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*Objective*

In this experiment, we will be investigating a number of emission spectra in a qualitative manner. The hydrogen emission spectrum in particular will be examined in greater detail. The visible wavelengths in the hydrogen line spectrum will be measured with a spectroscope. These experimental values will be analyzed graphically to determine the principle quantum number associated with the Balmer Series of hydrogen and to calculate a value for the Rydberg constant.

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*Introduction*

An **emission spectrum** is electromagnetic radiation emitted by a substance. The emission spectrum of sunlight is a **continuous spectrum**; in other words, all wavelengths of visible light are represented in the spectrum and these can be observed if the beam of sunlight is split with a prism. The emission spectrum for an atom can also be observed if the sample absorbs energy in the form of heat or, for a gas, an electrical current. However, the emission spectra for atoms in the gas phase are not continuous; only a few colors are observed which correspond to different wavelengths in the visible region of the electromagnetic spectrum. Light emission that occurs only at specific wavelengths are called a **line spectrum**. Every element has a unique line spectrum and the characteristic lines are like fingerprints used for identification of unknown atoms.

There is a fundamental link between atomic spectra and atomic structure. Beginning with Thomson's discovery of the electron, the structure of the atom was revealed and a *planetary* model was proposed in which the electrons were thought to be in circular orbits around the nucleus. Although this model is no longer considered to be an accurate description of the atom, the notion of orbits survives. Modern interpretation of atomic structure still uses the idea of orbits which we refer to as energy levels or electronic shells. Niels Bohr presented an explanation for atomic spectra based on this idea of electrons orbiting a nucleus but he imposed a restriction on these orbits: For the hydrogen atom, the single electron can only be located in specific orbits. Therefore, the electron can only possess certain fixed energy values which correspond to the energies of the allowed orbits. In other words, the energy of the electron is **quantized**. Bohr had embraced the idea of **quantization** con-

ceived by his contemporaries, Max Planck and Albert Einstein and was awarded the Nobel Prize in Physics in 1922 for his theory explaining the spectrum of the hydrogen atom.

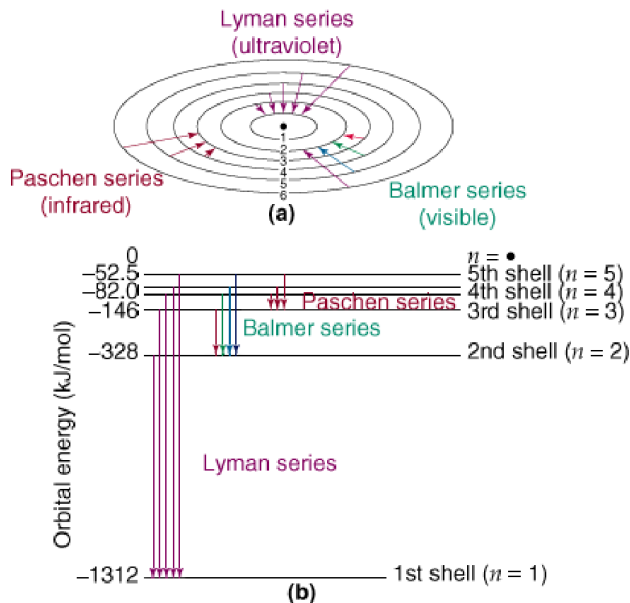
According to Bohr's theory, the energy values of an electron in a hydrogen atom are expressed by the equation

$$E = -B\left(\frac{1}{n^2}\right) \quad \text{(EQ 10.1)}$$

where  $B$  is a constant equal to  $2.18 \times 10^{-18}$  J and  $n$  is an integer called the principal quantum number with values equal to 1, 2, 3, ... etc. By convention, the negative sign signifies that the energy of an electron is less than the energy of a *free electron*, that is, an electron infinitely distant from the nucleus. The energy of a free electron is arbitrarily given a value of zero; this corresponds to  $n$  equal to infinity in the equation and  $E$  approaches zero. As the electron moves closer to the nucleus (as the value for  $n$  decreases),  $E$  becomes larger and more negative. The largest negative value is when  $n = 1$  which is the lowest energy state or **ground state** for the hydrogen electron. When  $n$  is greater than 1, the hydrogen atom is said to be in an **excited state**. Since the radius of each circular orbit depends on  $n^2$ , the size of the orbit increases as  $n$  gets larger and the electron is located further from the nucleus in any excited state.

Think about a hydrogen atom that absorbs energy. The energy absorbed causes the electron to move from a low energy state (small  $n$ ) to a higher energy state (larger  $n$ ). When the electron falls back to a lower energy state this energy is released as a photon. This quantized movement between energy states is like a ball moving up and down a stairway. The ball can rest on any step but is never located between steps. The energy associated with movement from one step to another is determined by the distance between the steps. For the hydrogen atom, the energy required to move an electron between energy levels depends on the difference in energy between the initial and final state. Movement of an electron between two energy states is called an **electronic transition** or simply a **transition**. When an electron is promoted to an excited state, there exists more than one emission pathway: The electron may return directly to the ground state by emitting a photon of frequency  $\nu$  which is equal to the energy difference between the ground state and excited state, or the electron may return to the ground state stepwise, emitting a photon for each successive movement to a lower energy level. These energy transitions are illustrated in Figure 10.1 on page 79.

FIGURE 10.1



Now consider a hydrogen atom in an excited state characterized by principal quantum number  $n_i$ . When the electron returns to a lower energy state, the energy of transition is simply the difference between the initial and final state (symbolized by subscripts  $i$  and  $f$ )

$$\Delta E = E_f - E_i \quad (\text{EQ 10.2})$$

and by substituting into equation 10.1, the energy for initial and final states can be calculated as

$$E_f = -B\left(\frac{1}{n_f^2}\right) \quad \text{and} \quad E_i = -B\left(\frac{1}{n_i^2}\right) \quad (\text{EQ 10.3})$$

where  $n_i$  refers to the shell number of the excited state and  $n_f$  refers to the shell number of the lower energy state. Remember that  $n_f$  is not necessarily the ground state shell number. An excited electron does not always return to the ground state in one step, therefore, we typically observe more than one wavelength for atomic emission spectra. Thus, the total energy change for a transition is given by

$$\Delta E = \left(\frac{-B}{n_f^2}\right) - \left(\frac{-B}{n_i^2}\right) \quad \text{or} \quad \Delta E = -B\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \quad (\text{EQ 10.4})$$

Using the relationships,  $E = h\nu = hc/\lambda$ , we can derive the familiar form of the Rydberg equation:

$$\Delta E = h\nu = \frac{hc}{\lambda} = -2.18 \times 10^{-18} \text{ J} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \quad (\text{EQ 10.5})$$

where  $B = 2.18 \times 10^{-18} \text{ J}$

Using the values of the constants, we have:

$$\frac{1}{\lambda} = \frac{-2.18 \times 10^{-18} \text{ J}}{hc} \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right) = \frac{-2.18 \times 10^{-18} \text{ J}}{6.626 \times 10^{-34} \text{ J} \cdot \text{s} (3.0 \times 10^8 \text{ m/s})} \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \quad (\text{EQ 10.6})$$

Multiplying through gives

$$\frac{1}{\lambda} = 1.097 \times 10^{-2} \text{ nm}^{-1} \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \quad (\text{EQ 10.7})$$

Equation 10.7 is called the Rydberg equation where  $1.097 \times 10^{-2} \text{ nm}^{-1}$  is the value of the **Rydberg constant for hydrogen** ( $R_H$ ).

