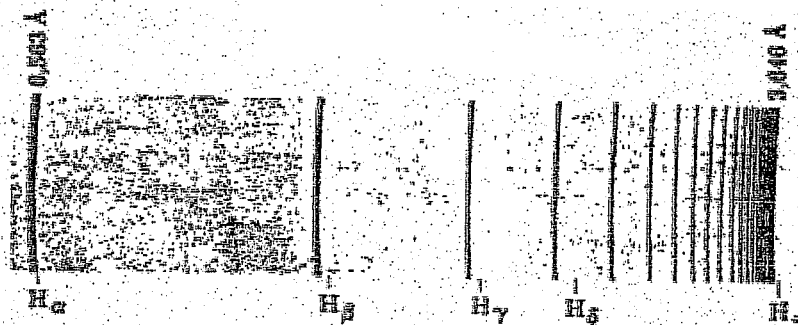


## THE BALMER SERIES OF HYDROGEN SPECTRUM

In the 19<sup>th</sup> century, long before the development of quantum mechanics, physicists devoted a considerable effort to spectroscopy trying to deduce some physical properties of atoms and molecules by investigating the electromagnetic radiation emitted or absorbed by them. Many spectra have been studied in detail. Among them the hydrogen spectrum (see Figure 1), which is relatively simple and shows regularity, was most intensely studied.



**Figure 1: The Balmer Series of Hydrogen Spectrum**

The obvious regularity of the H spectrum tempted several people to look for an empirical formula that would represent the wavelength of the lines. Balmer discovered such a formula in 1885. He found the simple equation,

$$\lambda = 3646 \frac{n^2}{(n^2 - 4)} \quad (\text{in units of } \text{\AA}) \quad (1)$$

where  $n=3$  for  $H_\alpha$ ,  $n=4$  for  $H_\beta$ ,  $n=5$  for  $H_\gamma$ , etc., was able to predict the wavelength of the first nine lines of the visible part, which were all known at the time, to better than 1 part in 1000. This discovery initiates a search for similar empirical formula that would apply to series of lines that can sometimes be identified in the complicated distribution of lines that constitute the spectra of other elements. Rydberg (ca. 1890, who found it convenient to deal with the wave number,

$$k = \frac{1}{\lambda}, \quad (2)$$

of the lines, instead of their wavelength. In terms of this quantity, the Balmer formula can be written

$$k = R_H \left( \frac{1}{2^2} - \frac{1}{n^2} \right), \quad n = 3, 4, 5, \dots \quad (3)$$

where  $R_H$  is the so-called Rydberg constant for hydrogen. For recent spectroscopic data, its value is known to be

$$R_H = (109677.576 \pm 0.012) \text{ cm}^{-1}.$$

This number is indicative of the accuracy possible in spectroscopic measurements.

A more general expression of the Rydberg formula for hydrogen is

$$k = R_H \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \quad (4)$$

where both  $n_f$  and  $n_i$  are positive integers with  $n_i > n_f$ . For each  $n_f$  the above formula gives a series of lines with different  $n_i$ . The Balmer series which falls in near ultraviolet and visible has  $n_f = 2$ . For  $n_f = 1, 3, 4, 5$ , the series are called Lyman (ultraviolet), Paschen, Brackett, Pfund (infrared). These transitions and the corresponding energies in eV are shown in Figure 2.

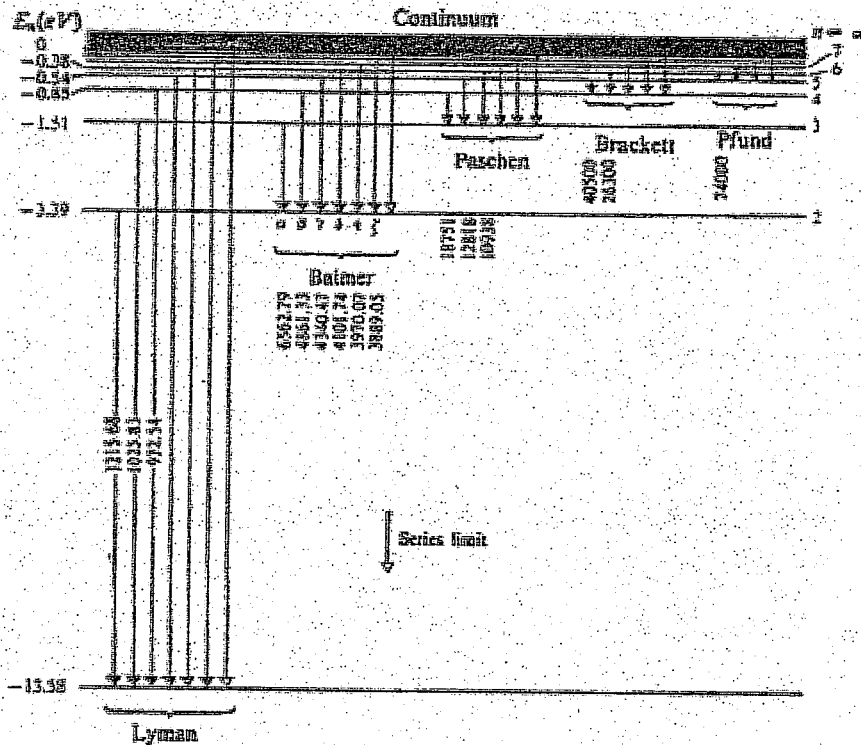


Figure 2

The Rydberg Formula which is empirical, as mentioned above, was not fully explained until 1913 when Bohr developed his quantum atomic model. From Bohr's theory, the energy of an electron in hydrogen was found to be discrete. The energy of the electron is given by

$$E_n = -\frac{me^4}{8\epsilon_0^2 h^2} \left( \frac{1}{n^2} \right) \quad (5)$$

where  $m$  is the mass of the electron,  $e$  is its electric charge,  $\epsilon_0$  is the permittivity of free space,  $h$  is Planck's constant, and  $n$  is an integer which is called the principle quantum number.

