EXPERIMENT 11
Atomic Spectra and Atomic Structure

INTRODUCTION

In the Beer's law experiment, you measured the absorption spectrum of a compound. This spectrum was *continuous*: the molecules absorbed light of all wavelengths in the range from about 300 – 700 nm. An *emission spectrum* is produced when electromagnetic radiation is given off rather than absorbed. A prism or diffraction grating can be used to separate the light given off into its component wavelengths. The emission spectrum from the sun is continuous; the visible part of this spectrum is a continuous range of colors commonly known as a rainbow. Different colors correspond to different wavelengths of light; the visible spectrum extends from about 400 nm (violet light) through about 700 nm (red light).

When a gas absorbs energy from an electrical discharge, it can also emit electromagnetic radiation. However, for gaseous elements, the emission spectrum produced is not continuous. Rather, only a few, separated wavelengths make up the spectrum, with gaps in between, so that it appears as a series of lines. This type of emission spectrum is known as a *line spectrum*. Each element has a unique emission spectrum; thus, an emission spectrum can be used to identify elements. In 1885 Johannes Balmer discovered a relatively simple formula relating the wavelengths present in the visible portion of the emission spectrum of hydrogen to a series of integers:

$$\frac{1}{\lambda} = R_H\left(\frac{1}{2^2} - \frac{1}{n^2}\right)$$

In this formula, λ is the wavelength of light, R_H is the Rydberg constant, and *n* is an integer. Each of the four wavelengths in the visible portion of hydrogen's emission spectrum is associated with one of the integers 3, 4, 5, or 6. Hydrogen also emits light outside the range of visible wavelengths (e.g., in the ultraviolet). These additional lines can be incorporated into a generalized version of Balmer's equation, known as the Rydberg equation:

$$\Delta E = h\nu = R_H\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$$

In this equation, n_i and n_f are integers (In the Balmer equation, $n_i = 2$, and n_f is just *n*. In the Rydberg equation, the energies may be negative (if energy is lost), while in the Balmer equation, only positive values of λ make sense.)

Niels Bohr came up with a theory to explain the hydrogen spectrum, and the success of the Rydberg formula at reproducing the experimentally observed lines. He postulated that the electron in a hydrogen atom is only allowed to take on certain energy values. Another way of stating this is to say that he postulated that the energy in the atom is *quantized*. The allowed energy values are known as *energy levels*, and are associated with a quantum number, *n*. Bohr also postulated that an electron can change from one energy level to another by emitting or absorbing energy in the form of a photon. [Although other parts of Bohr's model are no longer part of atomic theory, these two principles–that the energy levels of an atom are quantized, and that the atom emits radiation when it goes from a higher to a lower energy level–were an important step in understanding the hydrogen spectrum, and are part of the current atomic theory.]

In Bohr's theory, the atoms of hydrogen are normally in the lowest energy level, n = 1. The atom can absorb energy from an electrical discharge, which causes the electron to make a transition ("jump") into a higher energy level (*n* = 2, 3, 4…). Then, the energy will be reemitted in the form of electromagnetic radiation (light), as the electron changes (or "jumps down") into any of the lower energy levels. The second part of the process, in which the electrons emit energy on their way to a lower energy level, is depicted in the diagram below. Each arrow represents one of the possible transitions an electron might make. The Balmer series consists of the transitions that end at the level $n = 2$; the energy involved in these jumps happens to fall within the range of wavelengths that we can detect with our eyes (the visible portion of the spectrum). The energy of the photon emitted in a given transition is equal to the difference in energy between levels: (for example)

$$\Delta E = E_3 - E_2 = E_{photon} = h\nu$$

where ν is the frequency of the photon: $\nu = c/\lambda$, so $E_{photon} = hc/\lambda$

Since the atom can only occupy certain "allowed" energy levels, there is a limited number of transitions that can be made. Each of these corresponds to a specific wavelength, and it is only these allowed wavelengths that are seen in a line spectrum.

