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, which states that atoms can exist only at certain states that correspond to fixed energy levels. 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 a higher to a lower energy level. 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 with a specific amount of energy, \( E \). This energy is related to the frequency \( (\nu) \) and wavelength \( (\lambda) \) of light by the following equation:

\[
E_{\text{photon}} = h\nu = \frac{hc}{\lambda}
\]

where \( h = \text{Planck's constant} = 6.62608 \times 10^{-34} \text{ J} \cdot \text{s} \) and \( c = \text{speed of light} = 2.997925 \times 10^8 \text{ m} / \text{s} \)

The law of conservation of energy states that total energy is conserved. Thus, the change in energy of the atom must equal the energy change of the photon emitted. The energy change of the atom is equal to the energy of the upper energy level minus the energy of the lower level.

\[
\Delta E_{\text{atom}} = (E_{\text{final}} - E_{\text{initial}}) = E_{\text{photon}} = \frac{hc}{\lambda}
\]

The amount of energy in a photon given off when an atom changes from one level to another is very small, of the order of \( 10^{-19} \) joules. To avoid working with such small numbers, we will work with one mole of atoms. The above equation is multiplied by Avogadro's number, \( N \):

\[
\Delta E (kJ/mol) \approx \frac{Nh}{\lambda} = \frac{(6.02214 \times 10^{23})(6.62608 \times 10^{-34} \text{ J} \cdot \text{sec})(2.997925 \times 10^8 \text{ m}/\text{sec})}{\lambda} = 1.19627 \times 10^5 \frac{\lambda}{\lambda} (\text{nm})
\]

The above equation is useful in the interpretation of atomic spectra. For example, in the study of the atomic spectrum of sodium, a strong yellow line of wavelength 589.16 nm is observed. The above equation can be used to determine the change in energy. This in turn is corresponded to the transition in energy levels.

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. In 1913, Bohr explained the spectrum on a theoretical basis with his model of the hydrogen atom. According to Bohr's theory, the energies allowed to a hydrogen atom are given by the so-called Bohr's Equation:

\[
E_n = -\frac{B}{n^2} = \frac{-1312.04}{n^2}
\]

where \( B = \text{a constant (1312.04 kJ/mol)} \) and \( n = \text{the quantum number (1, 2, 3, ...)} \)

Bohr's equation allows you to calculate quite accurately 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 measure the wavelengths of the hydrogen spectrum and then determine the transition in energy levels associated with each wavelength. This lab consists of a worksheet that needs to be completed for credit; no formal typed laboratory report is due this week.

PROCEDURE: Part A: Visual Observation of a Hydrogen Discharge Tube Using a Spectroscope

The instructor will set up a spectroscope with a hydrogen discharge tube. Note the color of the emitted light without using the spectroscope.

Now view the hydrogen tube using the spectroscope. How many lines do you see? What color does each line have?

Now we shall use the Vernier system and an emission spectrometer to determine the wavelengths of the hydrogen lines you viewed in the spectroscope.

Part B: The Emission Spectrum of Hydrogen Using the Vernier LabQuest 2

Assemble the emission spectrometer and Lab Quest 2 per your instructor’s instructions. In the Lab Quest program, you should see “USB: Intensity rel” if everything is connected correctly.

Place the close to (but not touching!) the middle of a hydrogen discharge tube using a LabJack. Start the data collection by pushing the green “start” button (a green triangle) in the lower left of the Vernier LabQuest 2. **You should see at least three distinct peaks to perform the analysis:** the main central peak (656.3 nm) and at least two to the left of the main 656.3 nm peak (at 486.1 and 434.1 nm.) Ignore any peaks to the right (i.e. larger than 700 nm) – these are due to impurities in the hydrogen tube. Once you have at least three peaks visible, **stop** your experiment and turn off the hydrogen discharge tube.

Use the LabQuest 2 tools to find the wavelengths of the four emission peaks for hydrogen. Once the experiment is stopped, go “Graph – Graph Options”, then change the following: **Left** to 400, **Right** to 700 and **Top** to 0.400, then press **OK**. Your data points will be visible, and a fourth point should be apparent at about 410 nm.

