Chemistry 212

ATOMIC SPECTROSCOPY

LEARNING OBJECTIVES

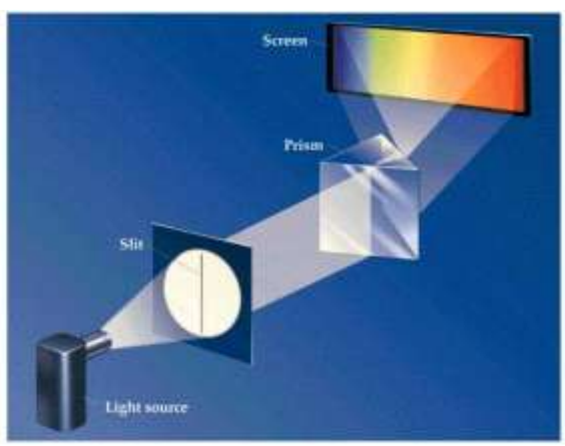
The emission and absorption of light energy of particular wavelengths by atoms and molecules is a common phenomenon. The emissions/absorptions are characteristic for each element's atoms and arise from transitions of electrons among the various energy levels of the particular atom under study. The apparatus used to study the wavelengths of light emitted/absorbed by atoms is called a **spectroscope.** You will use the spectroscope to determine the wavelengths of the emission lines of hydrogen, helium, mercury, and nitrogen.

BACKGROUND

The radiant energy emitted by the sun (or other stars) contains *all* possible wavelengths of electromagnetic radiation. The portion of this radiation to which the retina of the human eye responds is called the **visible light region** of the electromagnetic spectrum. The fact that the radiation emitted by the sun contains a *mixture* of radiation wavelengths may be demonstrated by passing sunlight through a prism. A prism *bends* light; the *degree* to which light is bent is related to the wavelength of the light. When sunlight (or other "white" light) containing all possible wavelengths is passed through a prism, each component color of the white light is bent to a different extent by the prism, resulting in the beam of white light being spread out into a complete rainbow of colors. Such a rainbow pattern is called a **continuous spectrum**.

It was discovered that the use of a narrow *slit* in the spectroscope between the prism and the source of white light sharpened and improved the quality of spectra produced by a beam of white light. See Figure 18-1.

Figure 18-1. The spectrum of "white" light. When light from the sun or from a high-intensity incandescent bulb is passed through a prism, the component wavelengths are spread out into a continuous rainbow spectrum.

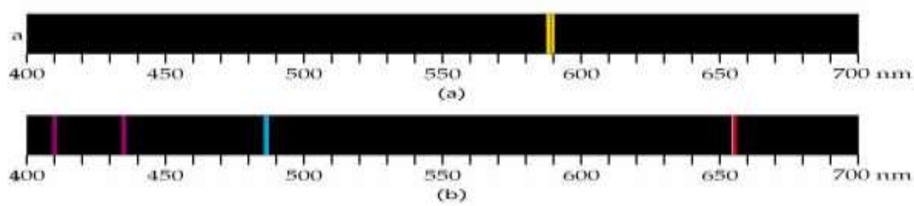


Most substances will emit light energy if heated to a high enough temperature. For example, a fireplace poker will glow red if left in the fireplace flame for several minutes. Similarly, neon gas will glow with a bright red color when excited with a sufficiently high electrical voltage; this is made use of in neon signs. When energy is applied to a substance, the atom present in the substance may *absorb* some of that energy. Electrons within the atoms of the substance move from their normal positions to positions of higher potential energy, farther away from the nuclei of the atoms. Later, atoms which have been excited by the application and absorption of energy will "relax" and will *emit* the excess energy they had gained. When atoms re-emit energy, more often than not, at least a portion of this energy is visible as light.

However, atoms do *not* emit light energy *randomly*. In particular, the atoms of a given element do *not* generally emit a continuous spectrum, but rather emit visible radiation at only certain discrete, well-defined, fixed wavelengths. For example, if you have ever spilled common table salt, NaCl, in a flame, you have seen that sodium atoms emit a characteristic yellow/orange wavelength of light.

If the light being emitted by a particular element's atoms is passed through a prism and is viewed with a spectroscope, only certain sharp bright-colored *lines* are seen in the resulting spectrum. The positions of these colored lines occur in the corresponding location (wavelength region) as in the spectrum of white light. See Figure 18-2, which illustrates the bright line spectrum of hydrogen.

Figure 18-2. The line spectrum of hydrogen (lower spectrum). The location of colored lines in the spectrum corresponds to the location of the same color in the spectrum of white light.



The fact that a given atom produces only *certain* fixed bright *lines* in its spectrum indicates that the atom can only undergo energy changes of certain fixed, definite amounts.

An atom cannot continuously or randomly emit radiation but can only emit energy corresponding to definite, regular changes in the energies of its component electrons. The experimental demonstration of bright line spectra implied a regular, fixed electronic microstructure for the atom and led to an enormous amount of research to discover exactly what that microstructure is.

Hydrogen is the simplest of the atoms, consisting of a single proton and a single electron. The emission spectrum of hydrogen is of interest because this spectrum was the first to be completely explained by a theory of atomic structure, by the Danish scientist Niels Bohr.