Finally, the Rydberg equation can be written as:

$$\frac{1}{\lambda} = -R \left( \frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \quad (\text{EQ 10.8})$$

which is a useful expression since it is an equation for a line ( $y = mx + b$ ). Thus, by graphing reciprocal wavelength versus the correct values for  $1/n_i^2$  a straight line should be obtained and from the graph, the slope can be determined which is of course the value for  $R$ , the Rydberg constant. Reciprocal wavelengths are also called wavenumbers symbolized by  $\bar{\nu}$ :

$$\bar{\nu} = -R \left( \frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \quad (\text{EQ 10.9})$$

factoring in  $R$  gives the equation:

$$\bar{\nu} = -R \frac{1}{n_i^2} + \frac{R}{n_f^2} \quad (\text{EQ 10.10})$$

where  $y = \bar{\nu}$ ,  $x = 1/n_i^2$ , the slope,  $m = -R$ , and the y-intercept,  $b = R/n_f^2$ .

Which wavenumbers and which values of  $n_i^2$  should be used? Wavenumbers are calculated from the observed wavelengths that are measured with the spectroscope. As for the  $n$  values, each wavelength corresponds to a transition from energy level  $n_i$  to level  $n_f$ . Energy level  $n_f$  is the same for all wavelengths in a particular series (Balmer, Paschen, Lyman) and  $n$  values are always integers. (As you know, the principle quantum number is always an integer). These are the spectral series are shown in Figure 10.1 on page 79 and the wavelengths for each series are illustrated in Table 10.1 on page 81.

TABLE 10.1

$n_i$	Pashen Series (Infrared light)	Brackett Series	Pfund Series	Humphreys Series
	$n_f = 3$	$n_f = 4$	$n_f = 5$	$n_f = 6$
	$\lambda$ (nm)	$\lambda$ (nm)	$\lambda$ (nm)	$\lambda$ (nm)
4	1870			
5	1280	4050		
6	1090	2630	7460	
7	1000	2170	4650	12370
8	954	1940	3740	7503
9	820	1820	3300	5910
10		1460	3040	5130
11			2280	4670
12				3280

### Procedure

1. Your instructor will explain the operation of the spectroscopes.
2. Take precautions so that you ...



**DO NOT** attempt to change a discharge tube while it is connected to a power supply. The system generates up to 15,000 volts.

**DO** wear the special protective tinted glasses which filter the ultraviolet radiation that comes from the discharge tubes. Your eyes may be damaged if left unprotected.

3. For purposes of comparison, observe and *sketch* the spectra of: sunlight (do not aim the spectroscope directly at the sun!), an incandescent bulb, a fluorescent bulb, and at least three elements (one of these must be the hydrogen discharge tube) Draw a rough scale below each sketch to identify the approximate wavelengths in each spectrum.
4. Carefully measure the visible wavelengths in the hydrogen line spectrum. Create a Table of wavelengths then convert these values into wavenumbers.

### Results and Calculations

1. Use a graphing program to plot these wavenumbers versus  $1/n_i^2$ , selecting the appropriate values for  $n_i$  for the visible wavelengths. The correct set of integer values will produce a straight-line plot  $\bar{\nu}$  vs.  $1/n_i^2$  as show in Equation 10.10.



**NOTE:** What is the ground state,  $n_f$ , for the visible spectrum? Refer to Figure 10.1 on page 79.

You may want to create a table like the one below:

TABLE 10.2

$\lambda$ (nm)	$n_i$	$1/\lambda$ (1/nm)	$\bar{\nu}$ (nm)	$1/n_i^2$

2. From your graph, determine the slope and compare your value of the Rydberg constant with the accepted value of  $1.097 \times 10^{-2} \text{ nm}^{-1}$ . Calculate the percent difference.
3. From your graph, find (and explain) the value of  $n_f$  from the y-intercept of your plot.
4. Also make graphs and analyze:
  - a.  $1/\lambda$  vs.  $1/n_i^2$  for the UV lines of Hydrogen (121.6 nm, 102.6 nm, 97.3 nm, 95.0 nm, 93.8 nm);



**NOTE:** What is the ground state,  $n_f$ , for the ultraviolet spectrum? Refer to Figure 10.1 on page 79.

- b.  $1/\lambda$  vs.  $1/n_i^2$  for the visible lines of Hydrogen from literature (656.3 nm, 486.1 nm, 434.1 nm, 410.2 nm).
5. Determine what electronic transitions were responsible for each of the spectral lines in both the UV and visible spectra.