**Determine** the four experimental emission wavelengths using the “left” and “right” buttons (which control the cursor; alternatively, use the pointer to select the exact point.) **Record** these values and **compare** them to the theoretical wavelengths for hydrogen to calculate the **percent error** for each line on the next page.

Part C: Calculations for the Energy Levels of Hydrogen Atom

Next, you can use the hydrogen wavelengths to calculate the **energy change** for each line in the observed hydrogen spectrum. Using Bohr's equation, calculate the **energy levels** ($\varepsilon_n$) in kJ/mole for each of the eight lowest allowed levels of the hydrogen atom starting with $n=1$ to $n=8$. Note that all the energies are negative, so that the lowest energy will have the largest allowed negative value.

The energy levels will allow you to determine the **energy transition** ($\Delta E$) that corresponds to the observed wavelengths. **Determine** the **quantum numbers** for the initial ($n_{hi}$) and final ($n_{low}$) states for these transitions.
The Atomic Spectrum of Hydrogen: Worksheet

Complete the following worksheet using the instructions provided.

Part A: Visual Observations – What color was the hydrogen discharge tube when you looked directly at it?

What four colors did you observe through the spectroscope?

Part B: The Emission Spectrum of Hydrogen – Use the Vernier system to find the hydrogen wavelengths.

<table>
<thead>
<tr>
<th>Color</th>
<th>( \lambda ) (Vernier, nm)</th>
<th>( \lambda ) (theoretical, nm)</th>
<th>Percent Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Red</td>
<td></td>
<td>656.3</td>
<td></td>
</tr>
<tr>
<td>Blue</td>
<td></td>
<td>486.1</td>
<td></td>
</tr>
<tr>
<td>Violet</td>
<td></td>
<td>434.1</td>
<td></td>
</tr>
<tr>
<td>Violet</td>
<td></td>
<td>410.2</td>
<td></td>
</tr>
</tbody>
</table>

Recall:

\[
\text{Percent Error} = \left| \frac{\text{absolute value (theoretical value - experimental value)}}{\text{theoretical value}} \right| \times 100\%
\]

Part C: Calculations for the Energy Levels of Hydrogen Atom

Find the energy level \( \varepsilon_n \) (in kJ/mol) for each quantum number from 1 through 8 using the following equation:

\[
\varepsilon_n = \frac{-1312.04 \text{ (kJ/mol)}}{n^2}
\]

Example: The \( n=1 \) energy level can be calculated as follows: \( \varepsilon_1 = (-1312.04/1^2) = -1312.04 \text{ kJ/mol} \)

Example: The \( n=2 \) energy level can be calculated as follows: \( \varepsilon_2 = (-1312.04/2^2) = -328.010 \text{ kJ/mol} \)

<table>
<thead>
<tr>
<th>( n ) value</th>
<th>( \varepsilon_n ) (kJ/mol)</th>
<th>( n ) value</th>
<th>( \varepsilon_n ) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-1312.04</td>
<td>5</td>
<td>_</td>
</tr>
<tr>
<td>2</td>
<td>-328.010</td>
<td>6</td>
<td>_</td>
</tr>
<tr>
<td>3</td>
<td>_</td>
<td>7</td>
<td>_</td>
</tr>
<tr>
<td>4</td>
<td>_</td>
<td>8</td>
<td>_</td>
</tr>
</tbody>
</table>
Now complete the table below. The first row has been partially completed for you.

