

THE ATOMIC SPECTRUM OF HYDROGEN

When atoms are excited, either in an electric discharge or with heat, they tend to give off light. The light is emitted only at certain wavelengths that are characteristic of the atoms in the sample. These wavelengths constitute what is called the atomic spectrum of the excited element and reveal much of the detailed information we have regarding the electronic structure of atoms.

Atomic spectra are interpreted in terms of quantum theory. According to this theory, atoms can exist only in certain states, each of which has an associated fixed amount of energy. When an atom changes its state, it must absorb or emit an amount of energy that is just equal to the difference between the energies of the initial and final states. This energy may be absorbed or emitted in the form of light. The emission spectrum of an atom is obtained when excited atoms fall from higher to lower energy levels. Since there are many such levels, the atomic spectra of most elements are very complex.

Light is absorbed or emitted by atoms in the form of photons, each of which has a specific amount of energy, ϵ . This energy is related to the wavelength of light by the equation

$$\epsilon_{\text{photon}} = \frac{hc}{\lambda} \quad (1)$$

where h is Planck's constant, 6.62608×10^{-34} joule seconds, c is the speed of light, 2.997925×10^8 meters per second, and λ is the wavelength, in meters. The energy ϵ_{photon} is in joules and is the energy given off by one atom when it jumps from a higher to a lower energy level. Since total energy is conserved, the change in energy of the atom, $\Delta\epsilon_{\text{atom}}$, must equal the energy of the photon emitted:

$$\Delta\epsilon_{\text{atom}} = \epsilon_{\text{photon}} \quad (2)$$

where $\Delta\epsilon_{\text{atom}}$ is equal to the energy in the upper level minus the energy in the lower one. Combining Equations 1 and 2, we obtain the relation between the change in energy of the atom and the wavelength of light associated with that change:

$$\Delta\epsilon_{\text{atom}} = \epsilon_{\text{upper}} - \epsilon_{\text{lower}} = \epsilon_{\text{photon}} = \frac{hc}{\lambda} \quad (3)$$

The amount of energy in a photon given off when an atom makes a transition from one level to another is very small, of the order of 1×10^{-19} joules. This is not surprising since, after all, atoms are very small particles. To avoid such small numbers, we will work with one mole of atoms, much as we do in dealing with energies involved in chemical reactions. To do this we need only to multiply Equation 3 by Avogadro's number, N :

Let

$$N\Delta\epsilon = \Delta E = N\epsilon_{\text{upper}} - N\epsilon_{\text{lower}} = E_{\text{upper}} - E_{\text{lower}} = \frac{Nhc}{\lambda}$$

Substituting the values for N , h , and c , and expressing the wavelength in nanometers rather than meters (1 meter = 1×10^9 nanometers), we obtain an equation relating energy change in kilojoules per mole of atoms to the wavelength of photons associated with such a change:

$$\Delta E = \frac{6.02214 \times 10^{23} \times 6.62608 \times 10^{-34} \text{ J sec} \times 2.997925 \times 10^8 \text{ m/sec}}{\lambda \text{ (in nm)}} \times \frac{1 \times 10^9 \text{ nm}}{1 \text{ m}} \times \frac{1 \text{ kJ}}{1000 \text{ J}}$$

$$\Delta E = E_{\text{upper}} - E_{\text{lower}} = \frac{1.19627 \times 10^5 \text{ kJ/mole}}{\lambda \text{ (in nm)}} \quad \text{or} \quad \lambda \text{ (in nm)} = \frac{1.19627 \times 10^5}{\Delta E \text{ (in kJ/mole)}} \quad (4)$$

Equation 4 is useful in the interpretation of atomic spectra. Say, for example, we study the atomic spectrum of sodium and find that the wavelength of the strong yellow line is 589.16 nm (see Fig. 10.1). This line is known to result from a transition between two of the three lowest levels in the atom. The energies of these levels are shown in the figure. To make the determination of the levels which give rise to the 589.16 nm line, we note that there are three possible transitions, shown by downward arrows in the figure. We find the wavelengths associated with those transitions by first calculating ΔE ($E_{\text{upper}} - E_{\text{lower}}$) for each transition. Knowing ΔE we calculate λ by Equation 4. Clearly, the $\text{II} \rightarrow \text{I}$ transition is the source of the yellow line in the spectrum.

