'll introduce a new idea:

Definition 183

A **buffer** is a solution which has constant pH even when small amounts of acid and base are added. Specifically, an **acidic buffer** contains a weak acid and its conjugate base (as a salt), and a **basic buffer** contains a weak base and its conjugate acid (as a salt).

For example, we can mix acetic acid (CH_3COOH) with an acetate salt (such as sodium acetate $NaCH_3COO$). Suppose we add these in equal amounts, and then we add a strong acid. Then we get the reaction

$$HCl(aq) + CH_3COO^-(aq) \rightleftharpoons CH_3COOH(aq) + Cl^-(aq),$$

so adding a bit of the strong acid doesn't do much – it increases the concentration of acetic acid and decreases the concentration of acetate, and the pH stays roughly the same. Similarly, if we add a strong base like OH^-, the neutralization reaction turns acetic acid into acetate. So again the additional ions are effectively removed from the picture and the pH stays the same. This means that our buffer is resistant to changes in pH.

However, we do need to make sure not to use a strong acid or a strong base (and its conjugate base / acid) to try to make a buffer, because the conjugate base/acid will be ineffective at neutralization and the pH will change dramatically.

Fact 184

In particular, if we have a weak acid and a strong base (not conjugate to each other), we should make a buffer of them by mixing at a 2:1 molar ratio. This is because in that proportion, half of the weak acid will be neutralized into its conjugate base (in a salt), so that we have equal contributions from the weak acid and its conjugate base.

Example 185

Suppose 1.00 moles of HCOOH and 0.500 moles of NaHCOO are added to water at 1 L. We'll calculate the pH of the solution given that the pK_a of HCOOH is 3.75.

We initially have 1 M of HCOOH, effectively 0 moles of H_3O^+, and 0.5 M of $HCOO^-$, so the equilibrium equation that's relevant here ($HCOOH + H_2O \rightleftharpoons H_3O^+ + HCOO^-$ is

$$K_a = 10^{-3.75} = 1.77 \times 10^{-4} = \frac{x(0.5+x)}{1-x}.$$

Again, we make an approximation $x \ll 0.5, 1$, so that we basically have

$$1.77 \times 10^{-4} = \frac{x \cdot 0.5}{1} \implies x = 3.45 \times 10^{-4} \text{ M} \implies \text{pH} = 3.45.$$

Remembering that the $\text{p}K_a$ of HCOOH is 3.75, we see that the pH has gotten a little bit lower.

Example 186

Now suppose we add 0.1 moles of HCl to the 1 L solution. Let's calculate the new pH.

The neutralization reaction here (because we have a buffer) is that HCl reacts with $HCOO^-$ via

$$\text{HCl (aq)} + \text{HCOO}^-\text{(aq)} \rightleftharpoons \text{Cl}^-\text{(aq)} + \text{HCOOH (aq)},$$

so 0.1 moles of HCl will all react with $HCOO^-$ to form an equal number of moles of HCOOH. This means we have 0.4 moles of $HCOO^-$ and 1.1 moles of HCOOH before accounting for the reaction between HCOOH and H_2O. The same equilibrium expression for K_a now gives us

$$K_a = 1.77 \times 10^{-4} = \frac{x(0.4+x)}{1.1-x} \implies x \approx 4.87 \times 10^{-4}\text{M},$$

which gives us a pH of about 3.31. So adding 0.1 moles of HCl (which has a pH of 1) only decreased the pH from 3.45 to 3.31.

Fact 187

The point of these calculations is that when thinking about the pH of a buffer that we are trying to create in the lab, we have to consider different factors, such as the $\text{p}K_a$ of our acid and the relative concentrations of A^- and HA.

In particular, notice that

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \implies [H_3O^+] = K_a \frac{[HA]}{[A^-]},$$

and taking logs on both sides gives us the equation

$$\text{pH} = \text{p}K_a + \log \frac{[A^-]}{[HA]}.$$

In a buffer, we can assume that weak acids and bases don't change their concentration very much during the evolution of a reaction, which leads us to the **Henderson-Hasselbalch equation**.

$$\boxed{\text{pH} \approx \text{p}K_a + \log \frac{[A^-]_{\text{initial}}}{[HA]_{\text{initial}}}}.$$

So if we're trying to make a buffer at some fixed pH, we should find an acid or base with $\text{p}K_a$ within about 1 of the desired pH, and then we should put in the conjugate acid and base at an appropriate concentration to make the log term work out. In particular, it's most important that the **ratio** is correct, though in a lab, the amount of acid and base that we put in does affect the **buffering capacity** (the amount of resistance to change in pH).

Remark 188. *In all of our calculations here in calculation equilibrium, for example in the equation* $1.77\times10^{-4} = \frac{x(0.5+x)}{1-x}$ *above, we've assumed that the initial concentration of* H_3O^+ *is zero. While water does have a concentration of* 10^{-7} *M for* H_3O^+*, that starting concentration is typically negligible and we can ignore it in this class – it only really comes up if we have extremely dilute acids and bases.*

24 April 8, 2022

We'll talk about the most complex part of acid-base chemistry today, calculating with titration curves. We're basically going to use chemical equilibrium concepts in an integrated manner to understand what happens to the pH of a solution.

Fact 189

Joan Feynman is an American astrophysicist (the sister of Richard Feynman) who was an expert in solar wind – specifically, she found that solar wind particles cause the aurora borealis and aurora australis, and she created a model that calculate how many high-energy particles hit a spacecraft over its lifetime.

Last lecture, we discussed the pH of salts and buffers. Specifically, using neutralization reactions between acids and bases, we can calculate the pH of salt solutions (which can be acidic or basic depending on the strength of the components), and we can product a pH of a buffer created from an acid HA and its conjugate base A^- using the Henderson-Hasselbach equation

$$\text{pH} \approx \text{p}K_a + \log \frac{[\text{A}^-]_{\text{initial}}}{[\text{HA}]_{\text{initial}}}.$$

Example 190

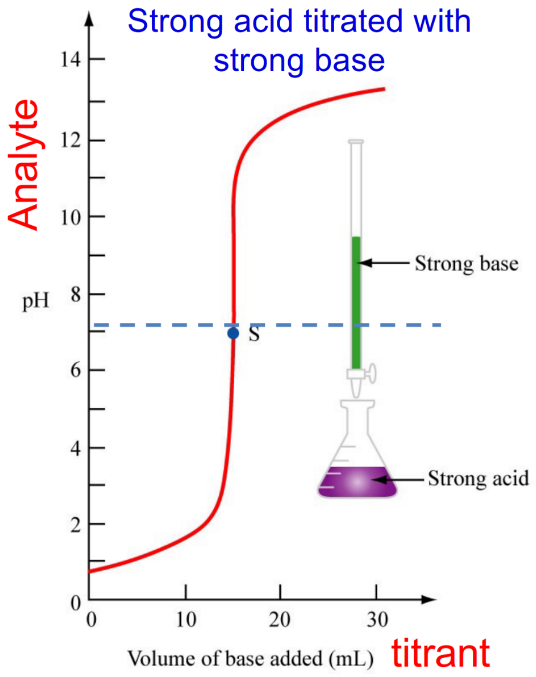
Blood is buffered by carbonic acid (H_2CO_3) and its conjguate base bicarbonate (HCO_3^-). Since the pH of blood is about 7.4, and the pK_a of carbonic acid is 6.47, the body has about 10 times more bicarbonate than carbonic acid.

We'll now move to the main topic of today's lecture:

Definition 191

An **acid-base titration** is a process in which a **titrant** (volume of base or acid of known concentration) is added to an **analyte** (a corresponding base or acid of unknown concentration).

The point of a titration is usually for determining concentrations of acids and bases in a given mixture, and a typical shape is shown below, in which we start with a strong acid (with low pH), and as we add more and more titrant (a strong base), the solution increases in pH until it becomes essentially a strong base in water:



(The curved shape goes in the opposite direction if we start with a base and add acid during the titration.) The point labeled S is called the **stoichiometric point** or **equivalence point** – that is the point at which the number of moles of acid and base in the solution are equal. Usually a titration solution contains an **indicator**, which changes color based on the presence of some chemical compound – the **end point** of a titration is where the indicator makes that change, and usually the end point is approximately the stoichiometric point (not the end of the whole titration).

Remark 192. *There are many different indicators with different transition pH colors. A* **universal indicator** *can take on various rainbow colors depending on how acidic or basic the solutoin is – red tends to indicate acidic, while purple tends to indicate basic. (because there is a change in structure for the indicator).*

Example 193

Suppose we titrate 25 mL of 0.250 M NaOH with 0.340 M of HCl. Let's calculate the pH when we add only a small amount – 5 mL – of 0.340 M HCl.

Here are the main steps of this calculation, where we want to look at the neutralization reaction $\text{NaOH} + \text{HCl} \rightleftharpoons \text{NaCl} + \text{H}_2\text{O}$:

1. We're told the molar concentrations of our various compounds, and we want to convert that to the number of moles of each compound that we have: we have 6.25 mmol of NaOH and 1.7 mmol of HCl.
2. We calculate the number of moles of H_3O^+ supplied by the titrant, and then we see how many moles of OH^- are remaining after reaction. After the neutralization reaction, we have 4.55 mmol of NaOH, 1.70 mmol of NaCl, and 1.7 mmol more of water.
3. The total volume of the liquid is 30 mL, so we can calculate the concentrations relative to this new volume. The only one in this case that influences the pH is the concentration of NaOH, because NaCl is completely ineffective for donating or receiving protons. We find that the OH^- concentration is 0.152 M, so the pOH is 0.818 and the pH is 13.18.

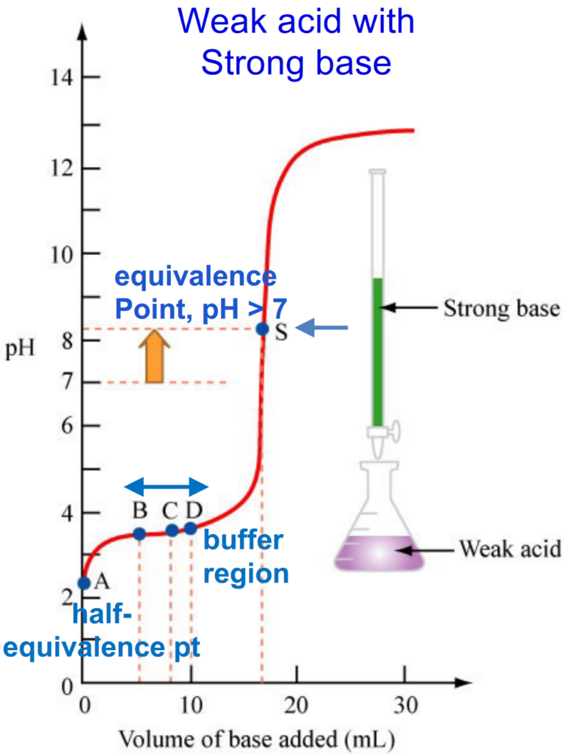
To reach the equivalence point in this example, we need to produce 6.25 mmol of HCl from our 0.340 M HCl solution, which tells us that we need 18.4 mL of HCl solution to completely neutralize the NaOH. And in this case, because we are titrating a strong base with a strong acid, the pH at the equivalence point will be exactly 7 because all that's left is NaCl and H_2O.

But beyond the equivalence point, we essentially end up with a strong acid in water problem, where we are just adding additional H_3O^+ molecules to the picture, and the only complication is making sure we account for the **extra volume** that was added during the titration. (For example, if 1 mL of 0.340 M HCl is added past the equivalence point of 18.4 mL HCl, we need to divide by (25.0 + 18.4 + 1.0 mL) to find our concentration.) What we'll find is that (as in the picture indicates) the pH changes dramatically around the equivalence point, because we go from having primarily base to primarily acid or vice versa, with no corresponding molecule to neutralize it.

Example 194

We'll now switch the direction, starting with an acid and titrating with a base, but this time we'll start with a weak acid.

The curve for a weak acid titrated with a strong base looks slightly different:



We'll explain all of the features of this updated picture, but we'll notice two qualitative changes: the equivalence point shifts up in pH, and there is a buffer region in which adding acid or base does not change the pH very much. That point C is known as the **half-equivalence point**, which is half of the total number of moles needed to reach the equivalence point. There are then a few important places in this picture to consider:

- At point A, we just have a weak acid sitting in water, so given the pK_a we can find the chemical equilibrium and find the initial pH.
- In the buffer region, notice that C is the point at which our weak acid and its conjugate base exist in equal concentrations. The purpose of the strong base is that once it neutralizes our weak acid, its ineffective conjugate

acid does nothing, so the solution's pH is affected by the relative concentrations of acid and conjguate base, and we can use Henderson-Hasselbach. (In particular, the pH is equal to the pK_a at the half-equivalence point.)

- At equivalence, we only have the conjugate base of our weak acid, and we again know how to calculate the pH of that solution from the pK_b.
- Finally, above the equivalence point, we essentially have a strong base in water problem.

We're now ready to do some more explicit calculations:

Example 195

25 mL of 0.10 M formic acid (HCOOH) is titrated with 0.15 M NaOH. The K_a of HCOOH is 1.77×10^{-4}.

1. (Point A) Before we add any NaOH, we calculate the pH by using the K_a equilibrium constant for formic acid. We start off with 0.10 M of HCOOH, so the equilibrium equation is
$$1.77 \times 10^{-4} = \frac{x^2}{0.10 - x} \approx \frac{x^2}{0.10} \implies x \approx 4.21 \times 10^{-3},$$
(remembering to check that x is less than 5 percent of 0.10, which is true), which tells us that the pH of the solution is $-\log x \approx 2.38$.

2. (Point B, or a similar calculation at point D) Next, suppose that we add 5 mL of 0.15 M NaOH, which is before the equivalence point. This is a **buffer calculation**: hydroxide ions OH^- of NAOH will react (essentially) completely with HCOOH via the equation
$$\text{HCOOH (aq)} + \text{OH}^-\text{(aq)} \to \text{H}_2\text{O}(\ell) + \text{HCOO}^-\text{(aq)}$$
(the K_{eq} of this equation is much larger than 1), and thus we find that our 2.5 mmol of HCOOH reacts with 0.75 mmol of OH^- to create 1.75 mmol of HCOOH and 0.75 mmol of $HCOO^-$ (with the Na^+ ions essentially ineffective in changing the pH, so that they can be ignored). Thus by the Henderson-Hasselbalch equation, we have
$$\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]_{\text{initial}}}{[\text{HA}]_{\text{initial}}} = -\log(1.77 \times 10^{-4}) + \log \frac{0.75}{1.75} \approx 3.38.$$
(Note that we should technically be putting in molar concentrations into the fraction instead of number of moles, but because the acid and conjugate base are in the same solution the volume factor will cancel out.) And note that even if we forget the Henderson-Hasselbalch equation, we can always convert the NCOOH and $HCOO^-$ amounts into concentrations and use the equilibrium constant.

3. (Point C) Now at the half-equivalence point, we know that the concentrations of HCOOH and $HCOO^-$ will be equal (because half of the acid was neutralized). Thus, the pH is exactly the pK_a of the weak acid, which is 3.75. (And we can calculate how many moles of NaOH must be added for this to happen using stoichiometry.)

4. (Point S) At the equivalence point, the amount of of NaOH added is exactly the amount of HCOOH initially present (which again we calculate with stoichiometry). At equivalence, we have 2.5 mmol of $HCOO^-$, and the total volume turns out to be 25 mL + 16.7 mL. Dividing tells us that the molarity of $HCOO^-$ is 0.0600 M, and now we can do a weak base in water problem:
$$\frac{x^2}{0.0600 - x} = K_b = \frac{10^{-14}}{K_a} = 5.6 \times 10^{-11} \implies x \approx 1.83 \times 10^{-6} \text{ M}.$$
Noticing here (if we write out the reaction with water) that x indicates the number of moles of OH^-, we find

that the pOH is 5.74, so the pH at equivalence is 8.26. So the key point is that **there are two reactions to take into account here**!

5. (Point E, not labeled above but further to the right on the titration) If we add any more NaOH, there is no acid to counter the base, and thus we have a pure strong base problem (because the conjugate base from our weak acid only contributes a very small amount of OH^- ions relative to the strong base). So in this case, if we go 5 mL past the equivalence point, we have 0.75 mmol of excess OH^- and a total volume of $5 + 25 + 16.7$ mL, giving us a a 0.016 M OH^- contribution from the strong base (yielding pOH of 1.79 and pH of 12.21). And again, in comparison, the weak base gives a much smaller concentration of OH^-.

Remark 196. *These five problems are the relevant calculations we'll have to do with titrations, and we should always make sure to write down the relevant neutralization and equilibrium reactions. And because it doesn't make sense to account for two different conjugate acid-base pairs, we will not be titrating with a weak acid or base.*

25 April 11, 2022

As a reminder, next Monday is a holiday (Patriots' Day), and next Wednesday is our third midterm exam. The midterm exam will cover lectures 17 through 26 (up until next lecture).

Fact 197

Maria Goeppert Mayer was a theoretical physicist who was the second woman to win a Nobel Prize in physics for proposing the nuclear shell model of the atom, explaining why having 2, 8, 20, 28, 50, 82, and 126 nucleons in a nucleus result in stable configurations. Her PhD was written on 2-photon absorption by atoms – the cross section for this 2-photon absorption is named the GM unit.

We'll be discussing **oxidation-reduction (redox) reactions** today, which are reactions involving electron transfer from one molecule to compound to another. Combustion, corrosion, metal extraction, photosynthesis, and many other reactions in the real world make use of this principle, and oxidation of copper and bronze produce a naturally occurring green **patina** (we can see this for instance on the Statue of Liberty).

Example 198

Firework colors come from the **oxidation** of various metals (magnesium produces white color, copper produces blue, and other salts and compounds produce red, yellow, and green colors). An example of such a reaction is $2\text{ Mg (s)} + O_2\text{(g)} \rightleftharpoons 2\text{MgO (s)}$, in which electrons are transferred from magnesium to oxygen.

Definition 199

Oxidation is the term for a compound "losing electrons," and **reduction** is the term for "gaining electrons."

In other words, magnesium is oxidized and oxygen is reduced in the reaction above. We can understand which species are being reduced or oxidized by thinking about **oxidation numbers**, which increase when an atom loses (donates) electrons and decrease when an atom gains electrons. In the reaction above, we start with oxidation numbers of 0 and end up with an oxidation number of +2 on Mg and −2 on O. Similarly, if we have an equation like $\text{Mg (s)} + Cl_2\text{(g)} \rightleftharpoons MgCl_2\text{(s)}$, we start with oxidation numbers of 0 and end up with +2 on Mg and −1 on Cl. (All of these oxidation numbers are consistent with the **groups** (columns) in which the elements appear on the periodic table.)

Proposition 200

Oxidation numbers are basically like formal charges, but instead of equally sharing electrons between atoms in a bond, we imagine that the electrons all go towards the **more electronegative atom**. The following rules apply for assigning oxidation numbers N_{ox} in a reaction:

- Oxidation numbers in free elements (pure elemental species) are always 0, and oxidation numbers for ions of only a single atom (e.g. $Li^{+}1$ are equal to the charge of the ion (in this case $+1$).
- Group 1 (resp. 2) metals always have N_{ox} of $+1$ (respectively $+2$), consistent with them being stable when losing 1 (resp. 2) electrons. Aluminum always has an oxidation number of $+3$.
- Oxygen almost always has an oxidation number of -2, except for peroxides like H_2O_2 and O_2^{-2} (where it's -1), superoxides O_2^- (where it's $-1/2$), and ozonides O_3^- (where it's $-1/3$). In particular, note that **oxidation numbers are not always integers**.
- The oxidation number of Hydrogen is $+1$ when forming compounds with nonmetals and -1 when forming compounds with metals.
- Fluorine always has an oxidation number of -1. Other halogens (Cl, Br, I) have negative oxidation numbers when occurring as halide ions, but positive oxidation numbers when combined with oxygen.
- The sum of the oxidation numbers of all elements is equal to the charge of the molecule or polyatomic ion that they make up.

Example 201

The oxidation numbers in NH_4^+ are $+1$ for Hydrogen (because it's forming a compound with a nonmetal) and -3 for Nitrogen (to get a total sum of $+1$; this is consistent with its position in the periodic table). Similarly, the oxidation numbers in N_2O are $+1$ for N and -2 for O.

Definition 202

The **oxidizing agent** in a reaction is the reactant that is reduced (gaining electrons), and the **reducing agent** in a reaction is the reactant that is oxidized (losing electrons).

For example, in the equation $Mg\ (s) + 2\ HCl\ (aq) \rightleftharpoons H_2(g) + MgCl_2(aq)$, HCl is reduced and is thus the oxidizing agent, and Mg is oxidized and thus the reducing agent. And in the thermite reaction $2Al(\ell) + Cr_2O_3(s) \rightleftharpoons Al_2O_3\ (s) + 2Cr(\ell)$, Chromium(III) is the oxidizing agent (reduced from +3 to 0) and aluminum is the reducing agent (oxidized to a number of +3).

Definition 203

A **disproportionation reaction** is a reaction in which a reactant element is both oxidized and reduced.

For example, in the thermal decomposition $2\ H_2O_2(\ell) \rightleftharpoons 2H_2O(\ell) + O_2(g)$, the oxygens in hydrogen peroxide have oxidation number -1, but the oxygens in the products have oxidation numbers -2 and 0.

Remark 204. *Such a reaction is slow when at low temperatures and in dilute solutions, though, without an enzyme that is present in the body. (And in the past, the class used to do an* **elephant toothpaste** *demonstration in 5.111, but the exothermic nature of the reaction made it slightly dangerous and it's not done anymore.)*

Redox reactions are particularly difficult to balance because the charges on the two sides need to be balanced as well. Here's the step-by-step idea: imagine that we have a reaction in aqueous solution which looks like

$$Fe^{2+} + Cr_2O_7^{2-} \rightleftharpoons Cr^{3+} + Fe^{3+}.$$

Such reactions suppress the involvement of H_2O, H^+, and OH^-.

Proposition 205

To balance a redox reaction, follow the steps below:

- Write down the **half-reactions** (oxidation and reduction), and balance them separately except ignoring the contributions to H and O.
- If we are in an acidic solution, balance the Os on both sides by adding H_2O, and then balance the Hs by adding H^+ on the appropriate side. If we are in a basic solution, we instead first balance the number of Hs and Os by adding H_2O, and then we finish balancing by adding OH^- ions (or for an easier argument, see the argument below).
- Match the net electron charges on the two reactions and add them together.

In this example case, our two half-reactions are the **reduction reaction**

$$Cr_2O_7^{2-} \rightleftharpoons Cr^{3+}$$

(because the Cr atoms go from +6 to +3) and the **reduction reaction**

$$Fe^{2+} \rightleftharpoons Fe^{3+}.$$

For the first equation, we must balance the number of Cr atoms on the two sides, and then we add water to balance out the oxygens, and then balance out H^+ atoms after that if we're in an acidic solution. To finish balancing the reaction, we check the charges and make sure they are equal:

$$\boxed{6\ e^- + 14\ H^+ + Cr_2O_7^{2-} \rightleftharpoons 2\ Cr^{3+} + 7\ H_2O}.$$

The reduction reaction is much simpler to balance:

$$\boxed{Fe^{2+} \rightleftharpoons Fe^{3+} + e^-}.$$

To finish balancing our redox reaction, we need to make sure an equal number of electrons are being transferred on the two sides: multiplying the second reaction by 6 and adding the two half-reactions together gives us our final solution in **acidic solution**:

$$\boxed{14\ H^+ + Cr_2O_7^{2-} + 6Fe^{2+} \rightleftharpoons 2\ Cr^{3+} + 7\ H_2O + 6Fe^{3+}}.$$

(This is indeed balanced: we have 14 H, 2 Cr, 7 O, 6 Fe, and a net charge of +24 on both sides of the equation.) On the other hand, if our reaction is happening in a **basic solution**, we can "adjust pH" by adding OH^- ions to both sides. Adding 14 OH^- ions on both sides will make H^+ and OH^- combine to water:

$$14\ H_2O + Cr_2O_7^{2-} + 6\ Fe^{2+} \rightleftharpoons 2\ Cr^{3+} + 7\ H_2O + 6Fe^{3+} + 14\ OH^-.$$

Finally, canceling out the water molecules gives us our final equation in **basic solution**:

$$\boxed{7\ \mathrm{H_2O} + \mathrm{Cr_2O_7^{2-}} + 6\ \mathrm{Fe^{2+}} \rightleftharpoons 2\ \mathrm{Cr^{3+}} + 6\mathrm{Fe^{3+}} + 14\ \mathrm{OH^-}}.$$

We'll do one more example: consider the unbalanced equation $\mathrm{MnO_4^-(aq)} + \mathrm{H_2C_2O_4(aq)} \rightleftharpoons \mathrm{Mn^{2+}} + \mathrm{CO_2(g)}$. Since Mn goes from an oxidation number of +7 to +2, $\mathrm{MnO_4^-}$ is reduced, and $\mathrm{H_2C_2O_4}$ is oxidized (because C goes from +3 to +4). Thus, our half-reactions (balanced out) end up being

$$\mathrm{MnO_4^-} + 8\ \mathrm{H^+} + 5\ \mathrm{e^-} \rightleftharpoons \mathrm{Mn^{2+}} + 4\ \mathrm{H_2O}$$

(we first balance everything except Hs and Os, then add water to balance Os, then add $\mathrm{H^+}$ ions, then balance the charge), and

$$\mathrm{H_2C_2O_4} \rightleftharpoons 2\ \mathrm{CO_2} + 2\ \mathrm{H^+} + 2\ \mathrm{e^-}.$$

Adding 2 times the first reaction to 5 times the second reaction gives us (canceling common terms)

$$\boxed{2\mathrm{MnO_4^-} + 5\ \mathrm{H_2C_2O_4} + 6\ \mathrm{H^+} \rightleftharpoons 2\ \mathrm{Mn^{2+}} + 10\ \mathrm{CO_2(g)} + 8\ \mathrm{H_2O}}.$$

26 April 13, 2022

We'll be discussing **reactions with electrochemical cells** today, which studies redox reactions at electrodes and has applications to how batteries work. In particular, we'll think about how to obtain electricity from a spontaneous reaction or using electricity to drive a non-spontaneous one.

Fact 206

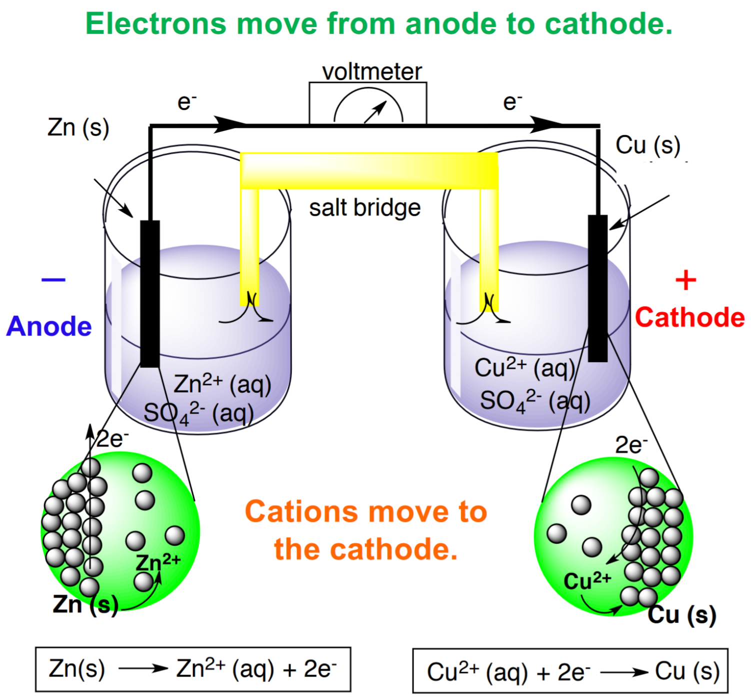
Percy Lavon Julian was an American chemist who was a pioneer in synthesizing medicinal drugs from plants – he pioneered the synthesis of cortisone, progesterone, and testosterone. He was the first person to synthesize physostigmine, used to treat glaucoma, and he was the first African-American chemist inducted into the National Academy of Sciences.

As a review of last time, redox (reduction-oxidation) reactions involve electron transfer between species, and we can figure out which substance gains electrons (is **reduced**) and which loses electrons (is **oxidized**) by assigning oxidation numbers to the various elements. As we saw last time, this balancing requires us to keep track of elements but also charges.

Definition 207

An **electrochemical cell** contains **electrodes** (which are conductors through electrons can travel). There are two types of electrochemical cells: a **galvanic cell** is one produced by a spontaneous chemical reaction, and a **electrolytic cell** is one that is used to cause a non-spontaneous chemical reaction to occur. A **battery** is then a collection of galvanic cells that are joined together.

Below is a conceptual diagram of a galvanic cell:



The idea is that electrons flow from one metal to the other – in the diagram above, solid Zinc gets dissolved into the solution (Zn(s) is being **oxidized** – this means that we call the zinc electrode an **anode**), and the two electrons that are freed flow along the current at the top of the diagram. Then the two electrons combine with aqueous copper to form Cu(s) – because Cu^{2+} is being reduced to Cu(s), we call the copper electrode a **cathode**. The main rule here is that **electrodes always move from anode to cathode** (from oxidation to reduction). The two solutions are not in contact, but there is also a **salt bridge** along which ions (cations and anions) can flow to maintain electrical neutrality. (In particular, cations will migrate to the cathode, and anions will migrate to the anode.) In particular, as this process continues, we will see a net current measured at the voltmeter, and that current can be used to do work.

Remark 208. *A mnemonic often used is "an ox" versus "red cat:" oxidation occurs at the anode, and reduction occurs at the cathode.*

The half-reactions in play are listed in the picture above, and combining them together gives us the overall reaction

$$\boxed{\text{Zn (s)} + \text{Cu}^{2+}\text{(aq)} \to \text{Zn}^{2+}\text{(aq)} + \text{Cu (s)}}.$$

But if we place Zn metal and $CuSO_4$ into a solution together, the idea is that the Zinc metal will slowly disappear, and the copper will **plate out** into a solid. Since Copper (II) ion looks blue, that color will disappear, and at the end there will only be copper metal left. However, **no electrical work will be generated** in such a case, because we need to be able to separate the reactants, and that's why we have the galvanic cell setup listed above.

In our particular boxed equation above, the ΔG_r° is -212 kJ/mol. The reason that this reaction is spontaneous is that Zn metal has a relatively weak cohesive energy, while Cu metal is more stable because of covalent bonding. So Zn is often the anode for household alkaline batteries. And the key point is that **no bond formation needs to occur, only electron transfer**, so the atoms and ions do not have to be spatially close as long as there is a wire that connects the cells.

Remembering the valence shell electron configurations of our various metals, Zn has a filled 3d and 4s shell, so it can only lose electrons – Zn^{2+} is still very stable because it has a filled 3d shell. And Cu^{2+}, which has configuration [Ar] $3d^9$, can gain two electrons to get into the more stable [Ar] $3d^{10}$ $4s^1$ configuration. However, there are situations where the electron flow is opposite for the copper electrode (it depends on the relative energies at play): if we have a galvanic cell with Ag and Cu, then silver will plate out instead, and Copper will get oxidized into ions. In general, the cathode is where plating out will occur (because reduction creates pure metal).

Fact 209

A **silver tree experiment** was performed for us in class: a copper wire ("tree") was placed into silver nitrate solution. This changes the appearance of the solid metal (more whitish-grayish because of silver metal), and also the color of the solution will change (more bluish because of the Cu^{2+} ions).

The electrochemical cell above is represented in the following way:

$$\mathrm{Zn\ (s)} \,|\, \mathrm{Zn^{2+}(aq)} \,||\, \mathrm{Cu^{2+}(aq)} \,|\, \mathrm{Cu}(s).$$

Specifically, the oxidation reaction is written on the left, a single vertical line represents a phase boundary, and two vertical lines represent a salt bridge. The pure metals are typically written on the outside (we can think of this as having metal in a container), and the ions are written on the inside (thinking of electrolytes as being between metal electrodes).

Example 210

Consider the galvanic cell with half-reactions $\mathrm{Zn\ (s)} \to \mathrm{Zn^{2+}(aq)} + 2e^-$ and $\mathrm{Sn^{4+}(aq)} + 2e^- \to \mathrm{Sn^{2+}(aq)}$. In this case, Zinc is at the anode and Strontium is at the cathode, and we represent the cell diagram as $\mathrm{Zn\ (s)} \,|\, \mathrm{Zn^{2+}(aq)} \,||\, \mathrm{Sn^{4+}(aq)}, \mathrm{Sn^{2+}(aq)}$ (the tricky part here is that there is no phase transition boundary because both states of Strontium are aqueous).

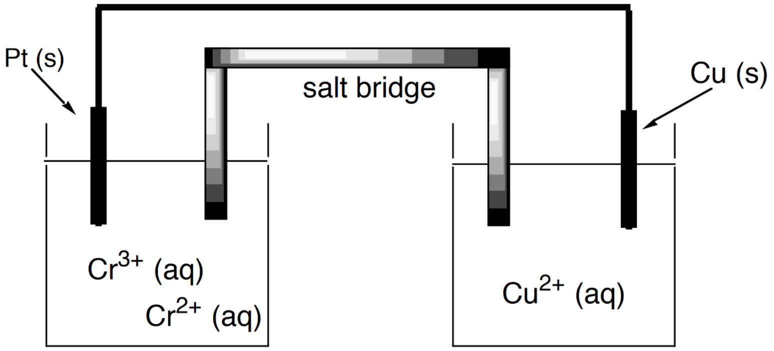
Proposition 211 (Faraday's law)

The number of moles of product formed (and also reactant consumed) in an electrochemical cell or reaction is proportional to the number of moles of electrons canceled. In particular, Faraday's constant tells us that there are $F = eN_A$ is 96485 Coulombs per mole of electrons.

Example 212

Suppose a current of 1 Ampere (1 Coulomb per second) flows for 1 second in our galvanic cell above. To calculate the amount of Zinc consumed and Copper deposited, we calculate that there were 3600 Coulombs of charge that passed through, which corresponds to 0.0373 moles of electrons that flowed through the wire. Since one mole of Zinc is consumed per two moles of electrons that flowed through, our answer is approximately 0.0187 moles of Zn and Cu, respectively, and we can convert those to answers in grams by stoichiometry.

It turns out that we do not always need to have anodes and cathodes by consumed in an electrochemical reaction – we can instead use an **inert Pt electrode**, as in the diagram below:



Anode (oxidation)
Cr^{2+} (aq) –> Cr^{3+} (aq) + e^-

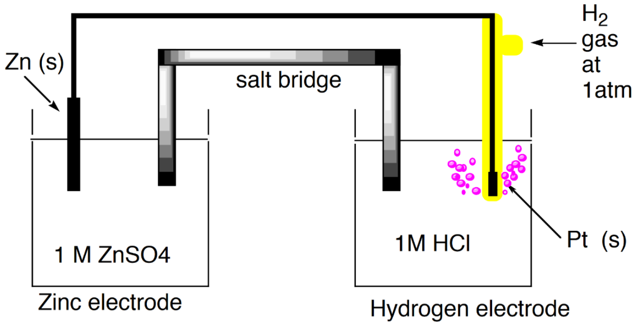
Cathode (reduction)
Cu^{2+} (aq) + $2e^-$ –> Cu (s)

In the diagram above, oxidation and reduction do occur, but the Pt(s) is not consumed and electrons still move along the wire. Such a cell is notated as

$$\text{Pt (s)} \,|\, \text{Cr}^{2+}\text{(aq)}, \text{Cr}^{3+}\text{(aq)} \,||\, \text{Cu}^{2+}\text{(aq)} \,|\, \text{Cu (s)},$$

In particular, platnium is often used to construct a **hydrogen electrode** in which hydrogen ions are reduced into hydrogen gas (or vice versa) – these **standard hydrogen electrodes** are often used to measure reduction potentials (which we'll discuss soon):

$2H^+$ (aq) + $2e^-$ –> H_2 (g)



Anode (oxidation)
Zn (s) | Zn^{2+} (aq)

Cathode (reduction)
H^+ (aq) | H_2 (g) | Pt (s)

We write those electrodes in different ways depending on whether hydrogen is acting as an anode (Pt(s) | $H_2(g)$ | H^+(aq)) or as a cathode (H^+(aq) | $H_2(g)$ | Pt (s)) – for example, if Pt(s) | $H_2(g)$ | H^+(aq) is acting as an anode, then hydrogen gas is being oxidized.

Definition 213
The **cell potential** ΔE_{cell} (measured in volts) is the ability of an electrochemical reaction to move electrons.

Just like a mass that falls through a gravitational potential does work, electrons that flow through a potential difference ΔE_{cell} will do electrical work (1 Joule is 1 Coulomb · 1 volt). In particular, **the maximum electrical work that can be done is the electrochemical cell's Gibbs free energy**, because the reaction can proceed until it is no longer spontaneous. We then get the equation for the maximum work that can be performed

$$\Delta G_{\text{cell}} = -nF\Delta E_{\text{cell}},$$

where n is the number of moles of electrons that pass through. (So a positive cell potential corresponds to a spontaneous reaction).

Definition 214

The **standard cell potential** in an electrochemical cell is the difference between the standard reduction potentials of two half cells (for the cathode minus the anode). (We will be provided the standard reduction potentials from thermodynamic tables.)

Example 215

For our electrochemical cell Zn (s) | Zn^{2+}(aq) || Cu^{2+}(aq) | Cu(s) from before, if we want to calculate the cell potential, we want the standard reduction potential for Cu^{2+} to be reduced into Cu, minus the standard reduction potential for Zn^{2+} to be reduced into Zn. Those numbers are 0.34 and −0.76 volts, respectively, so the standard reduction potential $\Delta E^\circ_{\text{cell}}$ will be 1.10 V. In particular, the flow of electrons will be spontaneous (meaning that we have a **galvanic** rather than an **electrolytic** cell).

27 April 15, 2022

We're finishing up the "redox module" today, talking about **electrochemical reduction potentials and the Nernst equation** – after the exam on Wednesday (no class on Monday because of the holiday), we'll dive into inorganic chemistry and chemical kinetics.

Fact 216

Virginia Apgar is an American physician and medical research known for the Apgar score (which helps assess a newborn child's health), which helped improve obstetric care. She entered the field of anesthesiology early on, establishing a new division at the New York Presbyterian hospital.Within the 1930s to 1950s,

Last lecture, we discussed galvanic cells (batteries) and their relevant concepts: when we connect two electrodes by a wire and salt bridge, oxidation will happen on one side (the anode) and reduction on the other (cathode). (We learned how to write down cell diagrams for such situations.) Faraday's law then tells us how to relate the charge transfer to the amount of metal reduced or oxidized, and the cell potential is related to the Gibbs free energy of the process via the equation $\Delta G^\circ_{\text{cell}} = -nF\Delta E^\circ_{\text{cell}}$, where the cell potential is usually calculated by comparing the standard reduction potentials (subtracting the one at the anode from the one at the cathode).

Note that the anode is always written on the left for a galvanic cell, which tells us the sign of the cell potential – a positive E° corresponds to a spontaneous reaction (meaning that reduction is favorable), and for a galvanic cell ΔE° should always be positive. In particular, a large positive E°_{red} for a half-reaction corresponds to an element that can easily be reduced. (The most easily reduced element is Fluorine F_2, for which $\Delta E^\circ_{\text{red}} = 2.87$ V – in other words, Fluorine is a very good oxidizing agent. On the other hand, because Li^+'s reduction reaction has potential −3.05 V, Li^+'s reduced form Li is a very good reducing agent and prefers to revert to the Li^+ form.)

Example 217

Suppose a Fe(s) | Fe^{2+} (aq) half cell is connected to another half cell with an unknown metal M in MNO_3 aqueous solution. If the full cell is a galvanic cell with $\Delta E^\circ_{\text{cell}} = 1.24$ V, the iron electrode was made lighter, and the unknown electrode was made heavier, then M was reduced (cathode). Thus the standard reduction potential x at the metal, minus the reduction potential of Fe^{2+}, which is -0.44 V, should be 1.24 V, and thus $x - (-0.44) = 1.24 \implies x = 0.80$, which tells us the metal is Ag.

Recall that these standard reduction potentials are always compared against a standard Hydrogen electrode, which we discussed last time. In more detail, what's going on here is that the reference reaction 2 H^+ (aq) + 2 e^- → H_2(g) is given a reduction potential of 0.00 V, so then we combine any electrode with a hydrogen electrode to measure E°_{red} with respect to this standard. So when we have a cell like

$$\text{Zn (s)} \mid \text{Zn}^{2+}\text{(aq)} \,||\, \text{H}^+\text{(aq)} \mid \text{H}_2\text{(g)} \mid \text{Pt}$$

has standard cell potential -0.76 V, meaning that Zinc likes to be oxidized by hydrogen and reduce H^+ ion (making gas bubble out), while cells with ΔE° positive cannot reduce H^+ ion.

On the other hand, notice that the actual reduction potential depends on the value of ΔE, which is not necessarily the standard potential ΔE° (and this shifts depending on the concentration of the various elements and thus how much work has already been done). In particular, at equilibrium we have an **exhausted battery**, and there is zero potential and $\Delta G = \Delta E = 0$. Remembering that we have the two equations

$$\Delta G = \Delta G^\circ + RT \ln Q, \quad \Delta G^\circ = -nF\Delta E^\circ_{\text{cell}},$$

doing some algebraic manipulation, we end up with the following characterizing equation:

Theorem 218 (Nernst)

The potential of a cell is given by

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{nF} \ln Q,$$

where Q is the reaction quotient (only taking into account the concentration of aqueous ions).

Example 219

Suppose we have a cell in which Zn^{2+} ions are at concentration 0.1 M, while Cu^{2+} ions are at concentration 0.0010 M. Then the standard cell potential is $E^\circ_{\text{cell}} = 1.10$ V as we've already calculated, and $Q = 1.0 \times 10^2$, so substituting into the Nernst equation (using the fact that $n = 2$ because we transfer 2 moles of electrons per mole of reaction) tells us that $E_{\text{cell}} = 1.0438$ V. (As a reference, remember that 1 Joule is equal to 1 Coulomb times 1 volt, so our energy units should still cancel out.) So the battery is not depleted yet.

In particular at equilibrium, we have $\Delta G = \Delta E = 0$, so plugging into the Nernst equation we find the equation

$$\ln K = \frac{nFE^\circ_{\text{cell}}}{RT}$$

for an electrochemical or redox reaction – in other words, we can calculate (fairly accurately) the equilibrium constant just by measuring standard cell potentials. It turns out that for a Cu/Zn cell to reach equilibrium, we must have a ratio of 10^{37} in the concentrations of the aqueous ions, which is huge. More generally, at room temperature, the coefficient

$\frac{RT}{F}$ in front of $\ln Q$ is equal to 0.0257. It turns out to be customary to switch to log base 10 instead of ln (base e), and plugging this number in gives us the equation (easier to work with)

$$\boxed{E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0592}{n} \log Q}.$$

Example 220

For an application of this material in biology, we'll talk about Vitamin B12 (found in fish, red meat, and poultry, which is important for preventing heart disease and preventing birth defects).

Vitamin B12 is a "coordination complex" of cobalt – Cobalt exists in a 3+ oxidation state here, but the vitamin needs to be reduced to a 2+ state to become active. A protein called **flavodoxin** reduces Vitamin B12 – the standard reduction potential for Vitamin B12 is -0.526 V, while the one for flavodoxin is -0.230 V. This means that vitamin B12 is a better reducing agent, and thus flavodoxin does not reduce vitamin B12 spontaneously (the E°_{cell} is -0.296 V, corresponding to a $\Delta G = 28.6$ kJ/mol).

It turns out that the energetic driving source comes from **folic acid** (coming from green vegetables, orange juice, and beer) – the cleavage of S-adenosylmethionine gives a ΔG° which is more negative than the ΔG for flavodoxin's reduction of vitamin B12. So electrochemical concepts actually factor into why nutrition can be complicated!

28 April 22, 2022

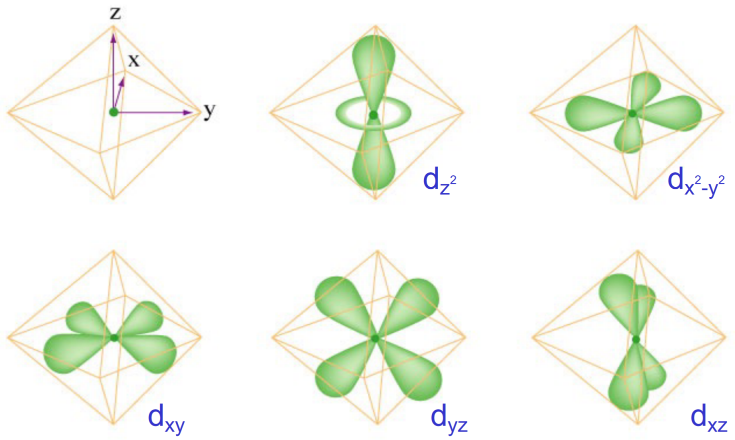
We'll start talking about **transition metals**, which make up the middle part of the periodic table (groups, or columns, 3 to 12). These metals are important in human civilization because of the Iron and Bronze Ages (reliant on copper and iron), coinage metals (copper, silver, gold), paint pigments, hydorgen fuel, and many other applications. (And living organisms have trace amounts of iron, copper, zinc, chromium, and manganese for various functions.)

Fact 221

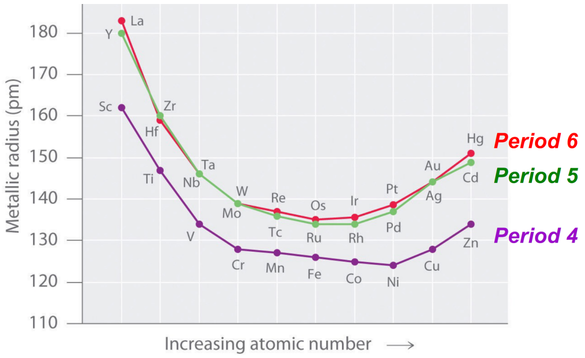
Caroline Lucretia Herschel is a German astronomer who discovered many comets and nebulae – her work was initially started as assistance to her brother William Herschel, but she became an independent astronomer who published a New General Catalog of stars and nebulae, still used today. She was awarded a Gold Medal for Science by the king of Prussia, and Asteriod 281 Lucretia is named after her.

Groups 3 to 12 are also known as **d-block metals**, and that's because many of them have valence electrons in the d orbitals. But as we discussed earlier on in the class, the electron configurations of d block elements have some special exception cases. In particular, recall that while Vanadium (in group 5) has electron configuration Ar$[3d]^3[4s]^2$, the next element Chromium (in group 6) has electron configuration Ar$[3d]^5 4s^1$ instead (because half-filled orbitals and fully filled orbitals) are more stable. This is followed by Manganese, which has configuration Ar$[3d]^5[4s]^2$, and then we return to filling the d orbital until Copper (in group 11) with configuration [Ar]$3d^{10}4s^1$.

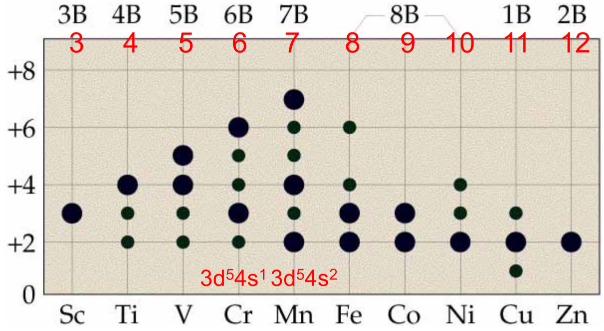
The key point here is that d orbitals are distributed more spatially than s or p orbitals, as we can see below:



All of these have electron density $\psi = 0$ at the nucleus, so *d* orbitals **do not shield charge very well**, and (based on their shape) there is little orbital overlap and thus **weak repulsion between d electrons**. This leads us to an interesting trend in **atomic radii** across the d atoms, in which the radius first decreases across a period / row (because of poor shielding initially) but then increases because of repulsion in a filled shell. (On the other hand, as usual the atomic radius does increase down the periodic table, but less so from period 5 to 6 because of the **lanthanide contraction** – poor shielding by f electrons and large effective nuclear charge Z.)



Additionally, as will be relevant to coordination of chemistry between d-block metals, **metals have multiple oxidation states**. This is shown below, with large circles denoting more common oxidation states:



In particular, it turns out that the valence shell s electrons are ionized first, followed by the d electrons. (So Chromium, with $3d^54s^1$ electrons in those orbitals, are commonly in the +3 or +6 states, which correspond to having electron configuration $3d^34s^0$ and $3d^04s^0$, respectively. Notice that elements in the middle of a row exhibit the largest range of oxidation states, and (for example) group 12 elements can only lose 2 s electrons.

Example 222

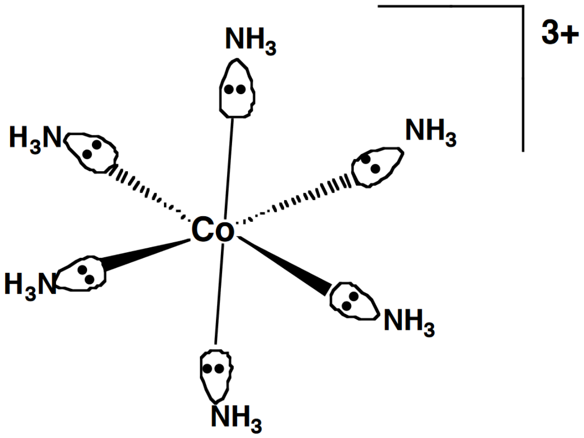
Iron (Fe) has an electron configuration of $[Ar]3d^6 4s^2$, so Fe^{2+} and Fe^{3+} have electron configurations of $[Ar]3d^6 4s^0$ and $[Ar]3d^5 4s^0$ (in particular, notice that Fe^{2+} does not have the same electron configuration of Cr).

Turning back to our discussion about redox reactions, notice that large positive oxidation states prefer to be reduced, so **high oxidation states correspond to strong oxidizing agents**. For example, the reduction potential for MnO_4^- (in which Mn is in the +7 oxidation state, but reacting with H^+ ions reduces us to Mn^{2+} state) is 1.51 V. We previously mentioned that reduction potentials of elements are more negative on the left of the periodic table (easily oxidized and are strong reducing agents) and more positive on the right of the periodic table (easily reduced and are strong oxidizing agents). Notice that copper and zinc, which were used even in the Bronze age, came first, followed by iron in the Iron age, followed by elements like titanium in the modern age. So indeed, the metals that are easier to smelt came first in the history of civilization.

Fact 223

One way to reduce iron is by taking a series of high-temperature redox reactions to make steel from hematite (Fe_2O_3) or magnetite (Fe_3O_4). This is usually done in a sequence of zones of different temperatures – limestone decomposes thermally into CaO and CO_2, then C and CO_2 form carbon monoxide, which reacts with hematite to produce magnetite. Magnetite then reacts with carbon monoxide to get FeO, and then finally FeO reacts with CO to get liquid Fe. So iron starts off in the +3 oxidation state in Fe_2O_3, and then it gets decreased to 8/3, then 2, then 0.

We can now turn to the concept of **coordination compounds** – the idea is that transition metals can form complexes with small molecules and with ions, because positive metal ions can attract electron density from transition metals (e.g. a lone pair of electrons), forming a **coordination complex**. These other atoms which donate lone pairs are then **ligands** – they donate electrons and are thus Lewis bases – and the corresponding acceptor atoms are the transition metals. So we can imagine having metals surrounded by ligands (which are neutral or negatively charged), and an example of such a coordination complex is a Co atom surrounded by NH_3 groups, shown below (in which if the complex has charge +3, that means the Co atom is in a +3 state). We place square brackets around these coordination complexes, so $[Co(NH_3)_6]^{3+}$ would be the notation for the complex shown below.



Definition 224

In a coordination complex, the **coordination number** (CN) is the number of bound ligands (ranging from 2 to 12, but 6 being the most common).

For example, even for a single transition metal like Cobalt, we can make different complexes by replacing some NH_3 groups with Cl atoms, and we'll be discussing the different isomers that may be formed when we consider the geometry of those situations. And for some special cases, coobalt (III) and chromium (III) always have a CN of 6, and Platinum (II) always has a CN of 4.

The VSEPR discussion from earlier on in the class now applies: for a CN of 6, 5, 4, 3, or 2, we want the ligands to be arranged in an octahedral (for 6), trigonal bipyramidal or square pyramidal (for 5), tetrahedral or square (for 4), trigonal planar (for 3), or linear pattern (for 2), where like before the number of lone pairs matters.

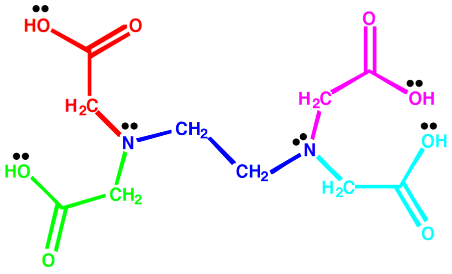
We also sometimes have **polydentate ligands** (also known as **chelating agents**), in which the ligands have multiple lone pairs of electrons and such that the shape allows the ligand to clamp down on the metal ion in multiple plays. ("Monodentate" refers to one point of attachment, "bidentate" refers to two points of attachment, and so on.) The picture in mind is that these ligands are grasping our transition metals like claws.

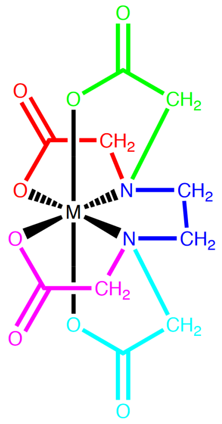
Example 225

Vitamin B12, which we discussed earlier in the course, is a Cobalt atom coordinate by a **tetradentate ligand** called corrin which completely wraps around the atom. But then there are two remaining ligands that complete the coordination complex.

Example 226

EDTA (ethylenediamine tetraacetic acid) is a **hexadentate chelate**, in which the OH groups and nitrogen atoms can donate lone pairs. The free structure of EDTA is shown on the left, and the structure when in complex with a metal ion of charge 2^+ is shown on the right.





EDTA chelation is used commonly in chemical research – the reason that this process is so favorable is that if we try to put a metal 2^+ ion into water, we'd need six water molecules to attach to it, while when EDTA chelates we only need one molecule. So the **chelating effect** basically explains that **metal chelates are stable because of the entropy increase that accompanies the release of water molecules**.

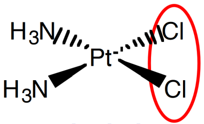
Fact 227

EDTA compounds are useful in the real world: chelation therapy is used for lead poisoning, bathtub cleaner chelates Ca^{2+} in bathtub scum, and EDTA is used as a food additive to prevent discoloration as well as bacterial and fungal activities.

Definition 228

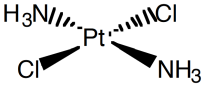
If we have multiple kinds of ligands in a metal, we can form **geometric isomers** in which the atoms are bound to the same ligands but in different locations, leading to different structures.

The strutures of cisplatin and translation are shown below: the difference in the locations of the Cl ligands affects whether the complex can crosslink with DNA.



cisplatin

potent
anti-cancer
drug



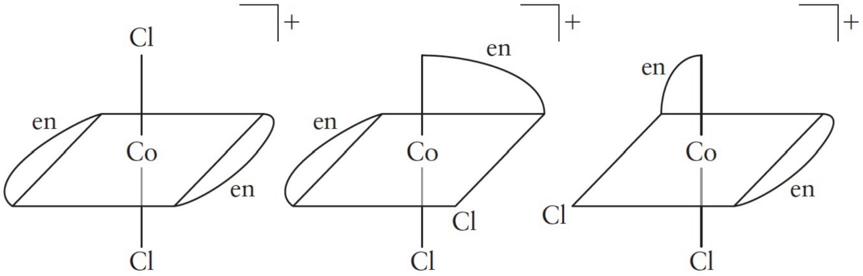
transplatin

no
known
function

Definition 229

Optical isomers are mirror images of compounds that are not superimposable. (A **chiral** molecule is a molecule not identical to its mirror image; in particular, all optical isomers are chiral.)

Below, we see three isomers, in which the middle and right pictures are optical isomers.



(a) *trans*-$[CoCl_2(en)_2]^+$ (b) *cis*-$[CoCl_2(en)_2]^+$ (c) *cis*-$[CoCl_2(en)_2]^+$

29 April 25, 2022

We'll discuss coordination complexes and transition metal ions, but specifically focusing on (a simplified version of) crystal field theory and magnetic properties that create colors.

Fact 230

Kelly Chibale is a South African organic chemist who developed treatments for HIV, cancer, malaria, and hypertension. He founded a drug discovery center, H3D, which discovered anti-malaria compounds that went into clinical trials. We may watch a conversation with him at this Youtube link.

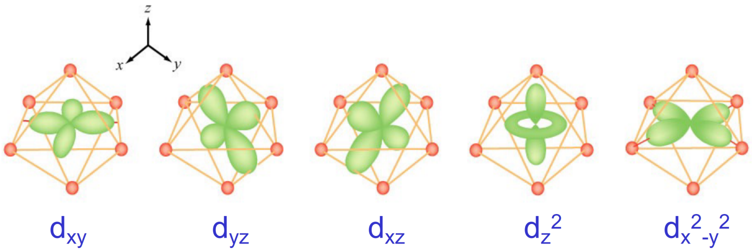
Last lecture, we introduced d block metals and how their electronic properties and trends lead us to coordination complexes in which ligands (Lewis bases) donate lone pairs to "attach" to the transition metal ions. (Recall that ligands can be neutral or negatively charged, and some ligands are polydentate.) Some common geometries for these coordination complexes are octehedral (coordination number of 6) or tetrahedral or square planar (coordination number of 4).

Fact 231

It is possible for d block metals to have +1 oxidation states as well – configurations based only atomic orbitals are oversimplified, and the diagram from last lecture is not complete.

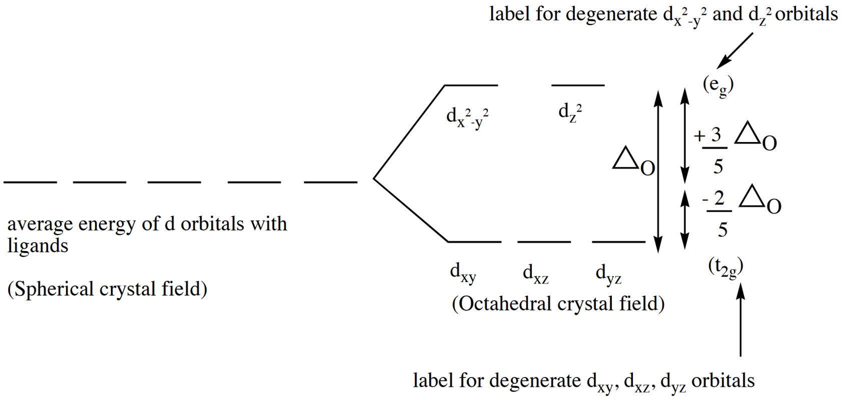
Our topic for today, **crystal field theory**, allows us to explain the different colors we see in transition metal ion solutions or complexes. The idea is that there are lots of *d* orbitals and thus a lot of d orbital electrons, and we need to think about **how ligands will adjust the energy levels of these orbitals** compared to for free metal ions. There are two ways to study this question – ligand field theory uses both covalent and ionic descriptions, while crystal field theory only uses an ionic description of the bonds.

Specifically, in crystal field theory, we think of ligands as negative point charges (for example, in an octahedral complex we imagine having negative point charges in an octahedron around the transition metal ion), and then we ask what happens to the various electron clouds. The shapes of the five d orbitals are generically shown below:



We can now think about what happens when the ligands come into play – if the ligands are at the tips of the orbital clouds, then we'll see a **large repulsion**. In particular, in the $d_{x}^{2}{}_{-y}^{2}$ and $d_z{}^2$ orbitals will be destabilized more than the other ones. On the other hand, the d_{xy}, d_{xz}, and d_{yz} orbitals are stabilized more. We end up finding that the latter three end up at a **lower energy** (but degenerate) and the former two end up at a **higher energy** than before.

We let Δ_O denote the crystal field splitting for **o**ctahedral complexes, and we show a diagram for the octahedral crystal field below (the labels e_g and t_{2g} come from group theory, but we won't get into that):



Another aspect to take into consideration here is how many d electrons end up being available for coordination with ligands, and that count is the **group number minus the oxidation number** of the metal. For example, for $[Co(H_2O)_2(NH_3)Cl_3]^-$ has oxidation number +2 for Cobalt (because we get a −1 from each of the three Cls, and we want the net oxidation number sum to be -1). Since Co is in group 9, we therefore have 7 d electrons available to work with. (If we have n d electrons available, we often say that we have a d^n complex.)

We now want to think about how they will fit into the crystal field splitting diagram. If we have n d electrons available, we often say that we have a d^n complex. But there is an important detail here instead of just using Hund's rule directly – **we must compare the crystal field splitting** Δ_O to the electron pairing energy to see which way to fill in the orbitals.

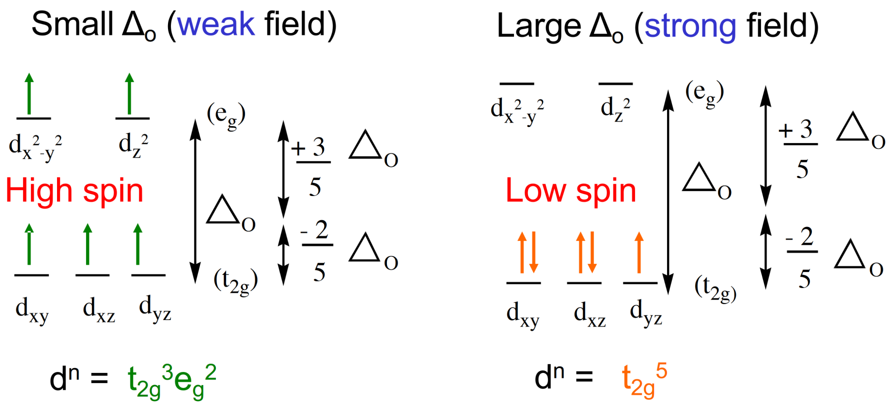
Fact 232

The Δ_O value depends on the ligands – a **strong field ligand** creates a large Δ_O, while a **weak field ligand** creates a small Δ_O. This leads us to the **spectrochemical series**, which indicates the various abilities of ligands to split d orbital energy levels. Specifically, from weak to strong (small to large Δ_O), we have I^-, Br^-, Cl^-, F^- (the halogen ions), followed by OH^-, H_2O (water is an intermediate-field ligand), NH_3, CO, and CN^-.

Example 233

Consider the octahedral complexes $[Fe(H_2O)_6]^{3+}$ and $[Fe(CN)_6]^{3-}$. Fe is in group 8, so the oxidation numbers of $+3$ in both cases give us d-counts of 5 in both complexes, and thus we have five electrons to fill the crystal field splitting diagram.

The key point from here is that for a weak field ligand like water, we can mostly ignore Δ_O compared to the repulsion between electrons in an orbital, and we fill with Hund's rule as usual. But with a strong field, we have to think of the two sets of d orbitals as being at significantly different energy levels and fill only the bottom set first:

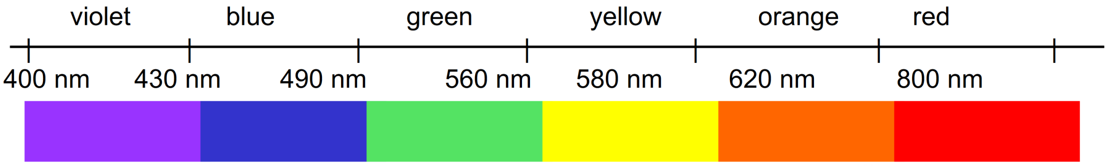


(We denote the complex with t_{2g} and e_g numbers to indicate how) The **crystal field stabilization energy** is then the energy change of our configuration compared to if it were completely spherical and with no splitting. We find that in the weak field case we get $3\left(-\frac{2}{5}\Delta_O\right)+2\left(\frac{3}{5}\Delta_O\right)=0$, while in the strong field case we get $5\left(-\frac{2}{5}\Delta_O\right)+2\text{PE}=-2\Delta_O+2\text{PE}$, where PE denotes the pairing energy for a set of electrons. And we can then predict the magnetic properties of these complexes: since both of these have unpaired electrons, we expect the compounds to be **paramagnetic**, meaning that they will be attracted by a magnetic field.

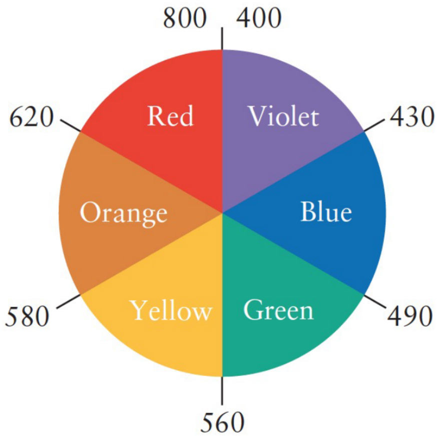
We'll now discuss how these energy level splittings correspond to colors and spectroscopy – recall that a substance absorbs photons if the energy $h\nu$ of the photon matches the energy difference between orbitals. Thus, in this case,

$$E_{\text{light}} = h\nu = \Delta_O.$$

It turns out that the splittings will typically be small enough to be in the **visible light range**, and here are the relevant wavelengths $\lambda = \frac{c}{\nu}$ for a complex absorbing different colors:



What's also important is that **the color that we see is the complementary color of the absorbed light** – for example, if we have a weak-field ligand, then we absorb longer wavelengths of light and thus transmit shorter wavelengths. Here "complementary" can be generally predicted from going across the "color wheel" below:



Fact 234

Coordination complexes may also be colorless if all of the d orbitals are filled, so that no d-d electron transitions can occur at all. This occurs for Zn^{2+} and Cd^{2+}, for example, in which we're in a 2+ oxidation state but 12 d electrons, and thus 10 electrons go into the d orbitals.

Example 235

Doing a concrete calculation, we can predict the color of the octahedral complex $[Co(H_2O)_6]^{2+}$, which has $\Delta_O = 239$ kJ/mol. We then find that $\frac{hc}{\lambda} = \Delta_O$, where we must convert the energy into energy per molecule / complex by dividing through by Avogadro's constant. Plugging in the numbers, we find that $\lambda = 5.00 \times 10^{-7}$ m (in the blue-green region), and thus we expect the color of the complex to be red-orange.

Fact 236

We can change the ligands around a metal to change the color: $CoCl_2$ will form $[Co(H_2O)_6]^{2+}$ (which is red) in solution, but it will form trans-$[CoCl_2(H_2O)_4]$ (which is blue) in solid state. So the complex will look red or blue depending on the mixture of ligands present, and we'll see that next lecture.

In general, the rule of thumb to keep in mind is that **strong field ligands** correspond to large splitting, low-spin complexes, less paramagnetism, and a red-ish color (because they absorb higher frequencies of light), and the opposite for weak field ligands. (And here, being "high" versus "low" spin basically means having many versus few unpaired electrons in the complex.)

30 April 27, 2022

Today's lecture will discuss **color, magnetism, and ligand geometries** for coordination complexes.

Fact 237

Mario Molina is a scientist known for his work on the ozone hole over Antarctica – he was a winner of the Nobel Prize in Chemistry in 1995, and he was the first person from Mexico to win a Nobel Prize in the sciences. As a postdoc, he co-authored a paper which highlighted the thread of chlorofluorocarbon (CFC) to the ozone layer, which led to a report that called for a complete ban on release of CFCs into the atmosphere and brought national attention.

Last time, we discussed how ligand electrons may split the d orbital energy levels for transition metal ions. In particular, this splitting allows for electronic transitions in the visible light region, and thus the color of our complexes depends on the energy splitting (for example, large splitting because of strong field ligands creates a more red-ish color), and the magnetic property depends on whether we have unpaired electrons in the d orbitals.

Example 238

For an octahedral d^7 complex, we may get different ground state electron configurations depending on whether we have a weak field or strong field ligand: in a weak field we fill all five d orbitals with a single electron first and then pair up two of them with the remaining electrons, but in a strong field we fill the three lower-energy d orbitals (xz, xy, yz) first and only place a single unpaired electron in the top level. Thus we get a $t_{2g}^5 e_g^2$ configuration (high-spin) in the weak field case, and we get a $t_{2g}^6 e_g^1$ configuration (low-spin) in the strong field case.

Example 239

For a high-spin d^4 complex, the crystal field stabilization energy will be $3 \cdot \left(-\frac{2}{5}\Delta_O\right) + 1 \cdot \left(\frac{3}{5}\Delta_O\right) = -\frac{3}{5}\Delta_O$, because three of the electrons are placed in the lower-energy orbitals and one is placed in the higher-energy one.

On the other hand, it's always important to remember that some ions have filled d orbitals, so that no visible-light transitions may occur at all, and that occurs in 2+ ions in Group 12.

Fact 240

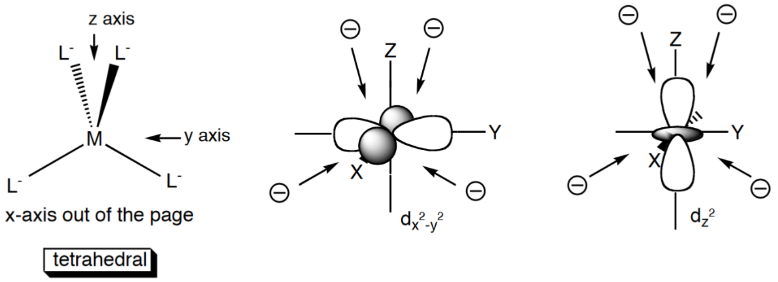
As mentioned last time, coordination complexes may change colors due to ligand changes. We'll look at four Ni(II) coordination complexes, namely $[Ni(H_2O)_6]^{2+}$, $[Ni(NH_3)_6]^{2+}$, $[Ni(en)_3]^{2+}$, and $[Ni(DMG)_2]^{2+}$ (notably red, square planar). If we add Ni(II) to water, we will form the first complex and create a light green color. But if we add ammonium hydroxide (originally colorless) to this solution, we will replace the water molecules and create the next complex, which creates a blue solution. We then get a purple color if we add ethylene diamine, and we get a red color if we add dimethylglyoxime.

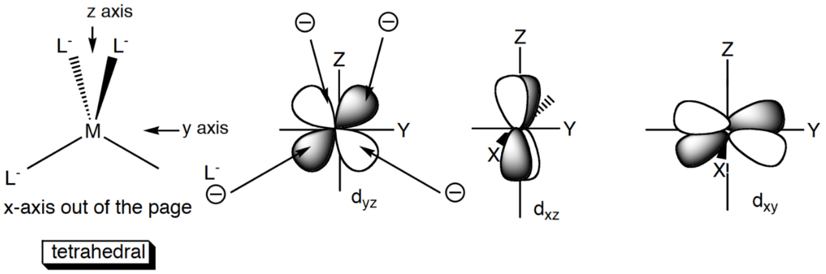
We can think about what this tells us about the various nickel complexes: seeing a greener color means that that **longer (redder) wavelengths** are absorbed, corresponding to a small Δ_O and thus a weak field ligand. On the other hand, as our color turns more blue, then violet, then red, our coordination complexes are absorbing light of shorter and shorter wavelengths, corresponding to larger Δ_Os and stronger ligands (explaining why we did indeed see a color change).

But the key point in our discussion above is that **we're now talking about a ligand geometry which is not octahedral**, and we'll be thinking about these different shapes that may be formed when the CN is not 6. For example, a CN of 4 can correspond to a square planar or tetrahedral geometry, and a CN of 5 can correspond to a square pyramidal geometry, and we'll next think about what the corresponding splitting diagrams look like.

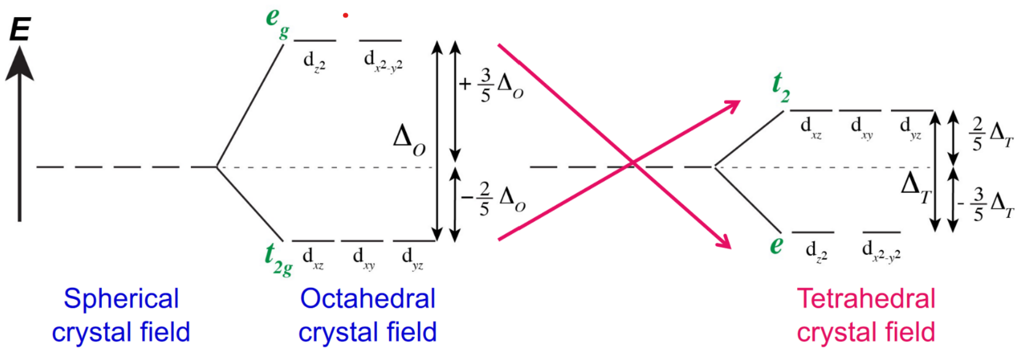
The strategy is again to think about how those geometries combine along with the shapes of the metal ion's d orbitals and understand which orbitals are more stable.

- Tetrahedral complexes are difficult to visualize, because they do not line up with the usual Cartesian coordinate directions. If we look at the diagram below, the top two orbitals will exhibit **less repulsion** than the bottom three orbitals, essentially because the orbitals aren't lining up exactly with the directions of the electrons. Thus we destabilize the xy, xz, and yz more (which is the opposite situation as in the octahedral case), making their energy higher:





Thus for a tetrahedral complex, **two** (rather than three) of the d orbitals are lower in energy than before, and we denote the splitting of energies as Δ_T. In general, we will have $\Delta_T < \Delta_O$ (because the point charges aren't directly pointed at any of the orbitals), and we denote the field states as e and t_2 instead of e and t_{2g}.



Fact 241

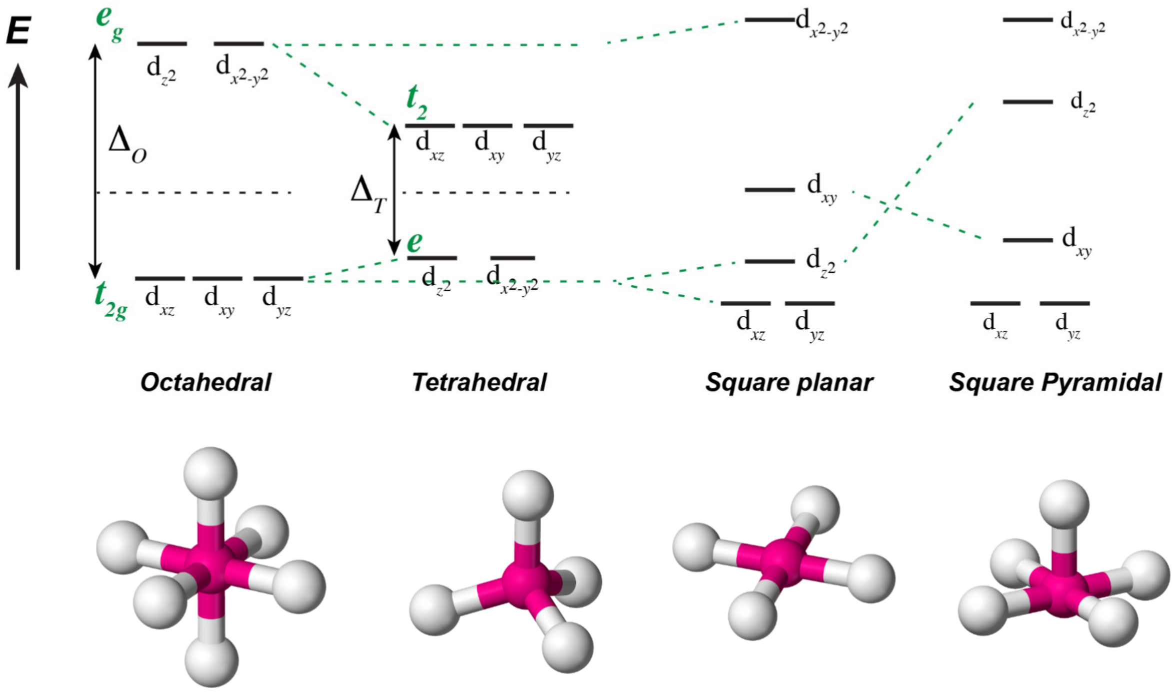
We may assume in this class that tetrahedral complexes are **high spin** in general, meaning that we will try to fill all five d orbitals before pairing up any electrons, because Δ_T tends to be small.

Example 242

Consider Cr^{3+}; because Chromium is in group 6, we will have a d^3 complex. If we consider a tetrahedral crystal field splitting diagram for such a complex, we will fill in one electron in each of $d_{x^2-y^2}$ and d_{z^2} (the lower energy orbitals), as well as one electron in either the xz, xy, or yz orbital. The d^n electron configuration is then $e^2t_2{}^1$ and we have three unpaired electrons.

- We may now think about the other case for a CN of 4, which is the **square planar** case. In this case, we destabilize the xy and x^2-y^2 orbitals the most if our coordination complex is aligned in the xy-direction, but the magnitudes of the repulsions will vary. It will turn out that the x^2-y^2 orbital is of the highest energy, followed by the xy orbital, followed by z^2 and then yz and xz together. (So there are **four different energy levels** for this case.)
- Finally, when we have a square pyramidal ligand geometry, we can also predict the extent of destabilization for all five of the d orbitals. We'll find that if the new ligand is added along the z axis, then the xz and yz orbitals will become more destabilized, and so will the z^2 orbital, relative to the square planar case.

Putting everything together, we can compare the crystal field splittings of all four geometries – for square planar and square pyramidal, we'll have to understand the balance between the energy splittings and the electron pairing energy on a case-by-case basis.



Example 243

A Nickel enzyme is made up of a Ni^{2+} center, and it is a diamagnetic d^8 complex. From this, we can **predict the geometry** (between octahedral, tetrahedral, and square planar): we may check that adding eight electrons to either the octahedral or tetrahedral splitting diagrams will always leave unpaired electrons (no matter whether the octahedral case is strong-field or weak-field), but for a square planar configuration we can fill all eight electrons with the four lower-energy orbitals. Thus this enzyme must indeed be square planar and have a CN of 4.

31 April 29, 2022

Today's lecture is an introduction to **chemical kinetics**, and it will also be the last demo of the semester (there used to be one more but it was a bit too hectic).

Fact 244

Rosalyn Sussman Yalow was a medical physicist who was one of the winners of the 1977 Nobel Prize in Medicine for developing RIA (radioimmunoassay), which was a method to measure the concentration of substances in blood. (She was the second Nobel Prize laureate after Marie Curie.) Over the course of her research, she mentored many students, such as the "queen of carbon" Mildred Dresselhaus.

Last lecture, we discussed crystal field splitting and how it affects electron configurations of various d-metal complexes, depending on both ligand type (strong-field versus weak-field) and coordination geometry. Today, we'll switch gears to **chemical reaction rates**, thinking about how fast reactions will go. This is a **different** question from that of thermodynamics and the spontaneous direction of reaction (which depends only on ΔG); the rate of reaction may instead depend on things like the energy barrier that needs to be overcome for the reaction to occur. We'll thus try to understand the overall rate at which concentration changes with time.

Fact 245

Questions about reaction rates (understanding why some reactions go faster and how to make them speed up with catalysts) have many applications. For example, it's interesting to ask why changes in temperature can have effects on cooking rates for food, and measured reaction rates may tell us about reaction pathways and mechanisms (how do the molecules actually come together). In general, kinetics is less well-understood than thermodynamics – we can measure equilibrium constants for a redox reaction with a galvanic cell, for example, but it's hard to determine the pathway and intermediate steps of those reactions because we do not always have simultaneous collision between all reactants.

Example 246

In Professor Hong's lab, the **tau protein** is an intrinsically disordered protein in neurons which stabilizes microtubules. Neurodegenerative diseases cause tau to misfold, and propagation of that misfolded structure will cause toxicity in neurons. It's thus important to understand the molecular mechanism by which misfolding and propagation may occur, and in the lab (depending on various factors) the assembly of fibrils occurs at various rates.

Before we describe kinetics in more detail, we'll consider the Briggs-Rauscher (oscillating clock) reaction

$$\mathrm{IO_3^-} + 2\ \mathrm{H_2O_2} + \mathrm{CH_2(COOH)_2} + H^+ \to \mathrm{ICH(COOH)_2} + 2\ \mathrm{O_2} + 3\ \mathrm{H_2O}.$$

Fact 247

A demo was performed in class: adding these various reactants to a beaker will give us a transparent solution, but then adding an indicator causes the color to repeatedly cycle between amber and dark blue.

What's really happening is that there is a **two-step reaction mechanism**: when we have a low concentration of I_2, the dominant reaction taking place will be

$$IO_3^- + I^- + 2\ H_2O_2 + 2\ H^+ \to 2O_2$$

where I_2 is causing the amber color. But when we have a lot of I_2, we instead get the reaction

$$I_2 + CH_2(COOH)_2 \to ICH(COOH)_2 + H^+ + I^-,$$

and $ICH(COOH)_2$ appears with a blue color. So the color changes are due to the relative concentrations of the colored compounds.

Remark 248. *As a sidenote, the first step of the reaction is a redox process:* IO_3^- *is reduced to* I_2 *(from +5 to 0), while* I^- *is oxidized to* I_2 *(from* -1 *to* 0*). On the other hand, one oxygen in* H_2O_2 *is oxidized to* O_2 *(from* -1 *to* 0*), while the other one is reduced to* H_2O *(from* -1 *to* -2*). But in this reaction,* H_2O_2 *is a good oxidizing agent.*

The key is that reaction rates depend on **both** the initial concentration of the reactants but also on the temperature in which the reaction is occurring.

Measuring reaction rates is difficult to do because the concentration of a reactant does not change in a linear way over time. For example, consider the reaction $NO_2(g) + CO\ (g) \to NO(g) + CO_2(g)$. Then we can define the **average rate** to be $\frac{\Delta[NO]}{\Delta t}$ over an interval of time Δt, though this average rate will depend on the interval that we choose. So if we want the rate at a particular time, it makes sense to instead take a derivative and define the **instantaneous rate** to be $\frac{d[NO]}{dt}$ in this case. (And if we can fit a curve to the experimental data, we can do the math explicitly.) In particular, the **initial rate** of the reaction is the instantaneous rate at time 0.

Definition 249

To measure reaction rate, we can either monitor the increase of products or the decrease of reactants. For example, in the reaction above, we can also define the instantaneous reaction to be $-\frac{d[NO]_2}{dt}$, or $-\frac{d[CO]}{dt}$, or $\frac{d[CO]_2}{dt}$. But if there are stoichiometric coefficients, and we have a reaction like $aA + bB \to cC + dD$, the instantaneous rate must account for these by defining the rate to be $-\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt} = \frac{1}{d}\frac{d[D]}{dt}$.

Recall that we've mentioned previously that at equilibrium, we talk about both forward and reverse rates being nonzero even though the net rate is zero. So the result above is really talking about **net** rates when we measure concentration.

Proposition 250

The instantaneous rate of a reaction is proportionally related to the concentration of our reactants or products. In particular, we may write the rate as

$$\text{rate} = k[A]^m[B]^n \cdots$$

for some rate constant k, and where m and n denote the **order of reaction** in the reactants or products A, B, and so on.

In particular, the order of reaction m and n do not need to be the same as the coefficients a and b, and they can be integers, fractions, negative, or positive – **we figure them out by measuring reactions experimentally**, and we can only predict the rate law from stoichiometry if we have an elementary reaction. (And it's important to mention that the rate law may have terms related to the products too, for example if having more products slows down the rate of a reaction.)

Thinking more about the implications of having an "mth order reaction," notice that in a **first order reaction** where the rate is of the form k[A], doubling the concentration of A will double the rate of the reaction. On the other hand, having a second order reaction with rate $k[A]^2$ will cause the rate to be quadrupled if we double [A], but having $m = -1$ or $m = -\frac{1}{2}$ will make the rate slower if we have more of the substance A. And there are some situations where we have zeroth order reactions, meaning that the rate is independent of the concentration of the relevant species.

Fact 251

While the reaction rate always has the same units of [M] per time, the units for the rate constant k may vary depending on the order of the reaction.

It is often difficult to measure instantaneous rates for reactions experimentally, and so it is easier to do integration to get a more tractable formula.

Example 252

Suppose we have a first-order reaction of the form A → B, meaning that the instantaneous rate is given by

$$-\frac{d[\text{A}]}{dt} = k[A].$$

If we use the usual method for solving such a differential equation, we find that (separating variables and integrating)

$$-\frac{1}{[\text{A}]}d[\text{A}] = -k\,dt \implies \ln[\text{A}] - \ln[\text{A}]_0 = -kt,$$

which gives us "exponential decay:" the reaction rate satisfies $\boxed{[\text{A}]_t = [\text{A}]_0 e^{-kt}}$, and this is called an **integrated rate law** for the reaction A → B. So if we're analyzing an experiment in a lab, we can plot $\ln[\text{A}]$ over time and see if it follows a straight line – if so, we have a first-order reaction and the slope is $-k$.

Definition 253

For any reaction, the **half-life** $t_{1/2}$ is the amount of time that it takes for the original concentration to be cut in half.

For a first-order reaction, this occurs when $e^{-kt_{1/2}} = 1/2 \implies t_{1/2} = \frac{\ln 2}{t} \approx \frac{0.6931}{t}$. In other words, the half-life does not depend on the initial concentration, only on the rate constant of the reaction, and our concentration will continue to be cut in half at increments of every $t_{1/2}$.

32 May 2, 2022

Our final exam (on Tuesday the 17th) will be cumulative but focus more on the second half of the class, and as usual, we'll have review sessions and materials available to us as the exam approaches. (And as a reminder, we should fill out the subject evaluations before next Friday.)

Fact 254

Mildred Dresselhaus is an American nanotechnologist who (as we mentioned last lecture) is known as the "queen of carbon," known for her work on graphite, carbon nanotubes, fullerenes, and low-dimensional thermoelectrics. (She was a pioneer in the field before it was popular, and the field has now blossomed.) She was the first female Institute Professor at MIT (she spent 57 years here!), and she received the Presidential Medal of Freedom in 2014.

We discussed **rate laws** last lecture, mentioning that reaction rates are measured in terms of changes of concentrations over time and can depend (in various orders) on the concentrations of reactants and products. In particular, a simple case where the rate is proportional to a single concentration [A] exhibits exponential decay for [A] with a half-life $t_{1/2} = \frac{\ln 2}{k}$ (where k is the rate constant).

Today's lecture will first cover **nuclear chemistry** as an application of first-order reactions (the idea being that even though most chemistry focuses on properties of electrons, the nucleus of our atoms may change as well). We'll be looking at symbols like ${}^{A}_{Z}\mathrm{X}_{N}$ today, where the Z represents the number of protons (giving us the atomic number) of an atom, the A represents the total number of nucleons (both protons and neutrons, giving us the atomic mass), and N represents the number of neutrons (often omitted because $A = Z + N$). In particular, electrons are written as ${}^{0}_{-1}\mathrm{e}$, since the mass of an electron is so much smaller than the mass of any proton or neutron.

Definition 255

An **isotope** of an element is defined by the values of Z and A. Since the element X written in the middle specifies the value of Z, we may also simplify our notation to ${}^{A}\mathrm{X}$ to designate a partiuclar isotope.

Example 256

Carbon always has 6 protons, but it has various isotopes Carbon-12, Carbon-13, Carbon-14, and Carbon-11. The most stable one is the former, ${}^{12}_{6}\mathrm{C}$, which makes up 99.0% of naturally occurring carbon and is a stable isotope with nuclear spin (spin number for the nucleus) 0. We also have ${}^{13}_{6}\mathrm{C}$, which appears 1.1% of the time and is a stable isotope with nuclear spin 1/2 (this is what is studied with NMR). The next isotope ${}^{14}_{6}\mathrm{C}$ is radioactive with a half-life of 5730 years, and thus it is used for **carbon dating** on the geological timescales. On the other hand, ${}^{11}_{6}\mathrm{C}$ is radioactive with a half-line of 20 minutes and is used in PET (positron emission tomography).

Example 257

Hydrogen has the isotopes ${}^{1}\mathrm{H}$ (a single proton, 99.98% of all hydrogen, stable, with a nuclear spin of 1/2), ${}^{2}\mathrm{H}$ (deuterium, stable, nuclear spin of 1, used to make **heavy (deuterated) water**), and ${}^{3}\mathrm{H}$ (tritium, rare, radioactive with a half-life of 12.3 years). In fact, the melting point for heavy water is 4 Kelvin higher than for ordinary water, and this causes it to have adverse biological effects.

We can study different isotopes with various chemical analysis methods: mass spectrometry allows us to measure A, neutron diffraction allows us to compare scattering lengths of different isotopes, and NMR lets us distinguish between spins. But what we're interested in for chemical kinetics purposes is the **spontaneous decay of radioactive nuclei** (which only occurs for unstable isotopes).

Proposition 258

In a nuclear decay reaction, atomic mass and number may both change, but mass and charge must balance out. And the reaction will be spontaneous (even if very slow) if products have lower energy than the reactants.

Definition 259

In **α decay**, we have the nuclear decay reaction

$$^{A}_{Z}\mathrm{X} \to {}^{A-4}_{Z-2}\mathrm{Y} + \alpha + 2e^{-}.$$

In particular, by balancing protons, neutrons, and charges, we see that an α-particle is an ejected Helium nucleus $^{4}_{2}\mathrm{He}^{2+}$.

Definition 260

In **β/β^{-} decay**, we have the nuclear decay reaction

$$^{A}_{Z}X \to {}^{A}_{Z+1}\mathrm{Y} + {}^{0}_{-1}\mathrm{e}$$

in which an electron is emitted. There is also a **β^{+} decay** in which a positron is emitted (which is what is used in positron emission tomography):

$$^{A}_{Z}X \to {}^{A}_{Z-1}\mathrm{Y} + {}^{0}_{+1}\mathrm{e}.$$

Definition 261

In γ radiation, we emit a photon via the equation

$$^{A}_{Z}X \to {}^{A}_{Z}X + \gamma.$$

We won't talk too much about these different processes, other than thinking about how **radioactive decay is a first-order reaction**. In nuclear decay kinetics, we can measure the rate of decay of nuclei with a **Geiger counter** (which detects radiation), where instead of measuring in terms of the changes in concentration [A], we measure in terms of number of nuclei we have. We get an equation of the form

$$N = N_0 e^{-kt},$$

where N_0 is the number of nuclei initially present, t is the time elapsed, and k is the decay constant. We may define the **activity** $A = -\frac{dN}{dt}$ to be the number of nuclei decaying per unit time – just like for a normal first-order reaction, we have the equation $A = kN$, and we in fact also get an exponential decay for the activity

$$A(t) = A_0 e^{-kt}$$

(since we've lost a fraction of the initial nuclei that may potentially decay). And just like other first-order reactions, we get $t_{1/2} = \frac{\ln 2}{k} = \frac{N_0 \ln 2}{A_0}$.

Fact 262

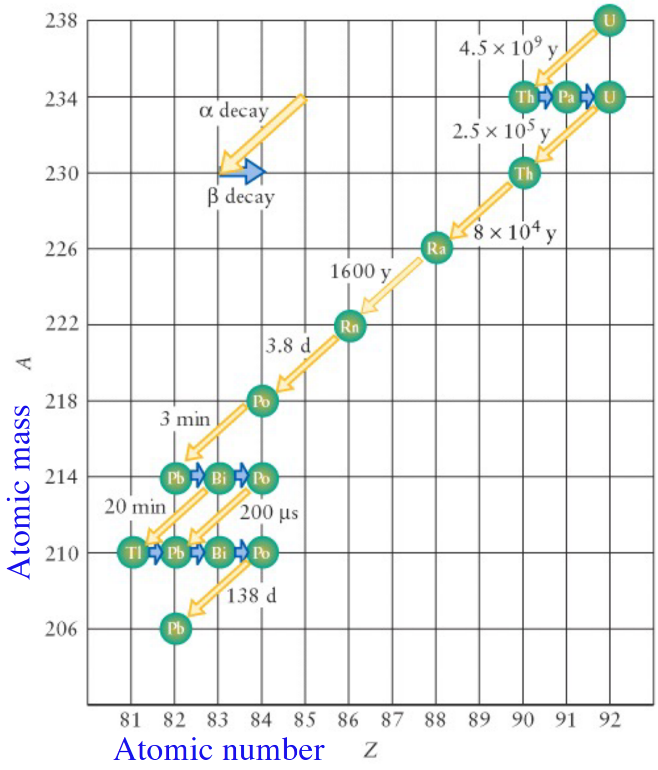
The SI unit for activity is the Becquerel (1 Bq is one nucleus decaying per second), though an older unit that used to be common was the Curie (1 Ci is 3.7×10^{10} decays per second).

In particular, given an amount of starting nuclei, the initial activity and half-life of the substance are **inversely related**. For example, tritium has a half-life of 12.3 years and an initial activity of 9621 Ci/g, while uranium-238 has a half-life of 4.5 billion years but an initial activity of 3.4×10^{-7} Ci/g. (In general, radioactive isotopes can have a huge variation in half-life!)

Fact 263

The element Radium (with atomic number 88) was discovered by Marie and Pierre Curie in 1898 – the α-decay that Radium-226 undergoes has a long half-life. But the product that it creates, Radon-222, is a significant health hazard (it has a half-life of about 3 days). For some other interesting examples, the largest source of natural radioactivity in animals comes from Potassium-40, though this decays very slowly. And Strontium-90 is a "bone seeker" that replaces calcium (which is bad for our bones).

For these kinds of discussions, the **nuclear decay series** is useful to considering the sequences of nuclear decays that a species can experience. We often plot these in a chart comparing atomic mass and atomic number, following the arrows downward (and indicating half-lives to see which reactions occur quickly).



(If we'd like an interesting read, we can check out "Days of our Half-Lives" by Mala L. Radhakrishnan, who got a PhD in chemistry from MIT and is now faculty at Wellesley.)

For the remainder of this class, we'll talk about **second-order reactions**, which are only slightly more complicated. Our rate law now looks like

$$-\frac{d[\mathrm{A}]}{dt} = k[\mathrm{A}]^2,$$

and again separating variables and solving for the integrated rate law gives us

$$-\frac{1}{[\mathrm{A}]^2}d[\mathrm{A}] = -kdt \implies \frac{1}{[\mathrm{A}]_0} - \frac{1}{[\mathrm{A}]} = -kt \implies \frac{1}{[\mathrm{A}]} = kt + \frac{1}{[\mathrm{A}]_0}.$$

In other words, if we plot the reciprocal of our concentration as a function of time and we get a straight line, we will have a second-order equation (and the way we distinguish between different orders of reactions is by making plots of $\log[\mathrm{A}]$ and $\frac{1}{[\mathrm{A}]}$ and seeing which one forms a straight line over time). And the half-life is the time t at which [A] is half of the initial $\frac{1}{[\mathrm{A}]_0}$; solving yields

$$\frac{1}{[\mathrm{A}]_0/2} = kt_{1/2} + \frac{1}{[\mathrm{A}]_0} \implies t_{1/2} = \frac{1}{k[\mathrm{A}]_0}.$$

In other words, the half-life is no longer an inherent property of the reaction and the rate constant – the half-life is shorter if we start off with a higher concentration, and thus that makes $t_{1/2}$ not a very useful quantity.

We'll now relate reaction rates and rate constants k back to the **equilibrium constants** K from earlier in the course: recall that at equilibrium the forward and reverse reaction rates are equal, and the relevant equations for a chemical reaction of the form $\mathrm{A} + \mathrm{B} \to \mathrm{C} + \mathrm{D}$ are

$$K_{\mathrm{eq}} = \frac{[\mathrm{C}][\mathrm{D}]}{[\mathrm{A}][\mathrm{B}]}, \quad \mathrm{rate}_{\mathrm{forward}} = k_1[\mathrm{A}][\mathrm{B}], \quad \mathrm{rate}_{\mathrm{reverse}} = k_{-1}[\mathrm{C}][\mathrm{D}].$$

where k_1, k_{-1} are the forward and reverse rate constants. Putting these equations together and noting that the reaction rates are equal at equilibrium, we find that

$$\boxed{K_{\mathrm{eq}} = \frac{k_1}{k_{-1}}}.$$

(So if $K > 1$, then the forward reaction is "much faster" in terms of rate constants, and vice versa.)

Reactions do not typically occur in a single step, though – they usually proceed through a series of steps known as **elementary reactions**. We'll explore this more next lecture, but the idea is that for elementary reactions we can directly figure out the rate laws. The **molecularity** of an elementary reaction (unimolecular, bimolecular, termolecular) is the number of reactant molecules that come together, and we'll see next time how we can use that information to predict the form of rate laws.

33 May 4, 2022

Last lecture, we discussed how different isotopes of an element have different properties – in particular, radioactive isotopes will undergo spontaneous decay (often through α, β^-, and β^+ decay) into other elements. Spontaneous decays thus follow first-order kinetics, and we keep track of such processes by tracking the number of nuclei and the activity of decay A. We also briefly discussed how nuclear reactions sometimes proceed in long decay series (such as the $^{238}\mathrm{U}$ series decaying into $^{206}\mathrm{Pb}$). And in the last part of the lecture, we discussed second-order reactions and their concentration-dependent half-life.

Today's lecture will study how **reaction rates depend on temperature** – the general rule of thumb is that rates tend to increase with temperature in the gas phase (and this will indeed be true for simple, elemental reactions). But with more complicated reactions, it's no longer as clear, and we'll see that later on in the lecture. We'll start with the simple case (which was studied by Arrhenius in 1889):

Proposition 264 (Arrhenius equation)

The rate constant k for an elementary reaction has a temperature-dependence given by

$$\ln k = \ln A - \frac{E_a}{R}\frac{1}{T} \iff k = Ae^{-\frac{E_a}{RT}},$$

where R is the gas constant, T is the temperature, A is a prefactor, and E_a is the **activation energy**.

In particular, the relationship between $\ln k$ and $\frac{1}{T}$ is linear – the larger $\frac{1}{T}$ is (the colder the temperature), the smaller $\ln k$ is (the slower the reaction proceeds). A is usually quite large, and in particular this means that as $T \to \infty$, the rate for the reaction will approach $Ae^{-0} = A$, some large finite constant. A is often called the **attempt frequency**, which can be thought of as the frequency with which molecules try to collide and make the reaction happen. And the meaning of this E_a term is usually thought of as an "energy barrier" that needs to be overcome for the reaction to actually proceed.

Fact 265

The value of E_a is typically temperature-independent, though if we change T wildly we might change the dynamics of the reaction. But for typical values this is not a major factor. In general, the larger E_a is, the more sensitive the rate is to changes in temperature (because, intuitively, large activation energy requires lots of kinetic energy from ambient temperature to allow the reaction to occur).

Example 266

Sucrose (from sugary food) hydrolyzes into glucose and fructose with the help of an acid catalyst during digestion. Given that $E_a = 108$ kJ/mol for this reaction, and given that $k = 1.0 \times 10^{-3}$ M^{-1}s^{-1} at body temperature (37 degrees Celsius), we can find k at 34 degrees Celsius (which would be a dangerous temperature for the human body).

Letting the rate constants at the two different temperatures be k_1 and k_2, we find that

$$\ln k_1 = \ln A - \frac{E_a}{R}\frac{1}{T_1}, \quad \ln k_2 = \ln A - \frac{E_a}{R}\frac{1}{T_2}$$

(assuming that E_a is constant over the temperature range, and so is A). Subtracting the two equations yields

$$\boxed{\ln \frac{k_2}{k_1} = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)},$$

and plugging in the values of E_a, T_1, T_2 that we have (remembering to use units of Kelvin instead of Celsius) and simplifying yields $k_2 = 6.6 \times 10^{-4}$ M^{-1}s^{-1}. So digestion of sucrose occurs at two-thirds the speed that it normally does if we only decrease the temperature by 3 degrees, and that kind of situation is why our body works much less well in the cold.

Fact 267

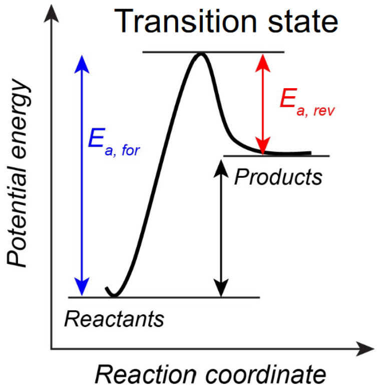
An activation energy below 10 kJ/mol is considered low (at that energy, decreasing temperature from 37 to 27 degrees Celsius decreases the rate constant by about 12 percent), and an activation energy above 60 kJ/mol is considered high (at that energy, decreasing the temperature in the same way decreases the rate constant by about 54 percent). And we can now compare those numbers to some of the values we've discussed earlier in the class to understand which processes have a high activation energy.

Going to a more extreme situation, if we look at enzymatic reactions at temperatures like 77 Kelvin (liquid nitrogen), rates will slow down far more. At an activation energy of 10 kJ/mol, $\ln \frac{k_2}{k_1} \approx -11.7 \implies \frac{k_2}{k_1} \approx 8.0 \times 10^{-6}$ (5 to 6 orders of magnitude slower), and even more dramatically at an activation energy of 60 kJ/mol, $\ln \frac{k_2}{k_1} \approx -70.4 \implies \frac{k_2}{k_1} \approx 2.5 \times 10^{-31}$. In other words, for fairly high activation energies, we will basically see almost no reaction at cryogenic temperatures in terms of molecular motions.

Fact 268

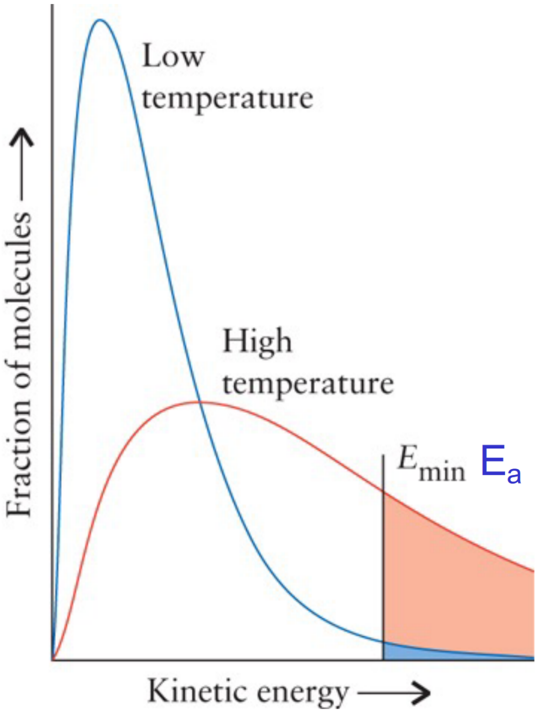
If we consider a simple reaction like CH_3 (g) + CH_3 (g) $\to$ C_2H_6 (g), we form the product by colliding two CH_3 molecules, but not every two molecules that collide will form a product. There is some critical energy $E_{\text{min}} = E_a$ that needs to be overcome when they collide, because **potential energy increases** as molecules get closer and the bonds distort. This encounter gives us an activated complex called a **transition state**, which is a (transient) combination of molecules that can either fall apart or form the product.

In this part of the course, we'll see the following diagram quite often:



On the x-axis, we graph the reaction coordinate (extent of completion of the reaction). In this case, what's important to notice is that there is a "hill" between the reactants and products (higher energy than both endpoints) which must be overcome to get over to the other side. We thus get a "forward" activation energy, as well as a "reverse" activation energy.

And yet another way to think about this situation is through a statistical mechanics approach: at higher temperature, the histogram of kinetic energies that the individual molecules will have is shifted more towards the right, so a higher fraction of the molecules will have enough energy to overcome the required E_a barrier.



But not every reaction goes faster at higher temperatures – this is only true when we have an **elementary reaction**, in which the activation energy barrier is positive. For more complicated, multi-step reactions, we have to look at the balance within the reaction:

Example 269

Consider the reaction $2\ NO+O_2 \to 2\ NO_2$, which has an enthalpy of $\Delta H^\circ = -114$ kJ/mol. This reaction involves three molecules, and in fact it actually occurs with a two-step mechanism: first, $NO + NO \rightleftharpoons N_2O_2$ is a fast and reversible step with a forward and reverse rate constant k_1 and k_{-1}, respectively. Then second, we have a slower step $N_2O_2 + O_2 \to 2NO_2$ with a rate constant k_2.

In such a situation, the rate of product formation is really **limited by the second step**, and thus the rate of product formation can be written as

$$\text{rate} = 2k_2[N_2O_2][O_2]$$

(factor of 2 because we form two NO_2 molecules). But because N_2O_2 is an intermediate product, we don't want to write our rate law in terms of it. Instead, since the first step is an elementary reaction, we can write its equilibrium constant (K_1 with a capital K) as

$$K_1 = \frac{[N_2O_2]}{[NO]^2} \implies [N_2O_2] = K_1[NO]^2.$$

(Because we're talking about chemical equilibrium, and this is not the fast part of the overall reaction, notice that the rate constants k_1, k_{-1} do **not** come into play.) We thus find that the overall rate is (plugging in)

$$\text{rate} = 2k_2K_1[NO]^2[O_2].$$

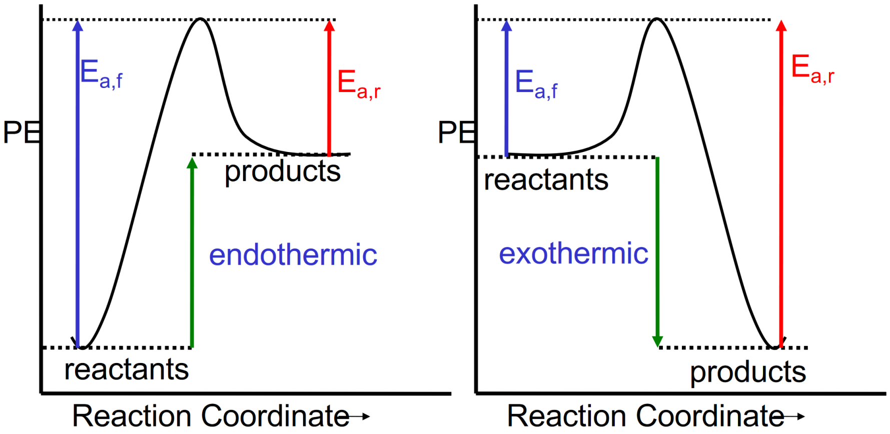
So now things get more complicated: the rate constant k_2 for an elementary reaction always increases with T, as we've been discussing. But on the other hand, the equilibrium constant K_1 for the other reaction may increase or decrease with temperature, depending on whether the reaction is exothermic or endothermic! In this case, since ΔH° is exothermic, increasing the temperature will decrease the equilibrium constant K_1, and we get an overall **observed rate** $k_{\text{obs}} = 2k_2K_1$, which will increase or decrease with T depending on E_a and ΔH.

Remark 270. *Notice that we have* **two very similar equations** *(Arrhenius and van't Hoff)*

$$\ln\frac{k_2}{k_1} = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right), \quad \ln\frac{K_2}{K_1} = -\frac{\Delta H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right),$$

and in particular a large E_a (resp. ΔH) means that k (resp. K_{eq}) is very sensitive to temperature. In the case above, it is the combination of the E_a and ΔH that affects whether the overall observed rate increases or decreases with T.

We can now connect kinetics and thermodynamics together by thinking more about these activation energy diagrams:



In particular, if we look at the left diagram (in which the reaction is endothermic and the forward activation energy $E_{a,f}$ is much larger than the reverse activation energy $E_{a,r}$), the idea is that **at higher temperatures** it becomes less difficult to overcome $E_{a,f}$ and thus the ΔE difference becomes less noticeable, shifting the reactions to products. And on the flip side, if we increase temperature for an exothermic reaction, it becomes easier to overcome $E_{a,r}$ and thus we shift the reaction towards reactants.

34 May 6, 2022

Fact 271

Professor McGuire is here to remind us that the final exam will be comprehensive, so in particular we should make sure to study information about the structure of the atom (shielding, periodic trends), molecular orbital digrams, and Lewis structures. (If we'd like tutoring for the class, it's still available – we should email the course staff.) And we can take 5.60 next spring with Professor McGuire if we want to learn more applications of thermodynamics and kinetics.

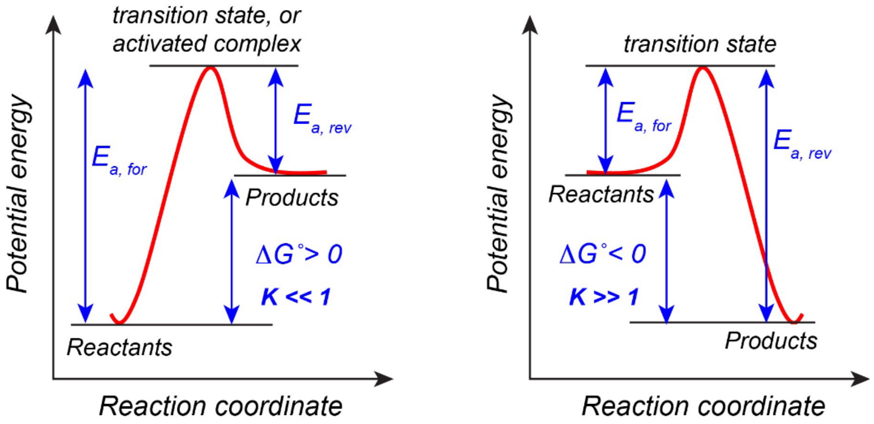
Fact 272

Irene Joliot-Curie (the daughter of Marie Curie) was a French chemist, physicist, and politician who co-won the 1935 Nobel Prize in Chemistry for synthesizing new radioactive materials. Her PhD thesis was on the alpha decay of polonium (an element discovered by her mother), and her major work was the discovery of positron emission and beta emission.

Last lecture, we discussed the temperature-dependence of reaction rates (via the Arrhenius equation) – intuitively, the activation energy E_a affects the fraction of collisions that have enough energy to form products. But today's lecture will discuss **reaction mechanisms**, discussing further the ideas from last lecture that a relevant question for determining reaction rates for more complicated reactions requires an understanding of which steps are fast or slow.

First, we should recall that there are different rate laws that may govern an elementary reaction: depending on whether we have a 0th, 1st, or 2nd order reaction, our rate will be proportional to k, $k[\mathrm{A}]$, or $k[\mathrm{A}]^2$, respectively. leading to different integrated rate laws, half-lives, and types of processes.

Additionally, we can also connect activation energy and Gibbs free energy together – looking at activation energy diagrams like the ones we drew last time, the sign of ΔG° is related to the question of whether the forward $E_{a,\text{ for}}$ or reverse $E_{a,\text{ rev}}$ activation energies are larger. And remembering that $\Delta G^\circ = -RT \ln K_{\text{eq}}$ and that $k = Ae^{-E_a/RT}$, we can relate the rate constants and equilibrium constants of a given reaction to the energies that we can read off such a diagram.



If we look at the forward and reverse "hills" in this diagram, we can in fact see that

$$\frac{k_f}{k_r} = e^{-(E_{a,f} - E_{a,r})/RT} = e^{-\Delta G^\circ/RT} = K_{\text{eq}},$$

so the equilibrium constants can be determined in terms of the rate constants. (We in fact derived this identity two lectures ago in another way by setting the forward and reverse rates equal at equilibrium.)

Fact 273

Reaction mechanisms are proposed to explain empirical, measured rate laws – whenever we have three or more reactant molecules, we usually need to think about multi-step elementary processes and see if the laws end up matching experimental results.

We'll do this by examining a few examples today – in this class, we'll be expected to do calculations like the following, given a proposed multi-step mechanism for the reaction.

Example 274

Consider the equation $2\ NO + O_2 \to 2\ NO_2$, which has an experimentally observed rate of formation of NO_2 of $k_{\text{obs}}[NO]^2[O]_2$ (where k_{obs} is some constant).

From the expression above, the overall order of this reaction is 3, but it's unlikely for all three molecules to collide together, so a single-step mechanism is not likely. Here's a proposed two-step elementary reaction mechanism: suppose that the first step

$$NO + NO \rightleftharpoons N_2O_2$$

is reversible and fast with rate constants k_1 and k_{-1} in the forward and reverse directions (this is the notation we'll use throughout the lecture), and the second step

$$N_2O_2 + O_2 \to NO_2 + NO_2$$

is slow and has a forward rate constant k_2. **If** this were the case, the rate of formation of N_2O_2 would be $k_1[NO]^2$, while the rate of decomposition of N_2O_2 would be $k_{-1}[N_2O_2]$ (we have to think about both the creation and destruction of this intermediate product from reaction 1). Then the rate of consumption in the second reaction is $k_2[N_2O_2][O_2]$, so overall there are three ways that the concentration of $[N_2O_2]$ can change:

$$\text{net rate} = k_1[[NO]^2 - k_{-1}[N_2O_2] - k_2[N_2O_2][O_2].$$

We will make the assumption that **the concentration of the intermediate product is nearly constant as the reaction progresses**, so this net rate should be zero. (In practice, this has to be experimentally verified.) We can then rearrange to find

$$[N_2O_2] \approx \frac{k_1[NO]^2}{k_{-1} + k_2[O_2]},$$

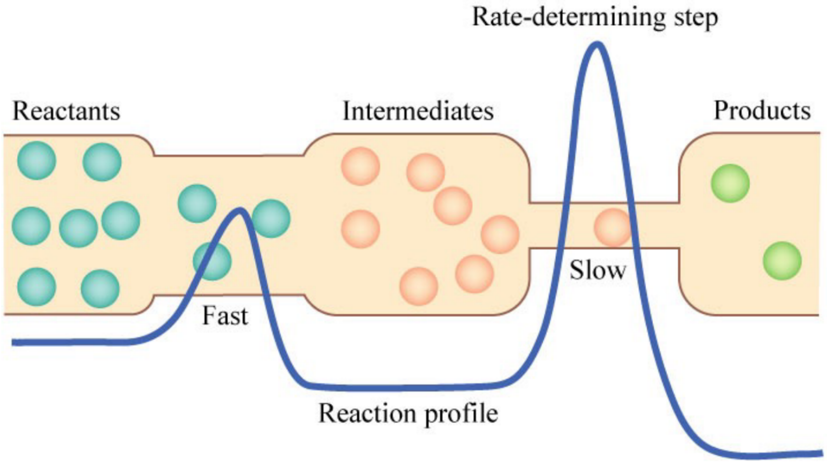
and then plug into the rate law of the second equation to find

$$\text{rate of formation of } NO_2 = 2k_2[N_2O_2][O_2] \approx \frac{2k_1k_2[NO]^2[O_2]}{k_{-1} + k_2[O_2]}$$

But this does not match the measured rate – there should be no denominator concentration dependence here – so there must be some overall **fast and slow** steps. But now we can use the assumption that the first step occurs much faster than the second – because of this, we can assume that the k_{-1} term in the denominator dominates, and then the rate of formation becomes $\frac{2k_1k_2}{k_{-1}}[NO]^2[O_2]$, which is indeed of the form that we want.

Definition 275

The slowest elementary step in a reaction, which often governs the overall rate of a multi-step reaction, is called the **rate-determining step**.



The diagram above gives us a general picture that we can keep in mind – because the reaction between the reactants and the intermediate product occurs much faster, we often have the first step approach equilibrium because only a small amount of the intermediate is proceeding onward. For this reason, we often call the intermediate (between the reactant and product) **pre-equilibriated**.

Example 276

Suppose we have an equation 2 $NO + Br_2 \to 2NOBr$, and we have two steps (1) $NO + Br_2 \rightleftharpoons NOBr_2$ and (2) $NOBr_2 + NO \to 2\ NOBr$. Also, assume that we know the measured rate law for this equation is $k_{obs}[NO][Br_2]$.

Like before, we must first calculate the rate of formation and decomposition of $NOBr_2$ from the first reaction, as well as the rate of consumption of $NOBr_2$ from the second reaction. Putting these together, the overall net rate of $NOBr_2$ is

$$\text{net rate} = k_1[NO][Br_2] - k_{-1}[NOBr_2] - k_2[NOBr_2][NO].$$

Making the steady-state approximation that this net rate is zero, we can rearrange to find the concentration of the intermediate

$$[NOBr_2] = \frac{k_1[NO][Br_2]}{k_{-1} + k_2[NO]},$$

and plugging this in gives us a rate of formation of NOBr:

$$\text{rate of formation} = 2k_2[NO][NOBr_2] = \frac{2k_2k_1[NO]^2[Br_2]}{k_{-1} + k_2[NO]}.$$

Now if the second step is fast and the first is slow, then $k_2[NO]$ will be much bigger than the other term in the denominator, k_{-1}. This simplifies out to a rate of $2k_1[NO][Br_2]$, and thus the order of the reaction would be 2. On the other hand, if the first step were fast and the second were slow, then we would find an overall rate of $\frac{2k_1k_2}{k_{-1}}[NO]^2[Br_2]$ and thus an overall order of 3. Experimental results are consistent with the former, so it must be true that the second step is fast.

Example 277

Finally, consider the reaction 2 $O_3 \to 3\ O_2$, given the mechanism (1) $O_3 \rightleftharpoons O_2 + O$ (fast, reversible) and (2) $O + O_3 \to O_2 + O_2$ (slow).

This time, we can again look at the rates relevant for the intermediate product O:

$$\text{net rate} = k_1[O_3] - k_{-1}[O_2][O] - k_2[O][O_3].$$

Again writing this intermediate concentration in terms of product and reactant concentrations, as well as rate constants, the steady-state approximation gives us

$$[\mathrm{O}] = \frac{k_1[\mathrm{O}_3]}{k_{-1}[\mathrm{O}_2] + k_2[\mathrm{O}_3]}.$$

Since the first step is fast, we can approximate the denominator with just the first term, and

$$[\mathrm{O}] \approx \frac{k_1[\mathrm{O}_3]}{k_{-1}[\mathrm{O}_2]} \implies \text{rate of formation of } \mathrm{O}_2 = 2k_2[\mathrm{O}][\mathrm{O}^3] = \frac{2k_2k_1[\mathrm{O}_3]^2}{k_{-1}[\mathrm{O}_2]}.$$

This agrees with the experimental data, and in particular notice that the order in O_2 is -1 (having more O_2 slows down the reaction). The overall order of such a reaction is then $2 - 1 = 1$, and we can predict how the rate will change depending on the concentrations of both O_3 and O_2 present.

35 May 9, 2022

As a final reminder, we should fill out the subject evaluations by Friday morning, and our final exam is the following Tuesday – detailed instructions for that exam are on Canvas. (In particular, we should arrive early for the exam because we're sitting by recitation section, and we should bring a calculator and not oversleep.)

Fact 278

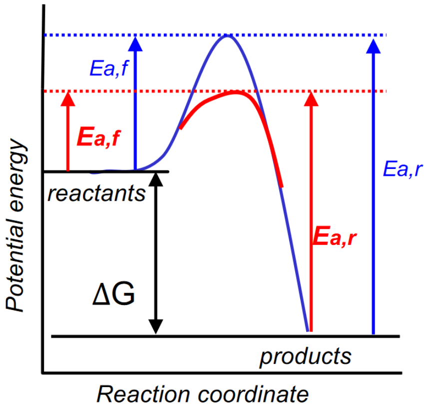
Rita Levi-Montalcini is an Italian and American neuroscientist who was a co-winner of the 1986 Nobel Prize in Physiology – her main contribution to science was the discovery of the **nerve growth factor** (NGF), which was important for understanding cell cancers and diseases like Alzheimer's and Parkinson's. She had to overcome family resistance and fascist laws to proceed in science, but she eventually became very well known; her 100th birthday was celebrated at the Rome city hall. (If we'd like to learn more scientific history, one nice resource is https://www.nobelprize.org/!)

Today's lecture will cover **catalysis**:

Definition 279

A **catalyst** is a substance that takes part in a chemical reacion and speeds up that reaction but does not undergo any permanent change.

In particular, catalysts are important for making reactions go faster, affecting the reaction rate and lowering the activation energy for them to occur. The diagram below describes a typical reaction coordinate diagram, where the red and blue correspond to the energy levels with and without a catalyst, respectively:



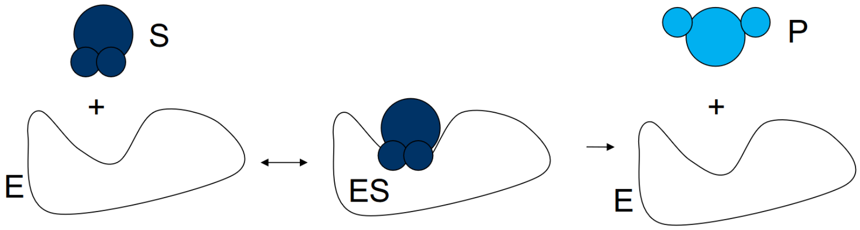
The idea here is that because catalysts reduce both the forward and reverse reaction rates (though they don't change the reactants and products and thus keep ΔG constant), they essentially **stabilize the transition state**, making it easier to reach.

We can get a sense of how dramatic the changes to reaction rates are by thinking about the Arrhenius equation $k = Ae^{-E_a/(RT)}$: if the catalyst reduces the activation energy by 50 kJ/mol (which is pretty typical for biological processes), then at $T = 300$ K (around room temperature), we have $RT \approx 2.5$ kJ/mol, and thus we are changing the rate constant by a factor of $e^{-\Delta E_a/(RT)} \approx e^{50/2.5} \approx 5 \times 10^8$, which is a huge number! So catalysts do make significant changes to whether processes noticeably occur.

Example 280

Catalysts in living organisms are called **enzymes** – they are often protein molecules (polypeptide chains) which are made of many amino acids linked by peptide bonds. The way these enzymes typically work is that we have a large protein molecule (enyzme) to which reactant molecules (called **substrates**) may bind, forming **enzyme-substrate complexes**. (These are typically quite stable because of complementary shapes or other reasons.) Such a complex can then dissociate to release a different product, with the enzyme staying behind and unchanged.

Below is a sketch of how such a reaction might occur:



In other words, we basically have a two-step reaction which we can describe as

$$\mathrm{E} + \mathrm{S} \rightleftharpoons \mathrm{ES} \to \mathrm{E} + \mathrm{P},$$

where we have a reversible step followed by a second step, meaning that the ES (enzyme-substrate complex) is an intermediate. We can thus apply our logic from last lecture: assume that the forward and reverse rate constants for the first step are k_1, k_{-1}, and the rate constant for the second step is k_2. Then the overall rate at which ES is being formed is

$$\text{rate} = \frac{d[\mathrm{ES}]}{dt} = k_1[\mathrm{E}][\mathrm{S}] - k_{-1}[\mathrm{ES}] - k_2[\mathrm{ES}]$$

(the rate of formation, minus the rate of consumption from each reaction). Applying the steady-state approximation from last lecture (meaning that we assume this rate is zero) yields

$$0 = k_1[\mathrm{E}][\mathrm{S}] - (k_{-1} + k_2)[\mathrm{ES}].$$

But this time, notice that we have some complication because enzymes can exist in two states (bound or free). In particular, if we let $[\mathrm{E}]_0$ be the total enzyme concentration at the start (which is easily experimentally measured), we know that we have the constraint

$$[\mathrm{E}]_0 = [\mathrm{E}] + [\mathrm{ES}] \implies 0 = k_1[\mathrm{E}]_0[\mathrm{S}] - k_1[\mathrm{ES}][\mathrm{S}] - (k_{-1} + k_2)[\mathrm{ES}].$$

We can now solve for the concentration of the intermediate ES to find that

$$[\mathrm{ES}]\,(k_1[\mathrm{S}] + k_{-1} + k_2) = k_1[\mathrm{E}]_0[\mathrm{S}] \implies [\mathrm{ES}] = \frac{[\mathrm{E}]_0[\mathrm{S}]}{[\mathrm{S}] + \frac{k_{-1}+k_2}{k_1}}.$$

We define the **Michaelis-Menten constant** $K_m = \frac{k_{-1}+k_2}{k_1}$ (this has units of M, so we should think of it in terms of concentrations) to get

$$[\mathrm{ES}] = \frac{[\mathrm{E}]_0[\mathrm{S}]}{[\mathrm{S}] + K_m} \implies \text{rate of product formation} = k_2[\mathrm{ES}],$$

which leads us to the **Michaelis-Menten equation**:

Proposition 281 (Michaelis-Menten)

The rate of product formation in a reaction catalyzed by an enzyme is given by

$$\frac{d[\mathrm{P}]}{dt} = \frac{k_2[\mathrm{E}]_0[\mathrm{S}]}{[\mathrm{S}] + K_m}.$$

We'll make sense of this mathematical expression by thinking about various limits, starting with the Michaelis-Menten constant K_m.

Fact 282

Because k_{-1} and k_2 are rate constants for first order reactions, they have units of s^{-1}. On the other hand, k_1 is a rate constant for a second order reaction and thus has units of $\mathrm{M}^{-1}\mathrm{s}^{-1}$, which justifies that K_m has units of M.

A small K_m corresponds to the reaction $\mathrm{E} + \mathrm{S} \to \mathrm{ES}$ occurring very fast relative to the other steps, meaning that we have **strong binding** of the enzyme-substrate complex. (So a large K_m would mean that the ES complex is quite weak.) In other words, K_m measures the affinity that the substrate has for the enzyme (considered strong if it's on the order of nM and weak if it's mM or μM).

We now look at the relevant regimes of behavior:

- When K_m is much smaller than [S] (so we have a significant excess of substrate), the Michaelis-Menten equation simplifies to

  $$\frac{d[\mathrm{P}]}{dt} = \frac{k_2[\mathrm{E}]_0[\mathrm{S}]}{[\mathrm{S}] + K_m} \approx \frac{k_2[\mathrm{E}]_0[\mathrm{S}]}{[\mathrm{S}]} = k_2[\mathrm{E}]_0.$$

  In other words, if we have strong binding and an excess of substrate, we reach a **maximum possible rate** $V_{\max}$ that we can achieve, proportional to the total amount of enzyme that we have and dependent on the second elementary reaction's rate constant. So even if we add more and more substrate, the rate of reaction will still level off because all of the active sites are filled.

- On the other hand, if [S] is small relative to K_m, the equation simplifies instead to

$$\frac{d[\mathrm{P}]}{dt} = \frac{k_2[\mathrm{E}]_0[\mathrm{S}]}{[\mathrm{S}] + K_m} \approx \frac{k_2[\mathrm{E}]_0[\mathrm{S}]}{K_m}.$$

  Thus the rate depends linearly on the amount of substrate and **also** the amount of enzyme added, because we have lots of free enzyme available.

- Finally, in the special case where $[\mathrm{S}] = K_m$, we find that

$$\frac{d[\mathrm{P}]}{dt} = \frac{k_2[\mathrm{E}]_0[\mathrm{S}]}{[\mathrm{S}] + K_m} = \frac{k_2[\mathrm{E}]_0[\mathrm{S}]}{2[\mathrm{S}]} = \frac{k_2[\mathrm{E}]_0}{2}.$$

  meaning that we're at half of the maximum reaction rate $V_{\max}$. So we can think of K_m as the **substrate concentration at which we reach half of the maximum reaction rate** (which can be useful in experiments).

Definition 283

The **turnover frequency** k_{cat} is the number of catalytic cycles that an enzyme produces per unit time, and the **catalytic efficiency** η is an enzyme is defined to be $\eta = \frac{k_{\text{cat}}}{K_m}$.

In particular, if we think about Michaelis-Menten kinetics, $k_{\text{cat}} = k_2 = \frac{V_{\max}}{[\mathrm{E}]_0}$, meaning that

$$\eta = \frac{k_2}{(k_{-1} + k_2)/k_1} = \frac{k_2 k_1}{k_{-1} + k_2}.$$

So when $k_2 \gg k_{-1}$ (the second step occurs much faster than the reverse first step), $\eta \approx k_1$. In other words, the efficiency of the catalyst is limited by the diffusion and encounter of the enzyme and the substrate – as soon as they find each other, the ES complex will quickly create the product, and the reverse reaction is negligible.

Example 284

Catalase (which catalyzes the decomposition of H_2O_2) has a typical turnover number of 4×10^7 molecules per second. But other enzymes work much slower – chymotrypsin, which hydrolyzes and cleaves peptide bonds, has a turnover number of 100 peptide bonds per second, and lysozyme, which hydrolyzes certain glycosidic bonds for carbohydrates, has a turnover number of only 0.5 bonds per second.

Example 285

As a numerical example, the conversion of CO_2 and H_2O in blood to carbonic acid is catalyzed by carbonic anhydrase. Given that the enzyme has concentration 5.0×10^{-6} M and $k_2 = 6.0 \times 10^{-5}\ \mathrm{s}^{-1}$, we have a maximum reaction rate of $k_2[\mathrm{E}]_0 = 3$ M/s. Thus, we'll observe half this maximum rate when the substrate concentration is $[\mathrm{S}] = K_m \approx 8.0 \times 10^{-5}$ M.