<table>
<thead>
<tr>
<th>Color</th>
<th>λ (actual, nm)</th>
<th>ν (s⁻¹)</th>
<th>ΔE (J/photon)</th>
<th>ΔE (kJ/mol)</th>
<th>n_hi</th>
<th>n_low</th>
</tr>
</thead>
<tbody>
<tr>
<td>red</td>
<td>656.3</td>
<td>4.568 x 10¹⁴</td>
<td>3.027 x 10⁻¹⁹</td>
<td>182.3</td>
<td>_____</td>
<td>_____</td>
</tr>
<tr>
<td>blue</td>
<td>486.1</td>
<td>_______</td>
<td>_______</td>
<td></td>
<td>_____</td>
<td>_____</td>
</tr>
<tr>
<td>violet</td>
<td>434.1</td>
<td>_______</td>
<td>_______</td>
<td></td>
<td>_____</td>
<td>_____</td>
</tr>
<tr>
<td>violet</td>
<td>410.2</td>
<td>_______</td>
<td>_______</td>
<td></td>
<td>_____</td>
<td>_____</td>
</tr>
</tbody>
</table>

Convert the wavelength values into ΔE (in kJ/mol) using the following equation:

$$ΔE (kJ/mole) = \frac{1.19627 \times 10^5}{λ (nm)}$$

The calculated ΔE values correspond to a transition between the various energy levels, $\varepsilon_n$, calculated previously. Determine which transition they correspond to by finding the change in energy (i.e. ΔE) between levels.

Example: Find the change in energy in a transition of hydrogen between the n=2 and n=1 energy levels.

The energy level, $\varepsilon_n$, for n=2 is $-328.010$ kJ/mol, and the energy level, $\varepsilon_n$, for n=1 is $-1312.04$ kJ/mol. A change in energy, ΔE, corresponds to the final energy state minus the initial energy state, or:

$$ΔE = \varepsilon_{\text{final}} - \varepsilon_{\text{initial}} = \varepsilon_2 - \varepsilon_1 = -1312.04 - (-328.010) = -984.03 \text{ kJ/mol}$$

If your calculated value of ΔE is about -984.03 kJ/mol, then your $n_{hi}$ would be 2 (the higher value of n) and your $n_{low}$ value would be 1 (the lower value of n).

Show the frequency calculation for the red line below:

Show the ΔE (J/photon) calculation for the red line below:

Show the ΔE (kJ/mol) calculation for the red line below:
**Post Lab Questions:**

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, as in your experiment. What common characteristic do the lines in the Balmer series have?

2. In the hydrogen atom, the electron is in its lowest energy state, \( n=1 \). The maximum electron 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 \( \text{H}^+ \) ion. How much energy does it take to ionize one hydrogen atom in kilojoules per mole and in Joules per atom? *(Hint: calculate \( \Delta E \) where \( \varepsilon_{\text{final}} \) is zero and \( \varepsilon_{\text{initial}} \) is –1312.04 kJ/mol.)*

Questions #3 through #5 will use the equation below for the helium ion. The helium ion, \( \text{He}^+ \), has energy levels similar to those of the hydrogen atom, since both species have only one electron. The energy levels of the helium ion are given by the following equation:

\[
E_n = -\frac{5248.16}{n^2} \text{ kJ/mol where } n = 1, 2, 3...
\]

3. Calculate the energies in kJ/mole for the four lowest energy levels of the helium ion using the equation above.

\[
\begin{align*}
\varepsilon_1 & \quad \varepsilon_3 \\
\varepsilon_2 & \quad \varepsilon_4
\end{align*}
\]

4. One of the most important transitions for the helium ion involves a jump from the \( n = 2 \) to the \( n = 1 \) level. Calculate the change in energy in kJ/mole for this transition. *(Hint: \( \Delta E = \varepsilon_1 - \varepsilon_2 \).)* Use the equation found in Part C of the worksheet to calculate the wavelength (in nm) of this transition.

5. Three of the strongest lines in the helium ion spectrum are observed at the following wavelengths. Find the quantum numbers of the initial and final energy states for the transitions that give rise to these three lines:

<table>
<thead>
<tr>
<th>( \lambda ) (nm)</th>
<th>( \Delta E ) (kJ/mol)</th>
<th>( n_{\text{hi}} )</th>
<th>( n_{\text{low}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>121.57</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>164.12</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>468.90</td>
<td></td>
<td></td>
<td></td>
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</tbody>
</table>