The simplest of all atomic spectra is that of the hydrogen atom. In 1886 Balmer showed that the lines in the spectrum of the hydrogen atom had wavelengths that could be expressed by a rather simple equation. Bohr, in 1913, explained the spectrum on a theoretical basis with his famous model of the hydrogen atom. According to Bohr's theory, the energies allowed to a hydrogen atom are given by the equation

$$e_n = \frac{-B}{n^2} \quad (5)$$

where B is a constant predicted by the theory and n is an integer, 1, 2, 3, . . . , called a quantum number. It has been found that all the lines in the atomic spectrum of hydrogen can be associated with energy levels in the atom which are predicted with great accuracy by

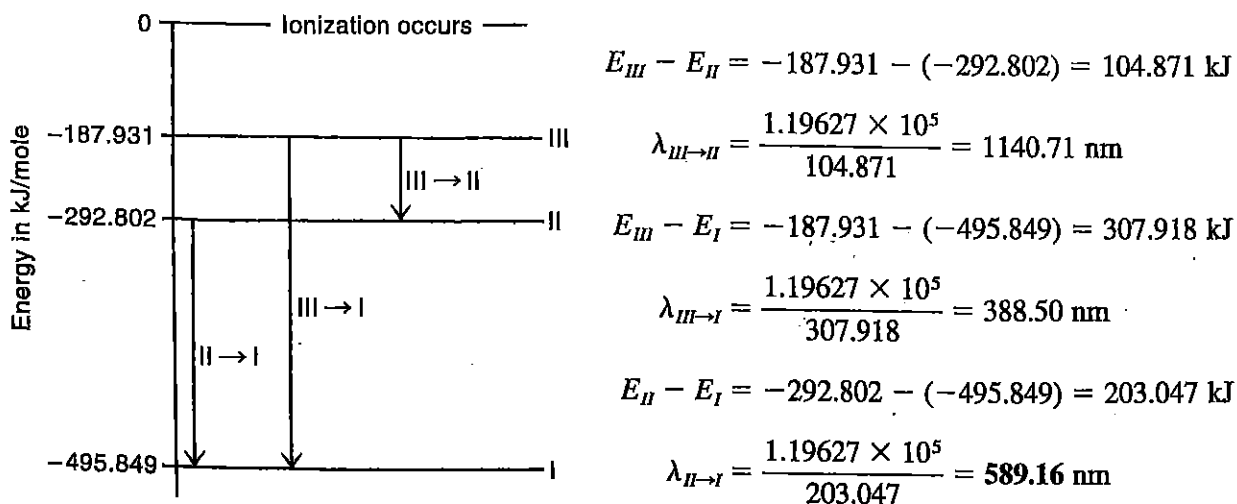


FIGURE 10.1 Calculation of wavelengths of spectral lines from energy levels of the sodium atom.

Bohr's equation. When we write Equation 5 in terms of a mole of H atoms, and substitute the numerical value for B , we obtain

$$E_n = \frac{-1312.04}{n^2} \text{ kilojoules per mole, } n = 1, 2, 3, \dots \quad (6)$$

Using Equation 6 you can calculate, very accurately indeed, the energy levels for hydrogen. Transitions between these levels give rise to the wavelengths in the atomic spectrum of hydrogen. These wavelengths are also known very accurately. Given both the energy levels and the wavelengths, it is possible to determine the actual levels associated with each wavelength. In this experiment your task will be to make determinations of this type for the observed wavelengths in the hydrogen atomic spectrum that are listed in Table 10.1.

Experimental Procedure

There are several ways we might analyze an atomic spectrum, given the energy levels of the atom involved. A simple and effective method is to calculate the wavelengths of some of the lines arising from transitions between some of the lower energy levels, and see if they match those that are observed. We shall use this method in our experiment. All the data are good to at least five significant figures, so by using electronic calculators you should be able to make very accurate determinations.