Bohr explained the Rydberg formula as follows. If the electron in hydrogen goes from a higher energy state (principle quantum number =  $n_i$ ) to a lower energy state (principle quantum number  $n_f < n_i$ ), the excess energy will be given out as a quantum of electromagnetic radiation (photon). But Einstein postulated that the frequency of a quantum of electromagnetic radiation is equal to the energy carried by the quantum divided by Planck's constant,

$$\nu = \left( \frac{E_i - E_f}{h} \right) \quad (6)$$

so the frequency of the photon emitted by the  $n_i \rightarrow n_f$  transition is

$$\nu = \frac{c}{\lambda} = \frac{1}{h} \left( -\frac{me^4}{8\epsilon_0^2 h^2} \left( \frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \right) = \frac{me^4}{8\epsilon_0^2 h^3} \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \quad (7)$$

and hence

$$k = \frac{1}{\lambda} = \frac{me^4}{8\epsilon_0^2 ch^3} \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right).$$

Comparing this equation with Rydberg's formula shows that

$$R_H = \frac{me^4}{8\epsilon_0^2 ch^3}.$$

### Experimental Procedure:

In this experiment we will use a small diffraction grating spectrometer to measure the wavelengths of the three strongest spectral lines of the Balmer series:  $H_\alpha$ ,  $H_\beta$ , and  $H_\gamma$ . The spectrometer scale is roughly correct but must be calibrated by reference to known wavelengths. Their prominent lines of the helium and mercury spectra will be used for this purpose. From the calibration, the wavelengths of the hydrogen spectrum can be determined.

Figure 3 is a schematic diagram of the spectrometer and the viewer's eye E (much enlarged). The spectrometer is enclosed in a hollow box blackened on the inside. A slit,  $S_0$ , of the adjustable width, is backed by a light source, L. One looks through the replica diffraction grating, G located in the spectrometer eyepiece. Inside the spectrometer, undiffracted light from  $S_0$  is imaged by the Eye, E, on the retina at  $S_0'$ . Diffracted light is imaged at points such as  $S_\gamma'$ . Here  $d$  is the spacing of the grooves on G and  $\theta$  is the angle between the rays to  $S_0'$  and  $S_\gamma'$  (see Figure 4). The colored image is seen against a scale incorporated in the spectrometer. Opening the shutter on the side of the spectrometer will illuminate the numbers on the scale so as to read them.

1. To calibrate the spectrometer, record the scale values of the various spectral lines from the helium or mercury bulb. Plot the scale values along the x-axis of a calibration graph with the corresponding wavelength from Table 1 along the y-axis. The scale is easily read to two significant figures; the third significant figure should be carefully estimated.

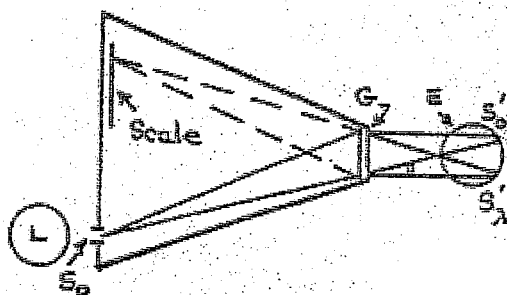


Figure 3

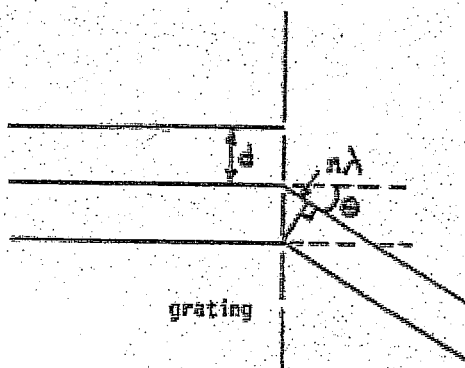


Figure 4

2. Perform a least squares fit of the data and obtain a slope value,  $m$ , and a  $y$ -intercept value,  $b$ .
3. Observe the hydrogen spectrum and obtain scale values for the prominent lines.
4. From the calibration equation  $y = mx + b$ , that linearly relates the scale values ( $x$ ) to the known wavelengths ( $y$ ), determine the hydrogen spectral wavelengths.
5. From the knowledge of the principle quantum numbers corresponding to the transitions that generate the spectral lines, use the wave number formula (3) to determine the Rydberg constant for each wavelength. Report an average for the three values.

Precautions:

1. HIGH VOLTAGE TERMINALS OR WIRES CONNECTED TO THE LUMINOUS TUBE SOURCES ARE DANGEROUS. DO NOT TOUCH THEM WHILE THE LIGHTS ARE PLUGGED INTO THE HOUSE PLUGS.
2. ALL THE LUMINOUS LIGHT SOURCES HAVE A LIMITED LIFE. DO NOT LEAVE THEM ON WHEN THEY ARE NOT BEING USED.

**Table 1: Mercury and Helium Approximate Wavelengths (nm)**

	<u>Mercury</u>	<u>Helium</u>	
Red		728	(weak)
		706	
		668	
Yellow	579		
	577	588	
Green		505	(weak)
	546	502	
Blue	(yellow green)	492	(turquoise)
		471	(weak)
Violet	436	447	
	405		