Elements other than hydrogen are more complicated because of the additional particles present (the most common isotope of hydrogen is composed of just one proton and one electron!). However, the same general principles apply: only certain energies are allowed, and the wavelengths of light present in an emission spectrum correspond to transitions between these allowed levels.

In this lab, you will use a spectroscope to observe the emission spectra of several elements. The spectroscope is used to measure the wavelength associated with each line in the spectrum. It consists of a box with a slit at one end for letting light in, and a diffraction grating, which, like a prism, splits up the incoming light into its component colors. When you look through the opening at the other end of the spectroscope, you will see the line spectrum on a numerical scale. This scale allows you to measure the wavelength of each line in the spectrum.

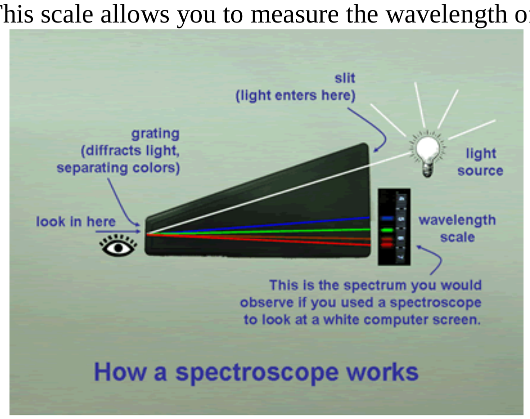
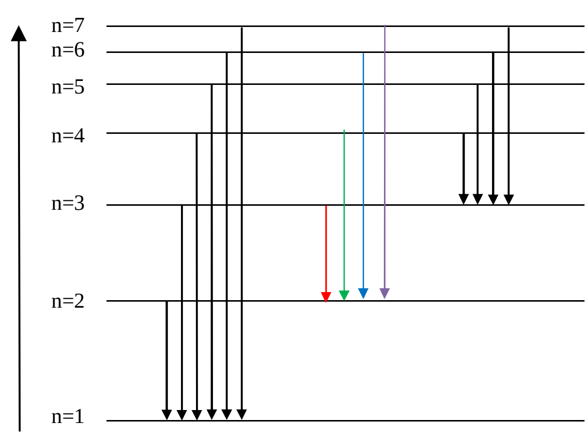


Image from: http://www.wellesley.edu/Chemistry/Chem105manual/Lab03/lab03_howitworks.gif

You will observe the spectrum from gas discharge lamps, as well as from flame tests of various salts. You will note down the colors you see and the numerical value for the wavelength, and use your observations to determine a value for the Rydberg constant. In the flame tests, the atoms absorb energy from the flame, then emit energy in the form of light, just as the atoms inside the lamp absorb electrical energy and then emit photons. Finally, you will use your observations from the flame tests of known cations to identify an unknown.



Lyman Series (ultraviolet) | Balmer Series (visible) | Paschen Series (infrared)

RELEVANT PROBLEMS FROM THE TEXT (Chang, 10e): 7.30, 7.31, 7.33, 7.34

PROCEDURE

1. Obtain a spectroscope from the stockroom.
2. Lamp observations will be easier if the room lights are off.
   For the hydrogen lamp:
   a. Make sure that the lamp is plugged in. Turn it on. DO NOT TOUCH THE TUBE ITSELF.
   b. Point the spectroscope at the lamp so that the slit is lined up with the lamp tube.
   c. You should see a series of 3 or 4 lines. (The violet line can be quite hard to see; you can still complete the lab without it, if you and your partner are unable to see it!) Record the color and the numerical reading for each line that you see, to the nearest ±0.01. (If you see a faint, fuzzy, yellowish line, ignore it!)

3. For the mercury lamp:
   a. Make sure that the lamp is plugged in. Turn it on. DO NOT TOUCH THE TUBE ITSELF.
   b. Point the spectroscope at the lamp so that the slit is lined up with the lamp tube.
   c. You should see a series of lines. Record the color and the wavelength reading of each line that you see, to the nearest ±0.01.