A. Calculations of the Energy Levels of the Hydrogen Atom

Given the expression for E_n in Equation 6, it is possible to calculate the energy for each of the allowed levels of the H atom starting with $n = 1$. Using your calculator, calculate the energy in kJ/mole of each of the 10 lowest levels of the H atom. Note that the energies are all negative, so that the *lowest* energy will have the *largest* allowed negative value. Enter these values in the table of energy levels, Table 10.2. On the energy level diagram provided, plot along the y axis each of the six lowest energies, drawing a horizontal line at the allowed level and writing the value of the energy alongside the line near the y axis. Write the quantum number associated with the level to the right of the line.

The Energy Levels of the Hydrogen Atom

Energies are to be calculated from Equation 6 for the 10 lowest energy states.

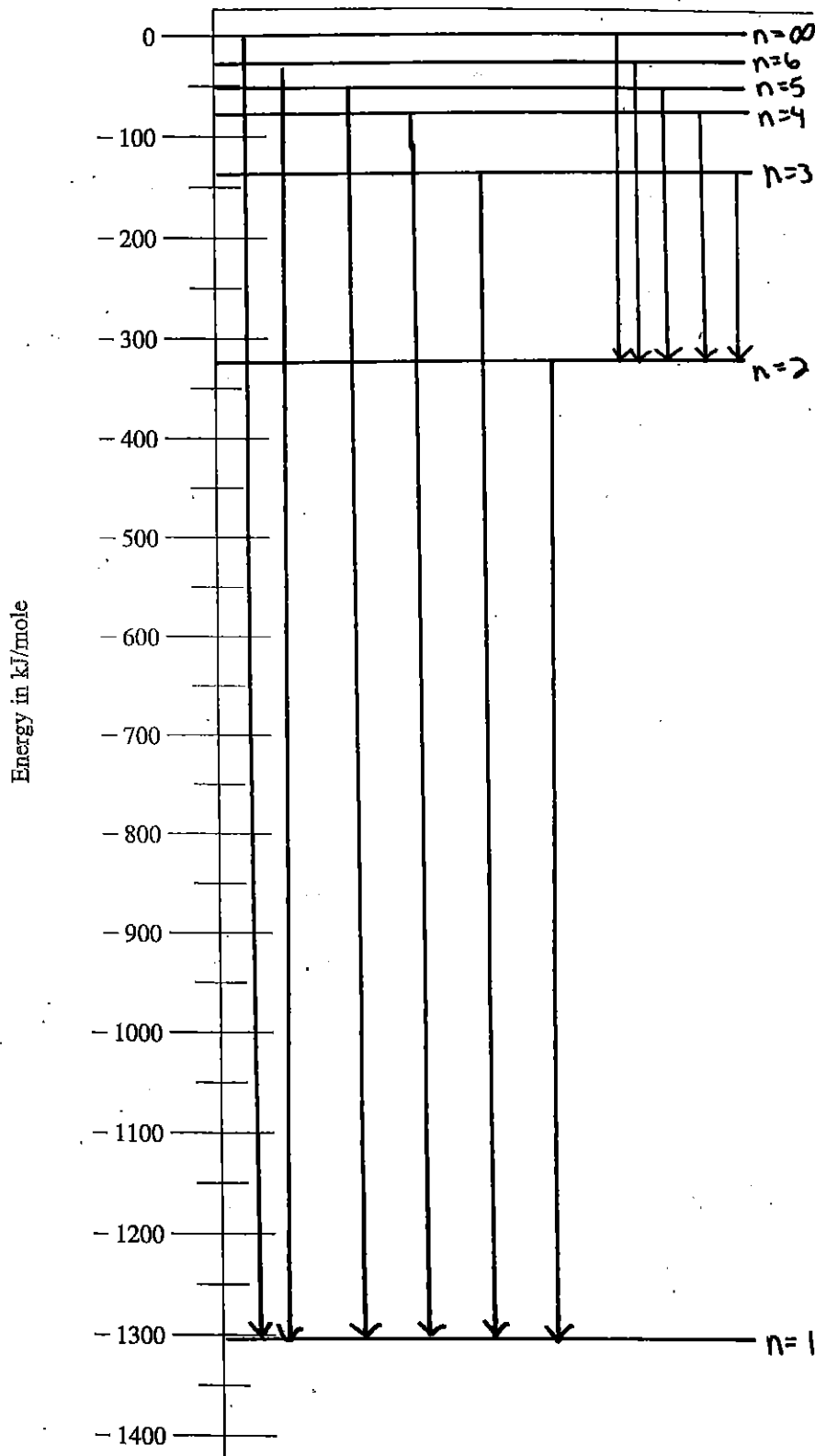
Table 10.2

5 sig figs

Quantum Number, n	Energy, E_n , in kJ/mole	Quantum Number, n	Energy, E_n , in kJ/mole
1	-1312.0	6	-36.446
2	-328.01	7	-26.776
3	-145.78	8	-20.501
4	-82.002	9	-16.198
5	-52.482	10	-13.120
		∞	0

The Atomic Spectrum of Hydrogen
Energy Level Diagram

(DATA AND CALCULATIONS)



Lyman —
(All levels to $n=1$)

Balmer —
(All levels to $n=2$)

Balmer —
(All levels to $n=2$)

B. Calculation of the Wavelengths of the Lines in the Hydrogen Spectrum

The lines in the hydrogen spectrum all arise from jumps made by the atom from one energy level to another. The wavelengths in nm of these lines can be calculated by Equation 4, where ΔE is the difference in energy in kJ/mole between any two allowed levels. For example, to find the wavelength of the spectral line associated with a transition from the $n = 2$ level to the $n = 1$ level, calculate the difference, ΔE , between the energies of those two levels. Then substitute ΔE into Equation 4 to obtain this wavelength in nanometers.

Using the procedure we have outlined, calculate the wavelengths in nm of all the lines we have indicated in Table 10.3. That is, calculate the wavelengths of all the lines that can arise from transitions between any two of the six lowest levels of the H atom. Enter these values in Table 10.3.

Calculation of Wavelengths in the Spectrum of the H Atom