*Post Lab Questions*

TABLE 10.3

Quantity	Symbol	Value
atomic mass unit	amu	$1.660565 \times 10^{-27}$ kg
Avogadro's constant	N or $N_A$	$6.022094 \times 10^{23}$ mol <sup>-1</sup>
electronic charge	$e$	$1.6021892 \times 10^{-19}$ C
Faraday constant	F	$9.648456 \times 10^4$ C/mol
gas constant	$R$	$0.0820568 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}$
		$8.314510 \frac{\text{J}}{\text{mol} \cdot \text{K}}$
mass of electron	$m_e$	$9.109534 \times 10^{-31}$ kg
mass of neutron	$m_n$	$1.6745943 \times 10^{-27}$ kg
mass of proton	$m_p$	$1.6726485 \times 10^{-27}$ kg
Planck's constant	$h$	$6.626176 \times 10^{-34}$ J s
Rydberg constant	$R_H$	$1.0967758 \times 10^7$ m <sup>-1</sup>
speed of light in vacuum	$c$	$2.997924 \times 10^8$ m/s

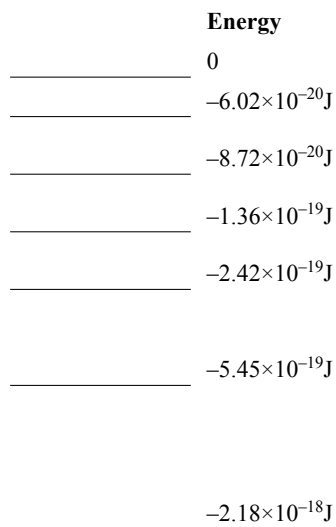
1. Determine the frequency of a photon of  $5.0 \times 10^{-7}$  meter wavelength.

2. What is the energy (in joules) of the photon in question 1?

3. If the threshold frequency,  $\nu_0$ , for a metal is  $1.0 \times 10^{14} \text{ s}^{-1}$ , what would be the velocity of an electron ejected from the metal surface by a photon of  $6.0 \times 10^{14} \text{ s}^{-1}$  frequency striking the metal? (kinetic energy =  $\frac{1}{2}mv^2$ )
4. Find the wavenumber of the photon in question 1.
5. Find the wavelength (in nm) of the light emitted by the  $n = 8$  to  $n = 2$  electronic transition in a hydrogen atom.



6. A stream of laser photons with a frequency of  $3.0 \times 10^{15}$  Hz excited electrons in the lowest energy of the hydrogen atom shown in the energy level diagram below



a. Show to what level the photon excited the electron.

b. Show all the possible emission transitions as the electron returns from the  $n = 3$  energy level to the ground state.

c. Calculate  $\Delta E$  for each line produced in b.

- d. What is the wavelength of the photon that would just ionize the ground-state atom to  $H^+$ ?

7. An energy of  $1.09 \times 10^3$  kJ/mol is required to convert gaseous carbon atoms to gaseous  $C^+$  ions and electrons. What is the maximum wavelength, in nm, of electromagnetic radiation with sufficient energy to cause ionization to a single carbon atom? In what region of the electromagnetic spectrum is this photon found?

8. Answer the following questions about the ground-state electron configuration of a neutral uranium atom.
- Write out the outer-shell ground-state electron configuration of the for the six electrons beyond the radon configuration of a neutral uranium atom.
  - Give the four quantum numbers that correspond to each of the six electrons beyond the radon configuration of a neutral uranium atom. Put your answers in Table 10.4 .

TABLE 10.4

Electron	$n$	$l$	$m_l$	$m_s$

9. What is the maximum number of electrons that can be accommodated in each representation below?

$2p$  \_\_\_\_\_  $l = 3$  \_\_\_\_\_  $m_l = 3$  \_\_\_\_\_

$n = 3$  \_\_\_\_\_  $4f$  \_\_\_\_\_  $n = 3, l = 2$  \_\_\_\_\_