   <u>Flame tests:</u>
4. Obtain 5 mL of 0.1 M NaCl solution in a clean dry test tube. Do the same for EACH of the remaining solutions, KCl, $CaCl_2$, $BaCl_2$, and an unknown: Place 5 mL of each solution in a separate test tube. Be sure to label all the test tubes.
5. Dip the wire loop in the NaCl solution and place it in the hottest part of the Bunsen burner flame (just above the blue inner cone).
6. Observe and record the color of the flame.
7. Dip the wire in HCl solution, and burn it off in the flame, to clean the wire.
8. Repeat steps 5 – 7 for the other solutions, and for your unknown. Determine the identity of the unknown by comparing the color observed with those of the known solutions.
9. Results: You will use your data and the Balmer equation to determine a value for R_H.

$$\frac{1}{\lambda} = R_H\left(\frac{1}{2^2} - \frac{1}{n^2}\right)$$

This equation can be rearranged to have the same form as the general equation for a straight line: $y = mx + b$

$$\frac{1}{\lambda} = -R_H\frac{1}{n^2} + R_H\frac{1}{2^2}$$

with y = $1/\lambda$, x = $1/n^2$, and m = $-R_H$. You will make a graph of your data to determine R_H.

   a. The spectroscope readings are in nm × 10^{-2}; that is, a reading of 4.00 corresponds to 400 nm. Convert your readings to nm, then to meters.
   b. From your hydrogen lamp data, calculate $\frac{1}{\lambda}$ in m^{-1}.
   c. For the Balmer series, the hydrogen atoms end up in the energy level $n = 2$. Each line in the spectrum represents a transition from a different initial energy level, with n = 3, 4, 5, etc. Identify the initial value of n for each of the lines you observed. That is, which line corresponds to the n = 3 to n = 2 transition? (This transition has the LOWEST energy: Which color, out of those you observed, does this correspond to?) The diagram above (and in the textbook on p. 286; Chang, 10th ed) may help.
   d. Calculate $\frac{1}{n^2}$ for each value of n.
   e. Plot a graph of $\frac{1}{\lambda}$ versus $\frac{1}{n^2}$.
   f. Draw a best-fit line and determine the slope of the line. Report your value of R_H to the appropriate number of significant figures.

Atomic Spectra and Atomic Structure

Name: ________________________________

Section: ________________________________

Unknown number: ________________________________

DATA

Hydrogen lamp

Color of line	Wavelength Reading

Mercury lamp

Color of line	Wavelength Reading

Flame Tests:

Solution	Color of flame	Wavelength Range for this color (look it up!)

RESULTS

1. Hydrogen lamp

Wavelength in nanometers	Wavelength in METERS	$\frac{1}{\lambda}$	n (integer)	$\frac{1}{n^2}$

Graph 1/λ versus $1/n^2$ (columns in bold) on the graph paper provided.

Calculation of slope:

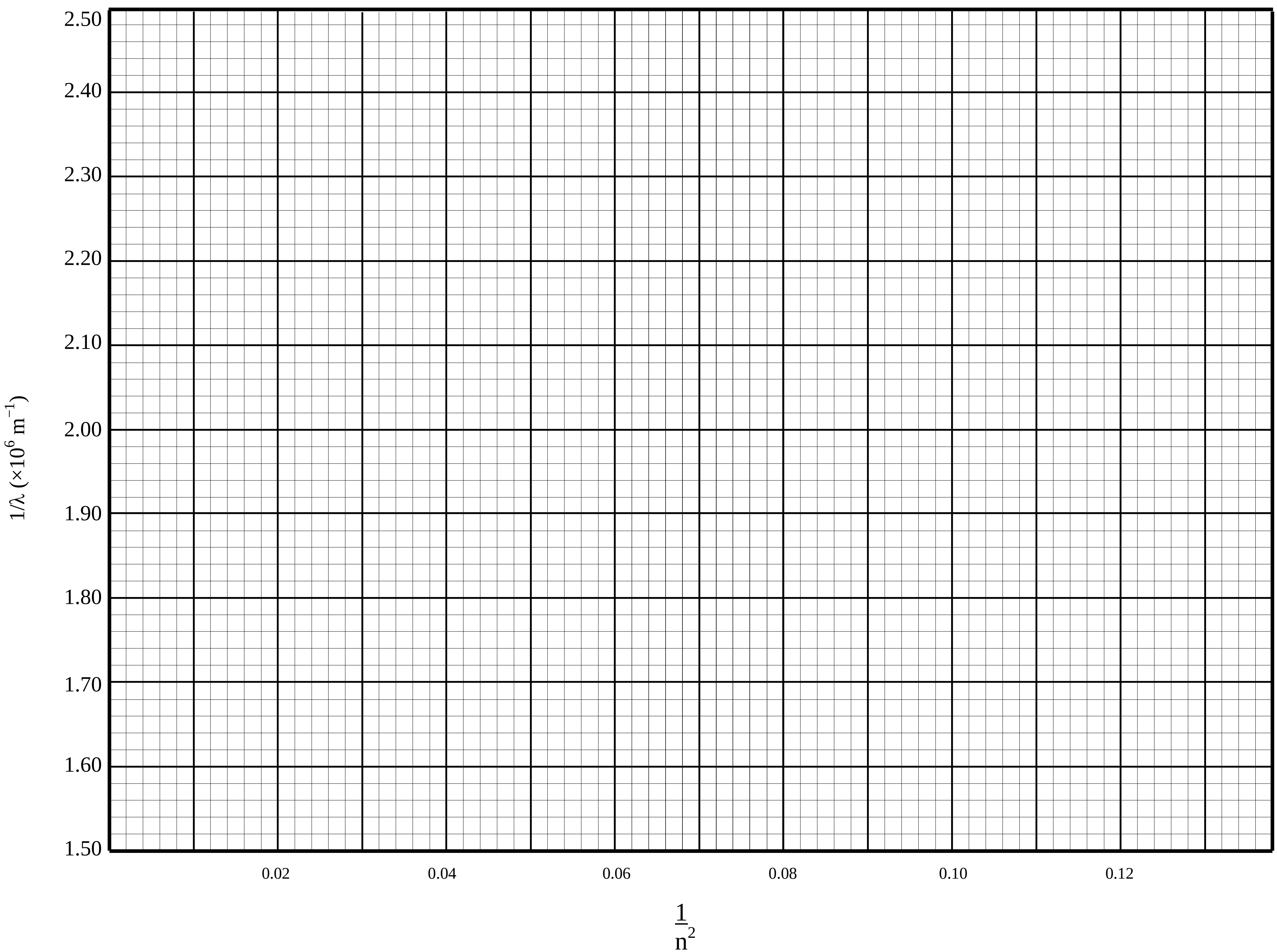
Value of R: ______________________________

The true value of R_H is 1.0737×10^7 m^{-1}. Calculate the % error in your value of R_H.

$$\% \text{ error} = \frac{|experimental\ value - true\ value|}{true\ value}$$

2. Mercury lamp: Convert your values to nm by multiplying by 100 and list them below. The literature values for some of the lines in mercury are 435.8 nm, 546.0 nm, 576.9 nm, and 579.0 nm. Compare your values with the literature values. Did you observe these lines? How accurate are your readings?

3. Identify the ion(s) present in your unknown solution: ________________________



2.50
2.40
2.30
2.20
2.10
2.00
1.90
1.80
1.70
1.60
1.50
1/λ (×10^6 m^-1)
0.02
0.04
0.06
0.08
0.10
0.12
1/n^2