In the upper half of each box write ΔE , the difference in energy in kJ/mole between E_{n_m} and E_{n_l} . In the lower half of the box, write λ in nm associated with that value of ΔE .

Table 10.3

n_{Higher}		6	5	4	3	2	1	
	n_{Lower}							
UV	1	ΔE	1276	1260	1230	1166	984.0	- Lyman Series (UV)
		λ	93.75	94.94	97.26	102.6	121.6	
Visible	2	ΔE	291.6	275.5	246.0	182.2		- Balmer Series (visible)
		λ	410.2	434.2	486.3	656.5		
IR	3	ΔE	109.3	93.30	63.78			- Paschen Series (IR)
		λ	1094	1282	1876			
Micro-	4	ΔE	45.56	29.52				- Brackett Series
		λ	2626	4052				
Short Radio	5	ΔE	16.04					- Pfund Series
		λ	7458					

4 sig figs

$$\Delta E = E_{n_m} - E_{n_l}$$

$$\lambda \text{ (nm)} = \frac{1.19627 \times 10^5}{\Delta E}$$

C. Assignment of Observed Lines in the Hydrogen Spectrum

Compare the wavelengths you have calculated with those listed in Table 10.1. If you have made your calculations properly, your wavelengths should match, within the error of your calculation, several of those that are observed. On the line opposite each wavelength in Table 10.1, write the quantum numbers of the upper and lower states for each line whose origin you can recognize by comparison of your calculated values with the observed values. On the energy level diagram, draw a vertical arrow pointing down (light is emitted, $\Delta E < 0$) between those pairs of levels that you associate with any of the observed wavelengths. By each arrow write the wavelength of the line originating from that transition.

There are a few wavelengths in Table 10.1 that have not yet been calculated. Enter those wavelengths in Table 10.4. By assignments already made and by an examination of the transitions you have marked on the diagram, deduce the quantum states that are likely to be associated with the as yet unassigned lines. This is perhaps most easily done by first calculating the value of ΔE , which is associated with a given wavelength. Then find two values of E_n whose difference is equal to ΔE . The quantum numbers for the two E_n states whose energy difference is ΔE will be the ones that are to be assigned to the given wavelength. When you have found n_{hi} and n_{lo} for a wavelength, write them in Table 10.1 and Table 10.4; continue until all the lines in the table have been assigned.