As described, we know that atoms absorb and emit radiation as light of fixed, characteristic wavelengths when excited. This absorption and emission of light is now known to correspond to electrons within the atom moving away from the nucleus (energy absorbed) or closer to the nucleus (energy emitted). Atoms emit and absorb energy of only certain wavelengths (bright or dark lines in the spectrum) because electrons do not move randomly away from and toward the nucleus, but may only move between certain fixed, allowed "orbits," each of which is at a definite fixed distance from the nucleus. When an electron moves from one of the fixed orbits to another orbit, the attractive force of the nucleus changes by a definite amount that corresponds to a specific change in energy. The quantity of energy absorbed or emitted by an electron in moving from one allowed orbit to another is called a **quantum (photon)**, and the energy of the particular quantum is indicated by the wavelength (or frequency) of the light emitted or absorbed by the atom. The energy of a photon is given by the Planck equation

$$\Delta E = hv = hc/\lambda$$

where v is the frequency of light emitted or absorbed and λ is the wavelength corresponding to that frequency.

Bohr postulated that the energy of an electron when it is in a particular orbit was given by the formula

$$E_n = -(\text{constant})/n^2$$

where n is the number of the orbit as counted out from the nucleus (n = 1 means the first orbit, n = 2 means the second orbit, etc.) and is called the **principal quantum number**. The proportionality constant in Bohr's theory is called the Rydberg constant (given the symbol R_H) and has the value 2.18 x 10^{-18} J. According to Bohr's theory, if an electron were to move from an outer orbit (designated as n_{outer}) to an inner orbit (designated by n_{inner}) a photon of light should be emitted, having energy given by

$$\Delta E = E_{inner} - E_{outer} = -R_H[(1/n_{inner}^2) - (1/n_{outer}^2)]$$

The wavelength (λ) of this photon would be given by the Planck formula as

$$\lambda = hc/\Delta E$$

Bohr performed calculations of wavelengths for various values of the principal quantum number, n, and found that the predicted wavelengths from theory agreed exactly with experimental wavelengths measured with a spectroscope. Bohr even went so far as to predict emissions by hydrogen atoms in other regions of the electromagnetic spectrum (ultraviolet, infrared) that had not yet been observed experimentally but that were confirmed almost immediately.

Bohr's simple atomic theory of an electron moving between fixed orbits helped greatly to explain observed spectra and formed the basis for the detailed modern atomic theory for more complex atoms with more than one electron. The spectra of larger atoms are considerably more complicated than that of hydrogen, but generally a *characteristic* spectrum is seen. Bohr's theory for hydrogen accounted on a microscopic basis for the macroscopic phenomena of spectral emission lines.

In this experiment, you will measure the wavelengths of the lines in the emission spectrum of hydrogen with a spectroscope and then determine by calculation to which atomic transition (of the electron between the various orbits) each of these spectral lines corresponds. You will also examine the emission spectra of nitrogen, which as a multi-electron atom is considerably more complicated to interpret.

Apparatus/Reagents Required

Spectroscope with illuminated scale, hydrogen lamp (discharge tube), nitrogen lamp, mercury lamp, helium lamp and high-voltage power pack with lamp holder.

Safety Precautions

- Wear safety glasses at all times in the laboratory.
- In addition to visible light, the hydrogen lamp and nitrogen lamps emit radiation at ultraviolet wavelengths. Ultraviolet radiation is *damaging* to the eyes. Wearing your safety glasses while taking readings with the spectroscope will absorb most of this radiation. Refrain from looking at the source of radiation for any extended period of time.
- The power supply used with the lamps develops a potential of several thousand volts. *Do not touch* any portion of the power supply, wire leads, or lamps unless the power supply is unplugged from the wall outlet.
- Always *unplug* the power supply before adjusting the position of the lamps or any other part of the apparatus.

EXPERIMENTAL PROCEDURE

Record al data and observations.

Look through the eyepiece, and adjust the slit opening of the spectroscope so that the spectral lines are as bright and as sharp as possible. If necessary, adjust the illuminated scale of the spectroscope so that the numbered scale divisions are easily read but do not obscure the hydrogen spectral lines.

Record the color and location on the numbered scale of the spectroscope for each line in the visible spectrum of hydrogen, helium and mercury on the data sheet.

Record observation of nitrogen spectra.

DATA ANALYSIS

Use the equations provided in the introduction to this choice to calculate the predicted wavelengths in nanometers (according to Bohr's theory) from the electronic transitions in the hydrogen atom (see question number one) corresponding to the following: $n = 3 \rightarrow n = 2$; $n = 4 \rightarrow n = 2$; $n = 5 \rightarrow n = 2$; $n = 6 \rightarrow n = 2$. How do these predicted wavelengths correspond to those you have measured for hydrogen?

The literature values for the lines in the helium spectrum are calculated in question number two. The values are given in terms of energy in Joules. Convert the energy values to wavelength in nanometers.

The literature values for mercury are:

Wavelengths (nm)	**Color**
404.7	Violet
435.8	Blue
546.1	Green
579.0	Yellow
623.4	Orange
690.7	Red

Atomic Spectroscopy

Data Sheet

Name____________________

Section___________________

Date_____________________

Hydrogen

Color	Observed λ (nm)	Literature λ (nm)	% Difference

Mercury

Color	Observed λ (nm)	Literature λ (nm)	% Difference

Helium

Color	Observed λ (nm)	Literature λ (nm)	% Difference

Nitrogen (Description only)

Chemistry 212

Pre-Laboratory Questions

ATOMIC SPECTROSCOPY

1. The spectral line observed in the visible spectrum of hydrogen arise from transitions from upper states back to the n = 2 principle quantum level. Calculate the predicted wavelengths for the spectral transitions of the hydrogen atom from the n = 6,5,4, and 3 to the n = 2 level in atomic hydrogen.

2. Calculate the theoretical spectral wavelengths of Helium given:

Energy	**Color**	**Wavelength**
(10^{-19} J)		**(nm)**
2.977	Red	
3.383	Yellow	
3.963	Light Green	
4.446	Blue-Violet	
4.937	Violet	

Show sample calculation: