8.3 Quantum Theory
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Key Equations:
$E = h\nu$
$h\upsilon = \frac{1}{2}mu^2 + \phi$ (Photoelectric Effect)
$h\upsilon = \frac{1}{2}mu^2 + h\nu_0$ (Photoelectric Effect)

Ok, I hope you are ready for 8.3 because it is going to be a long one. As I have done in 8.2, I will link the concepts with what we discussed before so you can see the bigger picture. Trust me, once you see how everything connects together, chemistry is an absolute beautiful science.

In 8.2 we said that energy is somehow quantized in atoms. Keep that in mind because this section will connect with 8.2.

Ok, lets start with Black-Body radiation. Ah, I was really horrible at explaining this on Sunday, sorry. You are probably more confused about this than ever before. No worries, I will make sure you are absolute clear about it this time!

What is a black body? Well a black body is an object that does not favor one wavelength over another. Think of it as a gate that accepts all travelers, regardless of racial, social, economical status. Except in this case the “gate” accepts all EMR equally, regardless of what wavelength they have.

Ok, so if it absorbs all EMR, it is going to release all EMR right? Right! Unlike an atomic spectra, blackbody will produce a continuous spectrum. Which region of the wavelength will the continuous spectrum be released the most depends on the temperature of the blackbody. If you look at the graph on the next page carefully, you will see that the curve never reaches 0 intensity, this would mean a blackbody releases EMR of ALL wavelengths but the temperature determines at which wavelength range the most intensity will be released. This is a conceptually diffcult section, I want you to read it a couple times. (The method in which it absorbs energy and emit EMR is assumed to the same as the process used in atomic spectra)

How do we use this blackbody? We don’t really use it. All objects above absolute zero (0 kelvin, which corresponds to -273 degrees Celsius) have this blackbody radiation affect. We heat blackbodies up so it releases the most EMR in the wavelength region we want! For our current discussion, we will say that iron is a blackbody (It is actually a blackbody, but not the perfect blackbody)

We all know that the hotter iron is, the bright it glows, and that color of light it gives off changes from red toward white as the temperature is raised. (The reason we don't observe a continuous spectrum is because we are not using a prism to disperse it! If we disperse the colored light, we will get a continuous spectrum!)Those are qualitative observations. (You know what that means from Biology) To study the effect quantitatively, we measure the intensity of the radiation over a wide range of wavelengths and repeat the experiment at different temperatures.

Ok, you are wondering.. what is intensity? Intensity is really the amplitude of the wave. At this period in time, we are still assuming that light behaves like a wave. So far so good?