Table 10.1 Some Wavelengths (in nm) in the Spectrum of the Hydrogen Atom as Measured in a Vacuum

Wavelength	Assignment		Wavelength	Assignment		
	$n_{hi} \rightarrow n_{lo}$			$n_{hi} \rightarrow n_{lo}$	$n_{hi} \rightarrow n_{lo}$	
97.25	4 → 1	vis	410.29	6 → 2	1005.2	?
102.57	3 → 1		434.17	5 → 2	1094.1	6 → 3
121.57	2 → 1		486.27	4 → 2	1282.2	5 → 3
	?		656.47	3 → 2	1875.6	4 → 3
389.02	?					
397.12	?	IR 954.86		?	4052.3	5 → 4 - Micro

Handwritten notes: UV bracket for 97.25, 102.57, 121.57; Visible bracket for 389.02, 397.12; IR bracket for 1005.2, 1094.1, 1282.2, 1875.6, 4052.3.

List below any wavelengths you cannot yet assign.

Table 10.4

Wavelength λ Observed	$\Delta E = \frac{1.19627 \times 10^5}{\lambda}$ ΔE Transition ($\frac{kJ}{mol}$)	Probable Transition $n_{hi} \rightarrow n_{lo}$	$\Delta E = E_{ki} - E_{lo}$ $E_{ki} = \Delta E + E_{lo}$
389.02	307.5	8 → 2	$n_{lo} = 2$ $(E_{lo} = -328.01 \text{ kJ/mol})$
397.12	301.2	7 → 2	
954.86	125.3	8 → 3	$n_{lo} = 3$ $E_{lo} = -145.78 \text{ kJ/mol}$
1005.2	119.0	7 → 3	

Measuring the Wavelength of Light Waves by Diffraction

Experimental Data:

D. The Balmer Series

This is the most famous series in the atomic spectrum of hydrogen. The lines in this series are the only ones in the spectrum that occur in the visible region. Your instructor may have a hydrogen source tube and a spectroscope with which you may be able to observe some of the lines in the Balmer series. In the Data and Calculations section are some questions you should answer relating to this series.

When light is incident upon a diffraction grating, it is diffracted by the slits in the grating. An interference pattern similar to the patterns you observed in Investigation 29, Diffraction and Interference of Waves, results. As you look through the grating, you will see the spectrum of the source to the right and left of the position of the source. The spectrum will consist of several lines of different-colored light.

In Figure 36-1, the light incident upon the grating is diffracted by the slits in the grating. The lines of colored light you observe are due to the constructive interference or reinforcement of the light waves. These lines of reinforcement are lines along which light waves from adjacent slits are in phase. In between these lines, the light waves are out of phase and cancel.

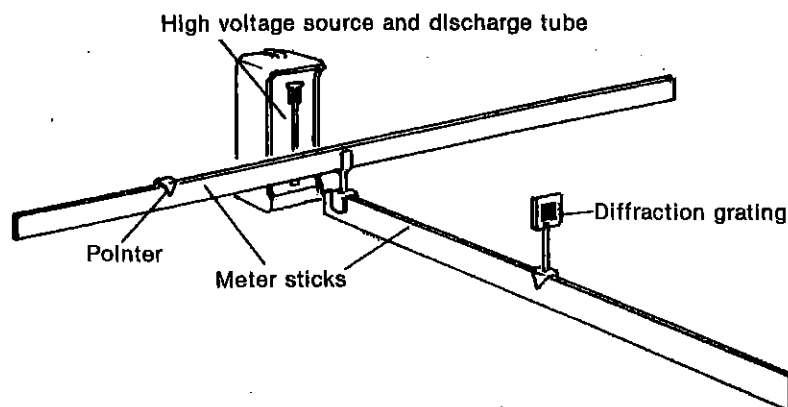


Figure 36-1. Apparatus for measuring wavelength. The high voltage source excites the atoms of gas in the discharge tube. The excited atoms emit a characteristic line spectrum. The spectrum is observed by means of a diffraction grating which makes use of the interference of waves so that each wavelength of light is reinforced at a particular distance from the center of the interference pattern. By measuring this distance and the distance between the grating lines, it is possible to calculate the wavelength of the light emitted from the source.

Consider the two slits A and B. The length of the path from B to the eye is one wavelength (λ) longer than the length of the path from A to the eye. The path difference (λ) is much too small to be measured directly. However, the triangle formed by the sides DLx is similar to the triangle dAb (two sides mutually perpendicular and one included angle being equal). The sides x and L are measurable along the meter sticks. From this you can find angle θ :

$$\frac{x}{L} = \text{tangent } \theta$$

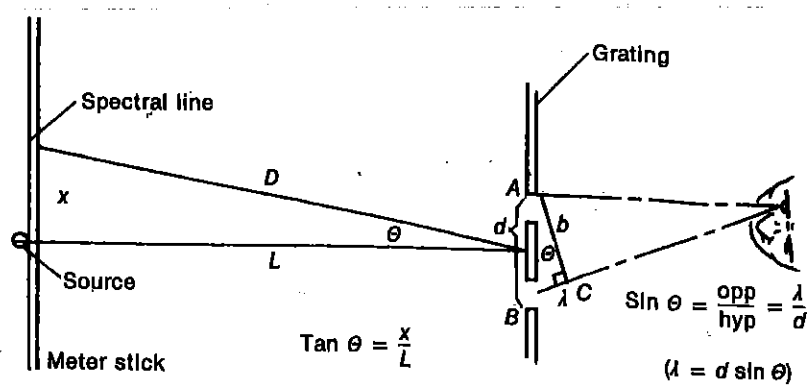
By measuring x and L and calculating the tangent of θ , you can look up the sine of θ . In the small triangle dAb,

$$\frac{\lambda}{d} = \sin \theta$$

and so,

$$\lambda = d \sin \theta.$$

You will use this equation to find the wavelengths of the light emitted by your source.



$$13,400 \frac{\text{lines}}{\text{inch}} \left(\frac{1 \text{ inch}}{2.54 \text{ cm}} \right) \left(\frac{1 \text{ cm}}{1 \times 10^7 \text{ nm}} \right) =$$

Data and Calculations

$$N = \frac{5280 \text{ lines}}{\text{cm}} = 5280 \text{ lines/cm}$$

$$d = \frac{1}{N} = 1894 \text{ nm}$$

Color of line	Distance from source to first-order lines (x) (cm)	Distance from source to first-order lines (x) (cm)	Distance from source to first-order lines (x) (cm) (Average)	Distance from source to grating (L) (cm)
Red	34.8 25.35	35.9 26.1	35.4 31.95	94.2 91.5
Blue/Green	25.7 28	25.9 29.5	25.8 28.75	94.2 91.5
Violet	23.6 22	20.8 26.4	22.2 25.7	94.2 91.5

Calculations

Tan theta $\frac{x}{L}$	Angle theta (°)	Sin theta	Wavelength, lambda = d sin theta (nm)
.375 169	20.6 22.3	.351 37	665.4 718.1
.274 295	15.3 164	.264 283	500.3 535.6
.236 264	13.3 14.8	.229	434.5 482.7

Wavelength lambda Observed	Delta E Transition (eV)	Probable Transition n _{hi} -> n _{lo}	lambda Calculated in nm (Eq. 4)
718.1	665.4	3 -> 2	665
535.6	500.3	4 -> 2	486.3
482.7	434.5	5 -> 2	434.2

(Compare Delta E to table 10.3)

$$E_{hi} = \Delta E + E_{lo}$$

$$\Delta E =$$

1. When Balmer found his famous series for hydrogen in 1886, he was limited experimentally to wavelengths in the visible and near ultraviolet regions from 250 nm to 700 nm, so all the lines in his series lie in that region. On the basis of the entries in Table 10.3 and the transitions on your energy level diagram, what common characteristic do the lines in the Balmer Series have?

They are all in the visible light spectrum.

What would be the longest possible wavelength for a line in the Balmer series?

$$\lambda = \frac{1.19627 \times 10^5 \frac{\text{kJ} \cdot \text{nm}}{\text{mol}}}{\Delta E (E_3 - E_2)} = \frac{1.19627 \times 10^5}{182.2} = \boxed{656.5 \text{ nm}} \quad \lambda = \underline{656.5} \text{ nm}$$

3-2

What would be the shortest possible wavelength that a line in the Balmer series could have? Hint: What is the largest possible value of ΔE to be associated with a line in the Balmer series?

↓
Largest $\Delta E = 291.6 \frac{\text{kJ}}{\text{mole}}$

$$\lambda = \underline{410.2} \text{ nm}$$

$$\lambda = \frac{1.19627 \times 10^5 \frac{\text{kJ} \cdot \text{nm}}{\text{mol}}}{291.6 \frac{\text{kJ}}{\text{mole}}} = \boxed{410.2 \text{ nm}}$$

Fundamentally, why would any line in the hydrogen spectrum between 250 nm and 700 nm belong to the Balmer series? Hint: On the energy level diagram note the range of possible values of ΔE for transitions to the $n = 1$ level and to the $n = 3$ level. Could a spectral line involving a transition to the $n = 1$ level have a wavelength in the range indicated? No, anything going to $n=1$ is lower λ than visible light

$$\lambda = 250 \text{ nm}$$

$$\Delta E = \frac{1.19627 \times 10^5 \frac{\text{kJ} \cdot \text{nm}}{\text{mol}}}{250 \text{ nm}}$$

$$\Delta E = 478.5 \frac{\text{kJ}}{\text{mole}}$$

$$\lambda = 700 \text{ nm}$$

$$\Delta E = 170.8 \frac{\text{kJ}}{\text{mole}}$$

$$\Delta E = E_{h_i} - E_{l_o}$$

$$E_{h_i} = \Delta E + E_{l_o}$$

The Ionization Energy of Hydrogen

2. In the normal hydrogen atom the electron is in its lowest energy state, which is called the ground state of the atom. The maximum electronic energy that a hydrogen atom can have is 0 kJ/mole, at which point the electron would essentially be removed from the atom and it would become a H^+ ion. How much energy in kilojoules per mole does it take to ionize an H atom?

$$\Delta E = E_{\infty} - E_1 = 0 - (-1312 \frac{\text{kJ}}{\text{mole}})$$

$$\underline{1312.0} \text{ kJ/mole}$$

The ionization energy of hydrogen is often expressed in units other than kJ/mole. What would it be in joules per atom? in electron volts per atom? ($1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$)

$$\underline{2.179 \times 10^{-18}} \text{ J/atom}; \quad \underline{13.6} \text{ eV/atom}$$

$$\left(1312.0 \frac{\text{kJ}}{\text{mol}}\right) \left(\frac{1000 \text{ J}}{1 \text{ kJ}}\right) \left(\frac{1 \text{ mol}}{6.02 \times 10^{23}}\right) = 2.179 \times 10^{-18} \frac{\text{J}}{\text{atom}}$$

$$\left(2.179 \times 10^{-18} \frac{\text{J}}{\text{atom}}\right) \left(\frac{1 \text{ eV}}{1.602 \times 10^{-19} \text{ J}}\right) = 13.6 \frac{\text{eV}}{\text{atom}}$$

Advance Study Assignment: The Atomic Spectrum of Hydrogen

1. The helium ion, He^+ , has energy levels similar to those of the hydrogen atom, since both species have only one electron. The energy levels of the He^+ ion are given by the equation

$$E_n = -\frac{5248.16}{n^2} \text{ kJ/mole} \quad n = 1, 2, 3, \dots$$

- a. Calculate the energies in kJ/mole for the four lowest energy levels of the He^+ ion.

$$\frac{-5248.16}{1^2}$$

$$\frac{-5248.16}{3^2}$$

$$E_1 = \underline{-5248.2} \text{ kJ/mole}$$

$$\frac{-5248.16}{2^2}$$

$$\frac{-5248.16}{4^2}$$

$$E_2 = \underline{-1312.0} \text{ kJ/mole}$$

$$E_3 = \underline{-583.13} \text{ kJ/mole}$$

$$E_4 = \underline{-328.01} \text{ kJ/mole}$$

- b. One of the most important transitions for the He^+ ion involves a jump from the $n = 2$ to the $n = 1$ level. ΔE for this transition equals $E_2 - E_1$, where these two energies are obtained as in Part a. Find the value of ΔE in kJ/mole. Find the wavelength in nm of the line emitted when this transition occurs; use Equation 4 to make the calculation.

$$\Delta E = E_{n_{hi}} - E_{n_{lo}}$$

$$\lambda \text{ (nm)} = \frac{1.19627 \times 10^5}{\Delta E}$$

$$n=2 \quad \Delta E = E_2 - E_1$$

$$n=1 \quad \Delta E = -1312.0 - (-5248.2)$$

$$\Delta E = 3936.2 \text{ kJ/mole}$$

$$\lambda = \frac{1.19627 \times 10^5}{3936.2 \text{ kJ/mole}} = \boxed{30.39 \text{ nm}}$$

In the upper half of each box write ΔE , the difference in energy in kJ/mole between $E_{n_{hi}}$ and $E_{n_{lo}}$. In the lower half of the box, write λ in nm associated with that value of ΔE .

n_{higher}	4	3	2
n_{lower}			
1	ΔE 4920.2	ΔE 4665	ΔE 3936
	λ 24.31	λ 25.64	λ 30.39
2	ΔE 984.0	ΔE 728.9	
	λ 121.6	λ 164.1	
3	ΔE 255.1		
	λ 468.9		

- c. Three of the strongest lines in the He^+ ion spectrum are observed at the following wavelengths: (1) 121.57 nm; (2) 164.12 nm; (3) 468.90 nm. Find the quantum numbers of the initial and final states for the transitions that give rise to these three lines. Do this by calculating, using Equation 4, the wavelengths of lines that can originate from transitions involving any two of the four lowest levels. You calculated one such wavelength in Part b. Make similar calculations with the other possible pairs of levels. When a calculated wavelength matches an observed one, write down n_{hi} and n_{lo} for that line. Continue until you have assigned all three of the lines.

(1) 4 → 2

(2) 3 → 2

(3) 4 → 3

MAJOR ASPECTS OF THE BOHR MODEL OF ATOMIC STRUCTURE (Based Upon the Hydrogen Atom)

1. The electron is held in the region of empty space within the atom by the electrostatic force of attraction between it and the positively charged nucleus (Coulomb's Law is obeyed).
2. The path of the electron is circular. The electron experiences a centripetal force equal to the electrostatic force (Newton's Laws hold).
3. The electron possesses angular momentum (mvr) which is quantized in units of $(h)/(2\pi)$. This is a key assumption without justification (except that it works).
4. Only certain orbits are possible, as a result of the above assumption. The radius of the orbits can assume only certain values which Bohr could calculate.
$$R = (5.29 \times 10^{-11})N^2 \text{ meters}$$
5. Each allowable orbit represents a specific energy state for the electron which Bohr could calculate.
$$E_N = (-1312.0 \text{ kJ/mol})/N^2$$
6. Each successive orbit represents a state of higher energy than the one beneath it. The smallest orbit in the hydrogen atom represents the lowest possible energy state for the atom ($N = 1$). This is called the ground state.
7. By absorbing a "quantum" of energy the electron can "jump" from the ground state to an orbit of higher energy. The atom is said to be in the excited state.
$$\Delta E = E_{hi} - E_{lo}$$
8. When the electron "jumps" back to an orbit of lower energy, a "quantum" of energy is emitted as light. The wavelength of the light can be calculated.
$$\lambda = (1.19627 \times 10^5 \text{ kJ nm/mol})/\Delta E$$
9. Each line in the hydrogen spectrum corresponds to a particular "jump" the electron makes between one orbit and another.