Here is a picture of what we are talking about…

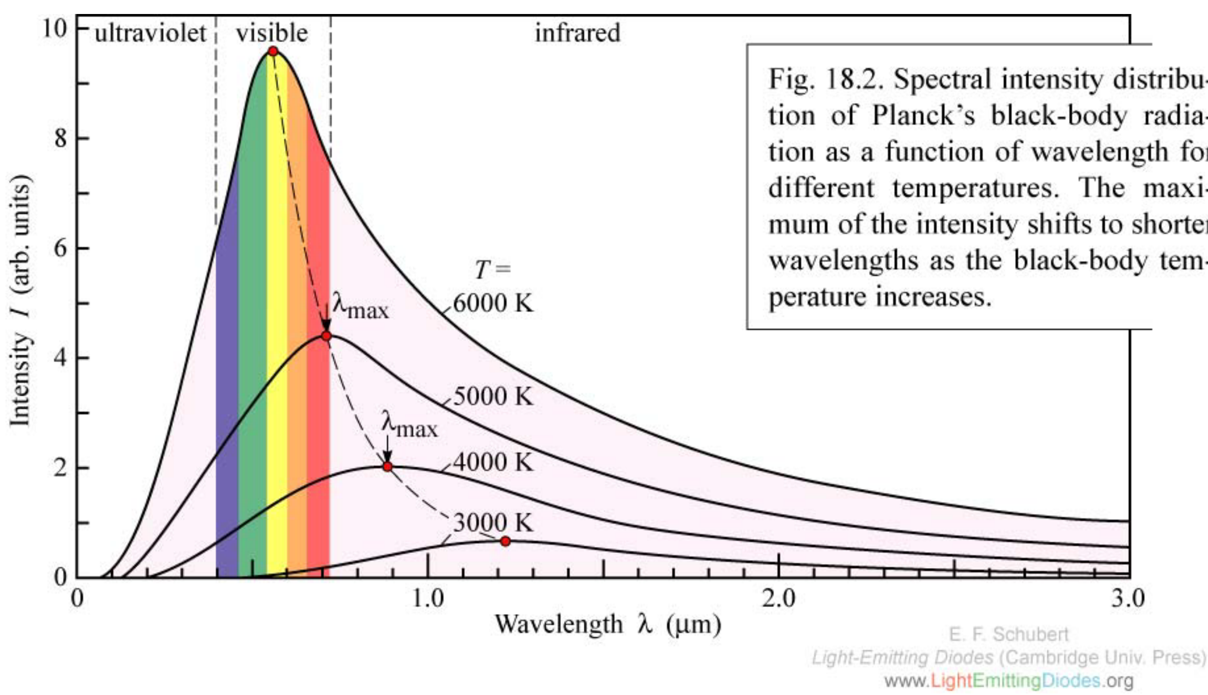


Fig. 18.2. Spectral intensity distribution of Planck's black-body radiation as a function of wavelength for different temperatures. The maximum of the intensity shifts to shorter wavelengths as the black-body temperature increases.

As you can see, higher temperature means that the peak wavelength is shifted more towards the UV region. At low temperatures, we have the peak in intensity at the red region of the visible spectrum. (Thus, we see observe red color because it overshadows all the other colors) With increasing temperature, we see that the peak moves to the yellow (which is white) region of the visible spectrum. With even higher temperature, the peak intensity is going to be at the blue region (Since you never took chemistry, you were probably never told that blue flame is the hottest..) With even higher temperature, we can't see the the color been emitted anymore because we are in the UV region! So far makes sense?

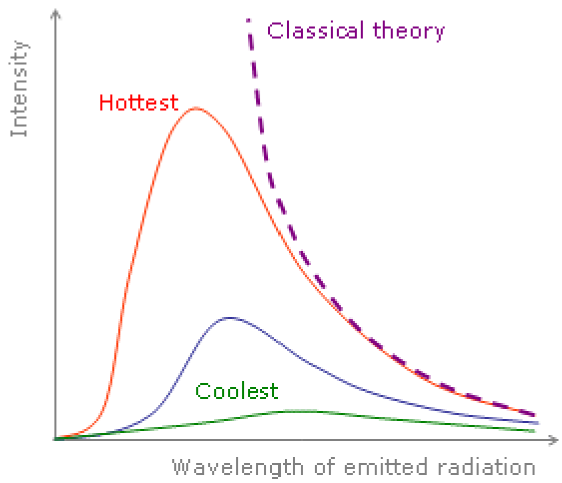
Ok, so. One of the major problems for physicists in the 19th century was to find out the intensity of the blackbody radiation at specific wavelengths. They set up a model of electromagnetic radiation based on waves and tried equations that would give them the intensity. One of the better equations was know as the Rayleign-Jeans Law. It had the following form:

$P(\lambda) = \frac{8\pi kT}{\lambda^4}$, where $P(\lambda) =$ intensity

K = some constant
T = absolute temperature

No, you DO NOT have to do any calculations with this equation. Just know the theory behind it, which I will explain.

Ok, this equation works great at the IR and visible range. The curve it predicted fitted perfectly, seems like a piece of cake right? NO! Look at what happens at the UV section of the wavelength! (I can't find a picture that shows the UV section clearly, sorry. This will have to do)



Intensity seems to go into infinity at smaller wavelengths! Lets check out our equation. UV as we know, as a wavelength of less than 320 nm. (because it to the left of the visible spectrum) Ok! As we as get closer and closer to 0 nm.. look what happens. Say for example

$8\pi kT = 4$ (It doesn't =4, we just assume it does so I can explain it)
We let $\lambda =$ 1m. We would get 4 as the intensity.. so far so good..
We let $\lambda =$ 0.1 m, we would get 40,000 as the intensity.. erm.. you see the problem now?
We let $\lambda =$ 0.01 m, we get 4.0 x 10^8 as the intensity….

We can go even smaller for λ but I think you have figured out that it intensity would be so large we can't even write it out.. Which means.. we get infinite intensity!

What does infinite intensity mean? Well, the thing is.. We get infinite intensity largely independent of which temperature the blackbody is at. Thus, we would get intense UV, x-ray and γ ray radiations from any blackbody at non-zero temperature. Any warm object would devastate the countryside and a human body with 37 Celsius would glow in the dark! This behavior is called the UV catastrophe.

Clearly, the wave model for EMR doesn't seem to work. This the first hint that there is something wrong with the wave model of light. Atomic spectra simply proved that energy within an atom is quantized. (Which hints that EMR might be quantized) It doesn't specifically point out that there is a problem with the old wave theory of light.

What do we do?!?!

Max Planck came along. He solved the UV catastrophe and along with it, proposed the theory of quantized energy.

What is this quantized energy? Well, we saw in the atomic spectra section that energy was ASSUMED to be continuous and it can have all values. Now, Planck said this assumption is TOTALLY wrong. He proposed that energy is discontinuous because it travels in packets called quanta and each quanta cannot have any value. It can only have E = hυ, where υ is the frequency of the radiation. There are two different ideas in Planck's hypothesis. I want to repeat them so that you don't see it as one idea. 1) Energy is discontinuous (unlike a wave), it travels in packets called quanta. 2) Each quanta can only have certain energy determined by hυ. With this hypothesis, he hit two birds with one stone. By saying that energy is discontinuous, he set down the idea that the wave theory of light is wrong. By saying that energy is quantized, he is able to explain both the UV catastrophe and the atomic spectra.

Lets do a quick recap.
Atomic spectra → energy is quantized within an atom
Blackbody Radiation → Wave theory of light is wrong
Planck's hypothesis → Solved both experiment by a single radical idea that said 1) energy is quantized 2) energy travels in quanta, not in waves.

Now, you must be wondering how the heck did Planck account for the UV catastrophe. Well, if you asked me 2 days ago, I wouldn't know. But now, I have finally find a well explained answer in one of my favorite chemistry book of all time. Here is their explanation, which I thought it to be very clear.

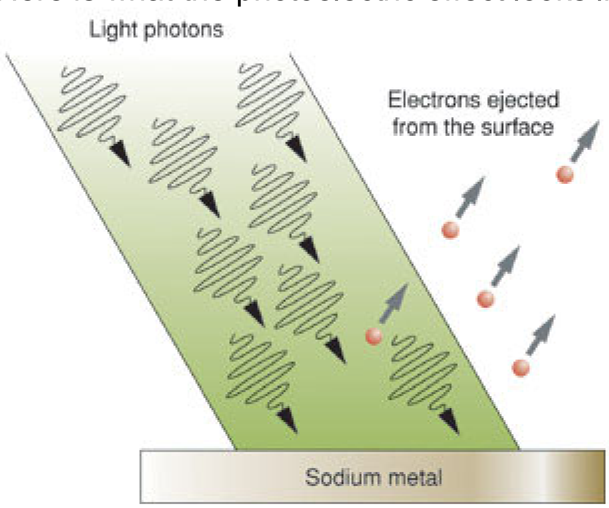
Lets look at Planck's famous equation: E = hυ. To generate radiation of a certain frequency υ, you need enough energy to do it. By heating a blackbody up, you see the shift in peak wavelengths towards the UV side because you are inputting high energy. However, with a cool blackbody, you do not have the energy to produce radiation of a high υ. Therefore, the intensity curve dies away at high frequencies and the UV catastrophe is avoided. I hope this makes sense to you, if not, come ask me and I will try my best to explain it to you.

Ok, one last thing before we move on to photoelectric effect. In classic waves, we associate intensity (amplitude) with the energy of the radiation. With Planck's new radical hypothesis, he associated frequency, υ, with energy of the radiation. What does intensity do then? Well, intensity of the radiation is an indication of the number of quanta that are generated. Why? I do not know. I doubt many people know the why of it and they certainly wouldn't ask you the why of it on the midterm. Yes I know, if you know the why of it, everything flows together instead of a collection of unrelated facts.

Now, finally! Photoelectric effect!

How does the photoelectric effect fit in with the Blackbody Radiation/Planck's Hypothesis? Well, you see. Planck's hypothesis is very good. He give it a hint of what's to come (hint: particle nature of light) but he didn't express it directly. It is up to Einstein to the express it clearly. Also, Planck's hypothesis has to be tested and the photoelectric effect is the experiment upon which Planck's hypothesis is tested.

Here is what the photoelectric effect looks like.



The basic idea is really simple. EMR, as you are already aware, contains energy. Ok, you take a piece of metal plate with a low ionization potential (which means that you need little energy to remove an electron from it), put it under EMR. Energy from the EMR will hit the metal atoms in the plate and bump electrons out in a process called ionization. Now, here is something I just learned, from you in fact. You see, in all the months I spent learning quantum mechanics I never formed an association between photoelectric effect and ionization. It never occurred to me that there would be a connection because all the textbooks I read never mentioned ionization in association with the photoelectric effect. So here I am, been spoon feeded by all the textbooks and it never occurred to me to stop and think about it. Then you came along and immediately pointed out the connection. Wow, that's just amazing.

Ok, back to the topic. What happens if EMR doesn't have energy to knock electrons out? Well, the electrons wouldn't move out and the energy would be wasted as heat. This happens when the energy of the EMR (which you can find out by using hν) < Ionization energy/Work Function/Threshold energy (all three of them means the same thing, they just use different terms to try and confuse you)

Now what exactly is work function/ionization energy/threshold energy? Think of this analogy. I have a basketball glued on to a table. I am going to take a hammer and whack the basketball. You know if I swing the hammer, I am to input energy into that swing, which would be transferred into that basketball. Now, that basketball won't come off easily because it is glued. If I don't swing hard enough, basketball won't move. The work function/ionization energy/threshold energy is the amount of energy I need to input that would break the glue bond between the table and basketball. The bond would break but the basketball won't move because the energy I input is exactly equal to the amount of energy need to break the glue bond. If I put more energy than that, the ball would fly off with a velocity that depends on how much I went over the "energy barrer".

Now, threshold frequency, ν_0. This can be a confusing concept because your EMR already has a ν associated with it. What does it need another ν for ?!?! Well, you know that E = hν right? ν_0, the threshold frequency x h, will give you threshold energy E_0. Threshold energy, as I already said, is = to work function (ϕ) = to ionization energy. Therefore, ν_0 is the minimum frequency of EMR that you need to bump an electron off the metal plate. That's all.

When the EMR have more energy than the work function/ionization energy/threshold energy, that energy automatically becomes kinetic energy of the electron. Objects possess kinetic energy due to their movement. Thus, once you know the kinetic energy of the electron, you can use E_k (Kinetic Energy) = $\frac{1}{2}m\mu^2$ to find the velocity of the electron.

Another way to view the photoelectric effect is by using frequencies ν. To do this, however, requires that you are given the threshold frequency ν_0. ν_0 is easy to find if you are given the work function/ionization energy/threshold energy since you can use the fact that $E_0 = h\nu_0$ (where work function/ ionization energy/threshold energy = E_0) to find ν_0. Then you just do this…

If $\nu > \nu_0$ electrons are ejected with a velocity

If $\nu = \nu_0$ electrons are ejected with 0 velocity

If $\nu < \nu_0$ no electrons are ejected

The equation that organizes everything together is this:

$h\upsilon = \frac{1}{2}mu^2 + \phi$

$h\upsilon$ = total energy of the EMR

$\frac{1}{2}mu^2 = \text{kinetic energy}$

$\phi = \text{work function}$

Which basically says, if $h\upsilon > \phi$, you have $\frac{1}{2}mu^2 = h\upsilon - \phi$

If $h\upsilon = \phi$, $\frac{1}{2}mu^2 = 0$, electrons ejected

If $h\upsilon < \phi$, $\frac{1}{2}mu^2 = 0$, electrons not ejected

I hope everything makes sense so far.

We touched a bit on the experiment, lets talk about the results of the experiment. What we observed using photoelectric effect are the following:

1) No electrons are ejected unless the radiation has a frequency above a certain value characteristic of the metal (In other words, the frequency of the EMR must be bigger than the threshold frequency)
2) Electrons are ejected immediately, however low the intensity of the radiation (Remember, in blackbody radiation, we said that intensity only affects the number of quantas or packets that pass through. It is the same thing here)
3) The kinetic energy E_k of the ejected electron varies linearly with the frequency of the incident radiation. (We talked about this above, it simply means that whatever energy you added to the incident radiation will be reflected in the kinetic energy of the electron provided that incident radiation has energy > that of the threshold energy. I.e. if incident radiation has an energy of 3 and threshold energy is 1. Your kinetic energy is 3-1 = 2. If you make your incident radiation's energy into 7 by adding 4, your kinetic energy also adds 4 and becomes 5. The threshold energy does not change unless you change the metal plate)

Then Einstein came and he took one look at the experiment.. and proposed the following:

Energy travels in packets called quantas with each of the packets containing quantized energy. (This is what Planck proposed) Einstein took this one step further by saying EMR consists of particles called photons. Each photon can be regarded as a packet of energy. Energy of a single photon is related to the frequency of the radiation by $E = h\nu$.

There is really nothing new here. You see, photoelectric effect confirmed Planck's hypothesis by showing that yes, energy is quantized since energy depends on frequency. It also showed that EMR can not be waves because intensity has no effect on energy (Classical wave theory states that energy of the wave is dependent on the wave's intensity. Since EMR do not exhibit this behavior, they can't be waves)

With Planck's hypothesis proved by photoelectric, Einstein added a physical dimension to the quanta of energy by saying that these quanta are really particles called photons. (Energy does not really exist in the physical sense, particles, however, do exist physically) So now when we think of the EMR, we think of it as a beam of photons rather than a wave.

With the picture of photons in mind, we can explain the photoelectric effect in another way:
A streams of photons with energy determined by $h\nu$ collides with the electrons in the metal.
1) An electron can be driven out of the metal only if it receives at least a certain minimum energy from the photon during the collision.
2) Provided a photon has enough energy, a collision results in the immediate ejection of an electron
3) If an energy E_0 is needed to remove an electron from the metal and if the phton has an energy $h\nu$, then the difference $h\nu - E_0$ will appears as the kinetic energy of the electron

Oh my! 8.3 is done finally! Next section is 8.4!